

Structural, Ferroelectric, and Transport Properties of Nb-based Double-Layered Perovskites

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論 文 内 容 の 要 旨

The rigid 3D frameworks of simple perovskites constrain atomic displacements and structural distortions, resulting in their crystallization predominantly in highly symmetric, centrosymmetric space groups. In contrast, layered perovskites disrupt these frameworks by introducing cationic layers, allowing the $[\text{BO}_6]$ oxygen octahedra to rotate and tilt, thereby inducing structural distortions. Based on the structural characteristics of the inserted layers, layered perovskites are classified into three main groups: Ruddlesden-Popper (RP), Dion-Jacobson (DJ), and Aurivillius perovskites. These structural distortions in layered perovskites can give rise to fascinating physical properties. The layered structures are particularly favorable for ion migration, while distortions of oxygen octahedra hold significant potential for inducing ferroelectricity, provided these distortions lead to polar structures. Niobate perovskites, as a notable subgroup of perovskites, are particularly appealing due to their non-toxic nature and cost-effectiveness, which has consistently attracted considerable research interest. The overarching objective of this research is to explore the relationship between crystal structures and physical properties, such as ferroelectricity and transport behavior, by tuning cation compositions within the structures. The organization of this thesis is as follows.

Chapter 1 is dedicated to share the background and the purpose of this study.

In Chapter 2, a Dion-Jacobson (DJ) double-layered perovskite $\text{CsNdNb}_2\text{O}_7$ is one of the extensively studied hybrid improper ferroelectric (HIF) materials, in which a coupling of two nonpolar oxygen octahedral rotation (OOR) modes triggers the spontaneous polarizations. Although the La counterpart $\text{CsLaNb}_2\text{O}_7$ has also been reported to be an HIF material, its polar structure and ferroelectric properties have not been intensely investigated so far. In this study, the temperature-composition phase diagram of complete solid-solution $\text{CsLa}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_7$ ceramics ($x = 0, 0.25, 0.5, 0.75$, and 1) has been constructed by variable-temperature synchrotron X-ray diffractometry, with the aid of first-principles calculations based on the density functional theory, dielectric measurements, and optical second harmonic generation. Upon cooling, the Nd-rich $\text{CsLa}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_7$ samples ($x = 0.5, 0.75$, and 1) samples undergo phase transitions from an aristotype $P4/mmm$ phase without OORs, to a $C2/m$ phase with $a^-b^0c^-$ -type OORs, to a polar HIF $P2_1am$ phase with $a^-a^-c^+$ -type OORs. Both phase-transition temperatures decrease with increasing La concentration. Room-temperature ferroelectricity has been demonstrated for the $\text{CsLa}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_7$ samples ($x = 0.75$ and 1), which adopt the polar $P2_1am$ structure at room temperature. Meanwhile, La-rich $\text{CsLa}_{1-x}\text{Nd}_x\text{Nb}_2\text{O}_7$ samples ($x = 0$ and 0.25) exhibit only $P4/mmm$ -to- $C2/m$ phase transitions on cooling. The end member $\text{CsLaNb}_2\text{O}_7$ is found to crystallize into the centrosymmetric

$C2/m$ phase at room temperature, although it has been reported to be noncentrosymmetric. Our theoretical calculations suggest that a symmetry trapping effect due to the absence of group-subgroup relationship between the $C2/m$ and $P2_1am$ phases suppresses the phase transitions between these phases.

In chapter 3, two Dion-Jacobson (DJ) double-layered perovskites $\text{CsNdNb}_2\text{O}_7$ and $\text{RbNdNb}_2\text{O}_7$ exhibit hybrid improper ferroelectricity, in which spontaneous polarization is induced by coupling of two types of nonpolar oxygen octahedral rotations (OORs). Their crystal structures adopt common polar distortion modes, although they exhibit distinct OOR patterns. In this study, complete solid-solution $\text{Cs}_{1-x}\text{Rb}_x\text{NdNb}_2\text{O}_7$ ceramics ($x = 0, 0.25, 0.5, 0.75, \text{ and } 1$) have been synthesized by conventional solid-state reaction methods, and the corresponding temperature-composition phase diagram has been established by various methods including variable-temperature synchrotron X-ray diffractometry, differential scanning calorimetry, optical second harmonic generation, and dielectric permittivity measurements. The powder X-ray diffractometry reveals that Cs-rich compounds ($x \leq 0.25$) crystallize into polar $P2_1am$ structures with $a^-a^-c^+/a^-a^-c^+$ OORs at room temperature, while Rb-rich compounds ($x \geq 0.5$) adopt polar $I2cm$ structures with $a^-a^-c^+/(a^-a^-c^+)$ OORs. All the solid solutions exhibit ferroelectricity at room temperature. Upon heating, successive phase transitions involving the loss of polar distortions and OORs have been observed. The phase transition temperatures of the solid solutions with intermediate compositions are lower than those predicted based on Vegard's law, indicating structural frustration effects due to the random arrangement of two alkali metal ions. This work provides insight into the influence of alkali metal ions in the intervening layers on the structural and ferroelectric properties of DJ layered perovskites.

In Chapter 4, the strategy of aliovalent substitution of Sr^{2+} by La^{3+} at A -site was used to obtain RP layered perovskite $\text{Li}_{2-x}\text{Sr}_{1-x}\text{La}_x\text{Nb}_2\text{O}_7$ ($x = 0, 0.1, 0.2, \text{ and } 0.3$) ceramics by a conventional high-temperature solid-state method. Variable-temperature synchrotron X-ray diffraction (SXRD) and permittivity reveal the nonpolar-to-polar phase transition that $Pnam$ -to- $A2_1am$ for $\text{Li}_2\text{SrNb}_2\text{O}_7$ below room temperature. Quantum paraelectric effects were detected for $\text{Li}_{2-x}\text{Sr}_{1-x}\text{La}_x\text{Nb}_2\text{O}_7$ ($x = 2$ and 0.3). The effects of A -site aliovalent substitution on Li^+ ionic conductivity and memristivity were also discussed based on temperature-dependent electrochemical impedance spectra and sweeping speed-dependent J - E curves.

Chapter 5 gives the overall conclusions of this study.

In summary, this thesis systematically investigates the crystal structures of Dion-Jacobson (DJ) and Ruddlesden-Popper (RP) Nb-based double-layered perovskites, exploring the intricate relationship between their structures and physical properties. The findings, which include insights into symmetry trapping, structural frustration, and the implementation of aliovalent substitution strategies, offer valuable guidance for researchers aiming to tailor physical properties by fine-tuning layered perovskite structures.

