

## Development of the mechano-optical conversion materials in piezoelectric semiconductors

塗, 東

<https://hdl.handle.net/2324/1544012>

---

出版情報：九州大学, 2015, 博士（工学）, 課程博士  
バージョン：  
権利関係：やむを得ない事由により本文ファイル非公開（3）

氏 名：塗 東 （トウ ドン）

論 文 名：Development of the mechano-optical conversion materials in piezoelectric semiconductors  
(圧電半導体を用いたメカノオプティカルコンバージョン機能の創出)

区 分：甲

### 論 文 内 容 の 要 約

Mechano-responsive optical materials, the optical properties of which can respond to mechanical stimuli have attracted considerable attention because of their wide applications. In this thesis, we focus on the most important type of mechano-responsive optical materials, mechano-optical conversion materials. Here, the mechano-optical conversion is defined as the repeatable variation of optical energy induced by the mechanical energy. As the most important type, mechano-optical conversion materials can further achieve the production, storage and consumption of optical energy by common mechanical energy, which shows great significance for both fundamental research and practical applications. However nowadays, the most studies of mechano-optical conversion were mainly concentrated in only single form, also the development of red emission ESL and improvement of tuning the mechano-optical conversion is still lacking.

Piezoelectric semiconductor materials can not only exhibit piezoelectric property, but also good electro-optical properties. In order to develop new type of mechano-optical conversion and improve the performance of mechano-optical conversion materials, incorporating with piezoelectric semiconductors can be expected to be an effective strategy because of their unique luminescent mechanism and good mechano-responsive performance. However previously, many piezoelectric semiconductors have been studied as the matrix of mechano-optical conversion materials, very few can be successful. Layered structural CaZnOS is a new piezoelectric semiconductor which shows large piezoelectric coefficient (38 pm/V), and chemical and thermally stability, which can be expected to be a good candidate matrix of mechano-optical conversion material. This thesis aims on developing the mechano-optical conversion materials in piezoelectric semiconductors. The emphases throughout this thesis are development of new type mechano-optical conversion and performance improvement of mechano-optical conversion in CaZnOS. In addition, improving the mechano-optical conversion in widely used piezoelectric material LiNbO<sub>3</sub> is also a part of this thesis.

At first of this thesis, a new type of mechano-optical conversion, elasto-quenching (ESQ), has been developed successfully in CaZnOS:Cu. Figure 1 displays the ESQ response with a compressive load and the ESQ images. The calculating ESQ intensity of the CaZnOS:Cu pellet immediately decreased linearly when a load was applied to the pellet. The ESQ was proportional to the applied load. After a compressive load was applied, the CaZnOS:Cu pellet showed substantial phosphorescence quenching areas at the top and bottom of the pellet where the compressive load was applied

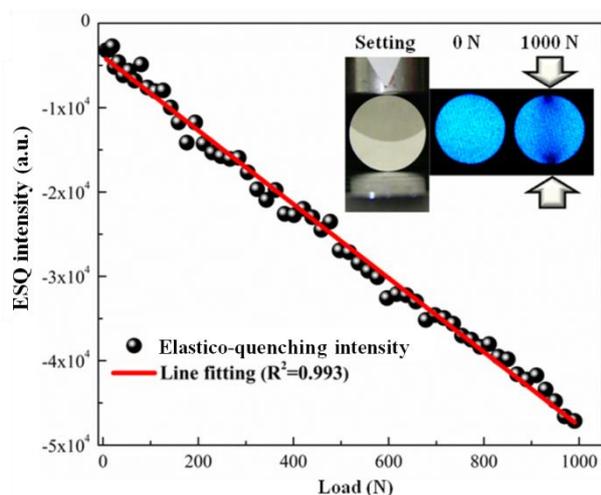


Fig. 1 The ESQ response for CaZnOS:Cu. The inset shows the image of ESQ.

(Fig.1 inset). In addition, the results indicated that ESQ intensity could also reflect well the stress distribution for quantitative analysis.

To understand the ESQ mechanism further, the ESQ properties of CaZnOS:Cu have been investigated in detail. As the decay time increases, the ESQ gradually swaps over to ESL under a compressive load. We proposed a mechanism based on the different roles of shallow and deep traps. When the load was applied, the trapped electrons could be excited to the non-radiative centers and conduction band, which may correspond to the ESQ and ESL, respectively.

In order to tune and improve the mechano-optical conversion further, the mechano-optical conversion properties have been investigated through changing the Cu concentration in CaZnOS. The ESQ intensity under 1000N load is also plotted as a function of Cu concentration in Fig. 2. It can be seen that the CaZnOS:Cu(0%) was initially a ESL material. However as the Cu concentration increased further, the ESL changed to ESQ and the ESQ intensity reaches maximum at the 0.01% Cu concentration (inset Fig. 2). After that, ESQ intensity decreased gradually as the Cu doping concentration increased which was due to the concentration quenching of excess Cu ions.

To consider the performance improvement of ESL, we also investigated the ESL properties of CaZnOS:Mn compared with MZnOS:Mn (M = Mg, Sr, Ba) samples and improved the ESL performance by co-doping the Li<sup>+</sup> ions. The synthesis, structure, luminescence properties were studied. Figure 3 shows the ESL curves of CaZnOS:Mn,Li compared with CaZnOS:Mn by compressive load up to 800 N, and the inset figures show the ESL distribution images of the corresponding composite pellets. The background intensities have been subtracted in this figure for the ESL comparison. As shown in Fig. 3, ESL intensity increased with increasing applied load, and the CaZnOS:Mn,Li showed stronger intensity growth trend. The ESL intensity of CaZnOS:Mn,Li was 4 times higher compared with CaZnOS:Mn when compressive load reached 800 N. It confirmed that ESL intensity had been greatly enhanced by Li<sup>+</sup> doping.

Finally, the ESL properties of piezoelectric material LiNbO<sub>3</sub>:Pr<sup>3+</sup> were also investigated by tuning the Li/Nb ratio. A series of LiNbO<sub>3</sub>:Pr<sup>3+</sup> with different Li/Nb ratio have been synthesized by the solid-state reaction and all these samples exhibited ESL corresponded to the applied load. With the increase of Li/Nb ratio, the phosphorescence intensity decreased, but the ESL intensity reached the maximum when Li/Nb was 1.8. The thermoluminescence indicated that the relative trap density of shallow trap V<sub>O</sub> increased with the increase of Li/Nb until 1.8.

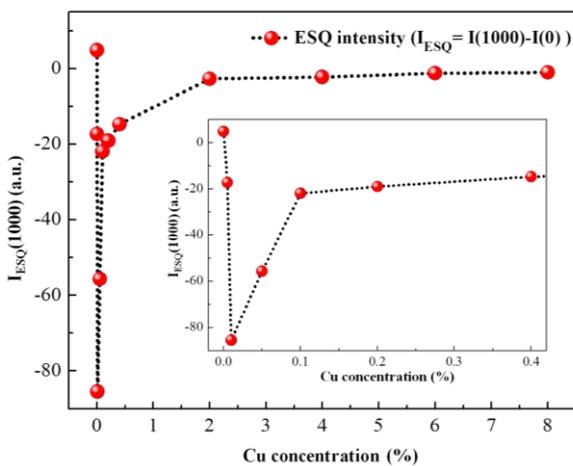


Fig. 2 Variation of ESQ intensity as a function of Cu concentration.

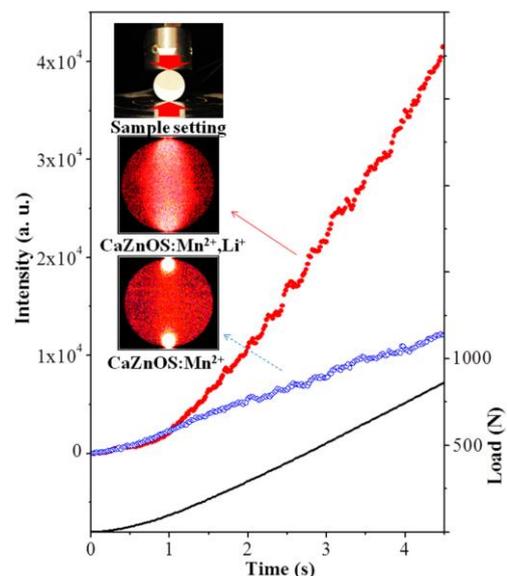


Fig. 3 The ESL response induced by compressive load and ESL images of CaZnOS:Mn and CaZnOS:Mn,Li.