

Exploration of Dielectric and Transport Properties Derived from A-Site Ordering in Simple Perovskite Oxides

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**Exploration of Dielectric and Transport Properties Derived
from A-Site Ordering in Simple Perovskite Oxides**

(単純ペロブスカイト酸化物における

A席秩序に由来する誘電および輸送特性の探究)

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CHAPTER 1 INTRODUCTION

1.1 Background of Perovskites

Perovskite structures, denoted by the general formula ABX_3 , are a cornerstone of modern materials science due to their versatile properties and applications. [1]–[8] The basic perovskite structure, a three-dimensional framework of corner-sharing octahedra, is exceptionally flexible, accommodating a wide variety of chemical compositions by incorporating almost every element from the periodic table. This flexibility enables perovskites to manifest a range of structural distortions and phase transitions, which critically influence their physical properties.

The structural flexibility of perovskites translates into a wide range of electronic, magnetic, dielectric, and optical properties. [1]–[8] Subtle changes in the symmetry, bond angles, and bond lengths can drastically affect the energy levels and the overall behavior of the material. Therefore, understanding the intricate relationship between the perovskite structure and its properties is essential for the rational design of new materials with tailored functionalities. This dissertation will explore various aspects of the structural chemistry of perovskites, with a particular focus on *A*-site ordered perovskites, their unique properties, and potential applications.

1.1.1 Historical Background

The mineral perovskite ($CaTiO_3$) was first discovered in 1839 by Gustav Rose [9], who named it in honor of Russian nobleman Lev Perovskiy. The term "perovskite" has since been expanded to include any material that adopts the same structural framework, whether naturally occurring or synthesized in the laboratory. Early investigations into synthetic perovskites were led by V.M. Goldschmidt [10], who developed the concept of the "tolerance factor" to predict the stability of the perovskite structure based on the size of its constituent ions.

Perovskite-type minerals, particularly magnesium silicate perovskite ($MgSiO_3$), are believed to constitute a significant portion of the Earth's mantle, reflecting the structure's ability to withstand high-pressure environments. The dense, close-packed arrangement of ions within the perovskite structure makes it ideal for such conditions. In addition to their geological importance, perovskites have been recognized for their useful electronic

properties, such as ferroelectricity, superconductivity, and colossal magnetoresistance, which have spurred decades of research into their potential industrial applications.

1.2 Introduction to the Perovskite Structure

1.2.1 General Description of Perovskite Structures

The ideal perovskite structure, with the formula ABX_3 (where A is a large cation, B is a smaller cation, and X is an anion), forms a three-dimensional network of corner-sharing BX_6 octahedra. In the ideal cubic structure, the $B-X-B$ bond angles are 180° , and the A -cations are in octahedral cavities formed by eight surrounding octahedra. The space group of this undistorted structure is $Pm\bar{3}m$ (No. 211), with a schematic structure shown in [Fig. 1.1](#).

However, most real perovskites deviate from this idealized cubic structure due to size mismatches between the A - and B -site cations. These mismatches induce distortions such as octahedral tilting and rotations, which lower the symmetry of the crystal. These distortions are described using the Goldschmidt tolerance factor [\[10\]](#), defined as:

$$\tau = \frac{R_{A-X}}{\sqrt{2}R_{B-X}} \quad \text{Eq. 1.1}$$

When τ is close to 1, the perovskite adopts an ideal cubic structure. Deviations from this value result in various structural distortions, with smaller A -cations ($\tau < 1$) typically leading to tilting of the octahedra to relieve bond strain.

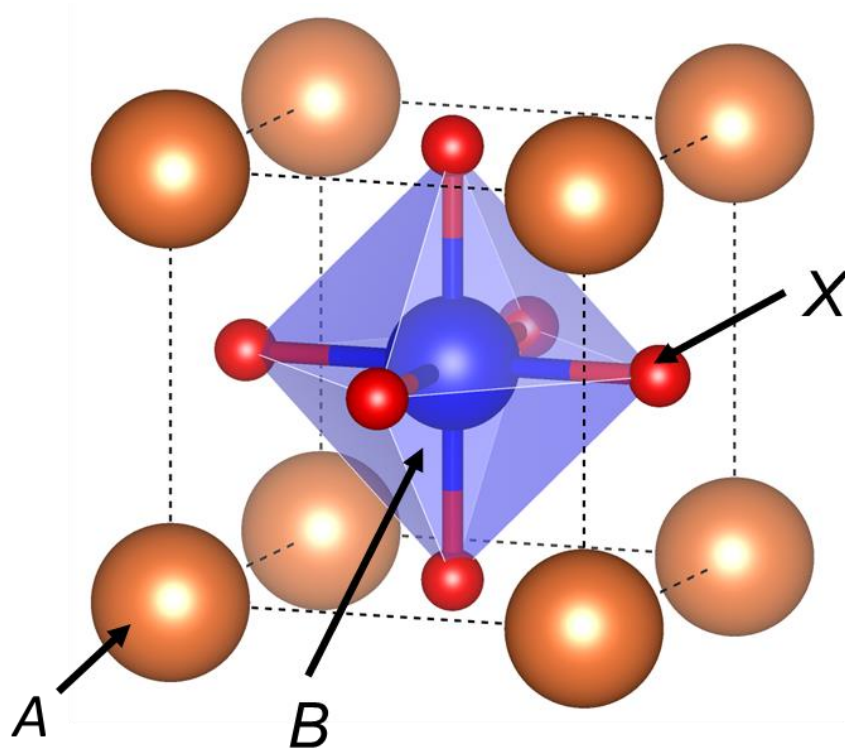


Fig. 1.1. Schematic structure of an ideal perovskite.

1.2.2 Octahedral Tilting and Notation Systems

Octahedral tilting is one of the most common distortions in perovskites, arising from mismatches in ionic radii. Tilting patterns can be described using Glazer notation [\[11\]](#), which uses a three-letter code with superscripts to indicate the type of tilting around the crystallographic axes. For example, $a^-b^+c^-$ describes out-of-phase tilting along the a and c axes, with in-phase tilting along the b axis. These tilts have profound effects on the electronic structure, altering the overlap of orbitals and thus affecting the properties.

In this thesis, Glazer notation will be used to describe the various tilting patterns and their impact on the properties of perovskites.

1.2.3 A- and B-Site Cation Ordering in Perovskites

A wide variety of perovskite structures can be obtained by elemental substitutions at the A and/or B sites. Due to the different ordering of the cations, a variety of exotic property changes can be induced. Usually, the arrangement of A-site cations is randomly distributed (disordered), layered, rock-salt, and columnar for 1 : 1 doping, as shown in Fig. 1.2. However, A-site ordering is actually rare, of which the more common is layered ordering, and other forms have rarely been reported. In contrast, B-site cation is usually ordered with rock-salt pattern rather than the others. This difference stems from the fact that A-site cations are usually alkali or alkaline-earth metals with large sizes and low charges, whereas B-site cations are usually transition metals with small sizes and high charges. [8] A schematical diagram illustrated in Fig. 1.3.

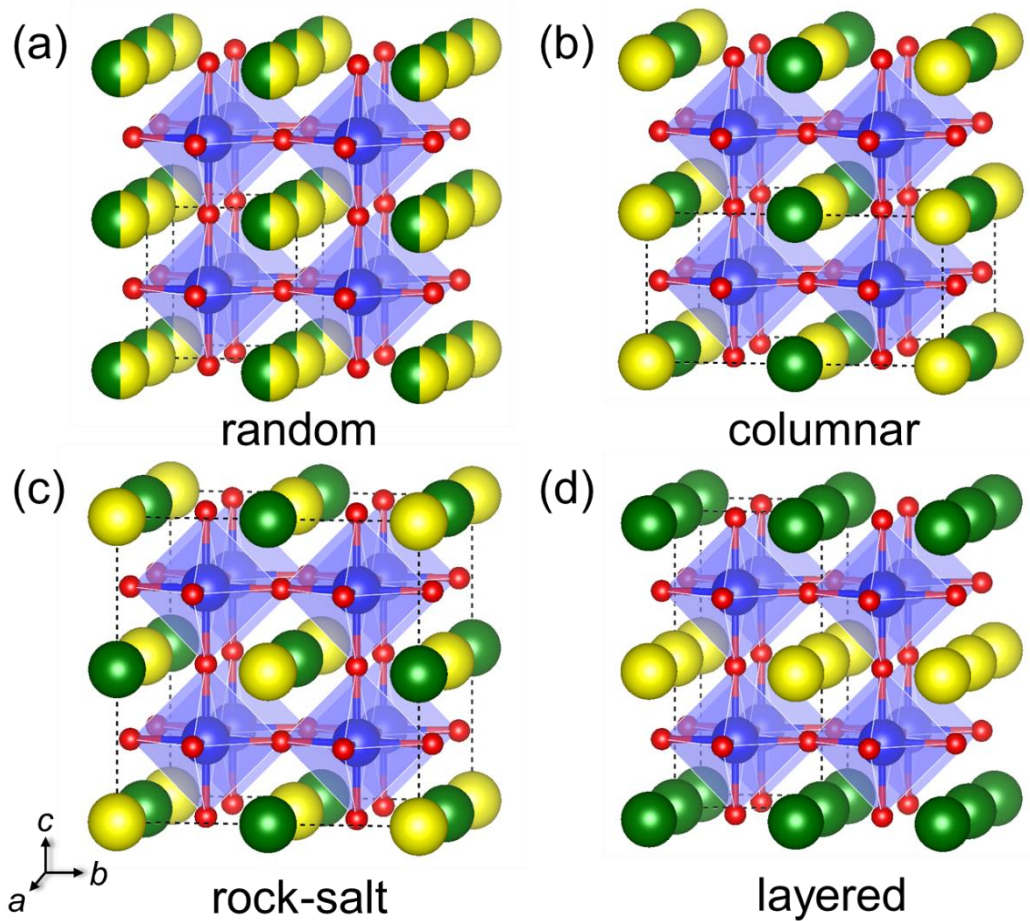


Fig. 1.2. A schematic diagram of the ideal configuration for 1 : 1 doping of A-site cations. The lattice vector is given according to the pseudo-cubic cell.

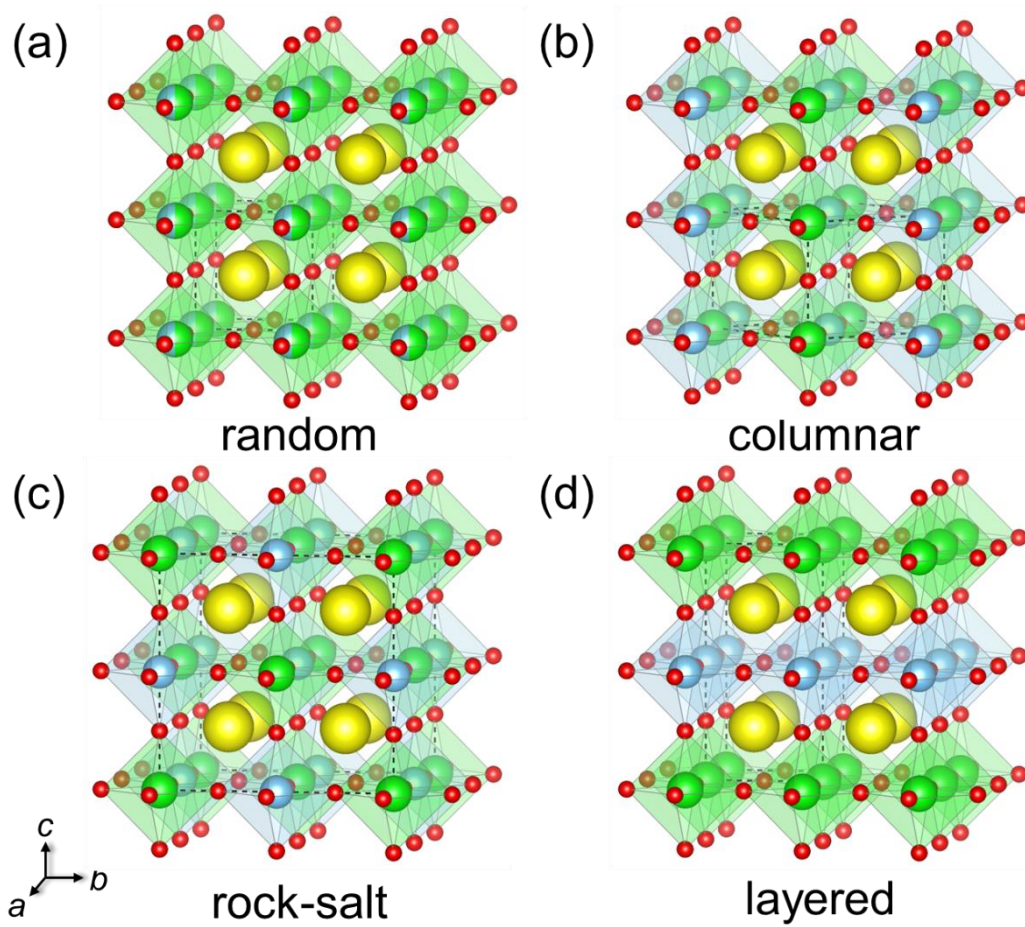


Fig. 1.3. A schematic diagram of the ideal configuration for 1 : 1 doping of *B*-site cations. The lattice vector is given according to the pseudo-cubic cell.

Ordered perovskites, in which two or more different cations occupy distinct crystallographic sites, can exhibit either *A*-site or *B*-site ordering. *A*-site ordering often leads to layered structures, while *B*-site ordering can result in double perovskites with alternating *B*-site cations. These ordered structures typically adopt rock-salt-like arrangements of cations, which affect the electronic and magnetic properties of the material. [3][4]

In double perovskites, the alternation of cations at the *B*-site creates a superlattice structure, which doubles the unit cell and introduces new electronic interactions. This ordered arrangement leads to the emergence of properties such as ferromagnetism, multiferroicity, and enhanced catalytic activity. Similarly, *A*-site ordered perovskites

exhibit unique dielectric and ferroelectric properties, making them suitable for applications in electronic devices and sensors.

Ordered perovskites exhibit a wide range of exceptional physical properties, stemming from the careful arrangement of cations at either the *A* site or *B* site within the perovskite lattice. These ordered structures often result in distinctive behaviors, such as ferroelectricity, tunable dielectric properties, and enhanced ionic conductivity, making them attractive for various technological applications. Below, we will discuss these properties in detail, focusing on the specific characteristics that arise due to cation ordering.

1.3 Properties of Simple Perovskites

Perovskite materials are widely used due to their exotic properties. One of the most well-known examples is barium titanate (BaTiO_3), which exhibits ferroelectric behavior, making it a critical material for high-permittivity dielectric applications. [12]–[14]

Another well-known material is lead zirconate titanate ($\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$, PTZ). It is a widely used piezoelectric ceramic material known for its exceptional electrical and mechanical properties. It can be regarded as a solid solution of lead zirconate (PbZrO_3) and lead titanate (PbTiO_3), which crystallizes in a perovskite structure. PZT exhibits a high piezoelectric coefficient, making it ideal for a variety of applications, including sensors, actuators, ultrasonic transducers, and energy harvesting devices. Its ability to convert mechanical stress into electrical charge, and vice versa, is a key feature that enables its use in precision instrumentation, medical imaging, and vibration control systems. [15][16]

1.3.1 Transport Properties

Perovskites exhibit a wide range of transport properties, including electrical, ionic, and thermal conductivity. These transport properties are largely determined by the perovskite structure, cation ordering, and the nature of the atomic species involved. Due to their structural flexibility, perovskites can be optimized for various applications by adjusting the composition and ordering, which influences the mobility of charge carriers, ions, and phonons.

Electrical conductivity. One of the most significant transport properties of simple perovskites is their electronic conductivity. In many perovskite materials, electronic

conduction occurs through mechanisms such as small polaron hopping or band conduction, depending on the nature of the *B*-site cation and the overlap of the transition metal *d*-orbitals with oxygen *p*-orbitals. [17] The degree of *B*-site ordering can significantly influence electronic conductivity by altering the bandwidth and electron mobility. [18] For example, in oxides like ABO_3 (where *B* is a transition metal), the oxidation state and electronic configuration of the *B*-site cation play a crucial role. Conductivity is typically enhanced when there is significant overlap between the *B*-site *d*-orbitals and the oxygen *p*-orbitals, which creates more extended electronic bands.

In certain perovskites, *B*-site ordering can lead to the formation of alternating chains of cations with different oxidation states, facilitating charge transfer via a hopping mechanism. For example, materials like LaMnO_3 [19][20] exhibit mixed-valence states ($\text{Mn}^{3+}/\text{Mn}^{4+}$) that promote double-exchange interactions, leading to high electronic conductivity. Such materials are also known for colossal magnetoresistance (CMR), where external magnetic fields drastically enhance conductivity.

Oxygen conductivity. Perovskites are also well known for their high ionic conductivity, especially in applications such as solid oxide fuel cells (SOFCs) and oxygen separation membranes [21][22]. Ionic conductivity in these materials arises from the mobility of oxygen vacancies, which are created by aliovalent substitution at the *A* or *B* sites. The arrangement and ordering of *A*-site cations can influence the distribution of these vacancies and thus the pathways for ion migration. In ordered perovskites, a more defined vacancy distribution can result in anisotropic ionic conductivity, where ions preferentially move along specific crystallographic directions.

Perovskites like yttria-stabilized zirconia (YSZ) [23] and doped ceria (CeO_2) [24] are widely studied for their high oxygen-ion conductivity. The presence of oxygen vacancies facilitates the hopping of oxygen ions between lattice sites, which is crucial for fuel cell performance. Additionally, certain *B*-site ordered perovskites have been explored for proton conduction, where hydrogen ions (protons) migrate through the lattice, offering potential in proton-conducting fuel cells.

A-site metal-ion conductivity. In addition to oxygen-ion conductors, certain perovskites are also being studied as lithium-ion conductors for applications in solid-state lithium batteries. Lithium-ion conduction in perovskites occurs via the migration of lithium ions through the *A*-site framework. The large, open structure of the perovskite allows lithium ions to move between interstitial sites, provided that there are sufficient vacant sites or pathways. The ordering of cations at the *A* and *B* sites can impact lithium-

ion mobility by altering the lattice symmetry and creating preferential conduction pathways.

For example, in lithium-ion conducting perovskites like $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ (LLTO), the degree of A-site cation ordering plays a crucial role in determining the ionic conductivity. LLTO has a cubic perovskite structure with ordered La^{3+} and Li^+ ions at the A-site. The partial occupancy of lithium at the A-site and the resulting lattice distortions create pathways for lithium-ion migration. This material is notable for having exceptionally high lithium-ion conductivity at room temperature, making it a promising candidate for solid-state electrolytes in lithium batteries. However, cation ordering, and the formation of grain boundaries can influence the ionic conductivity, and careful control of the material's microstructure is necessary to optimize performance. [25]–[30]

1.3.2 Ferroelectricity and Hybrid Improper Ferroelectricity (HIF)

Ferroelectricity is one of the most well-studied properties of ordered perovskites. In these materials, spontaneous electric polarization occurs as a result of structural distortions, such as the displacement of the B-site cations (commonly Ti^{4+} or Fe^{3+}) within their oxygen octahedral environment. This displacement leads to a non-centrosymmetric structure, which is essential for ferroelectric behavior. For example, in BaTiO_3 , the displacement of the Ti^{4+} ion induces a large polarization that can be switched by applying an external electric field, making it an ideal candidate for memory devices and capacitors. [31]–[34]

A more complex form of ferroelectricity is Hybrid Improper Ferroelectricity (HIF), which arises due to a combination of octahedral tilting and A-site cation ordering. In HIF materials, the ferroelectric polarization is not driven by a single ion displacement but results from the interplay of multiple structural distortions. These distortions break the symmetry and induce a net polarization. Such effects are commonly observed in layered perovskites and can lead to strong, tunable ferroelectric responses, even at room temperature. The ability to fine-tune the ferroelectric behavior through structural manipulations makes HIF systems valuable for advanced electronic devices. [35]–[39]

1.3.3 Dielectric Properties

The dielectric properties of ordered perovskites are another key area of interest, particularly for use in capacitors, sensors, and microwave devices. Dielectric materials store electrical energy in the form of an electric field, and the ability to modulate the dielectric constant is critical for optimizing performance in these devices.

In ordered perovskites, cation ordering can significantly affect the material's dielectric response. For instance, in doped BaTiO₃, the ordering of *A*-site or *B*-site cations can lead to variations in the dielectric constant (ϵ) and reduce dielectric loss. Moreover, ordered perovskites often exhibit temperature-dependent dielectric behavior, with phase transitions affecting the dielectric constant. The transition from a high-temperature paraelectric phase to a low-temperature ferroelectric phase is usually accompanied by a sharp peak in the dielectric constant, which is of great importance for temperature-sensitive applications. [12]–[14]

Relaxor ferroelectrics a subset of dielectric materials, demonstrate diffuse phase transitions and frequency-dependent dielectric constants, where nanoscale cation ordering leads to polar nanoregions. These regions, formed by partial disorder in an otherwise ordered lattice, give rise to high dielectric constants over a broad temperature range, useful for energy storage applications. [31][32]

Substitutions at the *A* and *B* sites of the perovskite structure enable fine-tuning of the dielectric constant, with the dielectric response varying according to the specific ions incorporated. The resonance frequency of dielectric materials often corresponds to a peak in the dielectric constant, and this response can be further modulated by the ordering of cations. Ordering also affects the temperature dependence of the dielectric constant, allowing these materials to be employed as dielectric relaxors or temperature-sensitive capacitors.

1.3.4 Other Properties

In addition to their ferroelectric and dielectric behavior, certain perovskites exhibit magnetic and colossal magnetoresistance (CMR) properties, particularly when transition metals like manganese (Mn) are present at the *B*-site. [19][20][40] In materials such as La_{1-x}Sr_xMnO₃ [40] the double-exchange mechanism, facilitated by the ordered arrangement of Mn³⁺ and Mn⁴⁺ ions, leads to strong coupling between magnetic ordering and electronic conductivity. This coupling gives rise to the CMR effect, where the material's electrical resistance dramatically decreases upon applying a magnetic field.

In addition, some perovskites have antiferroelectricity, piezoelectricity, photovoltaic conversion properties, and so on. They are not described in detail here. All in all, perovskites materials are rich in properties, and by modulating the composition and structure, they can induce exotic properties or combinations of properties, which have a strong potential for application.

1.4 Group-Theoretical Analysis for Perovskites

Common distortions in perovskites are rotations and tilts of the oxygen octahedron, according to the irreducible representations M_3^+ and R_4^+ of the $Pm\bar{3}m$ aristotype. [41] Group-theoretical analysis enables the prediction of phase transitions and the determination of space groups in materials, serving as a powerful tool for examining phase transitions and structures. The simple perovskites and cation-ordered double perovskites have been investigated by group theory, except for cases that are difficult to observe experimentally, such as layered ordering at the *B* site or columnar and rock salt ordering at the *A* site. There are more complex cases, such as those containing anionic defects, which are not described here.

1.4.1 Group-theoretical analysis of octahedral tilting in perovskites

Howard and Stokes [41] conducted a group-theoretic analysis of octahedral tilts in simple cubic perovskite. By treating the oxygen octahedral units as rigid, they identified 15 possible structures, which correspond to the 23 possibilities reported by Glazer [11]. The symmetries of the eight additional tilting systems exceed the requirements of the corresponding space groups and were therefore condensed to fifteen, as displayed in Fig. 1.4 with group-subgroup relationships schematically. Note that the octahedron does not need to be rigid, so the actual situation may be much more complicated, e.g. deformation of the octahedron or displacement of the central cation will lead to a further loss of symmetry. Nevertheless, these results of group theoretic analyses may simplify the determination of the structure.

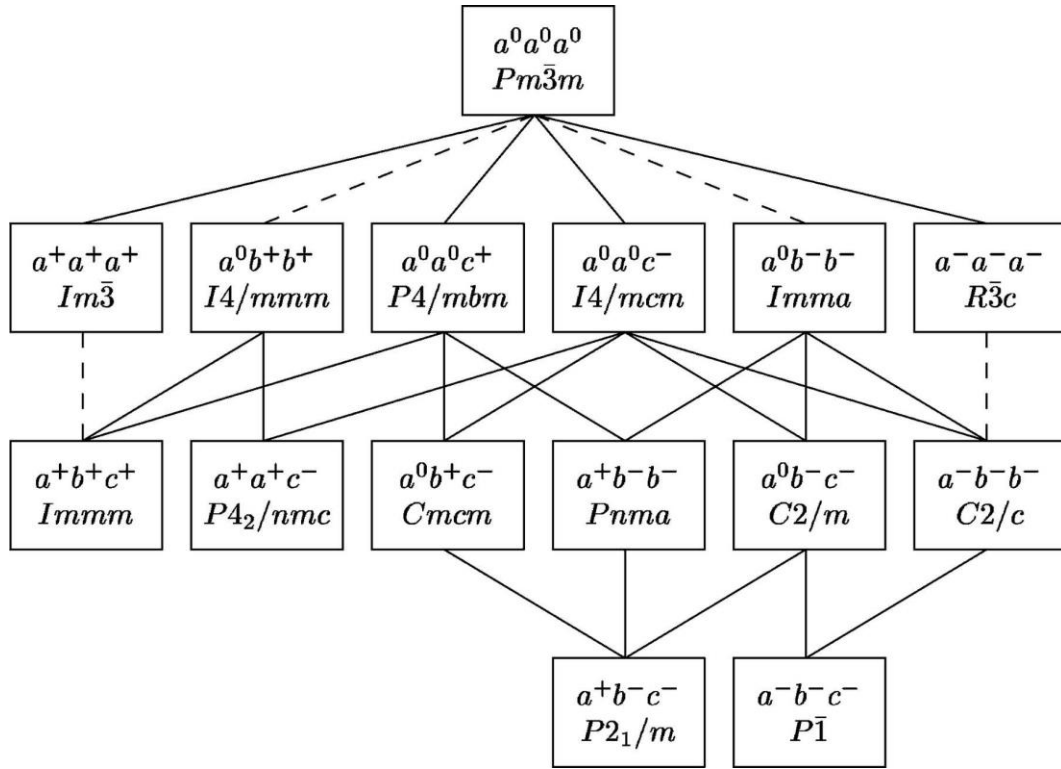


Fig. 1.4. A schematic diagram for the group-subgroup relationships among the 15 space groups. The dashed line connecting a group and its subgroups indicates that Landau theory requires the corresponding phase transition to be first order. [41]

1.4.2 Group-theoretical analysis of octahedral tilting in perovskites with layered ordered A site

Howard and Zhang [42] were the first to perform a group-theoretical analysis of the layered ordering of cations and vacancies on the A site of perovskite, with a formula of $AA'B_2X_6$. Though they initially offered a flawed version that was subsequently corrected. [43] The highest symmetry of perovskites with layered ordered A sites is $P4/mmm$, can be recognized as transforming according to the irreducible representation X_3^- of the $Pm\bar{3}m$ aristotype. When combined with rigid rotations and tilts of the octahedra, distorted structures can be produced, as illustrated in the group-subgroup relationship shown in Fig. 1.5. As previously stated, in practice the oxygen octahedron is unnecessarily rigid.

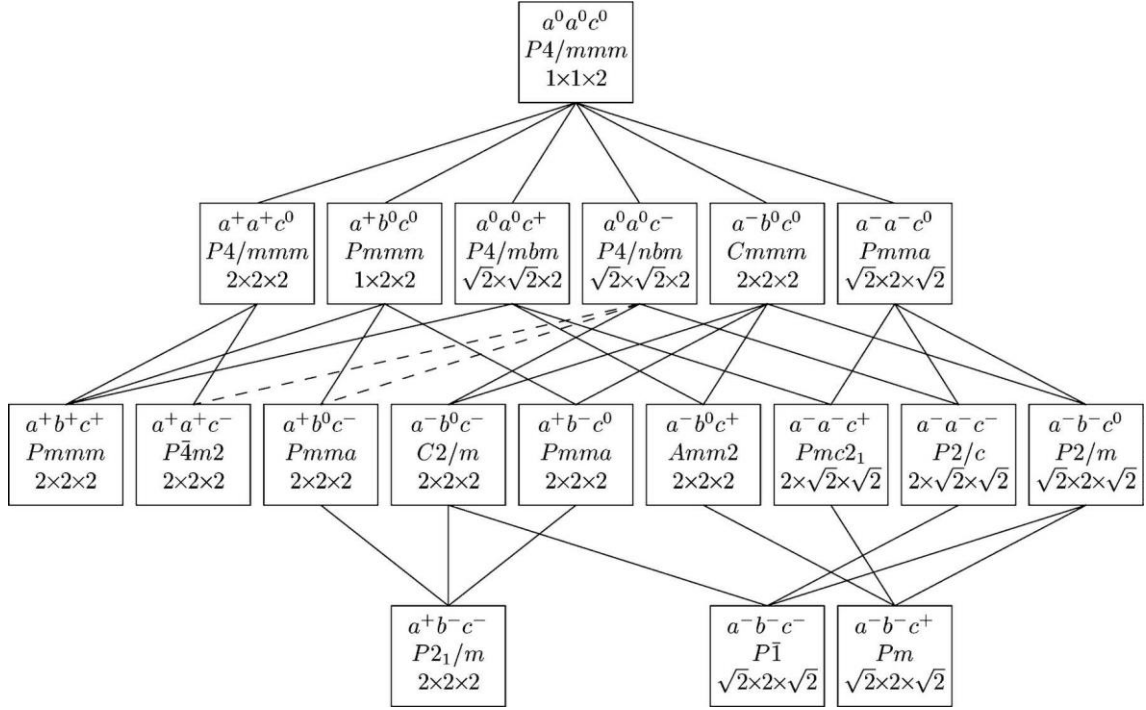


Fig. 1.5. A schematic diagram for the group-subgroup relationships among possible structures generated by the layered ordering of cations on the A site perovskite, followed by rotations and tilts of the BX_6 octahedra. The approximate cell dimensions are included in this diagram in terms of the $Pm\bar{3}m$ aristotype. The dashed line connecting a group and its subgroups indicates that Landau theory requires the corresponding phase transition to be first order. [43]

1.4.3 Group-theoretical analysis of octahedral tilting in perovskites with ordered B site

Although the double-B-site cations and their ordering are not mentioned in our experiments, $A_2BB'X_6$ perovskites are often found in actual double perovskites. Therefore, the following group theoretical findings of their structures are also briefly presented here. This group-theoretical analysis was performed by Howard, Kennedy, and Woodward [44], to tabulate the structures of B-site ordered double perovskites, $A_2BB'X_6$. The cation ordering on the B site is described by the irreducible representation R_1^+ of the $Pm\bar{3}m$ aristotype, and the octahedral tilts are described by irreducible representations M_3^+ and R_4^+ . Combining octahedral tilts and B-site ordering, a total of 12 different structures were identified. The group-subgroup relationships are shown in Fig. 1.6.

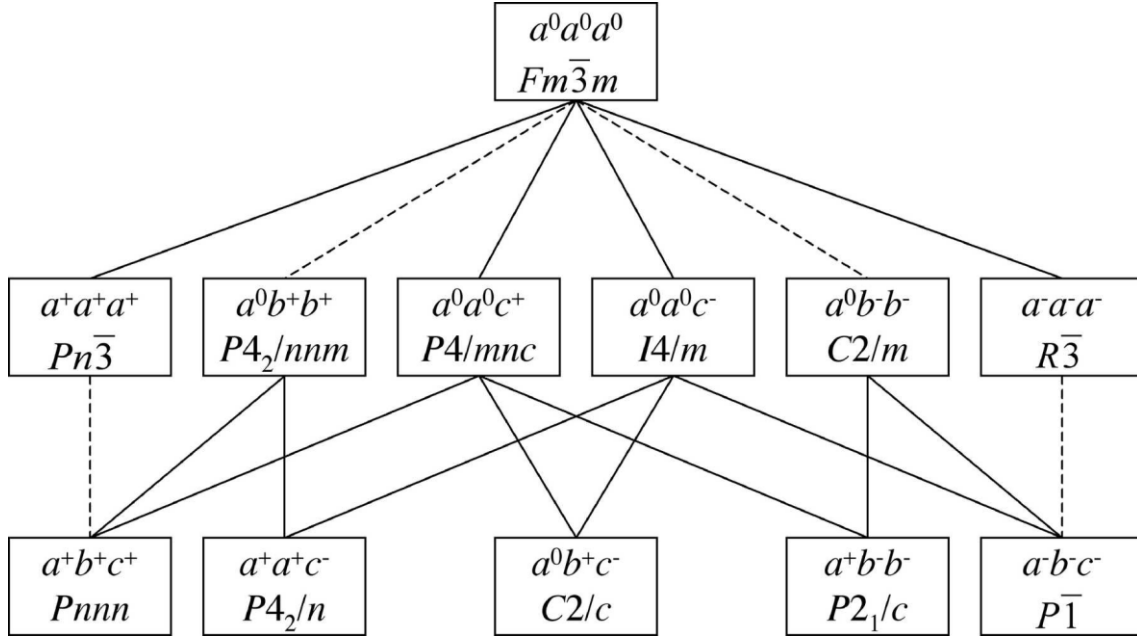


Fig. 1.6. A schematic diagram for the group-subgroup relationships among the 12 possible space groups for *B*-site ordered double perovskites. The dashed line connecting a group and its subgroups indicates that Landau theory requires the corresponding phase transition to be first order. [44]

1.5 Conclusion

The ordered arrangement of cations in perovskites allows for the tuning of properties, making these materials potential candidates for many fields. These diverse properties—ferroelectricity, dielectric behavior, ionic conductivity, and so on—highlight the immense potential of perovskites. Their unique ability to be finely tuned through compositional changes and structural modifications makes them key materials for cutting-edge applications in electronics, energy storage, and information technology.

In this thesis, the structures of some perovskites and the effect of the ordering and disordering of their *A*-site cations on the properties are investigated experimentally and computationally, and potential applications are also evaluated.

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CHAPTER 2 Thermally Controlled A-site Cation Ordering and Coupled Polarity in Double Perovskite $\text{NaLaZr}_2\text{O}_6$

2.1 Introduction

Perovskite structures, with a chemical formula of ABX_3 , are among the most extensively studied materials both theoretically and experimentally, due to their remarkable electrical, magnetic, and optical properties [1]–[4]. In these structures, the BX_6 octahedra share corners to form a three-dimensional network, with the A-site cations located at the center of the anion cuboctahedra, which are surrounded by eight BX_6 octahedra. The highest-symmetry configuration, referred to as an ideal or aristotype perovskite structure, belongs to the cubic $Pm\bar{3}m$ space group. Variations in A-, B- or X-site ions can induce octahedral distortions and rotations as well as ordered atomic arrangements, leading to a variety of hettotype structures.

Among these hettotype structures, considerable attention has been paid to A-site cation ordered perovskites, which possess more than two crystallographically unique A sites with distinct compositions and/or occupancies. Common examples of A-site ordered perovskite oxides include $AA'B_2O_6$, $AA'BB'O_6$, $AA_3'B_4O_{12}$ [5], as well as oxygen-deficient structures such as $AA'_2B_3O_{7-x}$ [6], $AA'_2B_2O_{5+x}$ [7], and $AA'_2B_3O_{8-x}$ [8]. Numerous studies have shown that the A-site cation ordering in the perovskites plays a crucial role in controlling their physical properties [5][10]. In particular, for $AA'B_2O_6$ and $AA'BB'O_6$, the combination of layered A-site ordering and octahedral rotations, represented by $a^-a^-c^+$ in Glazer notation [10], induces polar symmetry and so-called hybrid improper ferroelectricity [11]. However, since most part of $AA'B_2O_6$ and $AA'BB'O_6$ perovskites exhibit random occupation of A and A' cations, studies on perovskites with layered A-site ordering have been relatively limited.

The layered A-site ordering in the $AA'B_2O_6$ and $AA'BB'O_6$ perovskites commonly originates from a size and/or charge mismatch of A and A' cations, coupled with the charge and chemical ordering and cooperative Jahn-Teller distortions of the B-site octahedra [5]. Examples include $\text{LnBaMn}_2\text{O}_6$ (Ln = La [12], Nd [13][14], Pr [14], Sm [15]), $\text{LaBaCo}_2\text{O}_6$ [16] and so on. Although these compounds follow the nominal compositions of $AA'B_2O_6$, the B-site cations are not equivalent because their valence states differ; their true

compositions are written as $A^{(III)}A^{(II)}B^{(III)}B^{(IV)}O_6$. The layered A-site cation ordering is also seen in B-site co-ordered compounds $AA'BB'O_6$, such as $NaLnMnWO_6$ (Ln = La, Nd, Tb) [17][18], $NaYMnWO_6$ [19], $NaHoCoWO_6$ [19], $NaLnMWO_6$ (M = Fe, Co, Ni, Ln = lanthanoid) [20]–[25], and so on. In these compounds, the A-site ordering is driven by the B/B' rock salt ordering, coupled with Jahn-Teller distortions of the B-site octahedra.

Interestingly, layered ordering of A-site cations and vacancies is observed for A-site defective perovskites such as $Ln_{2/3}TiO_3$, $Ln_{1/3}NbO_3$ and $Ln_{1/3}TaO_3$ (Ln = lanthanoid) [26]. These ordered structures are stabilized by the displacements of second-order Jahn-Teller active tetravalent and pentavalent B-site cations such as Ti^{4+} , Nb^{5+} , and Ta^{5+} , with d^0 electronic configurations. Some of these materials have been studied as lithium-ion battery electrode or solid electrolyte materials, as the A-site vacancies facilitate the electrochemical insertion and migration of Li^+ ions. Among them, $Li_{3x}La_{2/3-x}TiO_3$ ($0 \leq x \leq 1/6$) exhibits high Li-ion conductivity, making it a promising candidate for use as a solid-state electrolyte [27]. Structural studies of $Li_{3x}La_{2/3-x}TiO_3$ have revealed that low Li concentrations lead to alternate stacking of cations and vacancies at the A sites. However, the degree of A-site ordering decreases with increasing Li concentrations [28]. The end member $LiLaTi_2O_6$ ($x = 1/6$) shows complete A-site disorder when quenched from high temperatures, whereas a slight A-site ordering can be observed on slow cooling [28]. A similar trend is observed in the Na counterpart $Na_{3x}La_{2/3-x}TiO_3$, although its end member $NaLaTi_2O_6$ ($x = 1/6$) shows complete A-site disordering even when cooled slowly from high temperatures [29]–[32]. Knapp *et al.* [32] reported that the X-ray diffraction (XRD) pattern of $NaLaZr_2O_6$ (NLZO) shows a slight ordering feature. Garcia-Martin *et al.* [33] observed superlattice reflections for NLZO using electron diffraction, attributing to A-site ordered nanodomains that cannot be detected by powder XRD. To the best of our knowledge, however, long-range Na/La layered ordering has not been reported for $Na_{3x}La_{2/3-x}ZrO_3$.

In this study, NLZO polycrystalline powders have been synthesized by solid-state reaction methods, and their crystal structures have been investigated by synchrotron XRD and optical second harmonic generation (SHG). The crystal structure of as-prepared samples was determined to be a polar $P2_1am$ phase (nonstandard setting for $Pmc2_1$, No. 26), which shows long-range layered A-site cation ordering and oxygen octahedral rotations (Fig. 2.1a). However, when quenched from high temperatures, NLZO adopts a nonpolar $Pnam$ phase (nonstandard setting for $Pnma$, No. 62) without A-site ordering (Fig. 2.1b), consistent with previously reported macroscopic and averaged structure for NLZO. These crystal structures and the associated structural distortions were analyzed using

group theory, and the origin of polarity was interpreted in the context of hybrid improper ferroelectricity. Notably, while *A*-site ordering has been controlled via heat treatments in other perovskites [28][34][35], NLZO is distinctive for its ability to manipulate both *A*-site ordering and polarity through thermal history.

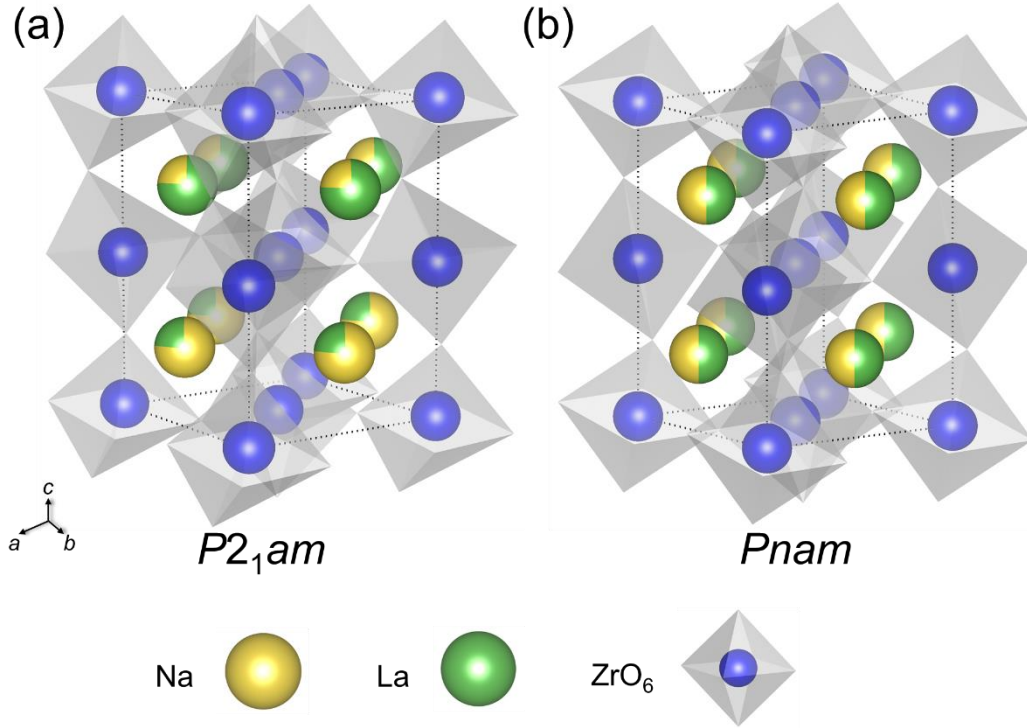


Fig. 2.1. Schematic crystal structures of NLZO with (a) $P2_1am$ and (b) $Pnam$ symmetry. The blue, green, and yellow balls represent Zr, La, and Na, respectively. Two-colored balls indicate that they are jointly occupied by two elements, and the proportion of the color indicates the occupancy of the elements. The gray octahedra represent ZrO_6 units, with the O atoms at the vertices omitted for clarity.

2.2 Experimental

2.2.1 Preparation of materials

Calcined powders. NLZO powders were synthesized by solid-state reaction methods. The reagent grade powders of Na_2CO_3 (Kojundo chemical laboratory, Japan; purity of 99%), ZrO_2 (Kojundo; 99.9%), and La_2O_3 (Kojundo; 99.9%) were weighed in a molar

ratio of Na : La : Zr = 1 : 1 : 2. To compensate for the loss of sodium during the high temperature process, an excess of sodium carbonate (0, 30%, 45%, 50%, 100, and 150%) was added. The mixture was ball-milled in a zirconia pot with anhydrous ethanol and zirconia balls at 350 rpm for 12 h using a Pulverisette-6 planetary mill (Friche, Germany). After drying at 60 °C, the mixture was pressed into pellets under a uniaxial pressure of 50 MPa. The pellets were placed in an alumina crucible, separated from the crucible by a platinum sheet to avoid reactions with the crucible during the high temperature process. The pellets were then heated to target temperatures (900, 1000, 1100, 1200 and 1300 °C) at a rate of 5 K min⁻¹ in the muffle furnace, held at the target temperatures for 2 h, and slowly cooled in the furnace.

Quenched powders. The powders calcined at 1200 °C were pressed into pellets, and subsequently heated again to the target temperatures (900, 1000, 1100, 1200, 1300 and 1400 °C). After holding the pellets for 1 h, they were taken out from the furnace and put onto a copper plate, allowing rapid cooling to room temperature.

Sintered pellets. Sintered bodies were prepared to measure electric polarization-field curves. The powders calcined at 1200 °C were reground by ball milling. The dried powders were sieved through a 75-μm stainless steel sieve to obtain fine powders. Approximately 1 g of the fine powders were then pressed using a graphite die and plungers with a diameter of 10 mm and sintered using a spark plasma sintering (SPS) technique. The samples were heated to 1100 °C at a rate of 100 K min⁻¹ and sintered for 20 min under the uniaxial pressure of 50 MPa under vacuum using an SPS-515B (Sumitomo Metal Mining, Japan / Fuji Electronic Industrial, Japan). The resulting SPS-sintered bodies were sliced and polished to a thickness of about 0.2 mm. They were then placed in a muffle furnace, and annealed at 800 °C in air for 8 h to completely burn off residual carbon and to relieve mechanical stress.

2.2.2 Characterization

X-ray diffraction. Crystalline phases in the powder samples were analyzed by X-ray diffractometry (XRD, Bruker AXS D8 Advance, Germany) with a Cu K α radiation at a diffraction angle step of 0.02° and an integration time of 0.6 s per step. High-resolution synchrotron powder diffraction data were collected at the beamline BL02B2 of SPring-8 with a wavelength of 0.774194 Å using a Debye-Scherrer camera with MYTHEN solid-

state detectors. Rietveld refinements were performed on the XRD data sets using FullProf software [36]. VESTA software package was used to visualize crystal structures [37].

Optical second harmonic generation measurements. The noncentrosymmetry of the pellet samples was confirmed by optical SHG measurements in reflection geometry. A Nd:YAG laser emitting a 1064 nm beam with 100 ps pulses and 10 Hz repetition rate was used, along with a 532 ± 10 nm bandpass filter for detection.

Ferroelectric hysteresis measurements. For the ferroelectric hysteresis measurements, the SPS-sintered bodies were ultrasonically cleaned in anhydrous ethanol and dried in air, followed by sputtering of Pt on the surface to form electrodes with a diameter of about 6 mm. A layer of Pt paste was applied over the sputtered Pt layer and heated at 200 °C to evaporate the solvent. The electric polarization-field (P - E) loops were measured in liquid nitrogen using a ferroelectric tester (Precision LCII, Radiant, U.S.) and a voltage amplifier (609B, Trek, U.S.). The switching frequency of the electric field was 10 Hz.

Crystallochemical and group theoretical analysis. The bond valence sums (BVSs) were calculated manually using parameters reported by Brown and Altermatt [38]. The group theory analysis was performed using the web-based software ISODISTORT [39] [40].

2.3 Results

2.3.1 Synthesis of NLZO perovskite

The synthesis conditions for NLZO phase were first investigated. Figure 2.2 shows the XRD patterns of the samples calcined at 1200 °C with varying amounts of excess Na. The main reflection peaks for all the samples align with the previously reported $Pnam$ (nonstandard setting for $Pnma$) phase, which is a common perovskite structure characterized by $a^-a^-c^+$ -type octahedral rotations [41]. However, small amounts of secondary phases, including $\text{La}_2\text{Zr}_2\text{O}_7$ and ZrO_2 , were also observed. Apart from these peaks, a distinct peak was detected at $2\theta = 10.9^\circ$, which is not ascribed to the $Pnam$ perovskite phase or any possible secondary phases. Indeed, the peak intensity does not strongly depend on the amount of excess Na. As discussed later, this peak plays a key role in determining the crystallography of the perovskite phase.

In the absence of excess Na, strong peaks corresponding to the impurities $\text{La}_2\text{Zr}_2\text{O}_7$ and ZrO_2 were detected. The contents of these secondary phases were decreased in the samples prepared with the excess Na, likely compensating for Na loss due to evaporation at high temperatures. When the amount of excess Na exceeded 45%, the peak intensities of $\text{La}_2\text{Zr}_2\text{O}_7$ and ZrO_2 were reduced to negligible levels. However, these phases could not be eliminated, even when the excess Na addition of up to 150%. Previous studies suggest the remarkable thermodynamical stability of $\text{La}_2\text{Zr}_2\text{O}_7$ [42]. Therefore, the persistence of $\text{La}_2\text{Zr}_2\text{O}_7$ may be derived from the decomposition via the reaction $\text{NaLaZr}_2\text{O}_6 \rightarrow 1/2\text{La}_2\text{Zr}_2\text{O}_7 + \text{ZrO}_2 + 1/2\text{Na}_2\text{O}$. Nevertheless, no peaks corresponding to Na_2O or Na_2CO_3 were observed, suggesting that the excess Na_2CO_3 , or the decomposition products of Na_2O , was almost entirely evaporated during the synthesis process.

Figure 2.3 shows the XRD patterns of the samples synthesized at various temperatures with 50% excess Na. The formation of NLZO begins above 900 °C, although several secondary phases, including $\text{La}_2\text{Zr}_2\text{O}_7$ and unreacted raw materials, remain. After heating to 1200 °C, only trace amounts of secondary phases were detected. However, their content rather increased at 1300 °C, probably due to the enhanced Na evaporation at high temperatures, promoting the decomposition of NLZO. Consequently, the optimal synthesis condition was determined to be the calcination at 1200 °C with 50% excess Na. Similar to the results in Fig. 2.2, a distinct peak at 10.9° was detected in all the samples, prompting a reevaluation of the NLZO crystal structure.

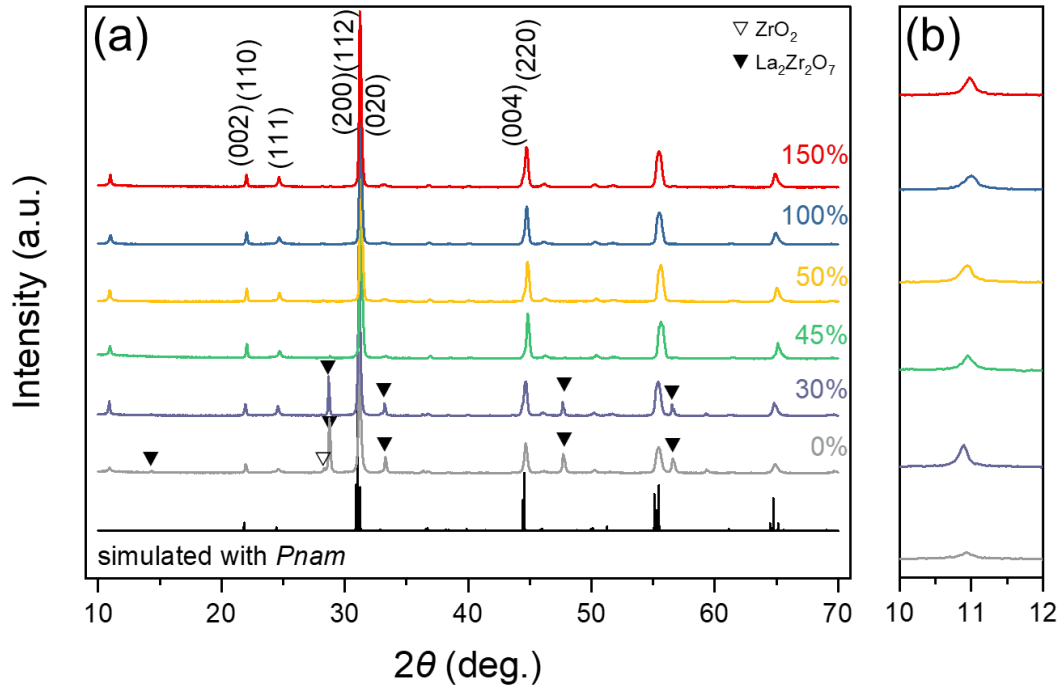


Fig. 2.2. (a) XRD patterns of the samples synthesized with varying excess Na amounts at 1200 °C, along with the simulated pattern for the $Pnam$ structure reported previously for NLZO. The Miller indices with respect to the $Pnam$ structure are assigned. (b) A magnified view of peaks at $2\theta = 10.9^\circ$, corresponding to forbidden 001 reflection in $Pnam$ symmetry.

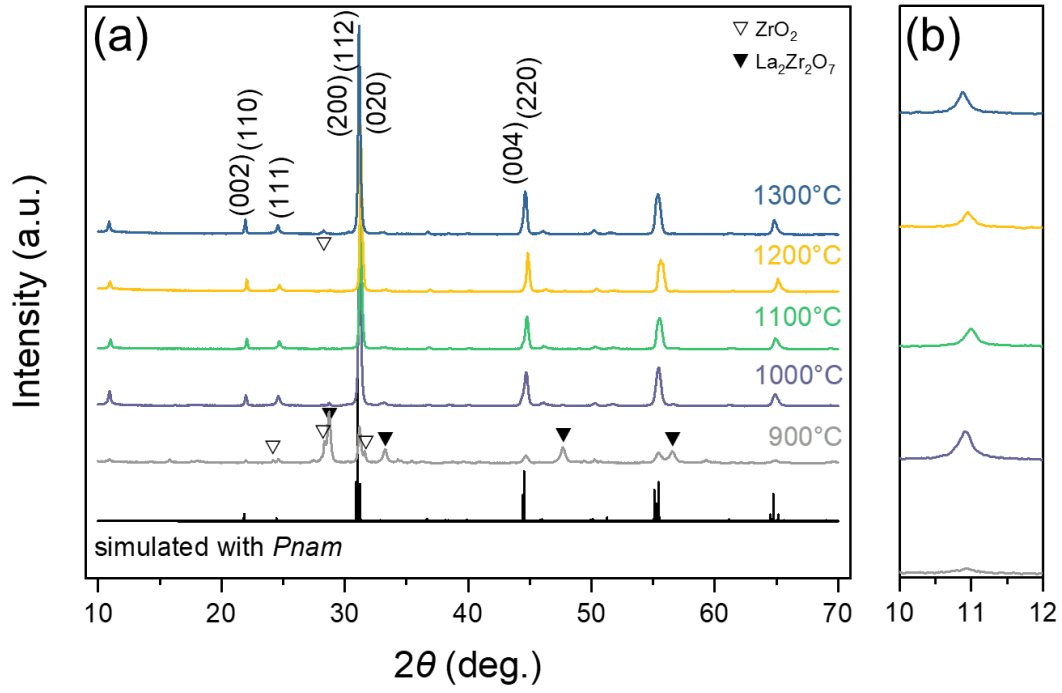


Fig. 2.3. (a) XRD patterns of the samples synthesized at different temperatures with 50% excess Na amounts, along with the simulated pattern for the *Pnam* structure reported previously for NLZO. The Miller indices with respect to the *Pnam* structure are assigned. (b) Enlarged view of diffraction peaks at $2\theta = 10.9^\circ$.

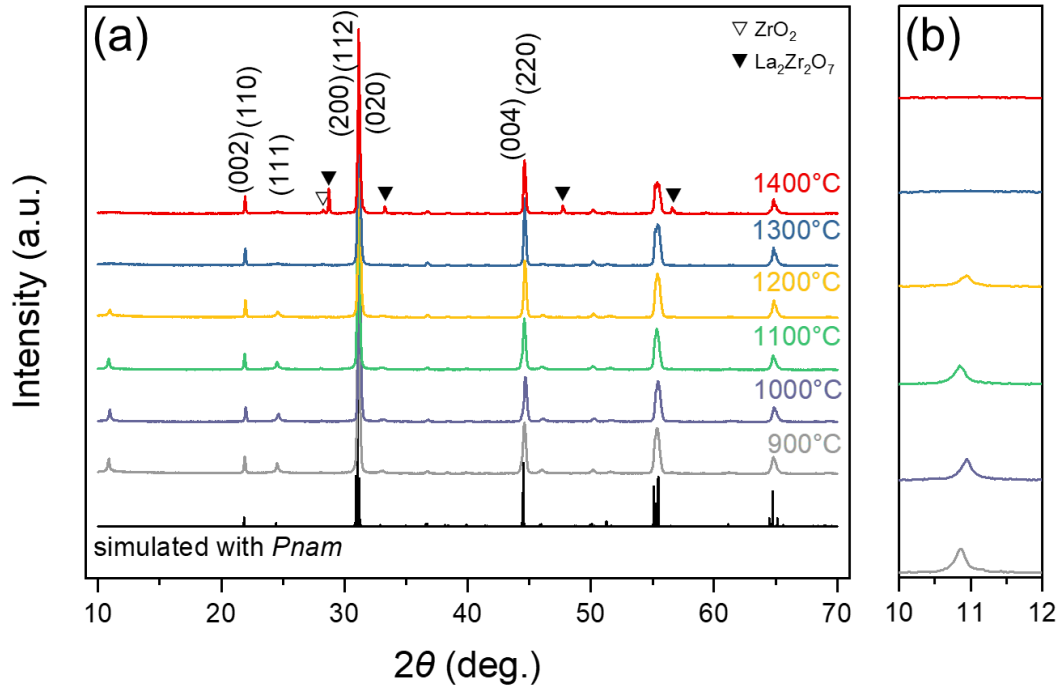


Fig. 2.4. (a) XRD patterns of the samples obtained by quenching the identical calcined powder from varied temperatures, along with the simulated pattern for the $Pnam$ structure reported previously for NLZO. The Miller indices with respect to the $Pnam$ structure are assigned. (b) Enlarged view of diffraction peaks at $2\theta = 10.9^\circ$.

2.3.2 Space group of the new NLZO phase

The diffraction peak at $2\theta = 10.9^\circ$ does not belong to the $Pnam$ phase, while the other main peaks are consistent with those expected from the $Pnam$ phase [41]. Therefore, it is most likely that these are indicative of a new phase of NLZO. Given that the additional peak arises from the absence of certain symmetry elements, it is hypothesized that this new phase belongs to the subgroups of the $Pnam$ phase.

The interplanar spacing corresponding to $2\theta = 10.9^\circ$ coincides with the lattice constant $c = 8.1426 \text{ \AA}$ [41] of the $Pnam$ phase. Therefore, this peak can correspond to the 001 diffraction for the $Pnam$ unit cell. However, in the $Pnam$ space group, $00l$ diffractions with odd l are forbidden due to the symmetry elements involving a $\frac{1}{2}c$ translation, specifically the 2-fold screw axis parallel to the c axis and the n -glide. The appearance of this peak suggests the lifting of these symmetry elements. The remaining symmetry elements form the two maximal subgroups, $P2_1am$ (nonstandard setting for $Pmc2_1$) and

$P2_1/a$ (nonstandard setting for $P2_1/c$). No peak splitting indicative of symmetry change from orthorhombic to monoclinic was observed in the XRD patterns, ruling out the monoclinic space group $P2_1/a$. As shown later, finite SHG signal will be detected for these samples, again excluding the centrosymmetric $P2_1/a$. As a result, the space group of the new phase of NLZO is determined to be $P2_1am$. Another possible assignment of the peak at $2\theta = 10.9^\circ$ is a $\frac{1}{2}(110)$ superlattice reflection of $Pnam$ phase. According to a group theory analysis [26], this structure belongs to the subgroup of $P2_1/m$ with an extension by $\sqrt{2} \times \sqrt{2} \times 1$ of the $Pnam$ unit cell. However, the $P2_1/m$ is centrosymmetric and hence again ruled out based on the observed SHG activity as well as the absence of monoclinic lattice deformation. Thus, the new NLZO phase is definitively assigned to the noncentrosymmetric polar space group $P2_1am$.

2.3.3 Effects of thermal treatments on the crystal structures of NLZO

To evaluate the equilibrium and nonequilibrium contributions to phase selection, samples were quenched from temperatures ranging from 1400 to 900 °C. The XRD patterns of these samples are shown in Fig. 2.4. The intensity of the peaks at $2\theta = 10.9^\circ$ decreased with increasing quenching temperatures, and became barely visible by quenching from 1300 °C, suggesting that NLZO adopt $Pnam$ at 1300–1400 °C. The sample quenched from 1400 °C contained secondary phases, likely due to the Na evaporation at high temperatures as mentioned above. Interestingly, the peak at $2\theta = 10.9^\circ$ appeared again when the quenched $Pnam$ sample was reheated to 1200 °C and slowly cooled to 900 °C at a rate of 5 K h⁻¹, followed by furnace cooling. These findings indicate that $P2_1am$ phase is thermodynamically more stable than the $Pnam$ phase below the transition temperature at 1200–1300 °C.

2.3.4 Noncentrosymmetry and ferroelectricity of the new phase of NLZO

Optical SHG is a powerful technique for probing noncentrosymmetry, as only noncentrosymmetric materials generate SHG signals. The SHG measurement was performed on both the sample prepared by calcination and those prepared by quenching from 1100–1400 °C, and the results are shown in Fig. 2.5. Finite SHG signals were detected in the samples quenched from the temperatures at or below 1200 °C, as well as the unquenched sample, indicating their noncentrosymmetry and supporting the assignment to the polar $P2_1am$ space group. In contrast, no SHG signals were observed

in the samples quenched from the temperatures at or above 1300 °C, indicating their centrosymmetry. These results in good agreement with the XRD data.

Polar materials are potentially ferroelectric. To confirm ferroelectricity for the polar $P2_1am$ phase of NLZO, polarization switching experiments were conducted on ceramic pellets obtained via SPS. XRD analysis confirmed the polar $P2_1am$ structure of the pellet sample. Due to high leakage currents at room temperature, the measurements were performed in liquid nitrogen at 77 K. Figures 2.6a and 2.6b show polarization-field (P - E) and remanent polarization-field (P_r - E) curves at 77 K, respectively. Although the P - E loops were nearly closed, weak hysteresis behavior was observed in the P_r - E curves. The value of remanent polarization under 100 kV cm⁻¹ was 4×10^{-4} μC cm⁻², which is significantly smaller than those of conventional ferroelectrics, such as BaTiO₃, (~ 24 μC cm⁻²) [44]. Based on the finite remanent polarization, $P2_1am$ NLZO is classified as a ferroelectric that exhibits the spontaneous polarization switching, the mechanism of which will be understood by hybrid improper ferroelectricity later.

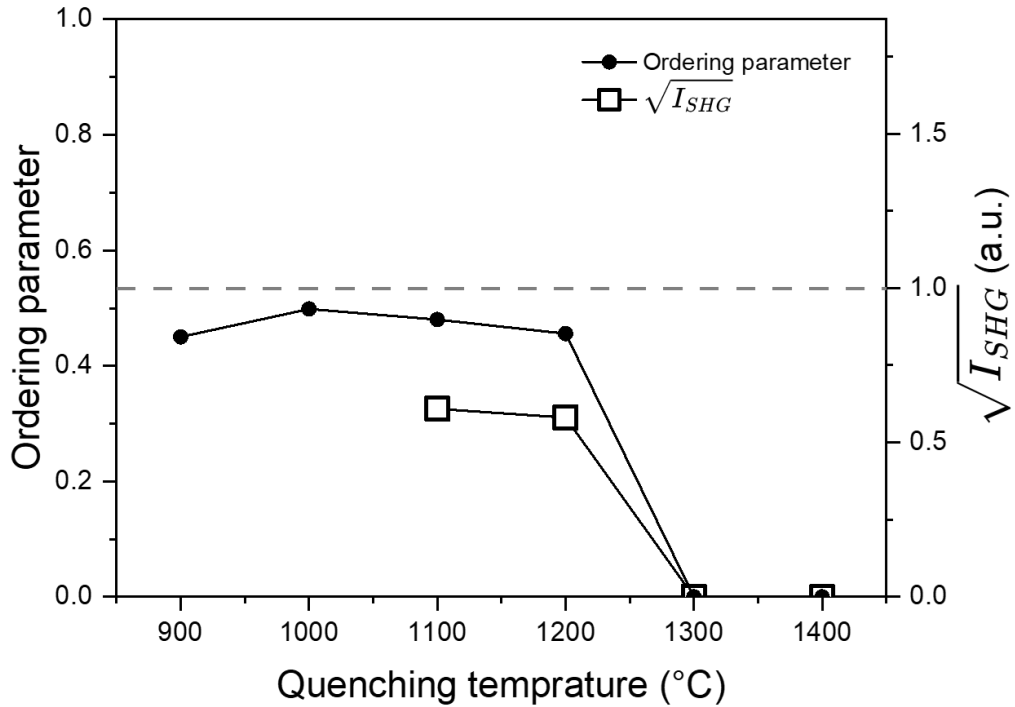


Fig. 2.5. Ordering parameters (solid circle) and optical SHG intensity (open square) for the quenched samples. The SHG signals are normalized with respect to that of the calcined (unquenched) powder. The dashed lines indicate the ordering parameter and optical SHG intensity for the calcined powder.

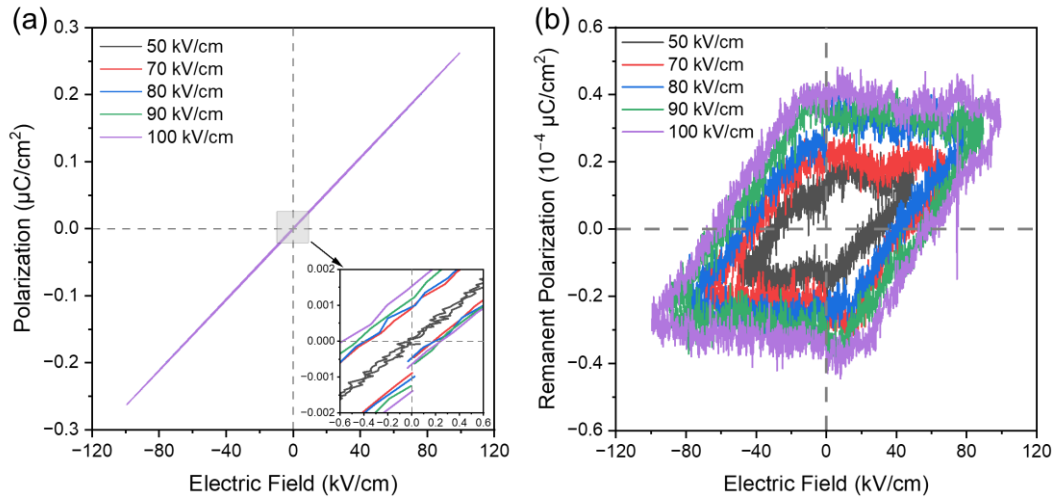


Fig. 2.6. (a) Polarization-field (P - E) curves and (b) remanent polarization-field (P_r - E) curves of the NLZO ceramic pellet at 77 K.

2.3.5 Structural refinements and parameters for NLZO

To determine the crystal structure of the new phase of NLZO, synchrotron XRD and Rietveld refinements were performed on both the unquenched and quenched samples (Fig. 2.7). The centrosymmetric samples quenched from 1300 and 1400 °C were readily refined with previously reported $Pnam$ $a^-a^-c^+$ model. The refined structural parameters are summarized in Table 2.1, and the corresponding structural model is illustrated in Fig. 2.8a. In contrast, the noncentrosymmetric samples with the ‘001 peak’ are refined using $P2_1am$ $a^-a^-c^+$ model. The refined structural parameters are summarized in Table 2.2, and the structural model is illustrated in Fig. 2.8b.

The crystal structure of the new phase features A -site cation ordering, forming a layered structure along the c axis. In the $Pnam$ structure, A -site cations are equivalent, with La and Na atoms evenly sharing the $4c$ positions. In contrast, the $P2_1am$ structure splits the $4c$ site into two distinct A sites, $2a$ and $2b$, with Na/La occupancies of 24/76% at $2a$ and 76/24% at $2b$, creating alternately stacked La-rich and Na-rich layers along the c axis.

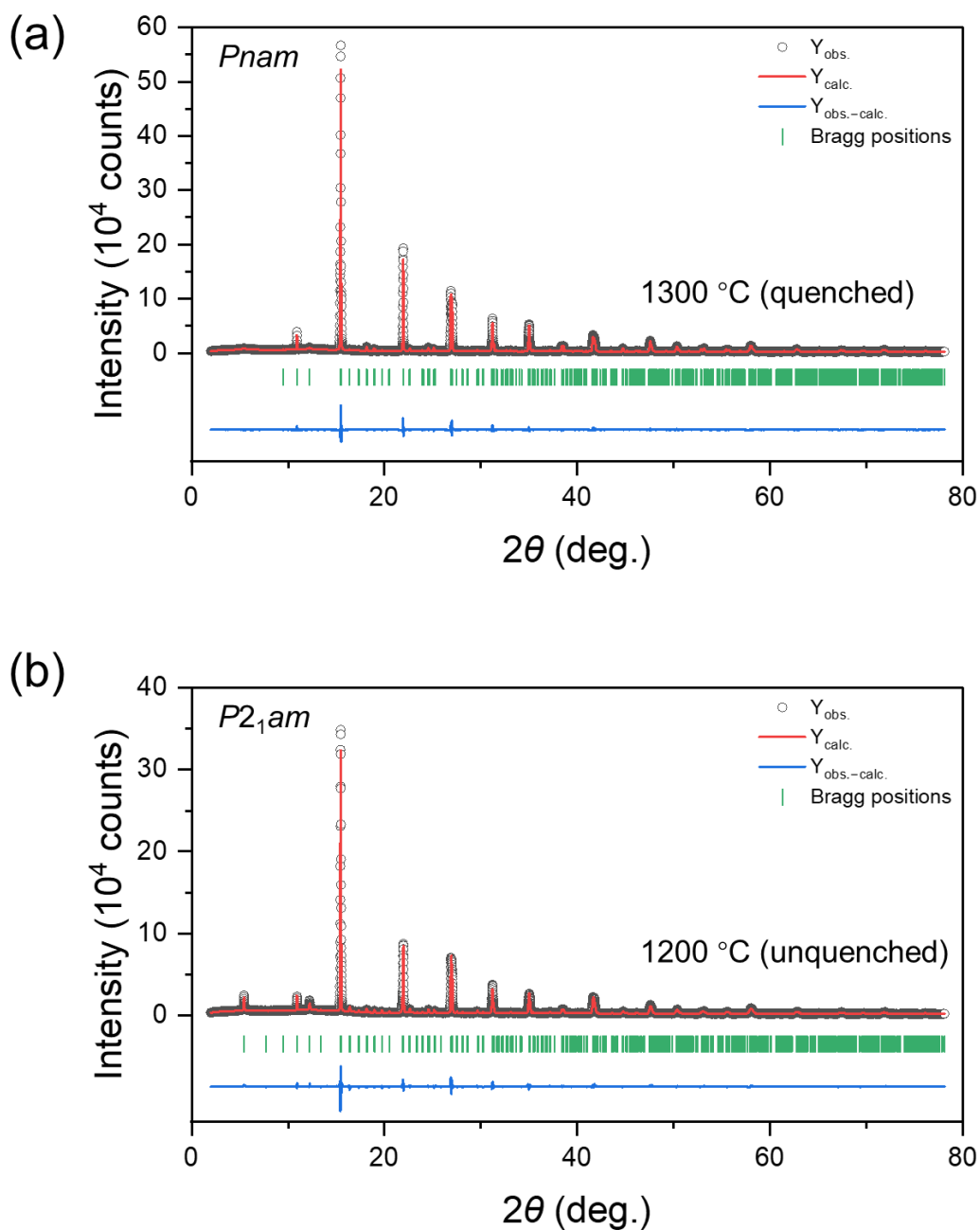


Fig. 2.7. SXRD patterns with refined profiles for the samples obtained by (a) quenching from 1300 °C and (b) calcination at 1200 °C without quenching. The refined structural parameters are shown in [Tables 2.1](#) and [2.2](#). Crystal models are shown in [Fig. 2.8](#).

Table 2.1. Rietveld Refined Parameters for NaLaZr₂O₆ Quenched Rapidly from 1300 °C.

Atom	Site ^{a)}	<i>g</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} (Å ²)
Na	4c	0.5	0.52447(11)	0.99393(20)	1/4	0.01536(14) ^{b)}
La	4c	0.5	0.52447(11)	0.99393(20)	1/4	0.01536(14) ^{b)}
Zr	4a	1	0	0	0	0.00625(9)
O(1)	4c	1	0.4821(10)	0.4134(9)	1/4	0.042(2)
O(2)	8d	1	0.2819(8)	0.78270(8)	0.0442(4)	0.0125(9)

Space group: *Pnam*, *a* = 5.775399(17) Å, *b* = 5.728000(17) Å, and *c* = 8.14465(2) Å, λ = 0.774194 Å, *R*_{wp} = 11.2%, *R*_B = 4.70%, and χ^2 = 19.35.

a) The occupancies of all the crystallographic sites, including 4c site, were fixed to unity.

b) The isotropic displacement parameter for Na and La is constrained to be the same.

Table 2.2. Rietveld Refined Parameters for NaLaZr₂O₆ Cooled Slowly from 1200 °C.

Atom	Site ^{a)}	<i>g</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} (Å ²)
Na(1)	2a	0.2410(18)	0.4763(5)	0.0025(16)	0	0.0136(6) ^{b)}
La(1)	2a	0.7590(18)	0.4763(5)	0.0025(16)	0	0.0136(6) ^{b)}
Na(2)	2b	0.7590(18)	0.4998(13)	0.996(3)	1/2	0.0136(6) ^{b)}
La(2)	2b	0.2410(18)	0.4998(13)	0.996(3)	1/2	0.0136(6) ^{b)}
Zr	4c	1	0 ^{c)}	0.7497(14)	0.7448(2)	0.0065(4)
O(1)	2a	1	0.100(4)	0.619(4)	0	0.045(7)
O(2)	2b	1	0.050(3)	0.849(3)	1/2	0.014(6)
O(3)	4c	1	0.726(3)	0.965(2)	0.7987(13)	0.000(3)
O(4)	4c	1	0.277(3)	0.539(3)	0.7373(13)	0.016(4)

Space group: *P2₁am*; *a* = 5.76356(5) Å, *b* = 5.72674(3) Å, and *c* = 8.15103(7) Å. λ = 0.774194 Å, *R*_{wp} = 13.8%, *R*_B = 4.68%, and χ^2 = 12.23.

a) The occupancies of all the crystallographic sites, including 2a and 2b sites, were fixed to unity.

b) The isotropic displacement parameter for Na and La is constrained to be the same.

c) The *x*-coordinate of Zr was set to 0 as the origin of the polar *a* axis.

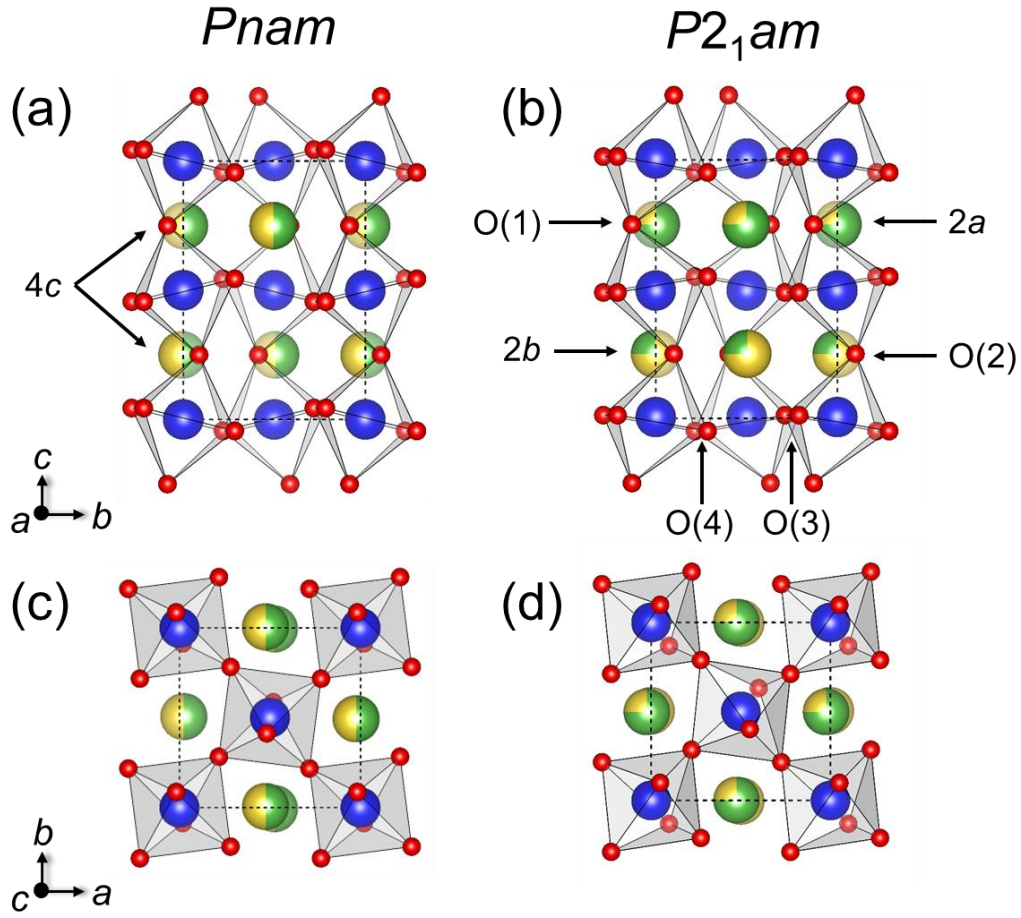


Fig. 2.8. Refined crystal structures for the samples obtained by (a) quenching from 1300 °C ($Pnam$, Table 2.1) and (b) calcination at 1200 °C ($P2_1am$, Table 2.2). Wyckoff positions for the A sites are labeled. Blue, red, green, and yellow balls represent Zr, O, La, and Na, respectively. Two-colored balls indicate an occupation by two elements, with the occupancies proportional to relevant colored areas.

To validate the $P2_1am$ structure (Table 2.2 and Fig. 2.8b) in terms of chemical bonding, the bond lengths and BVSs were analyzed, and these results are summarized in Table 2.3. The BVS for the i -th ion, S_i , was calculated using the following equation:

$$S_i = \sum_j e^{(R_0 - R_{ij})/b}, \quad \text{Eq. 2.1}$$

where R_0 is an empirical parameter specific to each ion pair, b is an empirical parameter taken to be equal to 0.37, and R_{ij} is the distance from the i -th ion to the j -th surrounding ions. The R_0 values determined by Brown and Altermatt [38] were used for the calculation.

At the Na-rich $2b$ site, the BVSs for Na and La are lower than the formal valences, 1 and 3, respectively, while the opposite is observed at the La-rich $2a$ site. These discrepancies are presumably due to the larger ionic radius of Na^+ (1.24 Å for 9-fold coordination) compared to La^{3+} (1.216 Å for 9-fold coordination). The BVSs of four sites of O are all close to the formal valence of 2. Notably, the chemical environments of the two oxygens at the apical sites of coordination octahedra differ significantly: O(1) is in the La-rich layer, while O(2) is in the Na-rich layer. The BVS for O(1) is slightly higher than that for O(2). Meanwhile, the BVSs of O(3) and O(4) at the equatorial sites are very similar, which is consistent with their comparable chemical environments. Overall, the refined $P2_1am$ structure is reasonable, based on the bond lengths and BVSs.

Table 2.3. Bond Lengths (Å) and BVSs in $P2_1am$ NaLaZr₂O₆ Calcined at 1200 °C.

Atom	Na, La ($2b$, Na-rich)		Na, La ($2a$, La-rich)		Zr ($4c$)	Oxygen BVS
O(1)	–		3.68(3) × 1 3.67(3) × 1 2.30(3) × 1 2.24(3) × 1		2.285(10) × 2	2.1
O(2)	3.42(3) × 1 3.23(3) × 1 2.66(3) × 1 2.34(3) × 1		–		2.094(6) × 2	1.8
O(3)	3.340(16) × 2 3.033(15) × 2		2.719(15) × 2 2.499(15) × 2		2.051(16) × 1 2.135(16) × 1	1.9
O(4)	2.993(18) × 2 2.607(17) × 2		3.221(16) × 2 2.720(14) × 2		2.095(19) × 1 2.002(18) × 1	1.9
Cation	Na	La	La	Na	3.8	
BVS	0.8	2.1	3.5	1.3		

A-site cation ordering.

To quantitatively describe the A-site cation ordering, the ordering parameter is defined by the following equation:

$$\frac{|g_{2a} - g_{2b}|}{g_{2a} + g_{2b}} \quad \text{Eq. 2.2}$$

where g_{2a} and g_{2b} are the occupancies of either Na or La ion at the two A sites, 2a and 2b, respectively, estimated by the Rietveld refinements. The ordering parameter as a function of quenching temperatures is plotted in Fig. 2.5, alongside the SHG intensity. The ordering parameters do not approach unity, indicating that complete layered ordering is not achieved. This can be explained by the temperature-dependent nature of ion mobility. At high temperatures, A-site cation disorder is entropically preferred. As the temperature decreases, the A-site cation ordering begins to develop. However, the reduced ion mobility at lower temperatures prevents the system from achieving full A-site cation ordering.

The ordering parameters are positively correlated with the square root of SHG intensity, which is related to the spontaneous polarization P according to the equation, $I_{\text{SHG}} \propto P^2$ [45]. The connection between the polarization and A-site ordering will be discussed later in terms of group theory.

Lattice constants and unit-cell volumes.

The lattice parameters and cell volumes of the quenched samples are given in Fig. 2.9 as a function of quenching temperature, where a , b , and c axes are defined as pseudocubic lattice constants, $a_p = a/\sqrt{2}$, $b_p = b/\sqrt{2}$, and $c_p = c/2$, respectively. The lattice constants a_p for A-site disordered samples are larger compared to those for A-site ordered samples. Meanwhile, the lattice constants b_p and c_p for A-site disordered samples are smaller than those for A-site ordered samples to compensate for the increase in a_p . The cell volume increases with increasing quenching temperature. It is well known that in ordered structures, the atoms are usually more efficiently stacked than in disordered ones, so that ordered atomic arrangements in complex perovskites usually lead to a decrease in unit-cell volume. This accounts for why the unit-cell volumes of $P2_1am$ are smaller than those of $Pnam$.

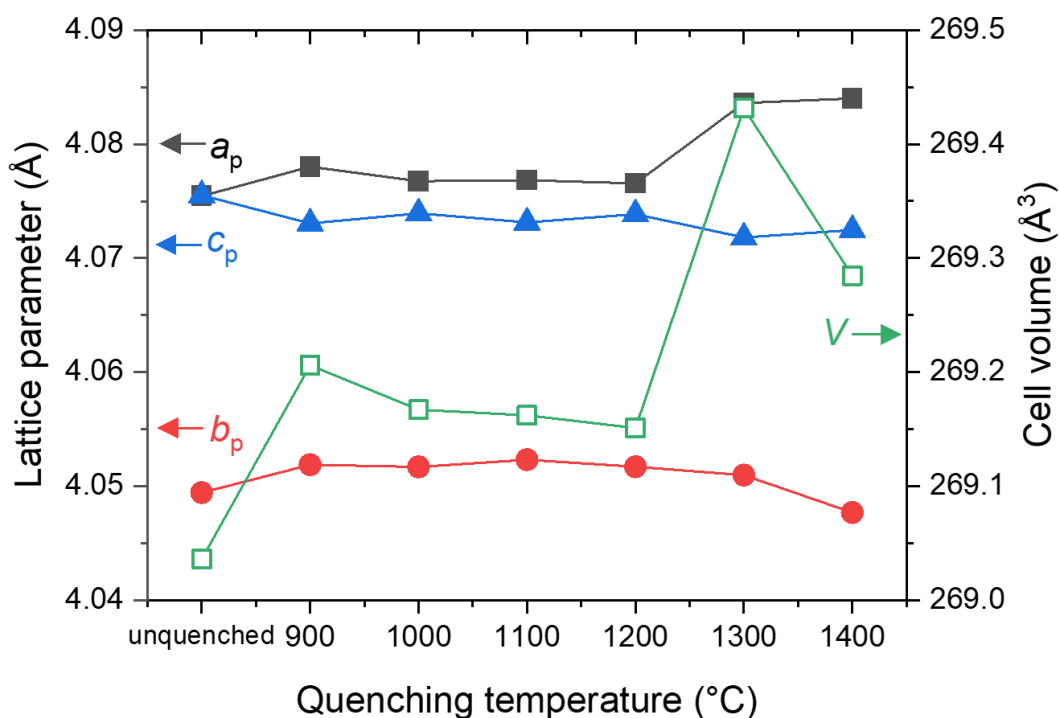


Fig. 2.9. Lattice parameters and cell volumes of the quenched samples as a function of quenching temperature.

2.4 Discussion

2.4.1 Stabilization of A-site cation ordering

Here we discuss how the A-site cation ordering is stabilized in NLZO. Knapp and Woodward [32] have shown that when two distinct A-site cations are alternately stacked in a layered manner, anions are displaced towards the layers consisting of smaller and/or more positively charged A-site cations to compensate for the A-site size and charge mismatch. However, such displacements do not fully stabilize the A-site ordered structures. The charge mismatch can be compensated only when the B-site cations are also significantly displaced. Therefore, layered ordering of the A-site cations commonly occurs when the B sites are occupied by the second-order Jahn-Teller active d^0 cations, which tend to show large off-centering displacements. These two distortions synergistically stabilize layered A-site ordered structure.

In this context, let us examine the refined $P2_1am$ structure of NLZO. In the refined structure, the B-site Zr ions are displaced from the centers of the oxygen octahedra towards the less positively charged Na-rich layers away from the more positively charged

La-rich layers along the c axis. The Zr ions move towards the apical O(2) ions within the Na-rich layers away from the apical O(1) ions within the La-rich layers, rendering the Zr-O(2) bonds much shorter than the Zr-O(1) bonds. The Zr displacements are most likely driven by the $4d^0$ electronic configuration of Zr^{4+} ions as well as a built-in electric field imposed by the layered A-site ordering. In addition, the octahedral tilt away from the c axis causes the equatorial O(3) and O(4) ions to move towards the La-rich and Na-rich layers, respectively, whereas the more positively charged La-rich layers attract the whole oxygen planes consisting of the O(3) and O(4) ions towards themselves. Thus, the deformation of the oxygen octahedra involving the Zr and O displacements occurs to compensate the charge mismatch between the La-rich and Na-rich layers, stabilizing the layered A-site ordered structure of NLZO. Thus, the atomic displacements in the $P2_1am$ structure agree with the mechanism behind the layered A-site ordering suggested by Knapp and Woodward.

2.4.2 Origin of polarization

Here, the origin of polarization in the $P2_1am$ phase of NLZO is discussed in terms of group theory. As mentioned above, $P2_1am$ is a subgroup of $Pnam$. Their structural difference is relevant to the polarization. Based on symmetry mode analyses, the structural difference was projected onto symmetry-adopted modes of the parent $Pnam$ phase, revealing that the A-site cation ordering Γ_3^- mode drives the $Pnam$ to the $P2_1am$ phases (Fig. A1a). However, it is not intuitive that the A-site ordering leads to its polarization. Here, we consider the structural modes with respect to other supergroups of the $P2_1am$ phases. Again, the $P2_1am$ phase encompasses the $a^-a^-c^+$ octahedral rotations and layered A-site ordering, whereas the $Pnam$ phase contains only the $a^-a^-c^+$ octahedral rotations without the layered A-site ordering. One of other possible subgroups is a $P4/mmm$ structure, which has the layered A-site ordering without any octahedral rotation. Rondinelli and Fennie [46] indeed proposed that the $a^-a^-c^+$ octahedral rotations eliminate the inversion symmetry and, in turn, induce a polar distortion and hence hybrid improper ferroelectricity in the layered A-site ordered perovskites with $P4/mmm$ symmetry.

Using symmetry mode analyses, the structural difference between the $P2_1am$ and $P4/mmm$ phase were projected onto symmetry-adopted modes of the parent $P4/mmm$ phase. The results are given in Table A1, respectively. The symmetry-adopted modes transforming like irreps M_2^+ (a) and M_5 (a, a) correspond to the in-phase rotation ($a^0a^0c^+$) and out-of-phase tilt ($a^-a^-c^0$) of the octahedra (Fig. 2.10a and b), respectively. Any single

irrep cannot establish the $P2_1am$ symmetry; the coupled modes transforming as $M_2^+M_5^-$ ($a \mid b, b$) lift the inversion symmetry and produce the $P2_1am$ phase (see Fig. A1b). The M_2^+ and M_5^- mode amplitudes are regarded as primary order parameters of the phase transition between the two structures. However, neither the nonpolar M_2^+ nor M_5^- can produce polarization. The symmetry mode analysis tells us that a polar Γ_5^- mode (Fig. 2.10c) occurs as one of the induced modes. Rondinelli and Fennie theoretically demonstrated that this polar mode is induced through a trilinear $Q(\Gamma_5^-)Q(M_2^+)Q(M_5^-)$ coupling term in the free energy, where $Q(X)$ is a mode amplitude of the distortion mode transforming like the irrep X . The polar Γ_5^- mode involves antiparallel displacements of the two crystallographically unique A-site cations, which produce finite polarization. This mechanism is so-called hybrid improper ferroelectricity.

It is instructive to see the structural distortion in the $Pnam$ phase in comparison. The distortion was decomposed into symmetry-adopted modes of a parent $Pm\bar{3}m$ phase. The results are provided in Table A2 (see also Table A3, which shows the results of symmetry mode analysis for the $P2_1am$ phase with respect to the $Pm\bar{3}m$ phase for a direct comparison). As in the case of $P2_1am$, the primary modes correspond to the in-phase rotation ($a^0a^0c^+$) and out-of-phase tilt ($a^-a^-c^0$) of the octahedra transforming like irreps M_3^+ ($a; 0; 0$) and R_4^+ ($0, a, a$) (Fig. 2.10d and e), respectively. A coupling of these modes establishes the $Pnam$ symmetry (see Fig. A1c). We note that the $a^-a^-c^+$ octahedral rotation modes induce a nonpolar X_5^+ mode involving antiparallel displacements of the crystallographically equivalent A-site cations (Fig. 2.10f), which is similar to the polar Γ_5^- mode in $P2_1am$. However, the induced X_5^+ mode in the $Pnam$ phase is completely antipolar because of the equivalence of the A-site cations. Meanwhile, the induced Γ_5^- mode in the $P2_1am$ phase is not antipolar but "ferrielectric" because of the inequivalence of the two crystallographically unique A-site cations. Thus, the combination of the layered ordering and antiparallel displacements of A-site cations produces finite polarization.

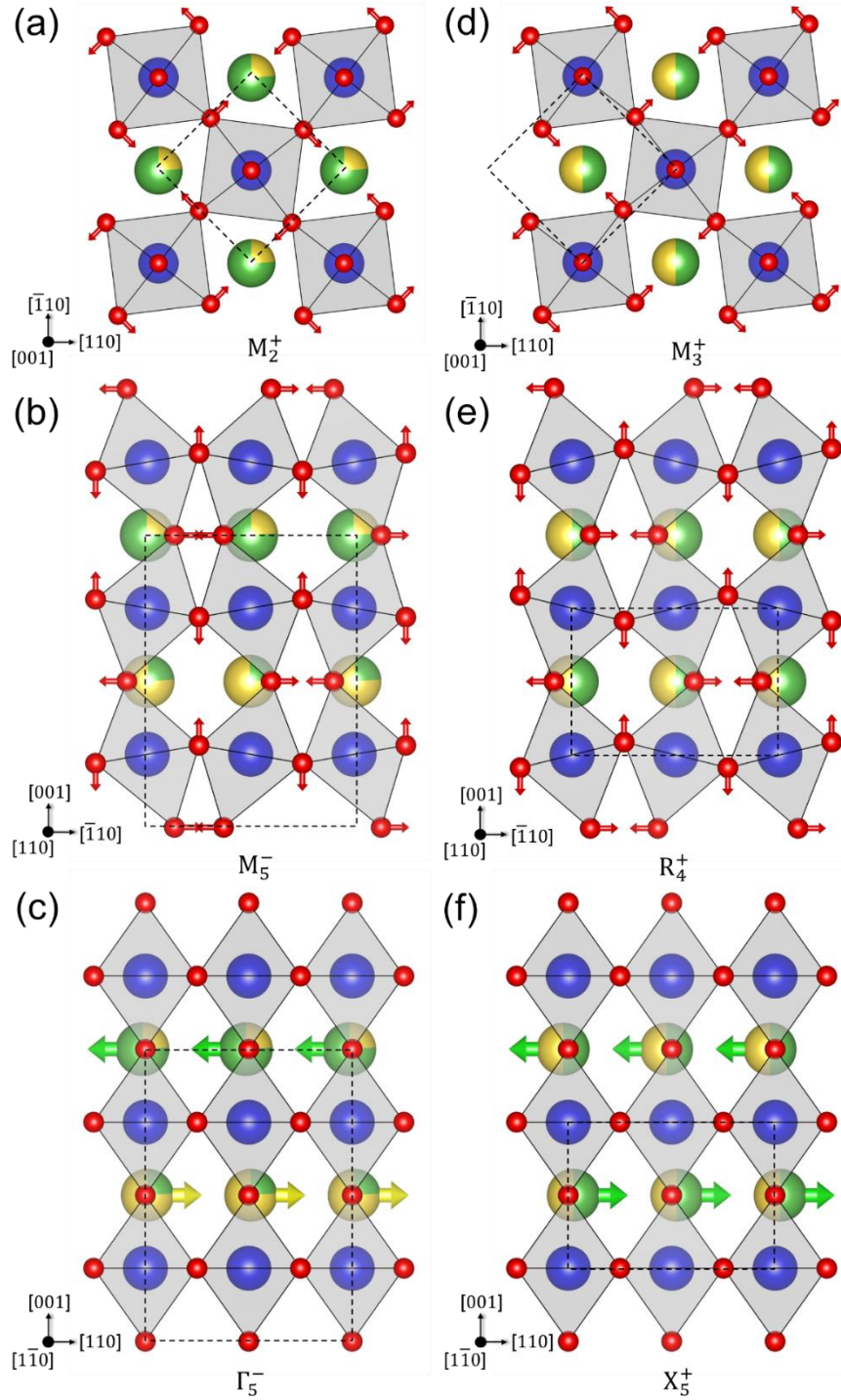


Fig. 10 Schematic illustration of the distortion modes transforming like the irreps (a) M_2^+ , (b) M_5^- , and (c) Γ_5^- of $P4/mmm$ in the $P2_1am$ phase, and those transforming like the irreps (a) M_3^+ , (b) R_4^+ , and (c) X_5^+ of $Pm\bar{3}m$ in the $Pnam$ phase. The lattice vectors are given according to the parent cell, which indicated by dash line.

2.4.3 Polarization switching mechanism

The $P2_1am$ phase of NLZO is potentially hybrid improper ferroelectric. Polarization switching mechanisms in hybrid improper ferroelectric perovskites have been studied theoretically [46]; the spontaneous polarization can be reversed by switching the direction of polar distortions, accompanied by reversal of either of the $a^-a^-c^0$ tilt or $a^0a^0c^+$ rotation, while keeping the A-site ordered arrangement. Tiny switchable polarization was observed for the $P2_1am$ NLZO, although a spontaneous polarization value of $\sim 7.5 \mu\text{C cm}^{-2}$ was calculated from the refined structure by the point charge model with nominal charges, which is comparable to those of typical hybrid improper ferroelectrics [11][18]. One possible explanation for the observed tiny switchable polarization is that the energy barriers for polarization switching in hybrid improper ferroelectrics is usually quite high, hampering full polarization switching, especially at low temperatures [47].

Another theoretically possible mechanism behind polarization switching involves the reversal of A-site ordering mode without the reversal of distortion modes. However, this mechanism is not plausible because a change in the A-site occupancy requires significant mutual diffusion of Na^+ and La^{3+} ions. The activation energy for their diffusion is most likely to be much higher than the switching barriers for the reversal of the polar and rotation modes, ruling out this mechanism.

2.5 Conclusion

In this study, polycrystalline NLZO samples were synthesized via solid-state reaction methods. The as-prepared samples crystallize into layered A-site ordered perovskites with polar $P2_1am$ symmetry, as revealed by XRD and optical SHG measurements, whereas the samples quenched from 1300 °C or higher adopt A-site disordered perovskite structures with nonpolar $Pnam$ symmetry, which was reported previously. The $P2_1am$ phase exhibits partial A-site cation ordering in a laminar pattern, leading to the splitting of crystallographically equivalent A sites with the Na/La ratio of 50/50 into two unequal A sites with the Na/La ratios of 24/76 and 76/24. The layered A-site ordering is stabilized by the displacements of O^{2-} ions and second-order Jahn-Teller active Zr^{4+} ions, which compensate the size and charge mismatch of the Na- and La-rich layers. The group theoretical analysis tells us that the nonpolar $a^-a^-c^+$ octahedral rotation modes induce a polar mode involving the antiparallel displacements of the two crystallographically unique A-site cations, producing spontaneous polarization. Ferroelectricity was

experimentally demonstrated for the $P2_1am$ phase, although its polarization is tiny. NLZO was found to be a rare and intriguing examples of the perovskites exhibiting thermally controllable A-site cation ordering and coupled polarity. To the best of our knowledge, this is the first report of the realization of switching from polar to nonpolar states and vice versa by thermal treatments.

2.6 References

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CHAPTER 3 Transport Properties of Perovskite-Type Sodium Lanthanum Zirconate Ceramics

3.1 Introduction

In recent decades, lithium-ion batteries have experienced rapid development, becoming indispensable power sources for portable electronic devices, electric vehicles, and energy storage systems. However, their widespread adoption has been hindered by safety concerns associated with the flammable nature of traditional organic electrolytes and the limited availability of lithium resources, coupled with high extraction costs. These limitations have prompted researchers to explore alternative energy storage solutions. One promising alternative is sodium-ion all-solid-state batteries, which have garnered significant attention due to the abundance of sodium ions and the inherent non-flammability of solid electrolytes. Among the key areas of research within this field, sodium-ion solid-state electrolytes stand out as a focal point. [1]–[7]

The research focus on classic sodium-ion conductors such as β -alumina and NASICON (Na super ionic conductor) has indeed demonstrated promising performance. However, these materials are still confronted with challenges, including poor high-voltage interface stability, obstacles in mass production, and low room-temperature conductivity. Therefore, the quest for new sodium-ion conductors is of paramount significance to address these limitations and advance sodium-ion battery technology. [8]–[13]

One promising system that has shown potential is the perovskite type lithium-ion conductor, $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ (LLT). This material exhibits high ionic conductivity (of the order of $10^{-3} \text{ S cm}^{-1}$ at room temperature) and a relatively wide electrochemical stability window (greater than 8 V), making it a promising candidate for solid-state electrolytes in lithium batteries. [14]–[16]

In this study, $\text{Na}_x\text{La}_{(2-x)/3}\text{ZrO}_3$ (NLZO) ($0.35 \leq x \leq 0.5$) we synthesized by solid-phase method. Expansion of the A-site vacancies by increasing the La content is thermodynamically limited. The conductivity of samples with high purity ($x = 0.5$) was investigated and the factors affecting the conductivity were analyzed by DFT calculations with KKR-CPA method.

3.2 Experimental

3.2.1 Preparation of materials

NLZO powders were synthesized by solid-state reaction methods. The reagent grade powders of Na_2CO_3 (Kojundo chemical laboratory, Japan; purity of 99%), (Kojundo; 99.9%), ZrO_2 (Kojundo; 99.9%), and La_2O_3 (Kojundo; 99.9%) were mixed according to the stoichiometric ratio with excess 50 mol% Na and ball milled with anhydrous ethanol and zirconia balls, noting that an additional amount of sodium carbonate was added to compensate for the loss of sodium during the high temperature process. After drying the mixture at 60 °C, the mixture was pressed into pellet under a pressure of 50 MPa. The pellet was then placed in an alumina crucible and separated from the crucible by a platinum sheet to avoid reaction with the crucible during the high temperature process, heated to 1200 °C at a rate of 5 °C per min and held for 2 hours. After cooling to room temperature along with the furnace, the calcined pellet was reground by ball milling. The dried powder was sieved through a 75- μm stainless steel sieve to obtain fine powder. About 1 g of the fine powder was then pressed into a graphite die with a diameter of 1 cm and sintered using spark plasma sintering (SPS) technique. It was heated to 1200 °C or 1100 °C at a rate of 100 °C per min and sintered for 20 minutes under the uniaxial pressure of 50 MPa under vacuum. Obtained sintered bodies were sliced, polished to a thickness of about 0.5 mm. They were then placed in a muffle furnace, heated to 800 °C and annealed in air for 8 hours to burn off residual carbon completely and to release mechanical stress.

3.2.2 Characterization

The phases of NLZO pellets were examined by X-ray powder diffraction (XRD) (Bruker D8 Advance XRD, Cu Ka-radiation, step size: 0.02°, time per step: 0.6 second, Panoramic Soller Slit). High-resolution synchrotron powder diffraction data were collected at the beamline BL02B2 of SPring-8 with a wavelength of 0.774194 Å using a Debye-Scherrer camera with MYTHEN solid-state detectors. The densities of the sintered bodies were evaluated using the Archimedes method and the relative densities were calculated. The microstructure and grain size of pellets were characterized by scanning electron microscopy (SEM, S-5200, Hitachi Ltd., Japan). The VESTA [17] software package was used to visualize crystal structure.

3.2.3 Electrochemical measurements

For the electrical measurements, Au electrodes were deposited by sputtering with about a 6 mm diameter and 40 nm thickness on both sides of the sample. The ionic conductivity was measured by the electrochemical impedance spectroscopy (EIS) using a Solartron 1260A impedance/gain-phase analyzer (Solartron Analytical, AMETEK Inc., U.S.) with a frequency range from 10 MHz to 10 Hz in a temperature range of 300–550 °C. Galvanostatic polarization measurement at room temperature using a Solartron S1287 electrochemical interface (Solartron Analytical, AMETEK Inc., U.S.). The impedance spectra were analyzed by equivalent circuit fitting with a (RQ) circuit using the Zview2 software (Scribner Associates Inc., U.S.) or observing the low-frequency real axis intercept to determine the total resistance.

3.2.4 Theoretical method

The density functional theory (DFT) calculations were performed using the Quantum Espresso software package [18]. The initial structure was based on the $P2_1am$ crystal structure of NLZO obtained in Chapter 2, with modifications to the A-site cation occupancy to reflect varying degrees of order, ranging from 0 to 1. For optimizing lattice constants and atomic positions, the vc-relax calculation was employed, using an $8 \times 8 \times 6$ k -point grid ($k_x \times k_y \times k_z$). The SG15 Optimized Norm-Conserving Vanderbilt (ONCV) pseudopotentials, generated with the scalar-relativistic ONCVPSP code (version 2.1.1, dated 03/26/2014, by D. R. Hamann), were used for the pseudopotentials. [19][20] The generalized gradient approximation (GGA) with the revised Perdew-Burke-Ernzerhof (PBEsol) [21] functional was applied for the exchange-correlation functional. The calculations employed the virtual crystal approximation (VCA), in which the pseudopotentials for La and Na atoms were mixed in proportion to their occupancies. A kinetic energy cutoff of 200 Rydberg and a self-consistent field (SCF) convergence threshold of 10^{-7} Rydberg were used to ensure high accuracy. Lattice constants and atomic positions were optimized by minimizing the total energy and forces, with atomic positions relaxed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm. The results of the vc-relax calculation yielded the updated lattice constants and atomic coordinates, which served as inputs for subsequent calculations.

The electronic structure calculations of NLZO were performed by AkaiKKR (MACHIKANEYAMA) [22] using the fully charge self-consistent Green's function Korringa-Kohn-Rostoker (KKR) method combined with the coherent potential approximation (CPA), which allows to account for disorder effects in the self-consistent

way. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) [23] functional was employed for the exchange-correlation functional. The computations were iterated until the total energy converged to 10^{-6} Rydberg. The muffin-tin potential approximation was applied to describe the potential and charge density. The maximum angular momentum $l_{\max}$ for the expansion of the scattering t -matrix was set to 3 for La and Na, and to 2 for O and Zr, respectively. Relativistic effects were included using the scalar relativistic approximation. It should be noted that the GGA-PBE tends to underestimate the values of energy band gaps.

3.3 Results and discussion

3.3.1 Synthesis of $\text{Na}_x\text{La}_{(2-x)/3}\text{ZrO}_3$

NLZO polycrystalline powders with different Na/La ratios were synthesized and the SXRD patterns are shown in Fig. 3.1. The main phase of all samples corresponds to the $P2_1am$ phase in Chapter 2. A large number of impurities are generated when lowering the Na/La ratio, i.e. decreasing x . The main impurities are $\text{La}_2\text{Zr}_2\text{O}_7$, and traces of ZrO_2 . This is consistent with previously reported thermodynamic limits. The phase fractions were obtained by two-phase refinement for SXRD pattern without considering ZrO_2 . The result shown in Fig. 3.2. The composition of NLZO was corrected according to the phase ratios and a pseudo-ternary phase diagram for ZrO_2 - La_2O_3 - Na_2O system was produced, as shown in Fig. 3.3. The actual composition deviates from the target composition due to the generation of pyrochlore. Furthermore, when the x of the target composition changes from 0.40 to 0.35, the corrected composition hardly changes anymore. The target and corrected compositions are listed in Table 3.1. The lattice constants obtained from the refinement were converted to a pseudo-cubic cell and plotted in Fig. 3.4. The lattice constant varies within $\pm 0.06\%$ using the sample with $x = 0.5$ as a reference. The slight decrease in cell volume with increasing sodium and decreasing lanthanum can be attributed to the fact that the radius of the Na^+ ion is smaller than that of the La^{3+} ion.

Although theoretically, due to the large radius and high charge of the La ion, increasing the amount of La in the lattice should have a large effect on the lattice constant because of and introduce vacancies. However, due to thermodynamic limitations, pyrochlore and NLZO chalcocite phases tend to coexist. As a result, the solid solution limit of $\text{Na}_x\text{La}_{(2-x)/3}\text{ZrO}_3$ is low and the amount of imported vacancies is limited.

Table 3.1. The target and corrected compositions for NLZO.

target composition		corrected composition	
Na	La	Na	La
0.35	0.55	0.44	0.52
0.40	0.53	0.44	0.52
0.45	0.52	0.46	0.51
0.50	0.50	0.50	0.50

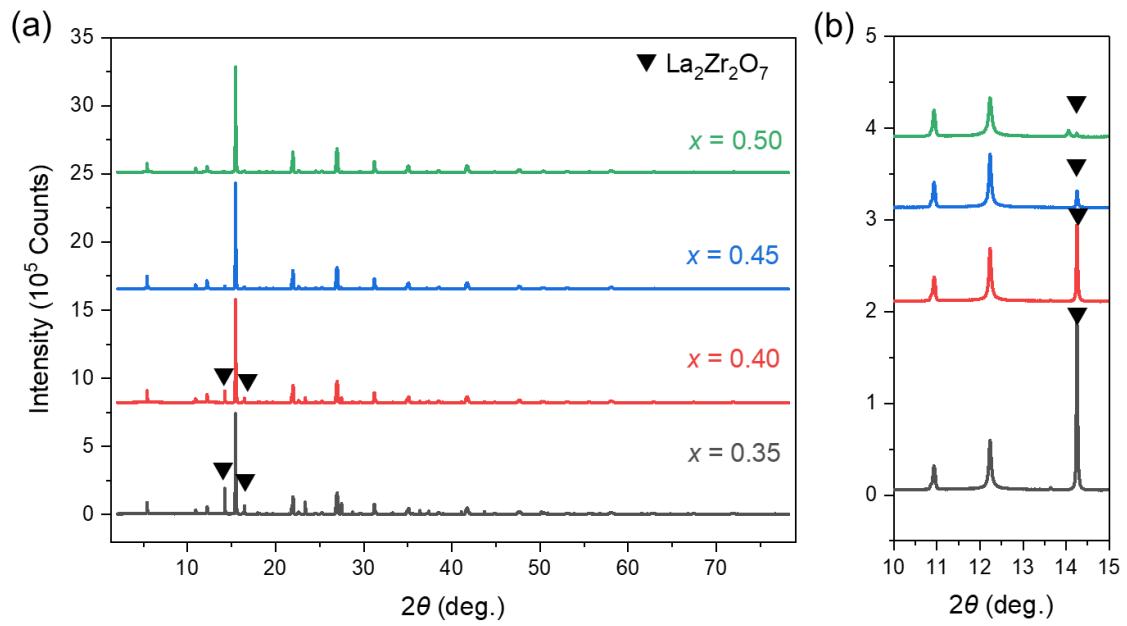


Fig. 3.1. (a) SXRD patterns of $\text{Na}_x\text{La}_{(2-x)/3}\text{ZrO}_3$ polycrystalline powders with different Na/La ratios. (b) Expanded region with main peak of pyrochlore $\text{La}_2\text{Zr}_2\text{O}_7$.

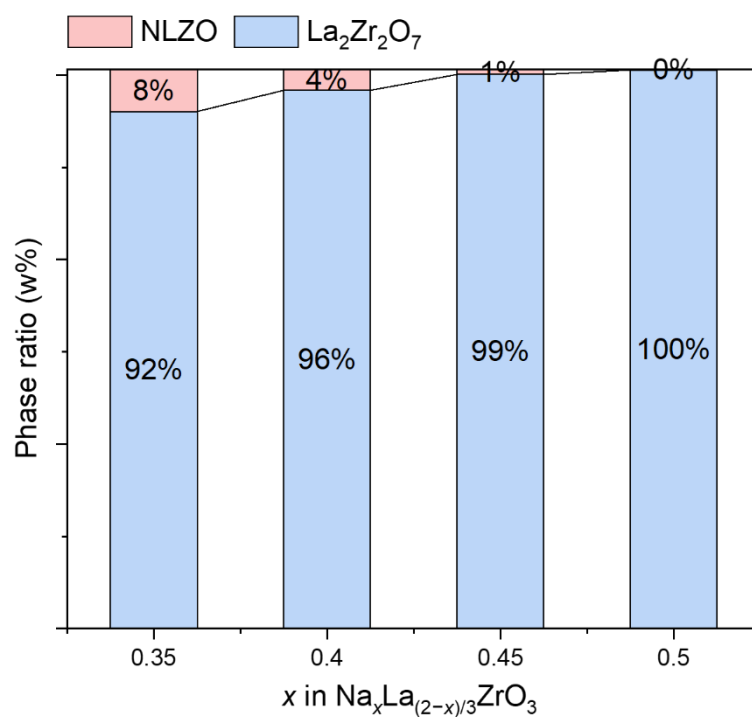


Fig. 3.2. Phase fractions of $\text{Na}_x\text{La}_{(2-x)/3}\text{ZrO}_3$ and pyrochlore $\text{La}_2\text{Zr}_2\text{O}_7$.

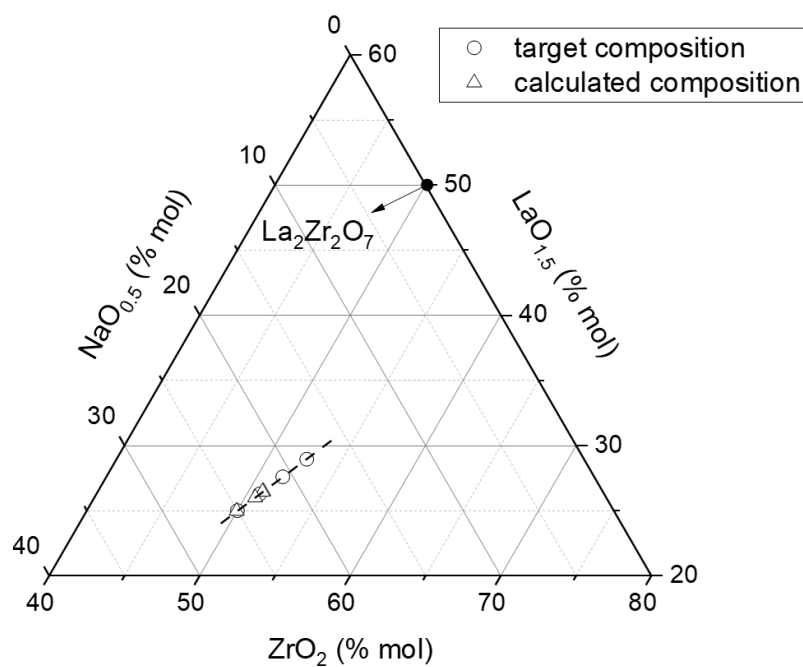


Fig. 3.3. The pseudo-ternary phase diagram of ZrO_2 - La_2O_3 - Na_2O , in which $\text{La}_2\text{Zr}_2\text{O}_7$ is labelled.

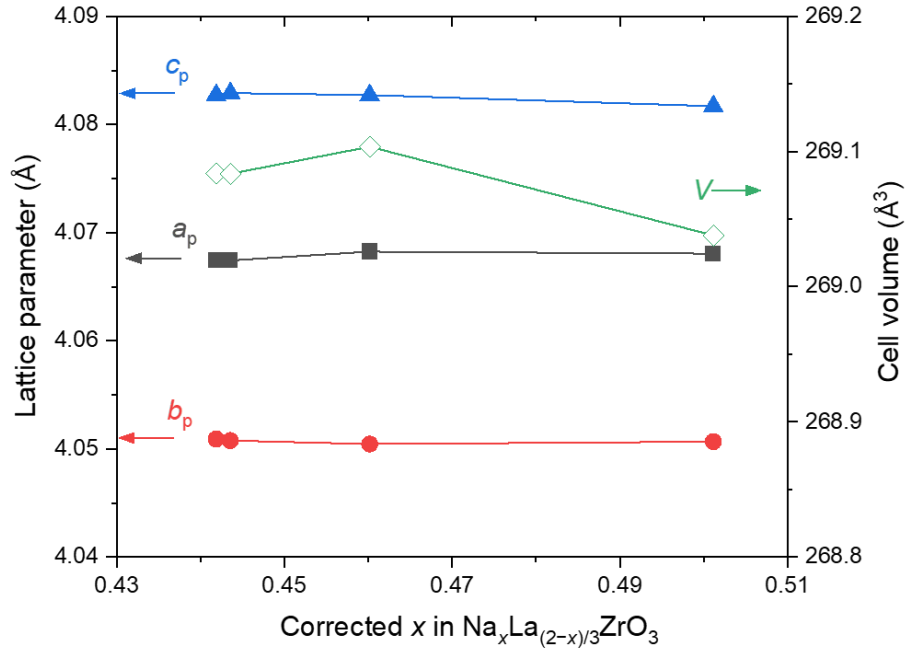


Fig. 3.4. Lattice constants of pseudo-cubic cells of NLZO, relative to the corrected x .

3.3.2 Transport properties of $\text{Na}_{0.5}\text{La}_{0.5}\text{ZrO}_3$

The presence of pyrochlore impurities has a non-negligible effect on the conductivity measurements, therefore, only samples without significant impurities ($x = 0.5$) were electrically measured. $\text{Na}_{0.5}\text{La}_{0.5}\text{ZrO}_3$ powders were sintered by SPS and the XRD results are shown in Fig. 3.5. The samples sintered at 1100 °C and 1200 °C are denoted as SPS1100 and SPS1200, respectively. The XRD pattern of SPS1200 was consistent with the $Pnam$ phase and SPS1100 was consistent with the $P2_1am$ phase. The difference in symmetry between SPS1100 and SPS1200 can be attributed to the fast cooling-rate during spark plasma sintering (SPS), which induces an approximate quenching effect. As mentioned in Chapter 2, quenching can change the symmetry of the NLZO.

Figure 3.6a shows a typical impedance spectrum of SPS1200 and SPS1100 at 500 °C with sputtered Au electrodes on both faces. Only one semicircle is observed in the mid-to high-frequency region and shows DC conductivity at low frequencies. The capacitance values were calculated by RC parallel circuit fitting of the spectra, showing values ~ 100 pF corresponding to the bulk phase. [24]

The conductivity of the samples in the temperature range 250–550 °C are given in the Fig. 3.6b along with the activation energy E_a , which is calculated from the Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad \text{Eq. 3.1}$$

where σ is the conductivity, T is the temperature, σ_0 is the pre-exponential factor, E_a is the activation energy, and k_B is the Boltzmann constant. The activation energy of SPS1100 is almost the same as that of SPS1200, 0.46 and 0.48 eV, respectively. However, the conductivity of SPS1100 is approximately one ten times greater than that of SPS1200. For example, at 500 °C, the conductivity of SPS1100 is $1.8 \times 10^{-5} \text{ S cm}^{-1}$ and of SPS 1200 is $1.9 \times 10^{-6} \text{ S cm}^{-1}$ respectively. Therefore, it can be assumed that the overall conductivity is highly depends on the pre-exponential factor σ_0 .

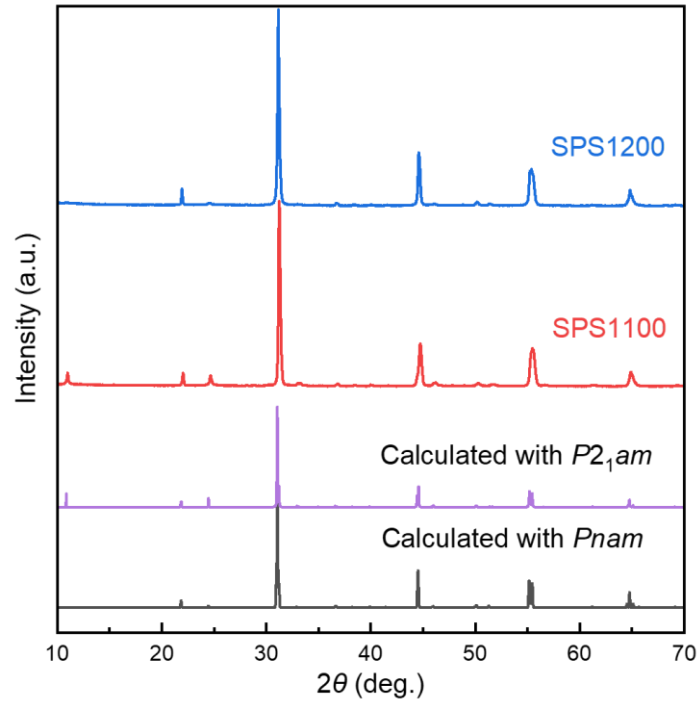


Fig. 3.5. XRD patterns of SPS1200 and SPS1100 for $x = 0.5$.

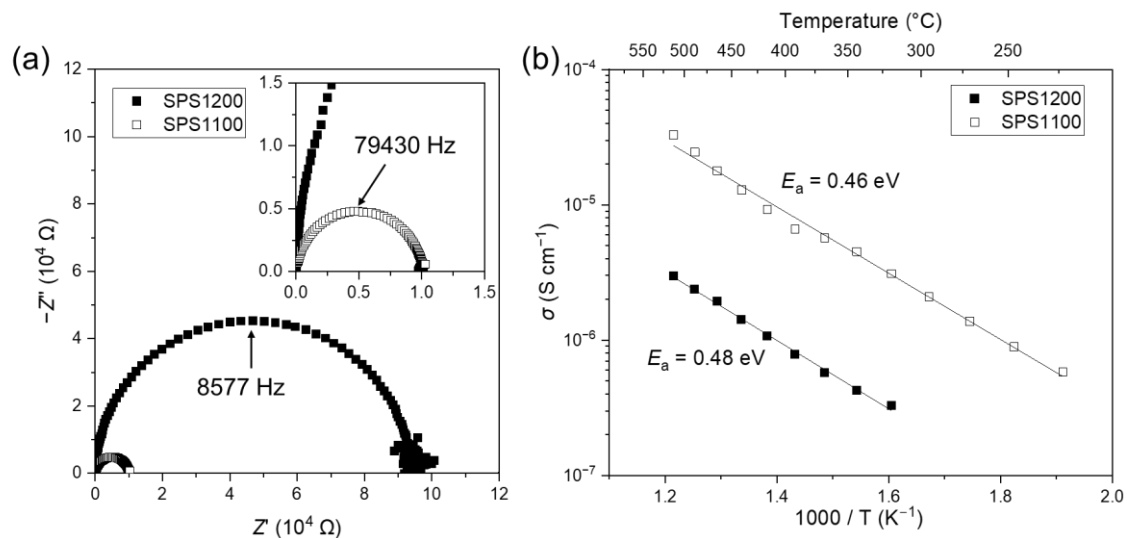


Fig. 3.6. AC impedance measurements and analysis results of SPS1200 and SPS1100. (a) AC impedance spectra at 500°C. (b) The conductivities (σ) in the temperature range 250–550 °C.

At high temperatures, the properties generally follow Arrhenius' law, while at low temperatures, the variation with temperature decreases. The low-temperature side can be interpreted as an electronic conduction due to variable-range hopping (VRH), which also supports that electrons are carriers. Conductivities are plotted in Fig. 3.7 as function of different d of $1/T^{1/(d+1)}$. A suitable linear interval can be identified for each d value. Although the appropriate d -value cannot be identified, a high possibility of VRH can be determined.

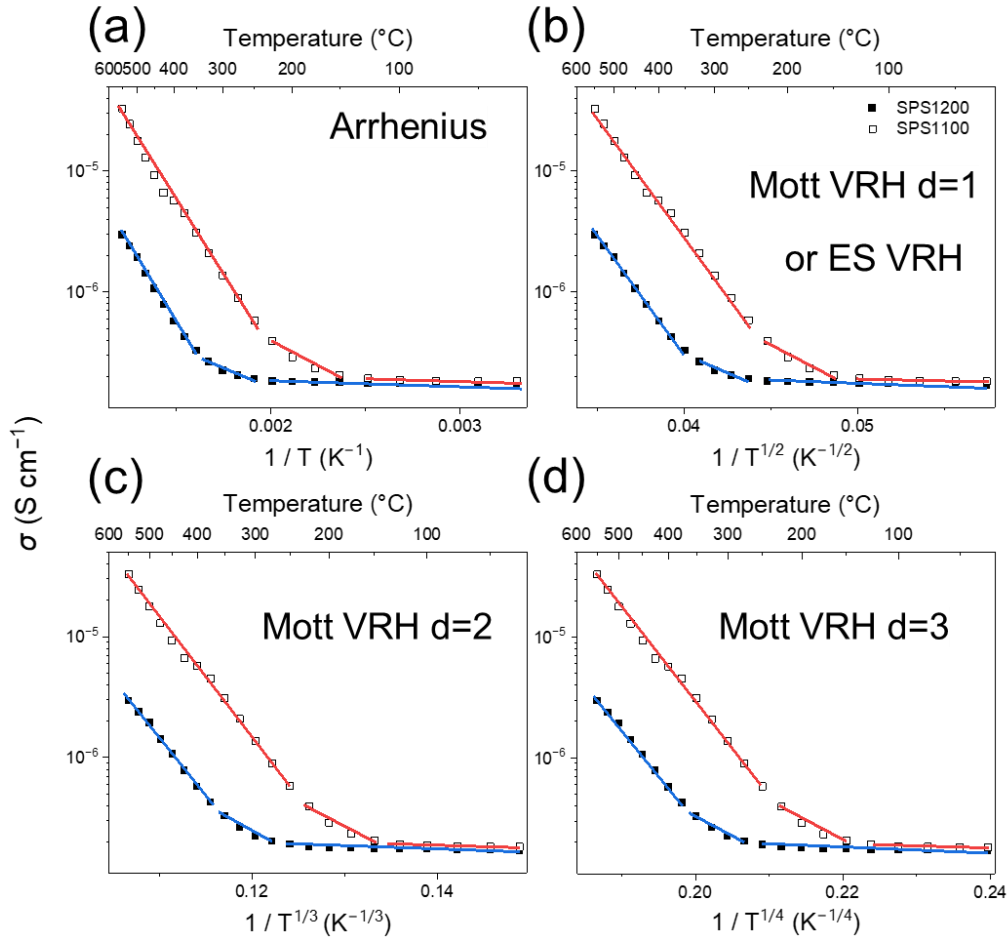


Fig. 3.7. The conductivities (σ) plotted as function of (a) $1/T$, (b) $1/T^{1/2}$, (c) $1/T^{1/3}$, and (d) $1/T^{1/4}$.

3.3.3 Results of DFT calculation

The difference in conductivity between SPS1100 and SPS1200 is likely to be related to their dissimilar crystal structures, and the main difference between the two is the order degree of the *A*-site cations, which is ~ 0.5 and 0 . The order degree is defined as:

$$\frac{|g_{2a} - g_{2b}|}{g_{2a} + g_{2b}} \quad \text{Eq. 3.1}$$

where g_{2a} and g_{2b} are the occupancies of either Na or La ion at the two *A* sites, $2a$ and $2b$. Therefore, theoretically investigating the effect of *A*-site cations ordering on the electron structure will help to understand the reason for the difference in conductivity.

Density functional theory calculations were performed for the $\text{Na}_x\text{La}_{(2-x)/3}\text{ZrO}_3$ system with order degree from 0 to 1. The order degree is modulated by varying the occupancy of La and Na in the La-rich and La-poor layers of the input file and keeping the total occupancy of La and Na as 1. For example, for an order degree of 0.5, the occupancy of La(2) and Na(2) in the La-poor layer is 0.25 and 0.75, respectively, while the occupancy of La(1) and Na(1) in the La-rich layer is 0.75 and 0.25, respectively. The notation for atoms corresponds to [Table 2.2](#) and [Fig. 2.8b](#) in Chapter 2.

Although the KKR-CPA method is well suited for calculating the electronic structure and properties of solid solutions, it is not well suited for geometry optimizations and energy calculations, and therefore geometry optimizations are performed by the VCA method. The VCA method is realized by mixing the pseudo-potentials of Na and La atoms using Quantum Espresso. The relative energies of each structure calculated by VCA method are plotted as a function of the relative order degree in [Fig. 3.8](#), using the lowest energy structure as a reference. It is observed that as the order degree increases, the energy decreases, with the lowest energy found in the fully ordered structure. This suggests that the fully ordered structure is more stable at 0 K, consistent with the experimental results presented in Chapter 2.

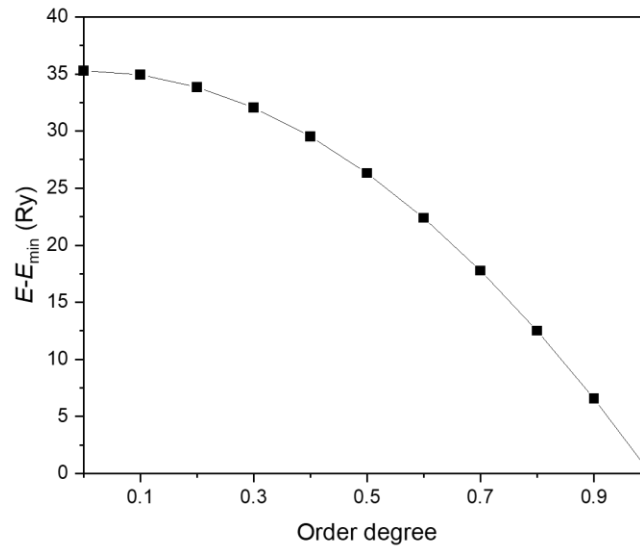


Fig. 3.8. The relative energy per cell calculated by VCA method plotted as a function of the relative order degree.

The optimized lattice vectors, converted to pseudo-cubic cells along with the cell volume, are plotted as a function of the order degree in Fig. 3.9. It is evident that both the a_p and b_p , as well as the cell volume, decrease with increasing order degree, whereas the opposite trend is observed for the c_p . It is well established that ordered structures typically exhibit higher stacking efficiencies, leading to smaller cell volumes. The elongation of the c axis may be attributed to the displacement of Zr ions due to the uneven charge distribution between layers, which enhances the covalent bonding between the Zr ions and the vertex oxygen atoms resulting in changes to the bond lengths. The maximum error between the lattice constants and the experimental values is $\sim 1\%$, within commonly reported ranges. [25]–[28]

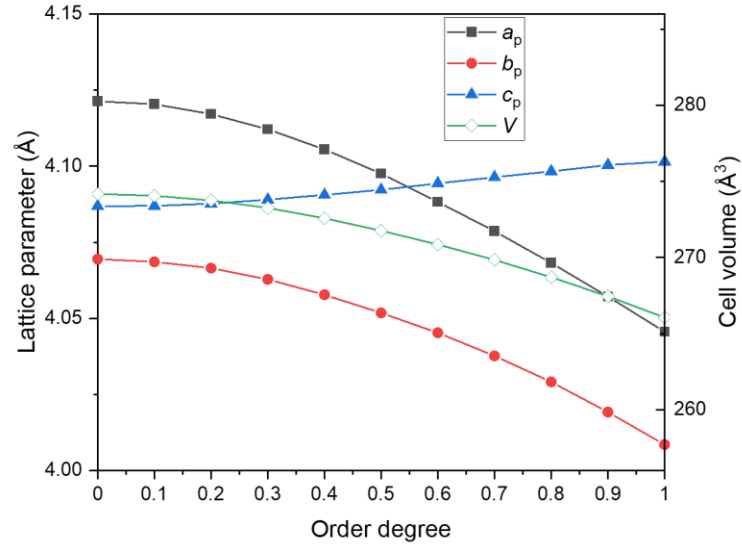


Fig. 3.9. The optimized lattice vectors, converted to pseudo-cubic cells along with the cell volume, plotted as a function of the order degree.

Electronic structure calculations were performed using the structure obtained from the VCA method, by KKR-CPA method. The total density of states (TDOS) for structures with varying degrees of ordering is plotted in Fig. 3.10, with the Fermi energy level defined as the zero point. As the degree of ordering increases, the conduction band minimum (CBM) lowers, indicating a narrowing of the bandgap. However, a notable exception occurs when the degree of ordering reaches unity (i.e., fully ordered): the CBM abruptly increases. In addition, new occupied states appear in the range of -5 to -15 eV

as the order degree rises. Analysis of the local density of states (LDOS) reveals that the new occupied states originate from 2p orbital of Na(1) located in La-rich layer. This can be attributed to the coulombic interaction of the La(1) ions with the electrons of Na(1). The CBM is primarily associated with La(2) atoms located in the La-poor layer. The LDOS for all atoms of the structure with an order degree of 0.5 is shown as an example in [Fig. 3.11](#).

The LDOS for La(2) atom in the La-poor layer for structures were shown in [Fig. 3.12](#). There are no data at order degree of units because the La(2) atoms disappear when the order degree is changed to units. With increasing degrees of ordering, the concentration of La atoms in the La-poor layer decreases, leading to a reduction in the CBM and its corresponding density of states. When the structure becomes fully ordered (degree of ordering = unit), La atoms are entirely absent from the La-poor layer, causing the abrupt change in the CBM. Therefore, it can be assumed that the main factor affecting the CBM as well as the band gap is the La(2) atom in the La-poor layer.

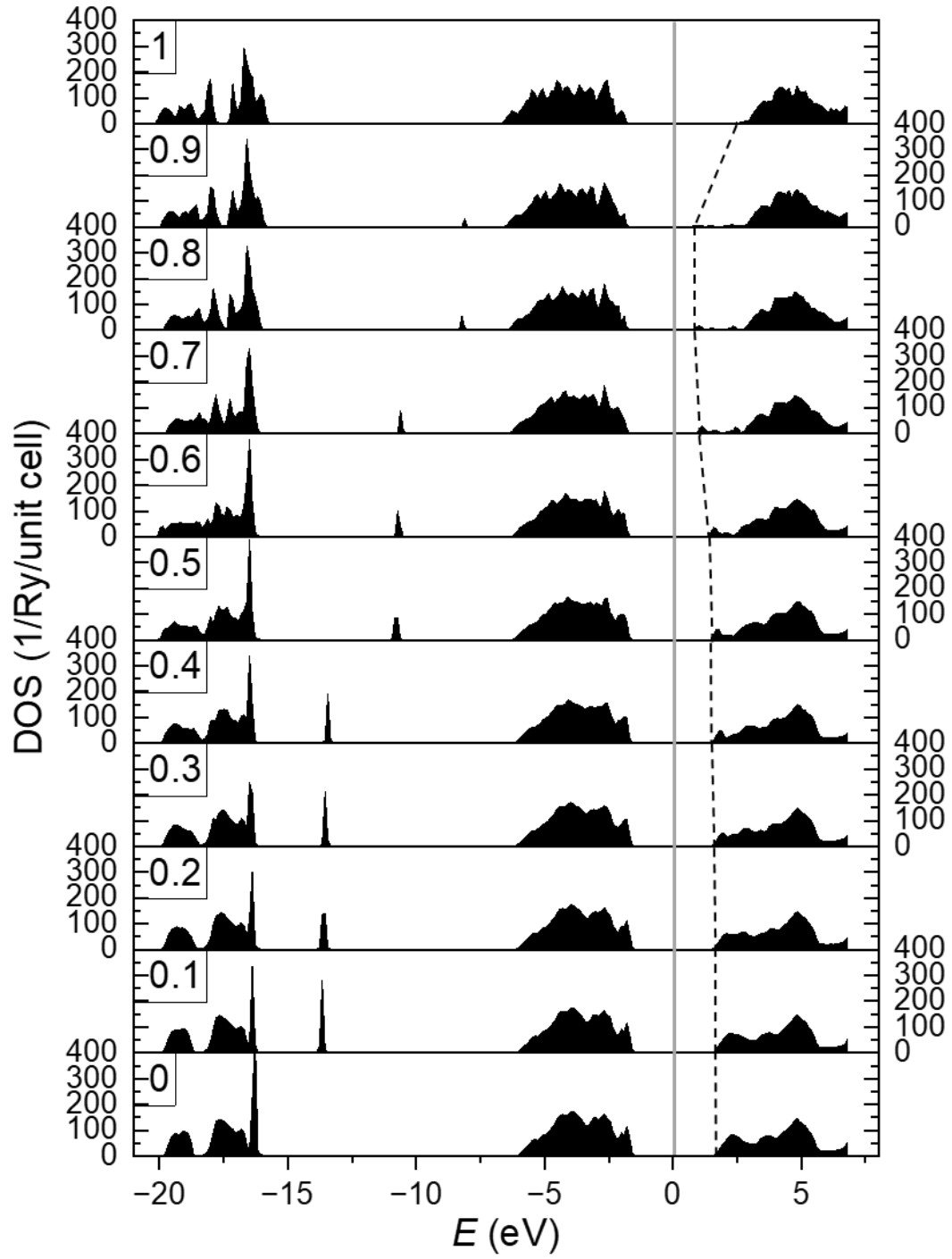


Fig. 3.10. The total density of states (TDOS) for structures with varying order degrees, with the Fermi energy level defined as the zero point. The solid grey line indicates the Fermi energy level as the zero point. The dashed line connects the CBMs.

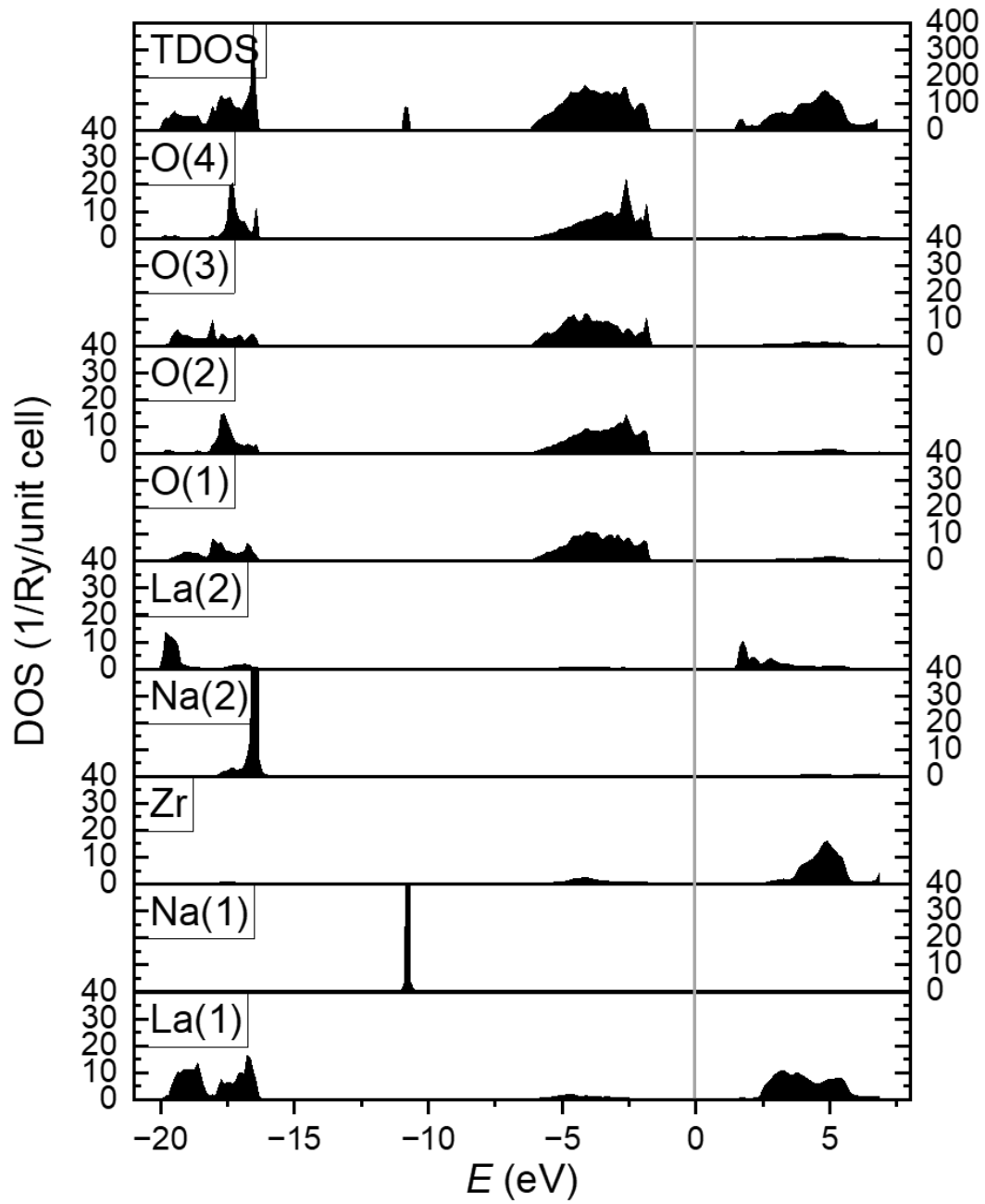


Fig. 3.11. The LDOS of the structure with an order degree of 0.5 for each atom. See Table 2.2 in Chapter 2 for the corresponding positions of the atoms, where La(2) is in the La-poor layer.

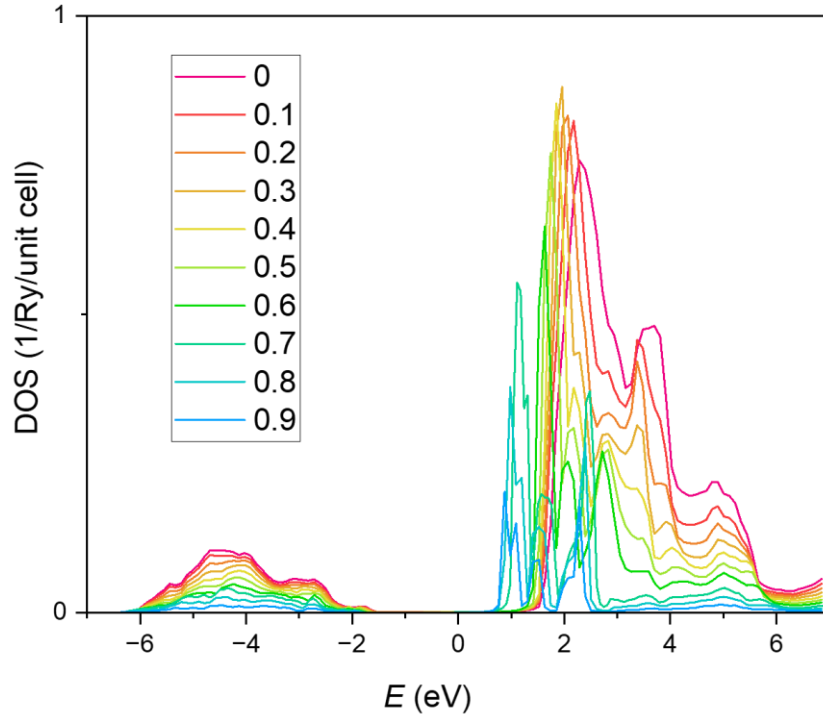


Fig. 3.12. The local density of states (LDOS) of La atom in the La-poor layer for structures with varying order degrees, with the Fermi energy level defined as the zero point. Since the La atom in the La-poor layer disappears when the order degree changes to unit, there is no data with the order degree of unit.

To further investigate the composition of the CBM, the DOS of La(2) was projected onto its orbitals and plotted in [Fig. 3.13](#) as an example of a structure with an order degree of 0.5. The CBM is mainly contributed by the 5d orbital of La(2), and the 5d electrons also have occupied states in the valence band. It is worth mentioning that the 4d orbital of Zr and 5d orbital of La(1) are also contribute to the conduction band. They have higher energies than the 5d orbital of La(2), but are more dispersed. When La(2) disappears, the 4d of Zr and 5d of La(1) become CBM, shown in [Fig. 3.14](#).

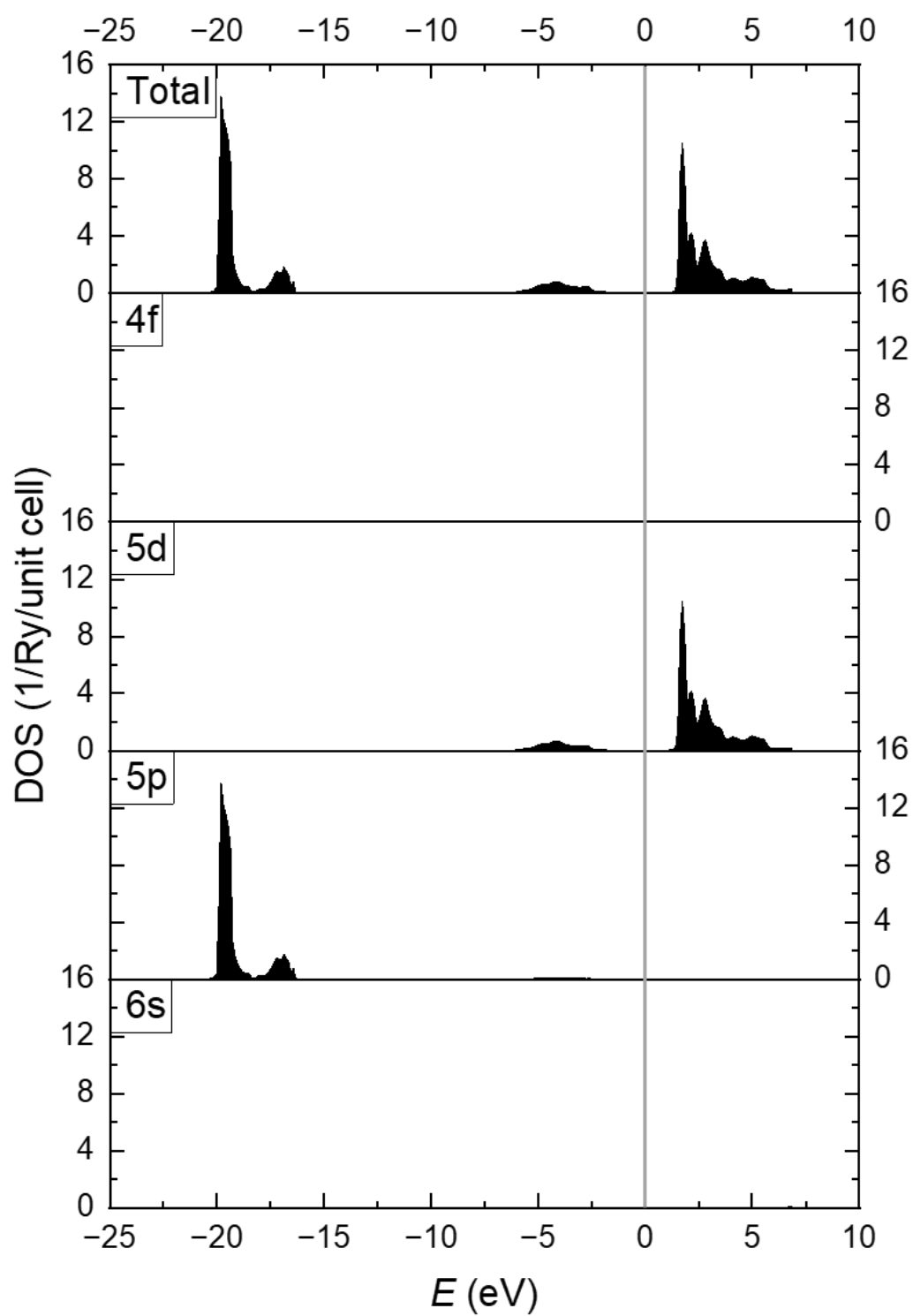


Fig. 3.13. The PDOS of the structure with an order degree of 0.5 for La(2) atom.

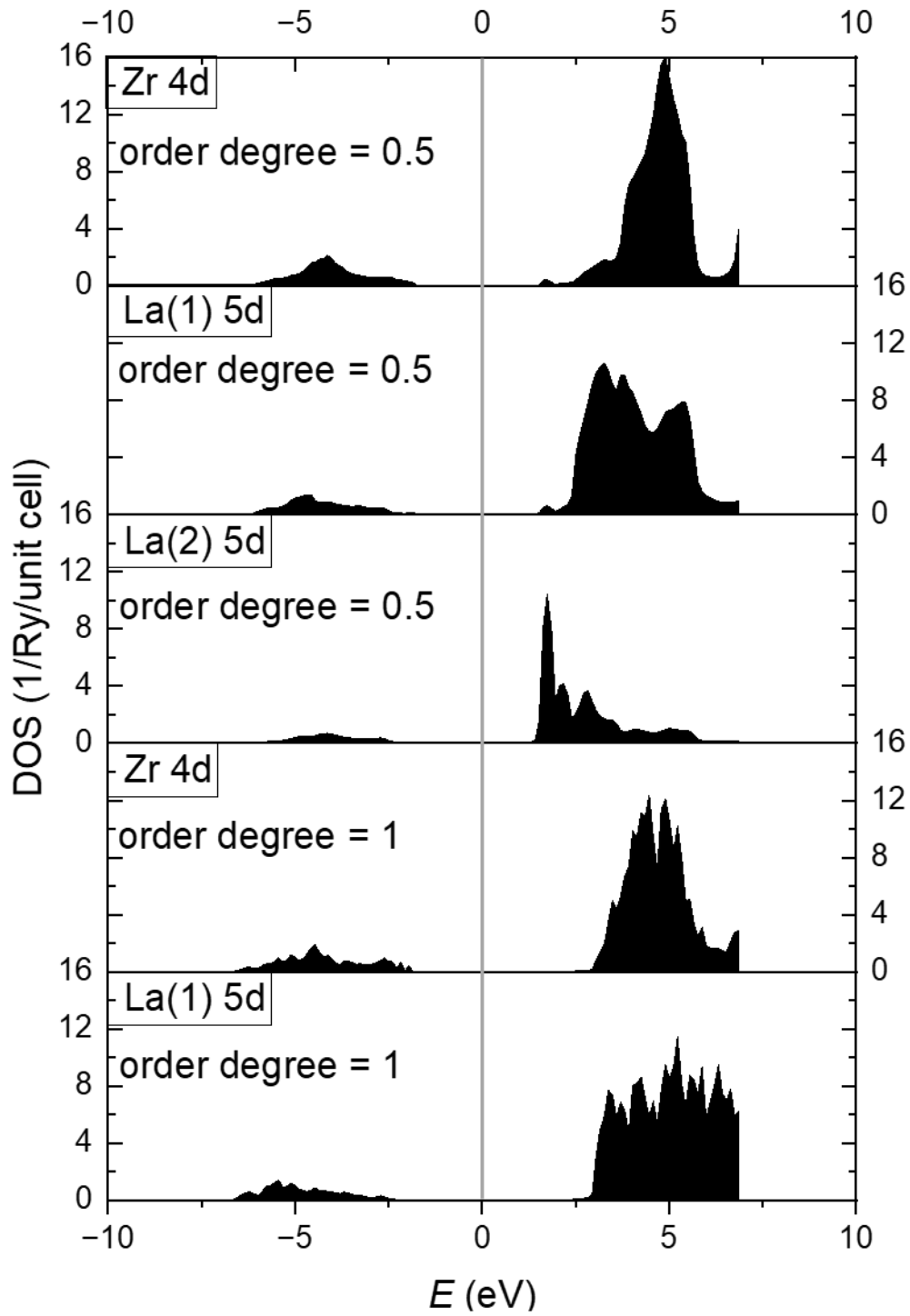


Fig. 3.14. The PDOS of the structures with order degrees of 0.5 and 1, for Zr, La(1), and La(2) atoms. When order degree = 1, no La(2) exists.

Bloch spectra (energy bands) were calculated along suitable high symmetry point paths in the Brillouin zone and displayed in Fig. 3.15. Changes of CBM can be found the same as the analysis for DOS. The blurred regions in the energy band diagram, arise from disorder effects. [22] In disordered structures, the eigenvalue of the crystal momentum is not well-defined, leading to a broadening of the Bloch spectral function. This blurring effect disappears when the structure becomes fully ordered. The changes in the CBM are particularly intriguing. As the degree of ordering increases, the CBM gradually decreases, accompanied by a blurring of the energy bands in its vicinity. These bands become discrete, then lose coherence and eventually disappear altogether. This transition leads to the emergence of new CBM states at higher energy levels when fully ordered. The energy values of these bands, which can correspond to the 5d orbitals of La(2) and have flat energy bands with strong localization effects, can be considered as the creation of defect energy levels by La(2). As the degree of ordering rises, the energy level corresponding to the 5d of La(1) decreases, and the energies of its bands are more dispersed, so that the carriers have a higher mobility. Excitations from these defect levels, which capture electrons, to the conduction bands consisting of La(1), are thought to correspond to the observed activation energy of 0.5 eV

Due to the broadening of the Bloch spectral function, reading the bandgap directly from the plot is limited by the energy resolution of the calculation. A better practice is to obtain it by fitting the Bloch spectral function with Lorentzian functions. For convenience, the band gap is estimated here by visually inspecting the peak positions of the Bloch spectrum. The results were plotted in Fig. 3.16, and the accompanying error bars indicate the energy resolution of the computational process. Note that GGA-PBE usually underestimates the bandgap, so it is more important to focus on the trend of the change as opposed to the absolute values. It can be found that despite the error due to the energy resolution, it can still be concluded that the band gap narrows with increasing order degree. In addition, to compare the bandgaps of NLZO with different order degrees, the UV-vis diffuse reflectance measurements were performed for SPS1200 and SPS1100, and the direct bandgaps were estimated by Kubelka-Munk equation shown in Fig. 3.17. It can be found that the band gap of SPS1200 is slightly higher than that of SPS1100, which is qualitatively consistent with the calculated results.

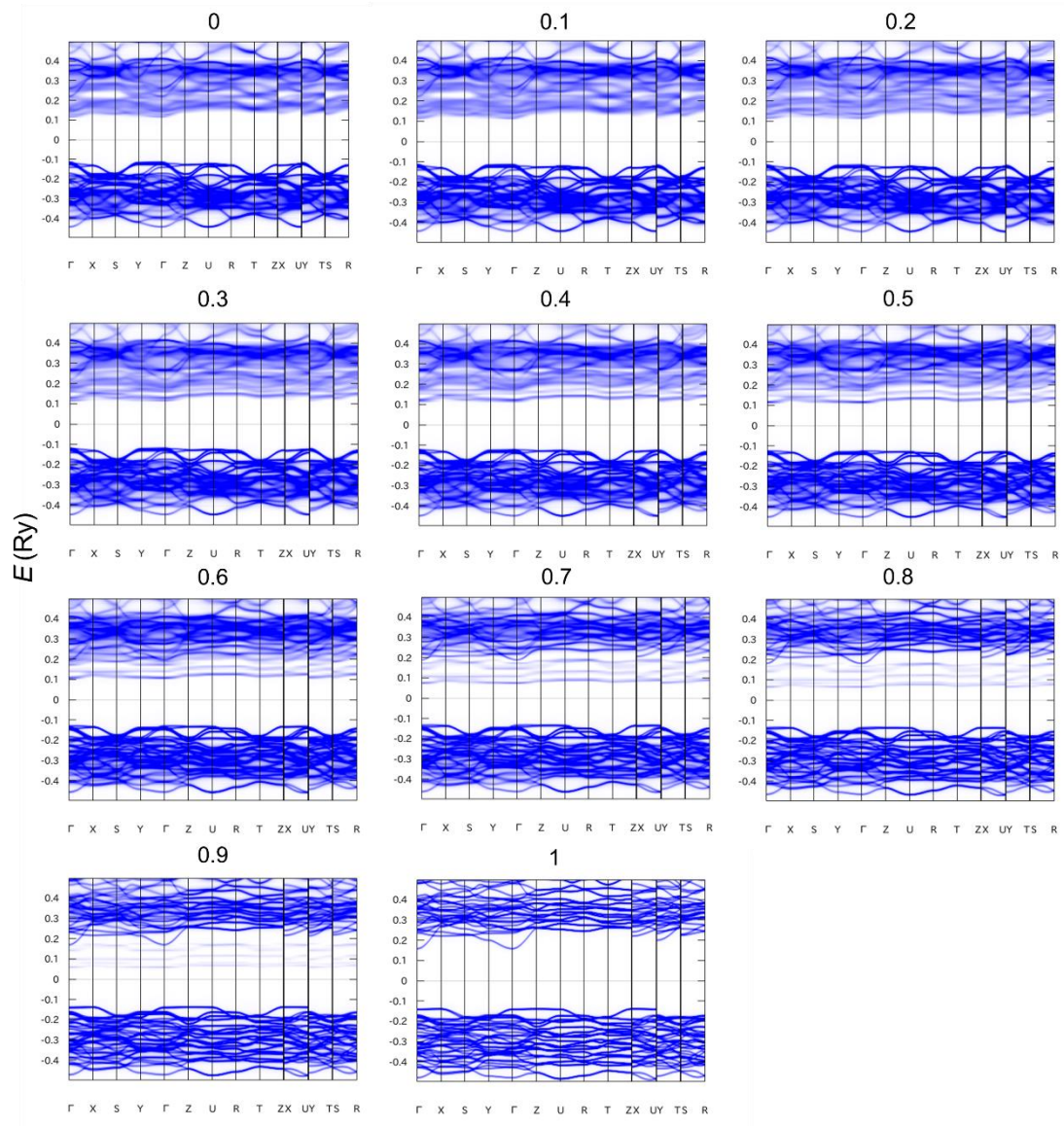


Fig. 3.15. Energy bands calculated along suitable high symmetry point paths in the Brillouin zone. The numbers above each figure represent the order degree.

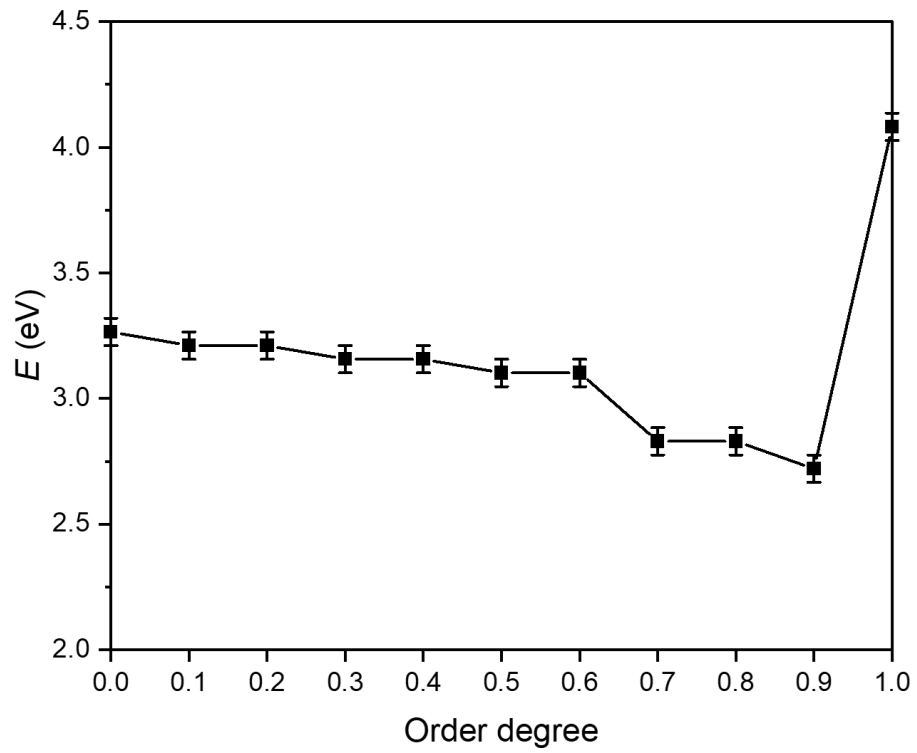


Fig. 3.16. Direct energy gap values estimated from band structures plotted as a function of the relative order degree. The error bars indicate the range of energy resolution of the computation.

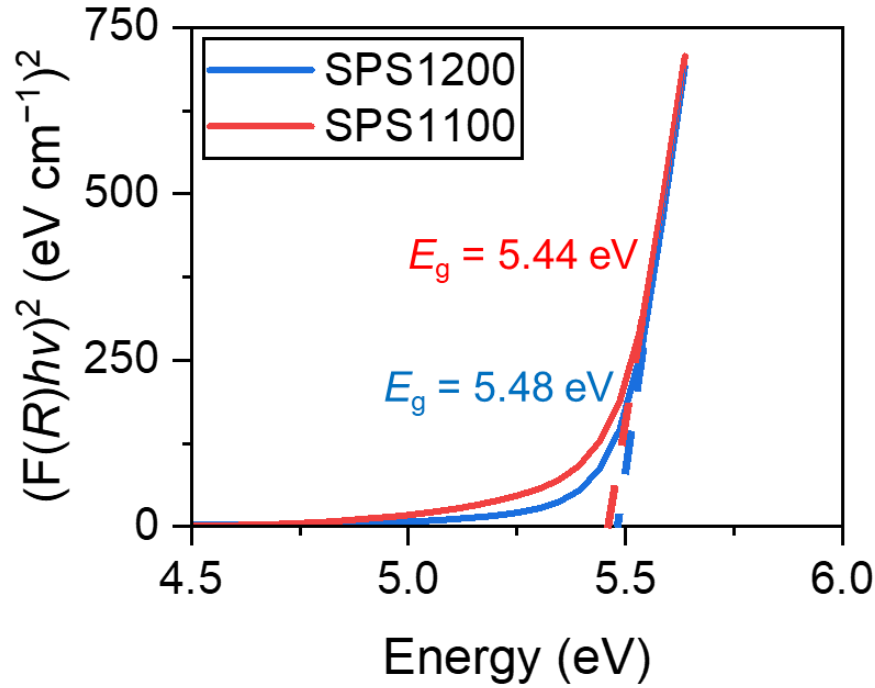


Fig. 3.17. Direct energy gap estimated from UV-vis diffuse reflectance by Kubelka-Munk function.

3.4 Conclusion

$\text{Na}_x\text{La}_{(2-x)/3}\text{ZrO}_3$ with different Na/La ratios were synthesized by solid-phase method. Due to thermodynamic limitations, when deviating from the ideal ratio $\text{Na/La} = 1$, the perovskite phase coexists with the pyrochlore phase. Compositional correction of $\text{Na}_x\text{La}_{(2-x)/3}\text{ZrO}_3$ by XRD refinement revealed a low solid solution limit.

$\text{Na}_{0.5}\text{La}_{0.5}\text{ZrO}_3$ powder were sintered by SPS, and the ceramics with two space groups were obtained. Electrical measurements revealed that the electrical conductivity of the SPS1100 ($P2_1am$ phase) is almost 10 times higher than that of the SPS1200 ($Pnam$ phase), and the conductivity is mainly electronic. The activation energies of the conductivity are similar and the main factor affecting the conductivity is the pre-exponential factor.

The electronic structures of $\text{Na}_{0.5}\text{La}_{0.5}\text{ZrO}_3$ with different order degree have been investigated based on the density functional theory. Sufficient relaxation of $\text{Na}_{0.5}\text{La}_{0.5}\text{ZrO}_3$ cells were carried out by the VCA method, and the increase in order degree improved the stacking efficiency and reduced the volume of cells, and the structure with higher order degree is more stable at low temperatures, which is consistent with the

experimental results in Chapter 2. The electronic structures were calculated by the KKR-CPA method. Density of States (DOS) and energy bands reveal that the 5d orbital of La(2) atoms in the La-poor layer exert a significant influence on the bandgap. As the order degree increases, i.e., the concentration of La(2) atoms in the La-poor layer decreases, the bandgap narrows. When the ordering degree reaches unit, the La atoms in the La-poor layer vanish, leading to an abrupt increase in the bandgap. The 5d orbitals of La(2) located in the La-poor layer form defect energy levels near CBM, while the 5d orbitals of La(1) located in the La-rich layer form conduction bands with dispersed energy, and these dispersed bands contribute to the carrier mobility. The difference in conductivity between the SPS1200 (*P_{nam}* phase) and SPS1100 (*P_{21am}* phase) can be mainly attributed to the difference in electronic structure due to the A-site cation ordering.

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CHAPTER 4 Sodium Ion Conduction in Perovskite-Type

Sodium Lanthanum Niobate Ceramics

4.1 Introduction

Sodium-ion batteries (SIB) offer a promising alternative to widely used lithium-ion batteries, featuring advantages in cost, safety, and battery performance particularly in terms of rate and temperature properties, as well as resource availability [1][2]. Sodium-ion all-solid-state batteries (Na-ion ASSB) may combine the benefits of sodium-ion batteries with those of solid-state materials and designs [3]–[5]; ASSBs provide superior thermal stability for wide temperature operation and circumvent the risk of fire and explosion by eliminating the liquid electrolytes in traditional batteries. To enhance the performance and manufacturability of these batteries, it is essential to explore solid electrolyte materials, electrode active materials, and their interface materials [6][7].

Various categories of Na-ion conductors have been investigated, including oxide-based Na- β/β' -Al₂O₃ [8] and NASICON type Na_{1+x}Zr₂(SiO₄)_x(PO₄)_{3-x} (NZSP) [9]–[12], sulfides [13], borohydrides [14], and halides [15][16]. The Li-counterpart of NASICON, such as Li_{3-x}Al_{2-x}Ti_x(PO₄)₃ (LATP) [17] and Li_{3-x}Ga_{2-x}Ti_x(PO₄)₃ [18], demonstrates good compatibility of ionic conductivity reaching 10⁻³ S cm⁻¹ at room temperature and sinterability as low as ~900 °C, making them suitable electrolytes for commercial oxide-based ASSBs.

Equivalent or higher Li ion conductivities have been observed in perovskite-type Li_xLa_{(2-x)/3}TiO₃ (LLT) [19]. The A site of perovskite LLT is described as Li_xLa_{(2-x)/3}□_{(1-2x)/3} with a formal composition range of 0 ≤ x ≤ 0.5, where □_{(1-2x)/3} represents the A-site vacancy and its ‘occupancy’. Although the Li⁺ ion migration is principally mediated by exchange with the vacancy, under certain condition, LLT crystal can accommodate interstitial Li⁺ ions, which enhance the concentration of the vacancy as well as the Li⁺ ion conductivity [20].

Following this, Na-based perovskites have been explored with expectation of achieving high Na⁺ ion conductivity among a variety of chemical composition and structure derivatives. Ruiz *et al.* [21] investigated the Na-counterpart of LLT, Na_xLa_{(2-x)/3}TiO₃ (NLT), and reported the total ionic conductivity on the order of 10⁻⁷ S cm⁻¹ at 400 °C for a ceramic sample with x = 0.42. NLT (0 < x < 0.5) crystallizes in space group *Ibmm* and

$Z = 4$, in which TiO_6 octahedra are tilted in the manner of $a^-a^-b^0$ in Glazer notation [22]. The limited conductivity compared to LLTs is attributed to the narrower bottlenecks formed by four adjacent TiO_6 octahedra, restricting the passage of Na^+ ion to neighboring vacant sites.

The Na^+ ionic conductivity in the Zr^{4+} -substituted derivative of NLZ, $\text{Na}_x\text{La}_{(2-x)/3}\text{ZrO}_3$ (NLZ) was investigated by Toyomura *et al.* [23], aiming to expand the Na^+ ion migration bottleneck by replacing Ti^{4+} with the larger Zr^{4+} ions. They reported a higher bulk conductivity of $7.2 \times 10^{-5} \text{ S cm}^{-1}$ at 350°C and a lower activation energy of 0.26 eV in a spark plasma-sintered ceramic sample with a composition of $\text{Na}_{0.32}\text{La}_{0.48}\text{ZrO}_{2.9}$. The unit cell of NLZ is characterized by $Pnma$ symmetry and $Z = 4$ with a different type of octahedral tilting, $a^-b^+a^-$. An experimental and theoretical collaboration study [24] suggested that a limited concentration of A-site vacancies is a crucial for the limited ion conductivity in NLZ perovskites, in which Na^+ ion interstitial is not favorably formed. In addition, the poor sinterability and eliminating secondary phases are challenges for NLZ perovskites.

Compared to the perovskites with tetravalent B-site cations, $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$ (NLN) with pentavalent Nb^{5+} can incorporate higher concentration of A-site vacancies. The A-site formula $\text{Na}_x\text{La}_{(1-x)/3}\square_{(2-2x)/3}$ with $x = 0$ gives twice as high as vacancy concentration compared to the Ti-counterpart, and formally allows for a wider x range of $0 \leq x \leq 1$. Furthermore, better sinterability has been suggested for preparation of NLN ceramics. To date, $\text{La}_{1/3}\text{NbO}_3$ and NLN have been investigated as microwave dielectrics [25][26], and the electrical conductivity has been reported only for $x = 0.25$ [27].

Therefore, this study investigates the electrical conductivity of $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$ ceramics over a broader composition range ($0.15 \leq x \leq 0.45$) to identify the best conductive condition and to elucidate the structural and chemical factors to determine the Na^+ ion conductivity. We demonstrate that dense ceramics are obtained through conventional pressureless sintering, and the best Na^+ ion conductivity is available for $x = 0.25$. Its conductivity of $7.0 \times 10^{-4} \text{ S cm}^{-1}$ at 350°C is approximately two orders of magnitude higher than the highest conductivity found in NLZ perovskites. High dielectric constant >200 is also characteristic for NLN perovskites. A brief experimental evaluation and its relevance to the Na^+ ion conduction will be described, although a more detailed investigation about dielectric properties will be presented elsewhere.

4.2 Experimental

4.2.1 Preparation of Materials

The reagent grade powders of Na_2CO_3 (Kojundo chemical laboratory, Japan; purity of 99%), Nb_2O_5 (Fujifilm Wako pure chemical corporation, Japan; 99.9%), and La_2O_3 (Kojundo; 99.9%) were weighed in ratios to obtain $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$ ($x = 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45$), for which 20 mol% excess of Na_2CO_3 for the formal amount was added for a compensation for sodium component loss during high-temperature processes. Their mixture was ball-milled in a zirconia pot with anhydrous ethanol and zirconia balls at 350 rpm for 12 h using a Pulverisette-6 planetary mill (Friche, Germany). After drying at 80 °C, the mixture was pressed into pellets under a uniaxial pressure of 40 MPa. The pellets were placed in alumina crucibles with inserting a platinum sheet for preventing a reaction with alumina, followed by heating at 900 °C for 12 h in air. The calcined pellets were ground again by ball milling at 350 rpm for 12 h, and dried again. The powder of ~0.2 g was uniaxially pressed and further cold-isostatically pressed (CIP) into a disk with 12 mm in diameter at 270 MPa. Finally, the pellets were sintered at 1350 °C for 12 h, followed by furnace cooling in air.

4.2.2 Characterization

Crystalline phases in the powdered samples were analyzed by X-ray diffractometry (XRD, Bruker AXS D8 Advance, Germany) with $\text{Cu K}\alpha$ radiation at a diffraction angle step of 0.03° and an integration time of 0.6 s per step. Rietveld refinements were performed for the measured patterns using TOPAS software (Bruker, Germany). Crystal structures were visualized using VESTA software [28]. The densities of the sintered bodies were determined using Archimedes method, and the relative density was calculated with respect to the theoretical density calculated from the crystallographic parameters determined by Rietveld analysis. Microstructure and element distributions of the ceramic samples were examined using a scanning electron microscope (SEM, JCM-700, JEOL, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS). Particle size was analyzed using SEM Particle Detector Tool (DP Technology, China) software.

4.2.3 Electrochemical measurements

For electrical measurements, Au electrodes with 6 mm in diameter and 40 nm in thickness were deposited on both sides of the samples by vacuum evaporation. Electrical properties were measured using an SP-150 potentiostat (BioLogic, France). The

temperature was controlled in a range from 30 to 350 °C using a sample stage and a temperature controller (THMS350V, LINKAM, UK) mounted in a home-made high-vacuum chamber, which was evacuated to the pressure lower than 10^{-3} Pa. Electrochemical impedance spectroscopy (EIS) was carried out with an AC modulation amplitude of 200 mV in a frequency range from 1 MHz to 0.1 Hz. The impedance spectra were analyzed by fitting with an equivalent circuit model using EC-Lab software (BioLogic). DC polarization measurements were performed by application of 0.5 V at 30 °C.

4.3 Results and discussion

4.3.1 Crystal chemistry

Sintered ceramic samples had ivory-colored appearances. XRD patterns were collected from powdered samples, and those for $x = 0.15$ and 0.25 are shown in Fig. 4.1a. (All XRD data are provided in Supplementary Fig. B1.) All peaks correspond to perovskite crystals except trace of secondary phase of LaNbO_4 . Due to its limited amount (~ 1 wt%), it does not significantly impact interpretation of experimental results. The XRD pattern of $x = 0.15$ aligns with that of orthorhombic $\text{Na}_{0.12}\text{La}_{0.29}\text{NbO}_3$ (ICSD-167753; space group *Pmmm* [26]), while the pattern of $x \geq 0.2$ closely resembles that of tetragonal $\text{Na}_{0.25}\text{La}_{0.25}\text{NbO}_3$ (ICSD-167754; *P4/mmm* [26]). To confirm the crystallization in perovskite structures and to determine their lattice parameters, XRD data were refined by the Rietveld method. (For detail, see Supplementary Fig. B2 and Table B1.) Both the orthorhombic and tetragonal unit cells of $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$ are doubled ($Z = 2$) with respect to the primitive perovskite unit along *c* axis, with no octahedral rotation, forming two crystallographically unique *A* sites in each symmetry (Fig. 4.1b). These two refined unit cells represent extreme cases among our samples. In $x = 0.15$, La and Na are almost separately distributed in the two *A* sites, forming an *A*-site ordered orthorhombic structure, while in $x = 0.25$, the degree of *A*-site ordering is very small, i.e., almost random distribution. In a previous report [26], superlattice reflections due to the *A*-site cation ordering was observed for $x \leq 0.2$. In our data, pronounced superlattice reflections are observed in $x = 0.15$, while they became very weak in $x = 0.2$. The discrepancy from the previous report may stem from a difference in synthesis conditions. Variations in lattice parameters versus x are plotted in Fig. 4.1c. There is a general trend that the unit-cell volume monotonically decreases with increasing x by substitution of smaller size Na^+ ion

for $1/3\text{La}^{3+}$ ion and $2/3$ vacancies. Along with the phase transition, deviated a , b and $c/2$ parameters tends to align so that $a = b \sim c/2$.

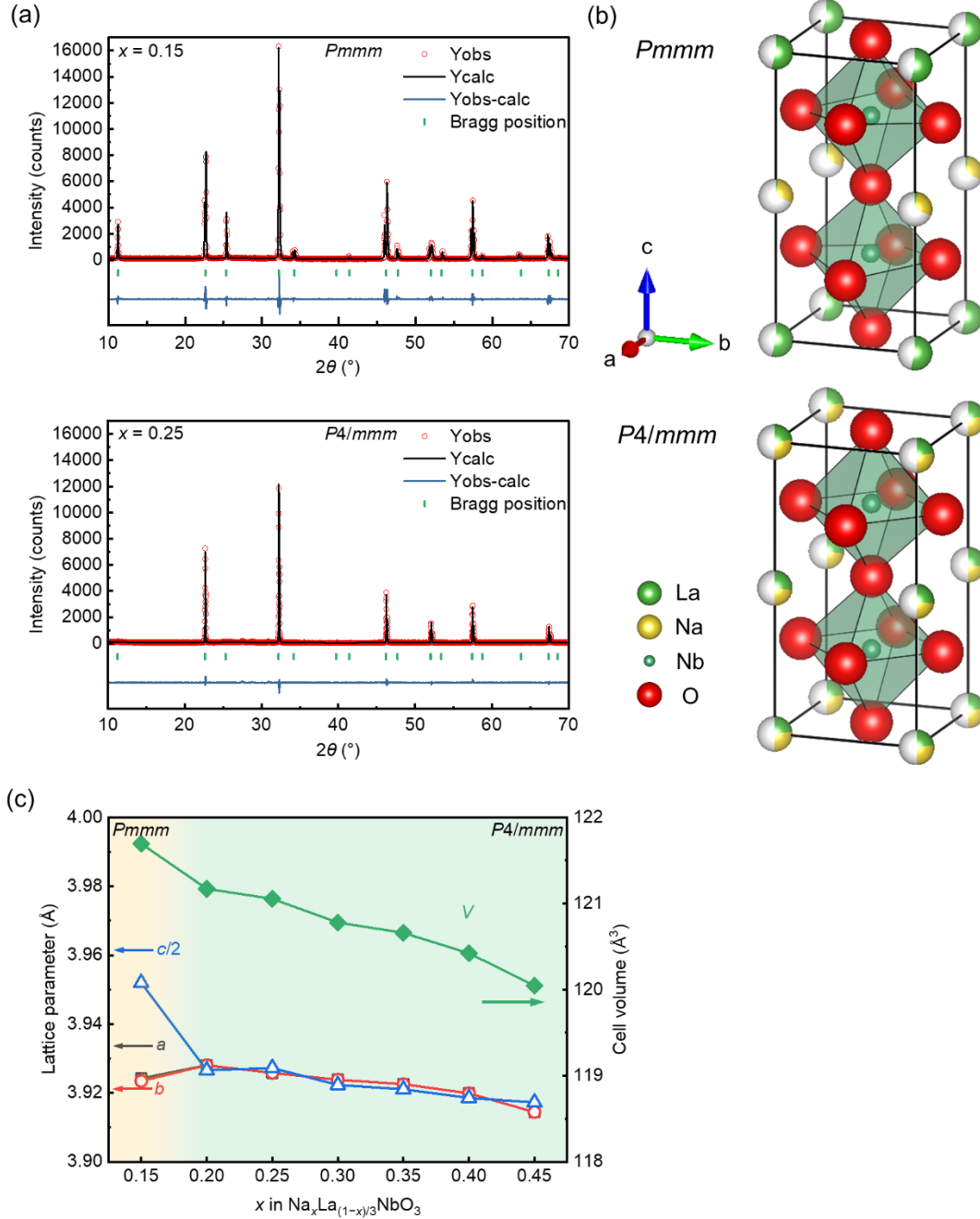


Fig. 4.1. Crystallography of $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$. (a) XRD patterns and Rietveld refinement of $x = 0.15$ and $x = 0.25$ samples; (b) the unit cells for $x = 0.15$ and 0.25 ; and (c) the change of lattice parameters against x .

4.3.2 Sinterability

The relative density of the sintered ceramics is calculated based on the Rietveld refined parameters, and shown in Fig. 4.2. The ceramic sinter of $x = 0.15$ has the highest relative density of 97.7% among all samples, and the density monotonically decreases with increasing the Na content. Nevertheless, the sample with the lowest density still exceed 95%, suggesting that the pores in sinters are mostly isolated to outside. The decreasing trend with increasing Na addition is possibly due to the high vapor pressure of Na component during sintering, which may hinder densification and pore annihilation but not the coarsening of grains.

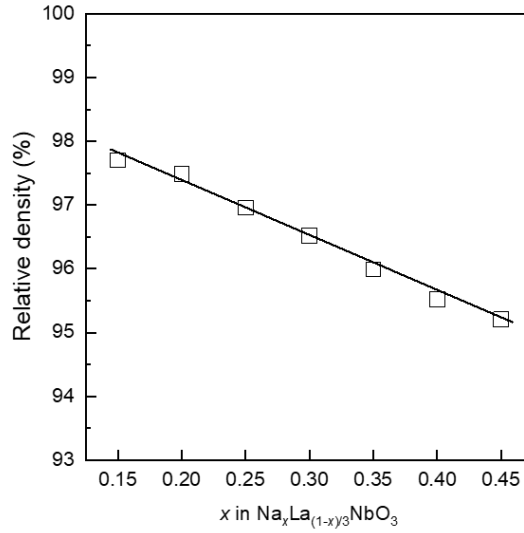


Fig. 4.2. Relative density of $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$ ceramic samples obtained by sintering at 1350 °C for 12 h in air.

The SEM images of the sintered sample surfaces are shown in Fig. 4.3. The absence of remarkable pores on the surfaces confirms the high density of the ceramics, as evaluated in Fig. 4.2. The average particle size as a function of x is plotted in Fig. 4.3h. The average size ranges from 1.2 to 2.0 μm , decreasing from $x = 0.15$ to 0.20 and then increasing with higher x value, i.e. the amount of Na. Notably, the particles in the samples with $x = 0.15$ and 0.45 exhibit partially truncated dice-like shapes, suggesting a formation of habit planes promoted by presence of liquid phases during sintering. According to a calculated ternary phase diagram in the system $\text{Na}_2\text{O}-\text{La}_2\text{O}_3-\text{Nb}_2\text{O}_5$ [29], there are two valleys on

liquidus surfaces near the compositions corresponding to $x = 0.15$ and 0.45 , supporting the formation of liquid phase. Chemical composition was analyzed by EDS. The Na, La, and Nb ratio reasonably agrees with those of formal chemical compositions. (For detail, see Supplementary Fig. B3.)

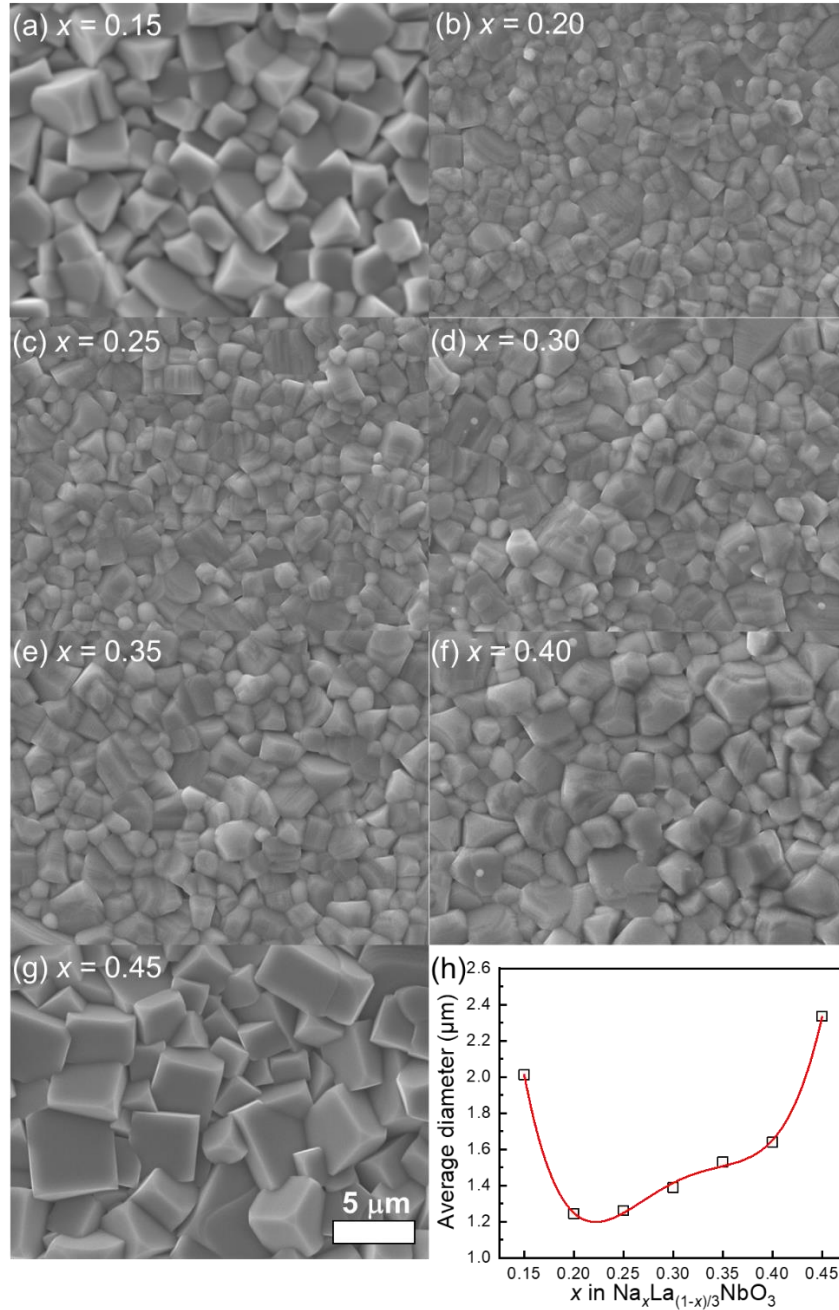


Fig. 4.3. Microstructures of $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$ ceramic samples obtained by sintering at $1350\text{ }^\circ\text{C}$ for 12 h in air. (a)–(g) SEM images and (h) the average particle size estimated from the SEM images.

4.3.3 Na⁺ ionic conductivity

Results of EIS measured for the $x = 0.25$ ceramic sample at selected temperatures are shown in Fig. 4.4a. (Full data are provided in Supplementary Fig. C1.) Each dataset was analyzed by fitting of equivalent circuit models, which are comprised of three sequential pairs of parallel resistance and constant phase element. From high to low frequency components, subscripts of 1, 2 and 3 are designated. (See the inset of Fig. 4.4a) Depending on the capacitance values of CPE₁, CPE₂, and CPE₃, which are typically 10–100 pF, 1–10 nF, and 1–10 μ F respectively, relevant components were assigned to bulk (R_{bulk}), grain boundaries (R_{gb}), and electrode interfaces, respectively. The total resistance (R_{total}) is the sum of the grain boundary and bulk resistances. The near-straight-line segment in the low-frequency region corresponds to an ion blocking behavior, suggesting that the conductivity is mainly contributed by ionic species. Semicircles in Fig. 4.4a assigned to bulk and grain boundary are clearly distinguishable at low temperature range 30–100 °C. At higher temperatures, however, it becomes impractical to distinguish the bulk and grain boundary components, and the interface component predominates. In this case, CPE₁ was omitted for the analysis, and resultant R_{bulk} and R_{gb} values are assigned with considering a continuity in the Arrhenius dependency (see Eq. 4.1). The conductivities were obtained from the reciprocal of the specific resistances, and denoted as the bulk (σ_{bulk}), grain boundary (σ_{gb}) and total (σ_{total}) conductivities.

Temperature-dependent σ_{bulk} and σ_{total} for all samples are plotted in Figs. 4.4b and c, respectively. (σ_{bulk} , σ_{gb} and σ_{total} for each sample are provided in Supplementary Fig. C2.) For samples with $x = 0.15$, 0.20 and 0.25, the bulk resistance dominates across the entire measured temperature range, while in samples with $x > 0.30$, the grain boundary resistance became comparable to the bulk resistance at lower temperatures. Exceptionally the grain boundary resistance was slightly reduced in $x = 0.45$, likely due to the marked grain growth. The chemical composition dependence of σ_{bulk} and σ_{total} at 30 °C is plotted in Fig. 4.4d. The $x = 0.25$ sample exhibits the highest conductivities around room temperature ($\sigma_{\text{bulk}} = 1.2 \times 10^{-6} \text{ S cm}^{-1}$ and $\sigma_{\text{total}} = 9.0 \times 10^{-7} \text{ S cm}^{-1}$ at 30 °C) among all samples. Its conductivity of $7.0 \times 10^{-4} \text{ S cm}^{-1}$ at 350 °C is approximately two orders of magnitude higher than the highest conductivity found in NLZ perovskites.

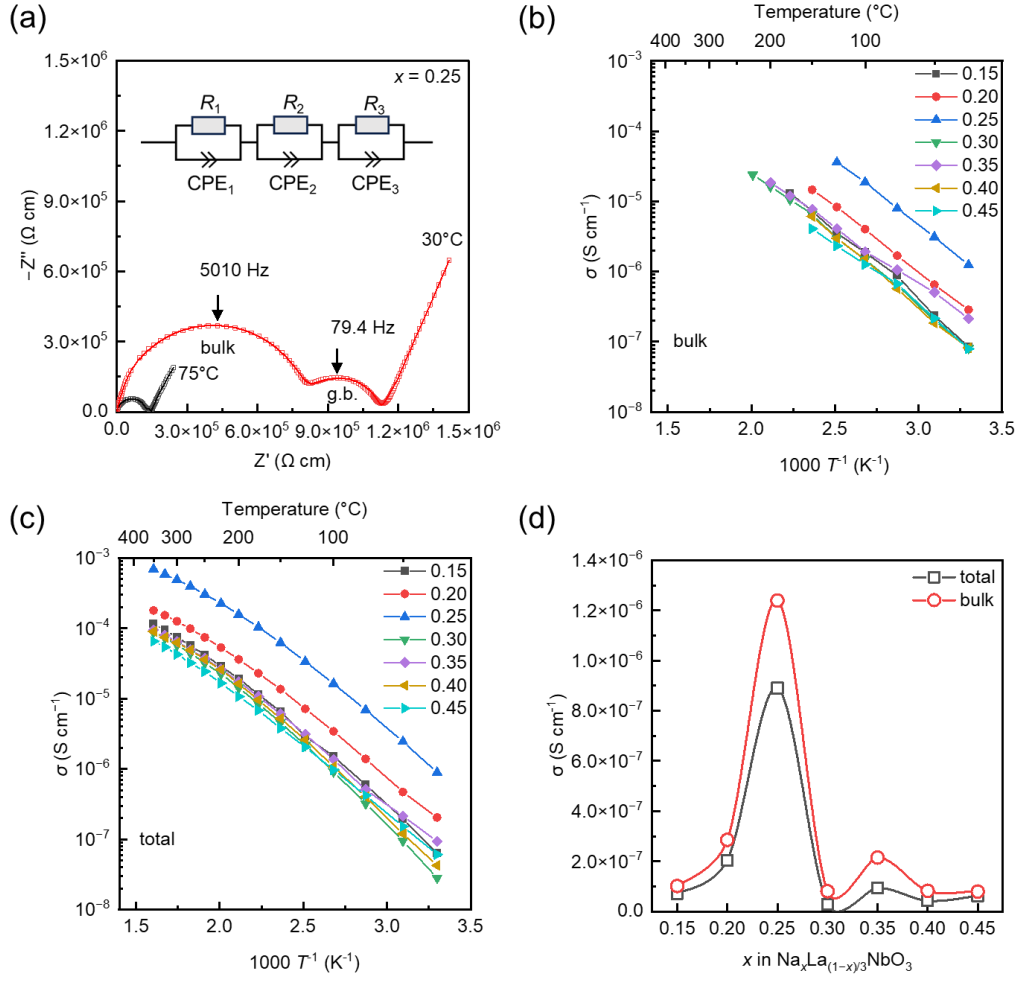


Fig. 4.4. Electrical conductivity in $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$ ($x = 0.15\text{--}0.45$) ceramics. (a) Nyquist plot of EIS measured in $x = 0.25$ sample at 30 and 75 °C. Solid curves calculated by the equivalent circuit model were fitted to measured data plotted by open circles. Arrhenius plots of (b) the bulk conductivity and (c) the total conductivity for all samples. (d) The bulk and total conductivities at 30 °C as a function of x .

The activation energy and the pre-exponential factor were estimated from the Arrhenius equation for ion diffusion-based conductivity:

$$\sigma T = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad \text{Eq. 4.1}$$

where σ is the conductivity, σ_0 is the pre-exponential factor, E_a is the activation energy, k_B is the Boltzmann constant, and T is the absolute temperature. Figure 4.5a shows the compositional dependence of E_a and $\log \sigma_0$, which are determined by a least-square fitting for bulk conductivity. (Those for grain boundary and total conductivities are shown in Supplementally Fig. C3.) Apparently, no clear trend in E_a against the chemical composition is found, although both parameters follow generally Meyer-Neldel rule [30], in which a decrease in E_a is offset by a decrease in $\log \sigma_0$. When $\log \sigma_0$ exceptionally increases and reaches a maximum value at $x = 0.25$, the bulk and total conductivities were maximized. For this composition, the value of E_a is 0.40 eV, which is not a minimum but close to it, while the minimum value of 0.39 eV was observed for different compositions of $x = 0.35$ and 0.45.

DC polarization measurements were carried out to confirm the contribution of Na^+ ion for the observed conductivity. From a result for $x = 0.2$ sample at 30 °C (Supplementary Fig. C4), the partial electronic conductivity was estimated to be $8.7 \times 10^{-10} \text{ S cm}^{-1}$. This value is approximately by 3 orders of magnitude smaller than the total conductivity, and thus the observed conductivity is almost pure ionic with the transport number of unity. The ionic species responsible for the ionic conduction is likely Na^+ , as suggested by the observed activation energy for bulk conductivity, which is around 0.4 eV— a typical range for the Na^+ ion [9]–[12][23][24][27] and lower for divalent or higher valent species [31]. Surface or bulk proton conductivities are also ruled out because of highly densified ceramic sample together with the high-temperature measurements in vacuum.

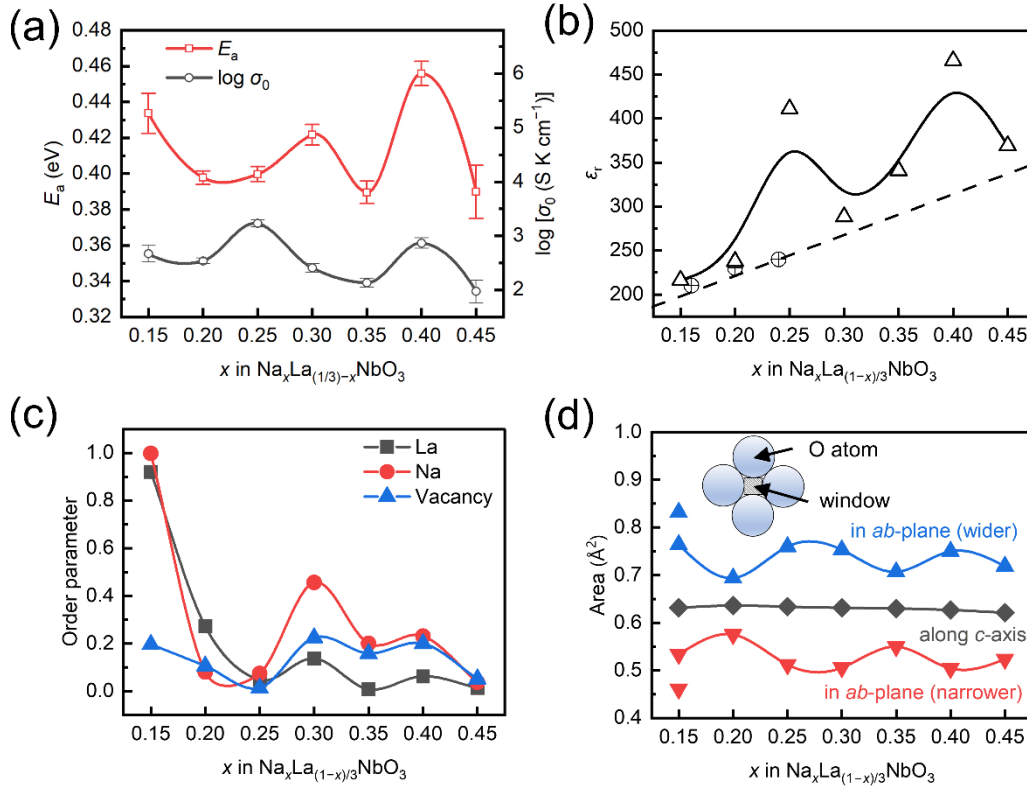


Fig. 4.5. Change of parameters for $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$ against x : (a) the activation energy and the preexponential factor for bulk Na^+ ion conductivity; (b) the relative dielectric constant at 30 °C; (c) the order parameters for A-site species; and (d) the areal sizes of bottleneck constructed by four-oxygens rectangular (inset).

4.3.4 Permittivity

The relative dielectric constant, ϵ_r , in $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$ at 30 °C, which was obtained by the equivalent circuit fitting for evaluation of CPE_1 , is shown in Fig. 4.5b. High values in a range of 240–470 are characteristic for this system, and seemingly inherited from the properties of endmember compounds, in which $\epsilon_r = 135$ for $\text{La}_{1/3}\text{NbO}_3$ [26] and $\epsilon_r = 200$ for NaNbO_3 [25] have been reported. In previous study of dielectric properties on the solid solution of $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$, a linear increase with x value up to $x = 0.5$ has been reported [25], as indicated by the dashed line in Fig. 4.5b. Although similar dependency is roughly observed in our data, there is a vibrational discrepancy from the reported values.

In this study, the enhanced Na^+ ion conductivity has been found ($\sigma_{\text{bulk}} = 1.2 \times 10^{-6} \text{ S cm}^{-1}$ for $x = 0.25$ at 30°C) in the system $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$. Simultaneously, the high permittivity ($\epsilon_r = 450$ for $x = 0.25$) and the suppressed electronic conductivity are available. These properties are advantageous for an interfacial layer between electrolyte and electrode active material in a sodium ion battery system [32]. Significant differences in the chemical potential of Na between the electrolytes and electrode active materials can lead to large built-in potentials at their interfaces, increasing the electrical resistance. This issue can be mitigated by inserting a material with a high dielectric constant at the interface.

4.3.5 Dominant factor of conductivity

This subsection is devoted to elucidate the dominant factor for the Na^+ ion conductivity. First, we consider the percolation theory with assuming a random distribution of cations in A site, and second the effect of A-site ordering will be examined.

Inaguma *et al.* [33] applied percolation theory to interpret the variation of Li^+ ion conductivity in perovskite-type $\text{Li}_x\text{La}_{(2-x)/3}\text{TiO}_3$, in which Li^+ ion migration with vacancy exchange mechanism among Li^+ -, La^{3+} - and vacancy-shared A sites are responsible for the ionic conduction. Interstitial Li^+ ion plays a crucial role, when crystallized in an orthorhombic (*Cmmm*) symmetry with an A-site ordering [20]. Again, when the A-site species are randomly distributed and the vacancy exchange dominates for the Li^+ ion diffusion, the composition dependence of conductivity can be described by:

$$\sigma \propto m(1 - m)(n' - n_c)^2 \quad \text{Eq. 4.2}$$

where n' is the sum of Li and vacancy concentration, $n_c = 0.31$ is the percolation threshold for 3-dimensional migration and m is the ratio of Li to the sum of Li and vacancy concentration. For the chemical formula $\text{Li}_x\text{La}_{(2-x)/3}\text{TiO}_3$, the expression is:

$$\sigma \propto \frac{x}{x + (1 - 2x)/3} \times \frac{(1 - 2x)/3}{x + (1 - 2x)/3} \times \left(x + \frac{(1 - 2x)}{3} - 0.31\right)^2. \quad \text{Eq. 4.3}$$

The model predicts that the conductivity will peak at $x = 0.34$. Experimentally, the highest conductivity is observed in the relevant composition, demonstrating the validity of the vacancy exchange percolation mechanism.

For the case of $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$ with pentavalent B site, the compositional dependence of the conductivity is rewritten as:

$$\sigma \propto \frac{x}{x + (2 - 2x)/3} \times \frac{(2 - 2x)/3}{x + (2 - 2x)/3} \times \left(x + \frac{(2 - 2x)}{3} - 0.31\right)^2. \quad \text{Eq. 4.4}$$

The maximum conductivity at $x = 0.55$ is predicted from Eq. 4. However, the experimental result in this study, $x = 0.25$, deviates markedly from the prediction, suggesting that percolation theory alone does not fully account for the conductivity properties. A similar discrepancy is observed in the Li-counterpart, $\text{Li}_x\text{La}_{(1-x)/3}\text{NbO}_3$, in which the highest conductivity appears at $x = 0.1$ [34][35].

Since the percolation theory based on the random distribution in the A site is insufficient for interpreting the compositional dependency of the conductivity, we now focus on the ordering in A site. The A -site order parameter, G , for each A -site specie, i.e., La, Na and vacancy, is defined by the difference in the occupation in the two crystallographically unique A sites as:

$$G = \frac{|g_{A_1} - g_{A_2}|}{g_{A_1} + g_{A_2}} \quad \text{Eq. 4.5}$$

where g_{A_1} and g_{A_2} are the occupancies at the two A sites, which are experimentally determined through Rietveld refinements. The order parameters for Na, La and vacancy are plotted in Fig. 4.5c. The $x = 0.15$ sample has an exceptionally high order parameter as compared with others, likely connecting the decrease in symmetry to the orthorhombic. There is again little systematic dependency on x , but a weak trend of a reduction with increasing x . However, a strong correlation between the order parameters and the activation energy is recognized, although they do not have a fully quantitative correspondence, but well reflecting the large/small relationship in adjacent compositions. Specifically, an inverse of the vacancy order parameter (Fig. 4.5c) has a close agreement with the conductivity (Fig. 4.4d). The random distribution of the vacancy may allow for three-dimensional migration of Na^+ ion, facilitating its diffusion, otherwise restricted in two-dimensionally along the ab -plane. Therefore, it is proposed that less ordered (or more random) distribution in the A site is a principal factor for reducing the activation barrier for Na^+ ion migration and enhancing the Na^+ ion conductivity.

The activation barrier for Na^+ ion migration is determined by the pathway from the initial equilibrium position to a neighboring vacant site. At the midpoint of this pathway, a rectangular gate formed by four oxygen atoms acts as a bottleneck. (See the inset of Fig.

4.5d.) Both A-site ordering and lattice parameters possibly influence this bottleneck. To investigate this, the window sizes of crystallographically independent rectangles formed by four oxygen atoms in each refined unit cell are plotted in Fig. 4.5d. A larger bottleneck size is generally associated with a lower activation energy. As the lattice contracts with increasing x , the bottleneck size decreases monotonically along the c axis, which is partially consistent with the observed trend of increasing activation energy with higher x values. Notably, the bottleneck sizes also show a general correlation with the order parameters. As the order parameter increases, the sizes of the two types of windows along the ab -plane (looser and tighter) deviate further; conversely, as the order parameter decreases, the window sizes converge. To further clarify the main influencing factors, we plot the products of the inverses of the order parameters of the vacancies and the areas of the oxygen bottlenecks against the Na content x in the Fig. 4.6, the result reproduce the trend of conductivity well.

Based on the factors examined so far, the most significant influence on Na^+ ion conductivity appears to be the disordering of A-site species, particularly vacancies. However, diffusion may also be affected by short-range ordering, strain, and chemical bonding. Additionally, the impact of oxygen vacancies has not yet been considered, and evaluating their effects is essential for fully understanding Na^+ ion conduction in this material system.

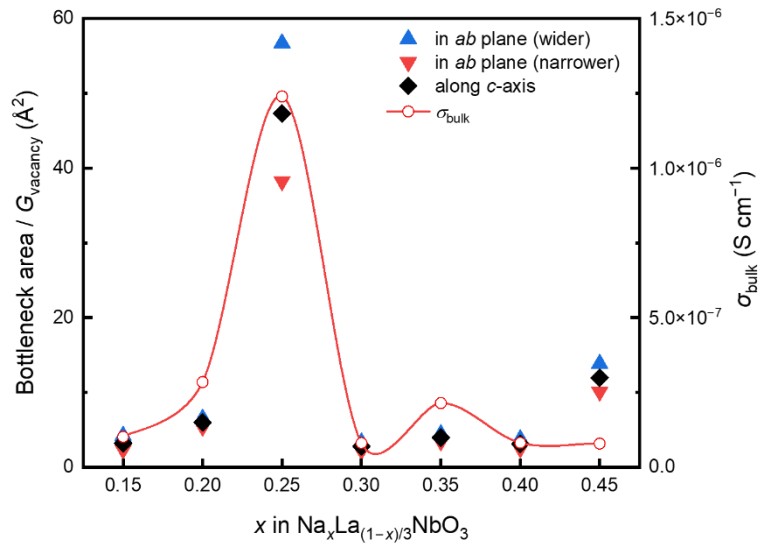


Fig. 4.6. Change of the product of the bottleneck area and the inverse of the vacancy order parameter for $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$ against x . Bulk conductivity data are replotted from Fig. 4d

4.4 Conclusion

Perovskite-type $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$ were synthesized by a conventional sintering technique, and the conductivity against the chemical composition ($x = 0.15\text{--}0.45$) was investigated. The samples demonstrated excellent sinterability, with the densest sample achieving a relative density of 97.7%. $\text{Na}_{0.25}\text{La}_{0.25}\text{NbO}_3$ demonstrated the highest conductivity, with a total conductivity of $7.0 \times 10^{-4} \text{ S cm}^{-1}$ at 350 °C with an activation energy of 0.37 eV. The percolation theory based on the Na^+ ion-vacancy exchange mechanism is insufficient for interpreting the chemical composition dependency on the electrical conductivity. Instead, the distribution of Na, La and vacancy across the two crystallographically unique A sites in the perovskite unit cells ($Pmmm$ or $P4/mmm$), i.e. A-site (dis)ordering, affects markedly the Na^+ ion conductivity, as inspected from the correlation with the activation energy for the Na^+ ion conductivity. The disordering in the A sites combined with wide bottleneck along Na migration pathway are likely crucial for enhancing the Na^+ ion conductivity. Additionally, high dielectric constant ($\epsilon_r = 220\text{--}470$) and suppressed partial electronic conductivity in the present system may be beneficial as an interface material to mitigate the chemical potential difference between an electrolyte and electrode active material in sodium ion batteries.

4.5 References

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CHAPTER 5 Conclusion

5.1 Summery

This dissertation examines A-site cation ordering and disorder in simple perovskites, exploring how they influences dielectric and transport properties. A chapter-by-chapter summary is provided below.

In Chapter 1, the history of perovskites is briefly reviewed, along with an introduction to key perovskite-type materials and their unique properties. The chapter also highlights cation-ordered perovskites and includes a group theoretical analysis. Additionally, the research background and objectives of this thesis are outlined.

In Chapter 2, $\text{NaLaZr}_2\text{O}_6$ polycrystalline samples were synthesized using solid-state reaction techniques. The untreated samples formed a layered A-site ordered perovskite structure with polar $P2_1am$ symmetry, as shown by X-ray diffraction (XRD) and second-harmonic generation (SHG) measurements. In contrast, samples that were quenched from 1300°C or higher adopted a disordered A-site structure with nonpolar $Pnam$ symmetry, which aligns with previous reports. The $P2_1am$ phase displays partial ordering of A-site cations in layers, splitting the initially equal Na/La ratio of 50/50 into two unequal ratios of 24/76 and 76/24. This ordering is stabilized by displacements of O^{2-} ions and second-order Jahn-Teller active Zr^{4+} ions, compensating for the mismatch in size and charge between the Na- and La-rich regions. According to group theoretical analysis, nonpolar $a^-a^-c^+$ octahedral rotations induce a polar mode, causing antiparallel displacements of the two distinct A-site cations, which results in spontaneous polarization. Although the polarization is small, ferroelectric behavior was confirmed in the $P2_1am$ phase. $\text{NaLaZr}_2\text{O}_6$ is a rare example of a perovskite with thermally tunable A-site ordering and associated polarity. To the best of our knowledge, this is the first observation of switching between polar and nonpolar states through thermal treatment.

In Chapter 3, $\text{Na}_x\text{La}_{(2-x)/3}\text{ZrO}_3$ perovskites with different Na/La ratios were synthesized using a solid-phase method. When A sites are not fully occupied, the perovskite phase coexisted with the pyrochlore phase due to thermodynamic limitations. X-ray diffraction (XRD) analysis revealed a low solid solution limit for the $\text{Na}_x\text{La}_{(2-x)/3}\text{ZrO}_3$ composition. The $\text{Na}_{0.5}\text{La}_{0.5}\text{ZrO}_3$ powder was sintered using spark plasma sintering (SPS), resulting in ceramics with two different space groups. Electrical conductivity measurements showed that the SPS1100 sample ($P2_1am$ phase) had conductivity nearly 10 times higher than the

SPS1200 sample (*Pnam* phase), with electronic conduction as the primary mechanism. Both samples had similar activation energies for conductivity, but the pre-exponential factor played the most significant role in the conductivity differences. Density functional theory (DFT) was used to investigate the electronic structures of $\text{Na}_{0.5}\text{La}_{0.5}\text{ZrO}_3$ with different levels of ordering. The virtual crystal approximation (VCA) method was applied to relax the $\text{Na}_{0.5}\text{La}_{0.5}\text{ZrO}_3$ cells. It was observed that increasing the degree of ordering enhanced stacking efficiency, reduced cell volume, and improved the stability of the structure at low temperatures, consistent with the experimental results in Chapter 2. The electronic structures were further analyzed using the KKR-CPA method. The density of states (DOS) and energy band calculations revealed that the 5d orbitals of La(2) atoms in the La-poor layer significantly influence the bandgap. As the degree of ordering increased, the concentration of La(2) in the La-poor layer decreased, narrowing the bandgap. When the ordering degree reached unity, the La atoms in the La-poor layer disappeared, causing a sharp increase in the bandgap. Additionally, the 5d orbitals of La(2) in the La-poor layer formed defect energy levels near the conduction band minimum (CBM), while the 5d orbitals of La(1) in the La-rich layer contributed to conduction bands with dispersed energy levels, enhancing carrier mobility. The conductivity difference between the SPS1200 (*Pnam* phase) and SPS1100 (*P2₁am* phase) was mainly attributed to differences in their electronic structures caused by the A-site cation ordering.

In Chapter 4, perovskite-type $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$ compounds were synthesized using a conventional sintering technique, and their conductivity was examined across a range of chemical compositions ($x = 0.15\text{--}0.45$). The samples exhibited excellent sinterability, with the densest sample achieving a relative density of 97.7%. Among them, $\text{Na}_{0.25}\text{La}_{0.25}\text{NbO}_3$ showed the highest conductivity, reaching a value of $7.0 \times 10^{-4} \text{ S cm}^{-1}$ at 350 °C, with an activation energy of 0.37 eV. The conventional percolation theory, based on the Na^+ ion-vacancy exchange mechanism, was inadequate to explain the composition-dependent conductivity behavior. Instead, it was found that the distribution of Na, La, and vacancies across the two distinct A-sites in the perovskite unit cells (*Pmmm* or *P4/mmm*), plays a more significant role in determining the Na^+ ion conductivity. A-site (dis)ordering was shown to influence conductivity, as evidenced by its correlation with the activation energy for Na^+ ion transport. The disorder at the A-sites, along with wider bottlenecks along the Na migration path, likely enhances Na^+ ion conductivity. Furthermore, the materials exhibited high dielectric constants ($\epsilon_r = 220\text{--}470$) and suppressed partial electronic conductivity, making them potential candidates for use as

interface materials to reduce the chemical potential difference between the electrolyte and electrode in sodium-ion batteries.

5.2 Perspective

For ease of comparison, the compositions and properties from this study are presented in [Table 5.1](#), alongside the reported materials. The following four perspectives on cation ordering in simple perovskites are presented below.

(1) In the synthesis of the perovskite phase, tetravalent Zr tends to form a pyrochlore phase together with La. Previous reports indicated that Ti also encountered this issue, but it was not as severe as with Zr. Therefore, it is difficult to synthesize a pure phase where the A-site is fully occupied in the NLZO system. By replacing Zr with pentavalent Nb, the formation of the pyrochlore phase was not observed. This may be related to the valence state. The presence of partially occupied perovskite phases of La is believed to enable the prediction of the dopability of materials. In the $\text{Ln}_{2/3}\text{TiO}_3$, $\text{Ln}_{1/3}\text{NbO}_3$, and $\text{Ln}_{1/3}\text{TaO}_3$ systems introduced in Chapter 2, it may be easier to introduce Na ions without forming secondary phases such as pyrochlore. We expect that various developments can be made in this area in the future.

(2) A-site ordering has different effects on various characteristics. For the induction of polarization (or ferroelectricity), A-site ordering must combine with octahedral rotation. Therefore, while polarization can be induced in the NLZO system, it cannot be induced in the NLNO system. This is because the NLNO system has a higher tolerance factor, making it more difficult for the oxygen octahedra to rotate. By replacing La with smaller Lanthanide atoms, the tolerance factor decreases, and octahedral rotation is likely to occur with proper selection, allowing polarization to be induced while maintaining A-site ordering.

(3) There are still unresolved issues in Chapter 3, but both experimental and computational results suggest that ordered structures exhibit higher conductivity. Designing materials with different order degrees for comparison might provide more information, but this is experimentally challenging. Moreover, while the arrangement of vacancies could affect conductivity, it is also not easy to experimentally obtain materials with different vacancy orders while keeping the composition constant. However, hints of this can be observed through theoretical calculations, and it could be explored as a future challenge.

(4) Regarding ion conductivity, ordering is generally considered undesirable, and the results of this study support this conclusion. The control of ordering is typically achieved through heat treatment and composition adjustments, both of which were applied in our research. Since both composition and the degree of ordering influence ion conductivity, controlling the combination of these two factors may be the key to achieving high ion conductivity. Additionally, although electronic conductivity is undesirable in sodium-ion electrolytes, for materials that require mixed ionic and electronic conductivity, such as electrode materials, tuning the degree of ordering may lead to the development of new practical materials.

Table 5.1, Comparison of the compositions and properties from this study alongside the reported materials.

Composition	$\text{Na}_x\text{La}_{(2-x)/3}\text{TiO}_3$	$\text{Na}_x\text{La}_{(2-x)/3}\text{ZrO}_3$	$\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$
Pyrochlore phase	light	critical	no
Polarity	no	inducible	no
Ionic conductivity	low	low	medium
Electrical conductivity	low	low	low
Existence of Ln_yMO_3	yes	no	yes
Octahedral rotation	yes	yes	no

Appendix A

This appendix contains tables and figures with information on additional group theoretical analysis.

Table A1. Symmetry-adopted mode decomposition of the $P2_1am$ structure with respect to an ideal $P4/mmm$ parent structure, in which Zr sits at $(1/2, 1/2, 1/4)$ and $(1/2, 1/2, 3/4)$ (Wyckoff 2h), Na(1) and La(1) sit at $(0, 0, 0)$ (Wyckoff 1a), Na(2) and La(2) sit at $(0, 0, 1/2)$ (Wyckoff 1b), O(1) sits at $(1/2, 0, 1/4)$, $(0, 1/2, 1/4)$, $(1/2, 0, 3/4)$, and $(0, 1/2, 3/4)$ (Wyckoff 4i), O(2) sits at $(1/2, 1/2, 1/2)$ (Wyckoff 1d) and O(3) sits at $(1/2, 1/2, 0)$ (Wyckoff 1c). Lattice vectors of subgroup $P2_1am = (\mathbf{a} + \mathbf{b}, -\mathbf{a} + \mathbf{b}, \mathbf{c})$, origin = $(1/4, -1/4, 0)$ in parent-lattice units, $s = 2$, $i = 8$.

$\mathbf{k}$ -point ^a	irrep ^b	OPD ^c	Isotropy subgroup ^d	s^e	i^f	Wyckoff ^g	Mulliken ^h	Amplitude ⁱ
[0, 0, 0]	Γ_5^-	(a, a)	$Amm2$	1	4	[Zr: h: dsp]	E (a)	0
						[La(1): b: dsp]	E_u (a)	-0.00166
						[Na(1): b: dsp]	E_u (a)	-0.00166
						[La(2): a: dsp]	E_u (a)	-0.19699
						[Na(2): a: dsp]	E_u (a)	-0.19699
						[O: i: dsp]	B_2 (a)	0.04114
						[O: i: dsp]	B_1 (a)	-0.00588
						[O: d: dsp]	E_u (a)	0.41560
						[O: c: dsp]	E_u (a)	0.83120
[1/2,1/2,0]	M_3^+	(a)	$P4/mbm$	2	2	[O: i: dsp]	B_1 (a)	0.73468
[1/2,1/2,0]	M_2^+	(a)	$P4/mbm$	2	2	[O: i: dsp]	B_2 (a)	-0.13518
[1/2,1/2,0]	M_5^-	(a, 0)	$Pmma$	2	4	[Zr: h: dsp]	E (a)	-0.00353
						[La(1): b: dsp]	E_u (a)	-0.03325
						[Na(1): b: dsp]	E_u (a)	-0.03325
						[La(2): a: dsp]	E_u (a)	0.02078
						[Na(2): a: dsp]	E_u (a)	0.02078
						[O: i: dsp]	A_1 (a)	-0.72175
						[O: d: dsp]	E_u (a)	0.82289
						[O: c: dsp]	E_u (a)	-1.08887

^aThe $\mathbf{k}$ -points in the first Brillouin zone of the parent structure associated with the distortion. ^bThe Irreducible representation (irrep) of the space-group symmetry of the parent structure. ^cThe Order parameter direction (OPD), a vector in representation space with the same dimension as the irrep. ^dThe subgroup of parent space-group operators which leave the OPD invariant. ^eThe size of the primitive unit cell of the isotropy subgroup relative to the parent space group. ^fThe index of the isotropy subgroup relative to the parent space group. ^gThe type of atom and its Wyckoff position in the parent phase, where ‘dsp’ denotes displacive mode and ‘occ’ denotes occupancy mode. ^hThe irrep of the point-group symmetry of the local Wyckoff position expressed in Mulliken symbols,

with the free variables from the OPD. ⁱThe standard supercell-normalized amplitude, in Å for displacive mode, and no unit for occupancy mode.

Table A2. Symmetry-adopted mode decomposition of the $Pnam$ structure with respect to an ideal $Pm\bar{3}m$ parent structure, in which Zr sits at (0, 0, 0) (Wyckoff 1a), La and Na sit at (1/2, 1/2, 1/2) (Wyckoff 1b) and O sits at (1/2, 0, 0), (0, 1/2, 0), and (0, 0, 1/2) (Wyckoff 3d). Lattice vectors of subgroup $Pnam = (\mathbf{a} + \mathbf{b}, \mathbf{a} - \mathbf{b}, -2\mathbf{c})$, origin = (0, 0, 0) in parent-lattice units, $s = 4$, $i = 24$.

$\mathbf{k}$ -point ^a	irrep _b	OPD ^c	Isotropy subgroup ^d	s^e	i^f	Wyckoff ^g	Mulliken ^h	Amplitude ⁱ
[1/2,1/2,1/2]	R_4^+	(0, a, a)	$Imma$	2	12	[O: d: dsp]	$E_u(a)$	-1.45460
[1/2,1/2,1/2]	R_5^+	(0, a, -a)	$Imma$	2	12	[La: b: dsp]	$T_{1u}(a)$	0.07135
						[Na: b: dsp]	$T_{1u}(a)$	0.07135
						[O: d: dsp]	$E_u(a)$	-0.01496
[0,1/2,0]	X_3^+	(0, 0; 0, 0; a, -a)	$Cmcm$	2	12	[La: b: dsp]	$T_{1u}(a)$	-0.28764
						[Na: b: dsp]	$T_{1u}(a)$	-0.28764
						[O: d: dsp]	$E_u(a)$	-0.21041
[1/2,1/2,0]	M_2^+	(a; 0; 0)	$P4/mbm$	2	6	[O: d: dsp]	$A_{2u}(a)$	0.00940
[1/2,1/2,0]	M_3^+	(a; 0; 0)	$P4/mbm$	2	6	[O: d: dsp]	$E_u(a)$	-0.75937

Table A3. Symmetry-adopted mode decomposition of the $P2_1am$ structure with respect to an ideal $Pm\bar{3}m$ parent structure, in which Zr sits at (0, 0, 0) (Wyckoff 1a), La and Na sit at (1/2, 1/2, 1/2) (Wyckoff 1b) and O sits at (1/2, 0, 0), (0, 1/2, 0), and (0, 0, 1/2) (Wyckoff 3d). Lattice vectors of subgroup $P2_1am = (\mathbf{a} + \mathbf{b}, \mathbf{a} - \mathbf{b}, -2\mathbf{c})$, origin = (1/4, -1/4, 1/2) in parent-lattice units, $s = 4$, $i = 48$.

$\mathbf{k}$ -point ^a	irrep ^b	OPD ^c	Isotropy subgroup ^d	s^e	i^f	Wyckoff ^g	Mulliken ^h	Amplitude ⁱ
[0, 0, 0]	Γ_4^-	(a, a, 0)	$Amm2$	1	12	[Zr: a: dsp]	$T_{1u}(a)$	0.00000
						[La: b: dsp]	$T_{1u}(a)$	-0.14047
						[Na: b: dsp]	$T_{1u}(a)$	-0.14047
						[O: d: dsp]	$A_{2u}(a)$	-0.00588
						[O: d: dsp]	$E_u(a)$	0.65249
[0, 0, 0]	Γ_5^-	(0, a, -a,)	$Amm2$	1	12	[O: d: dsp]	$E_u(a)$	0.59431
[1/2,1/2,1/2]	R_4^+	(0, a, a)	$Imma$	2	12	[O: d: dsp]	$E_u(a)$	-1.46624
[1/2,1/2,1/2]	R_5^+	(0, a, -a)	$Imma$	2	12	[La: b: dsp]	$T_{1u}(a)$	0.03820
						[Na: b: dsp]	$T_{1u}(a)$	0.03820
						[O: d: dsp]	$E_u(a)$	0.44552
[0,1/2,0]	X_3^-	(0, 0; 0, 0; a, -a)	$Cmcm$	2	12	[La: b: dsp]	$T_{1u}(a)$	-0.13812
						[Na: b: dsp]	$T_{1u}(a)$	-0.13812
						[O: d: dsp]	$E_u(a)$	-0.29387
[0,1/2,0]	X_3	(0; 0; a)	$P4/mmm$	2	6	[Zr: a: dsp]	$T_{1u}(a)$	-0.08644
						[La: b: occ]	$A_{1g}(a)$	0.51800
						[Na: b: occ]	$A_{1g}(a)$	-0.51800
						[O: d: dsp]	$E_u(a)$	0.42318
[1/2,1/2,0]	M_2^+	(a; 0; 0)	$P4/mbm$	2	6	[O: d: dsp]	$A_{2u}(a)$	0.13518

[1/2,1/2,0]	M_3^+	(a; 0; 0)	$P4/mbm$	2	6	[O: d: dsp]	$E_u(a)$	-0.73468
[1/2,1/2,0]	M_5^-	(a, -a; 0, 0; 0, 0)	$Pmma$	2	12	[Zr: a: dsp]	$T_{1u}(a)$	-0.00353
						[La: b: dsp]	$T_{1u}(a)$	0.00882
						[Na: b: dsp]	$T_{1u}(a)$	0.00882
						[O: d: dsp]	$E_u(a)$	-0.18808

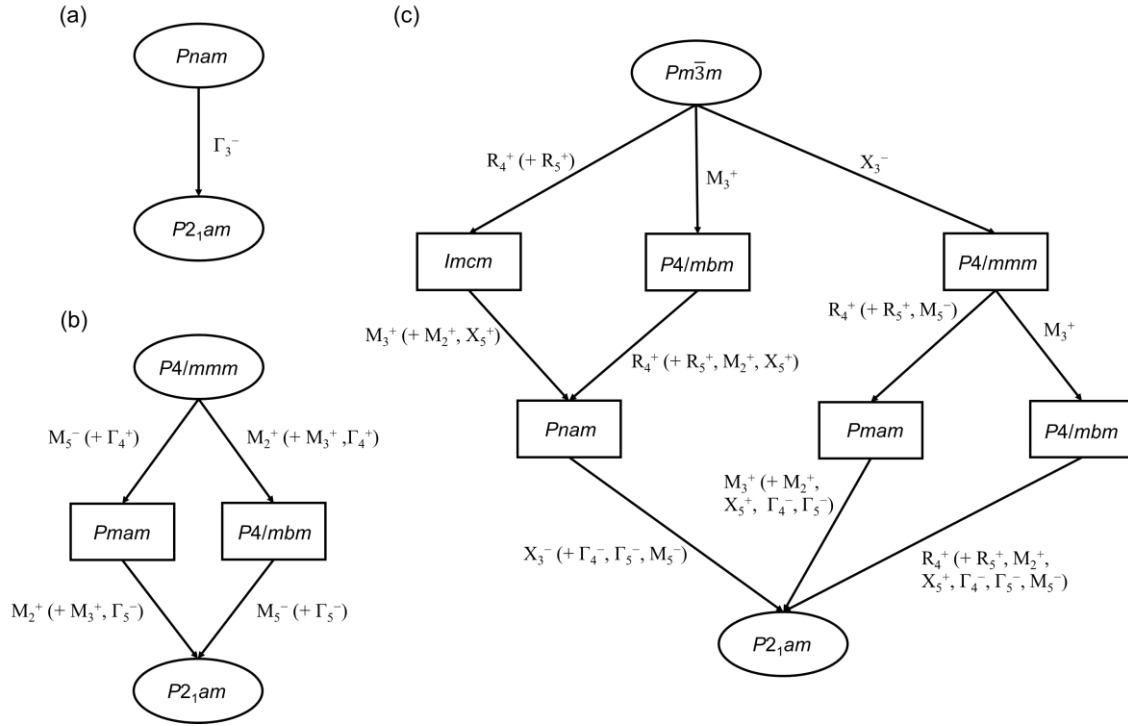


Fig. A1. Group-subgroup relationship (a) between the $Pnam$ and $P2_1am$ phases, (b) between the $P4/mmm$ and $P2_1am$ phases, and (c) between the $Pm\bar{3}m$ and $P2_1am$ phases.

Appendix B

This appendix contains X-ray diffraction patterns and refined crystallographic data sheets, as well as compositional data obtained by EDS.

Table B1. Rietveld Refined Crystallographic Data for $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$.

x		0.15	0.20	0.25	0.30	0.35	0.40	0.45
Space group		<i>Pmmm</i>	<i>P/4mmm</i>					
a (Å)		3.92425(17)	3.92804(6)	3.92582(4)	3.92383(5)	3.92253(9)	3.91990(6)	3.91442(8)
b (Å)		3.92346(17)						
c (Å)		7.90398(10)	7.8532(2)	7.85448(15)	7.84467(19)	7.8421(3)	7.83711(19)	7.8345(3)
V (Å ³)		121.695(8)	121.171(5)	121.054(3)	120.780(5)	120.660(7)	120.422(4)	120.046(6)
La(1)	x	0	0	0	0	0	0	0
	y	0	0	0	0	0	0	0
	z	0	0	0	0	0	0	0
	g	0.54(8)	0.1939(13)	0.2381(3)	0.2014(14)	0.2182(6)	0.2125(3)	0.1811(8)
	B	2.20(14)	2.53(11)	3.00(9)	3.86(12)	4.23(12)	4.74(13)	7.76(18)
Na(1)	x	0	0	0	0	0	0	0
	y	0	0	0	0	0	0	0
	z	0	0	0	0	0	0	0
	g	0.0(5)	0.216(7)	0.2686(14)	0.4368(7)	0.2797(3)	0.3077(17)	0.4344(4)
	B	2.20(14)	2.53(11)	3.00(9)	3.86(12)	4.23(12)	4.74(13)	7.76(18)
La(2)	x	0	0	0	0	0	0	0
	y	0	0	0	0	0	0	0
	z	1/2	1/2	1/2	1/2	1/2	1/2	1/2
	g	0.02(8)	0.3391(13)	0.2619(3)	0.2653(14)	0.2151(6)	0.1875(3)	0.1859(8)
	B	2.20(14)	2.53(11)	3.00(9)	3.86(12)	4.23(12)	4.74(13)	7.76(18)
Na(2)	x	0	0	0	0	0	0	0
	y	0	0	0	0	0	0	0
	z	1/2	1/2	1/2	1/2	1/2	1/2	1/2
	g	0.3(5)	0.184(7)	0.2314(14)	0.1632(7)	0.4203(3)	0.4923(17)	0.4666(4)
	B	2.20(14)	2.53(11)	3.00(9)	3.86(12)	4.23(12)	4.74(13)	7.76(18)
Nb	x	1/2	1/2	1/2	1/2	1/2	1/2	1/2
	y	1/2	1/2	1/2	1/2	1/2	1/2	1/2
	z	0.2609(3)	0.2493(4)	0.2505(7)	0.2517(9)	0.2518(10)	0.2511(9)	0.2517(10)
	g	1	1	1	1	1	1	1
	B	2.48(10)	2.22(8)	2.37(6)	2.72(8)	3.14(8)	2.90(8)	4.88(10)
O(1)	x	1/2	1/2	1/2	1/2	1/2	1/2	1/2
	y	1/2	1/2	1/2	1/2	1/2	1/2	1/2
	z	0	0	0	0	0	0	0
	g	1	1	1	1	1	1	1
	B	1.9(2)	2.44(18)	2.39(15)	1.93(17)	2.03(17)	2.32(17)	0.13(16)
O(2)	x	1/2	1/2	1/2	1/2	1/2	1/2	1/2
	y	1/2	1/2	1/2	1/2	1/2	1/2	1/2
	z	1/2	1/2	1/2	1/2	1/2	1/2	1/2
	g	1	1	1	1	1	1	1
	B	1.9(2)	2.44(18)	2.39(15)	1.93(17)	2.03(17)	2.32(17)	0.13(16)
O(3)	x	1/2	1/2	1/2	1/2	1/2	1/2	1/2
	y	0	0	0	0	0	0	0
	z	0.263(3)	0.2566(15)	0.264(2)	0.264(2)	0.259(3)	0.264(2)	0.261(2)
	g	1	1	1	1	1	1	1

	<i>B</i>	1.9(2)	2.44(18)	2.39(15)	1.93(17)	2.03(17)	2.32(17)	0.13(16)
O(4)	<i>x</i>	0	—					
	<i>y</i>	1/2						
	<i>z</i>	0.271(3)						
	<i>g</i>	1						
	<i>B</i>	1.9(2)						
<i>R</i> _{exp}		6.49	12.38	10.13	11.09	9.77	10.61	11.12
<i>R</i> _{wp}		14.43	16.18	14.17	16.74	17.52	17.85	20.63
<i>R</i> _p		10.80	12.18	10.22	12.36	13.36	13.63	16.11
GoF		2.22	1.31	1.40	1.51	1.79	1.68	1.86
<i>R</i> _{Bragg}		3.915	2.251	3.202	6.73	7.749	9.600	14.030

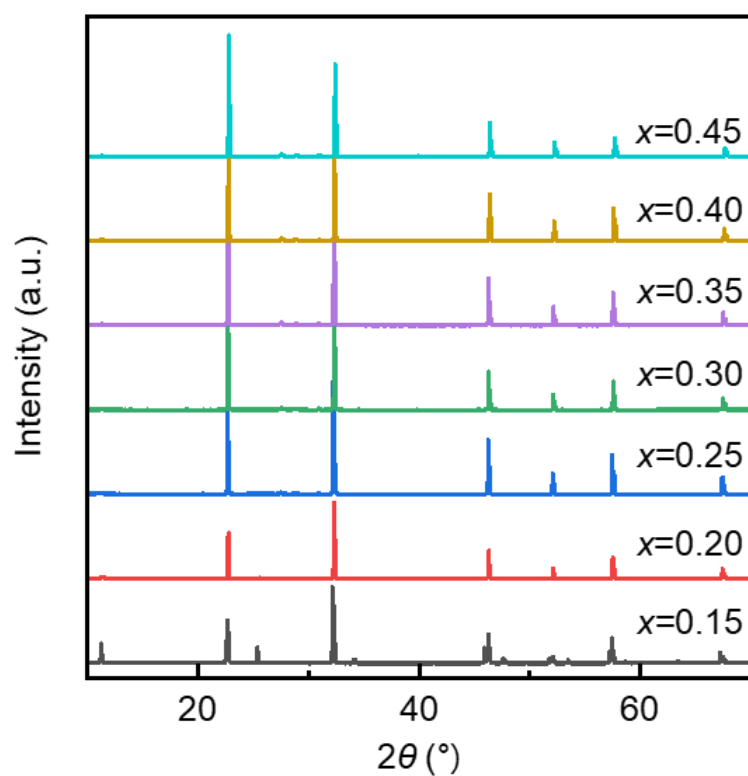


Fig. B1. XRD patterns for $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$ ($x = 0.15\text{--}0.45$) samples.

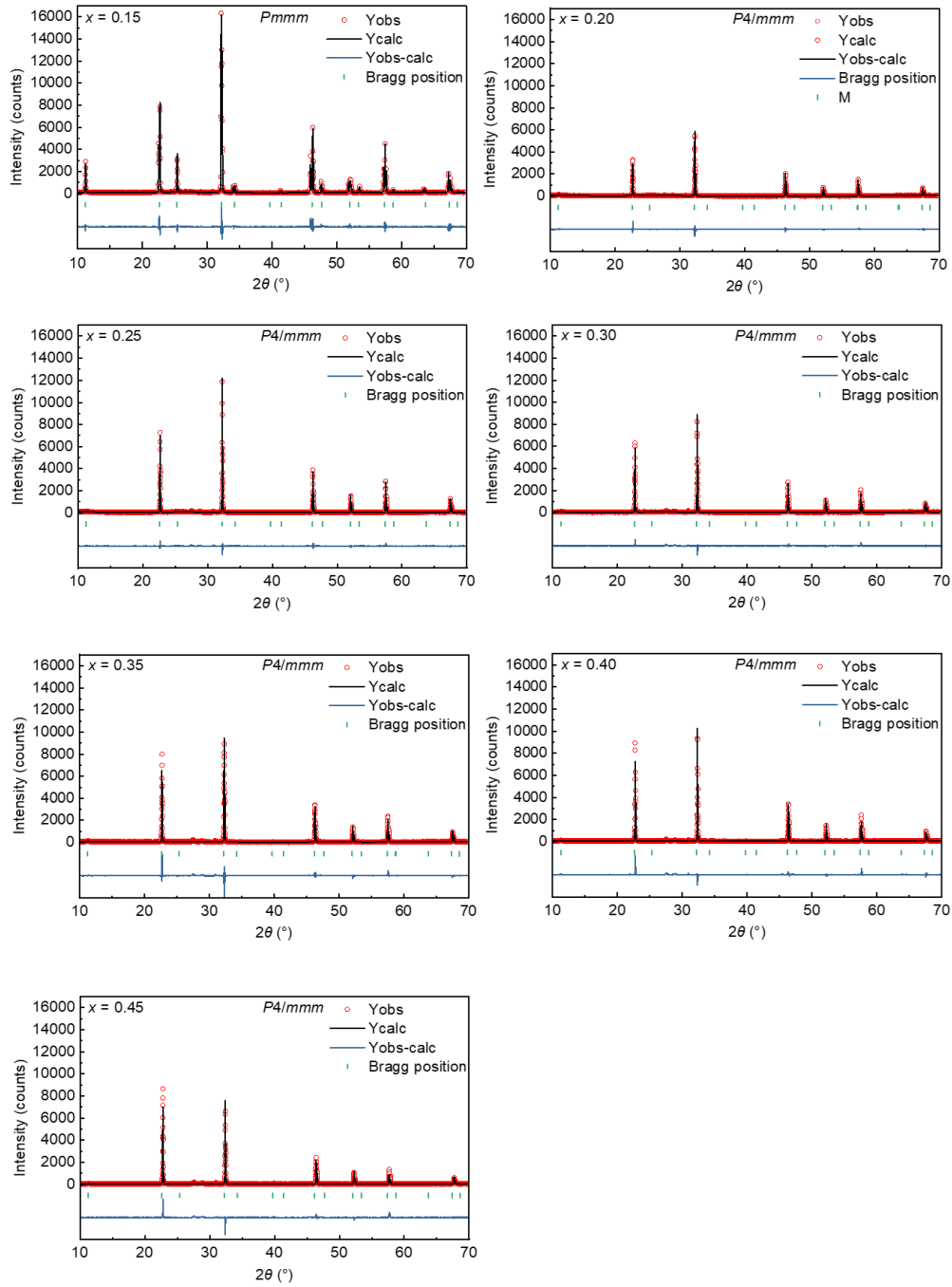


Fig. B2. The Rietveld refinement results for $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$ ($x = 0.15\text{--}0.45$) samples. XRD data for $x \geq 0.25$ were refined using $P4/mmm$ model, while XRD data for $x = 0.15$ were refined using Pmm model. The refinement for $x = 0.2$ were first examined using both models. Obtained R_{wp} , χ^2 and R_{Bragg} values for the Pmm model are slightly larger

than those for $P4/mmm$ model, implying that latter model is more favorable. In addition, a and b parameters refined using $Pmmm$ model was coincided to be $3.928(2)$ Å, which is also coincided to the value ($3.92804(6)$ Å) obtained from the $P4/mmm$ model, again validating the $P4/mmm$ model.

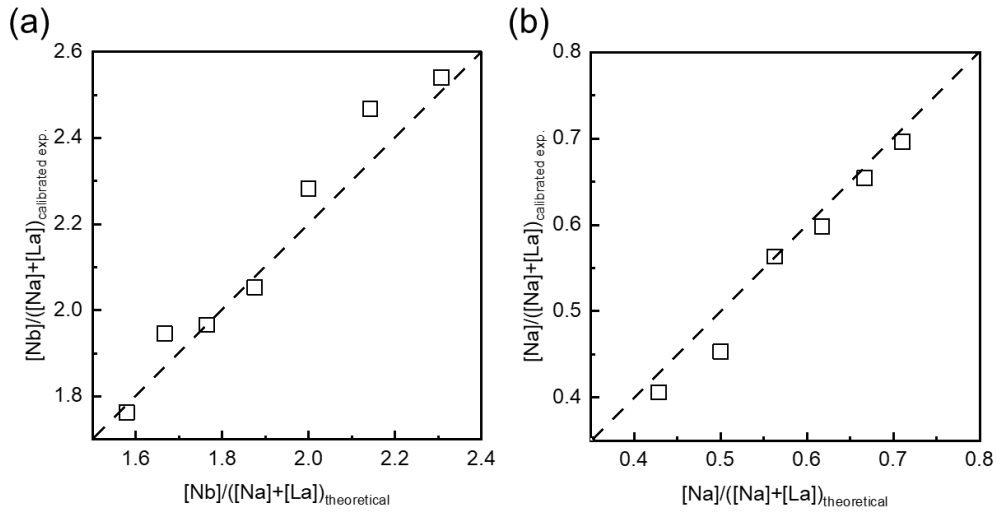


Fig. B3. Elemental ratios calculated from the result of EDS analysis, which are plotted for (a) the ratio of Nb to the sum of Na and La, and (b) the ratio of Na to the sum of Na and La. Intensity of EDS was calibrated using standard materials prepared by mixing Na_2CO_3 , La_2O_3 and Nb_2O_5 powders.

Appendix C

This appendix contains data on electrochemical properties.

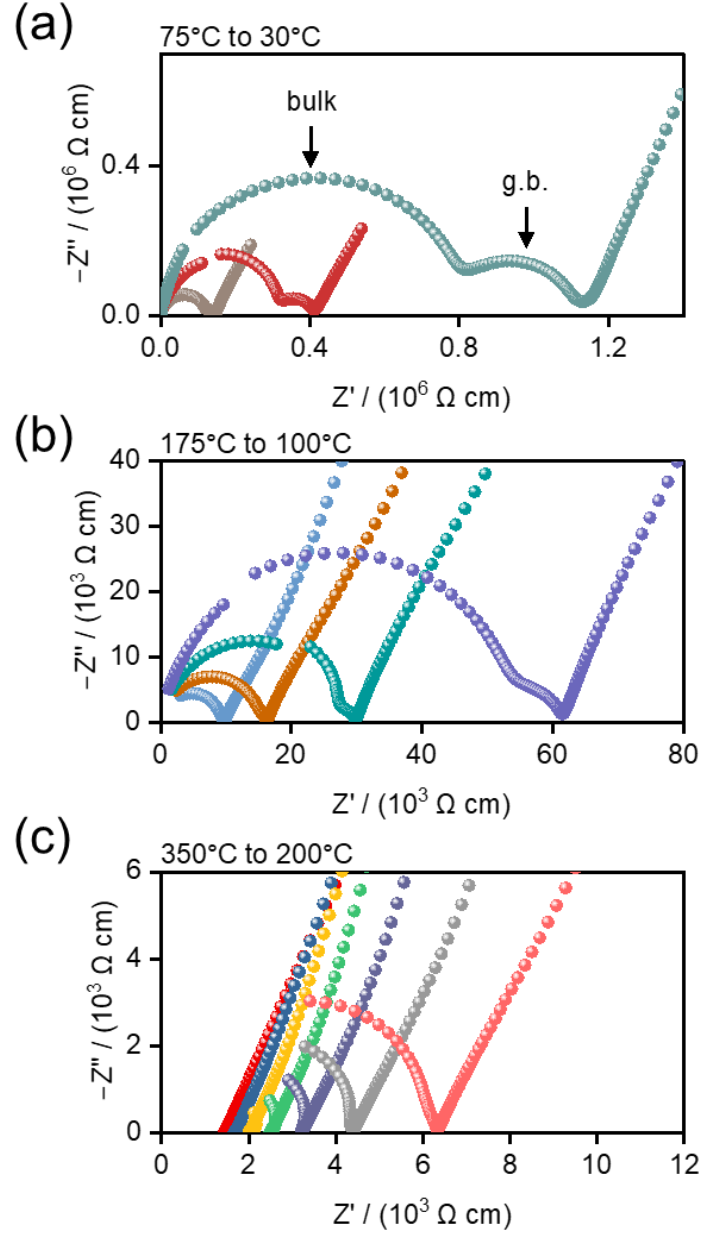


Fig. C1. Nyquist plot for sample $x = 0.25$ at the temperatures: (a) 30 °C, 50 °C, and 75 °C, (b) 100 °C to 175 °C with 25 °C interval, and (c) 200 °C to 350 °C with 25 °C interval.

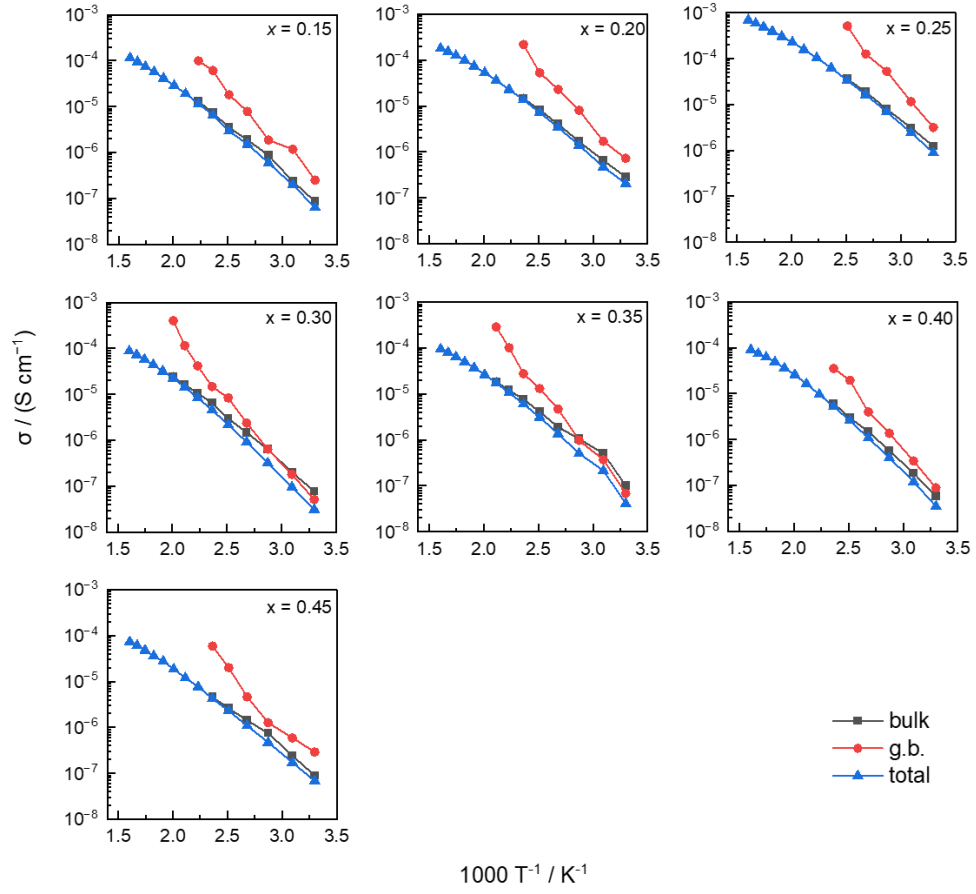


Fig. C2. The temperature dependence of bulk, grain boundary, and total conductivities for $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$ ($x = 0.15\text{--}0.45$) samples.

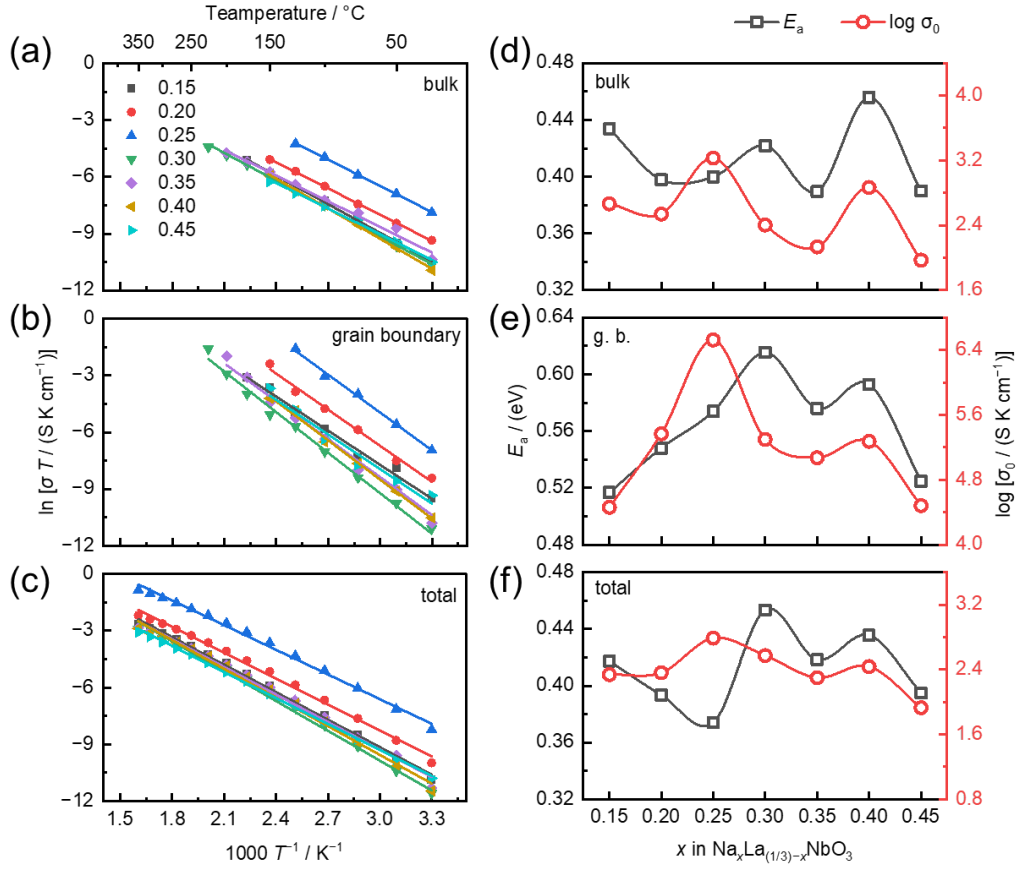


Fig. C3. Arrhenius plots ($\ln \sigma T$ vs. $1/T$) for (a) the bulk, (b) the grain boundary, and (c) the total conductivities. The activation energy (E_a) and logarithm of the pre-exponential factor ($\log(\sigma_0)$) of (d) the bulk, (e) the grain boundary, and (f) the total conductivities.

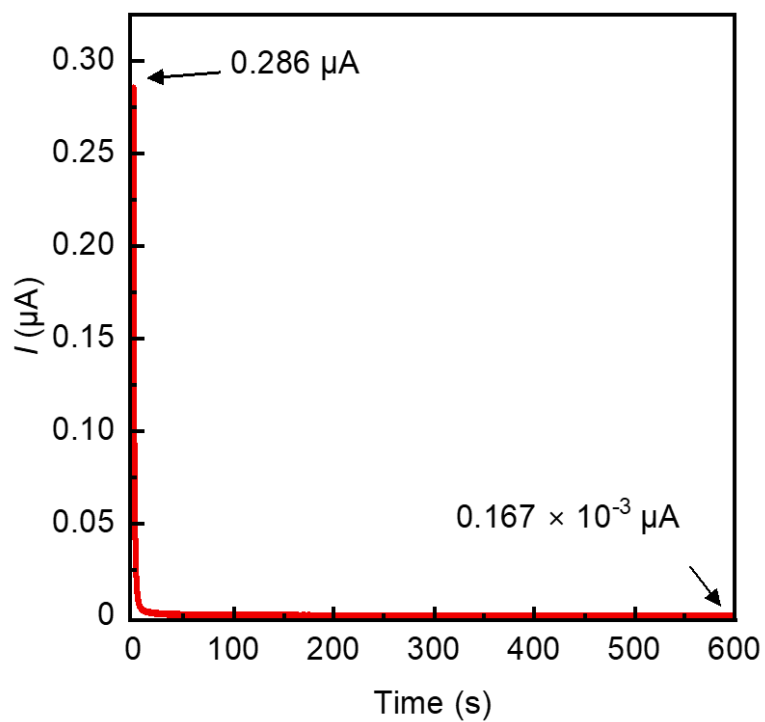


Fig. C4. DC polarization measured in $x = 0.2$ sample with symmetrical Au blocking electrodes at room temperature under constant voltage application of 0.5 V.

Publications

Original Papers

- 1) Jian Wang, Hirofumi Akamatsu, Katsuro Hayashi, “Sodium Ion Conduction in Perovskite-Type Sodium Lanthanum Niobate Ceramics,” *Journal of Alloys and Compounds*, 1010, 177335. (2025)
- 2) Jian Wang, Hirofumi Akamatsu, Yang Zhang, Tatsushi Kawasaki, Saneyuki Ohno, Koji Fujita, Katsuro Hayashi, “Thermally Controlled A-site Cation Ordering and Coupled Polarity in Double Perovskite $\text{NaLaZr}_2\text{O}_6$,” *Inorganic Chemistry*. (2025)

Joint Papers

- 1) Shufan Jia, Saneyuki Ohno, Jian Wang, George Hasegawa, Hirofumi Akamatsu, Katsuro Hayashi, “Enhanced Electrochemical and Transportation Properties in a NASICON-Type $\text{Na}_3\text{Zr}_2(\text{SiO}_4)_2(\text{PO}_4)\text{--Na}_3\text{Ti}_2(\text{PO}_4)_3$ Junction Prepared by Spin Coating and Glass-Ceramic Processes,” *ACS Applied Energy Materials* **6**, 317-325. (2022)
- 2) Bowei Xun, Jiang Wang, Yukio Sato, Shufan Jia, Saneyuki Ohno, Hirofumi Akamatsu, Katsuro Hayashi, “Bifunctional Al Dopant for Enhancing Bulk and Grain Boundary Conductivities in Sodium Ion Conducting NASICON Ceramics,” *Advanced Energy Materials*, 2402891. (2024)
- 3) Bowei Xun, Jiang Wang, Yukio Sato, George Hasegawa, Hirofumi Akamatsu, Katsuro Hayashi, “High-Conductivity, Low-Temperature Sintering-Compatible NASICON Solid Electrolyte for Enhanced Compositing with Hard Carbon Electrode in All-Solid-State Batteries,” *ACS Energy Letters*. (2024)

Academic conference

- 1) ○王 健, 赤松 寛文, 林 克郎, 高誘電率を有するペロブスカイト型 $\text{Na}_x\text{La}_{(1-x)/3}\text{NbO}_3$ セラミックスにおける Na イオン伝導, 第 50 回固体イオニクス討論会, 2024 年 12 月 9 日 (月) ~11 日 (水), 大阪千里
- 2) ○王 健, 赤松 寛文, 林 克郎, 二重ペロブスカイト $\text{NaLaZr}_2\text{O}_6$ における A 席カチオン秩序と極性の熱制御, 2024 年度日本セラミックス協会九州支部 秋季研究発表会, 2024 年 12 月 3 日 (火), 福岡博多

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