Intense red emitting mechanoluminescence from CaZnOS:Mn,Li with *c*-axis preferred orientation*

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We report that the co-doping of Li⁺ ions significantly enhances the crystallinity and mechanoluminescence (ML) intensity of CaZnOS:Mn. The prepared CaZnOS:Mn,Li showed a preferred orientation of *c*-axis, and the particles possessed a plate-like morphology, which could be attributed to the layered structure of CaZnOS. At the same time, the ML induced by compressive load exhibited intense red emission and obvious intensity enhancement by the Li⁺ co-doping.

Keywords: Mechanoluminescence; CaZnOS:Mn,Li; preferred orientation.

1. Introduction

There has been a growing interest in mechanoluminescence (ML), which means emitting light can be induced by the local mechanical energy.^{1–6} As a category of ML developed by our lab, elasto-luminescence can present an almost linearity of ML intensity against deformation energy, it is promising to monitor the two-dimensional stress distribution in artificial skin, engineering structure, and living body in view of the advantages of wireless, nondestructive, reproducible, real-time and reliable stress sensing.^{4–7} In order to promote the application, ML materials in various wavelength have been developed such as SrAl₂O₄:Eu²⁺ (green),^{1,6–8} CaAl₂Si₂O₈:Eu²⁺ (blue),⁹ SrMg₂(PO₄)₂:Eu²⁺ (purple),¹⁰ Sr_{n+1}Sn_nO_{3n+1}:Sm³⁺ (reddish)¹¹ and so on. One limitation of these materials is that, it needs to use rare earth ions and high sintering temperature, driving up the production cost and energy consumption. Thus, the development of new ML phosphors with low cost and low synthesis temperature is very important.

In the contrast, piezoelectric material CaZnOS-based semiconductors have been studied as the promising luminescent materials matrix without rare earth doping.^{12–15} CaZnOS was first discovered by Petrova *et al.* in 2003, and its synthesis, structure and piezoelectric property were reported in 2007^{12,13}; photoluminescence properties of Mn²⁺-activated MZnOS (M = Ca, Ba) were investigated in 2009,¹² and the ML property from CaZnOS:Mn was reported by our group in

2013.¹⁶ However, the ML intensity needs to be improved for application. In order to enhance the ML intensity, we have investigated the co-doping effects of various ions such as transition metal and alkali ions. Distinguished improvements have been reached by co-doping Li⁺ with Mn²⁺.

Here we initially investigated the red emission ML phosphor CaZnOS:Mn and then the enhancement of ML intensity by Li⁺ ions co-doping. It is especially noteworthy that the synthesized CaZnOS:Mn,Li phosphor exhibited highly *c*-axis oriented plate-like structure.

2. Experimental Procedure

CaZnOS:Mn and CaZnOS:Mn,Li powders were synthesized using a solid-state reaction. Stoichiometric amounts of starting materials CaO (99.99%), ZnS (99.999%), MnCO₃ (99.9%) and Li₂CO₃ (99.99%) were weighed and thoroughly mixed with a small amount of ethanol in a mortar, and then sintered at 1100°C for 3 h in a horizontal tube furnace under a flowing Ar atmosphere. Li⁺ ions are doped to substitute Ca site with taking charge balance into account.

The crystalline phase was characterized with a powder X-ray diffraction (XRD) instrument (RINT-2000, Rigaku Co., Japan) with CuKα (1.5418 Å and 2θ = 10–80°) radiation (cathode voltage: 40 kV and current: 40 mA). The morphology was studied using scanning electron microscope

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(SEM: JEOL JSM-7001F). Photoluminescence (PL) measurement was recorded with a fluorescence spectrometer (FP-6600, JASCO Co., Japan) by using a 150 W Xe lamp at room temperature.

For the ML measurement by the compressive load, pellets were prepared by mixing the powder with an optical epoxy resin, and solidify into a composite disk 25 mm in diameter and 15 mm thick. The pellets were exposed to UV light (254 nm) for 1 min and then ready to be detected. The ML measurement was carried out with the lab-made system, consisting of a universal testing machine (RTC-1310A, Orientec Corp.) and a photon-counting system: a photomultiplier tube (R585S, Hamamatsu Photonics) and a photon counter (C5410-51, Hamamatsu Photonics) controlled by a computer. The former applied mechanical load while the latter detected ML emission intensity simultaneously.

Fig. 1. The XRD patterns of the $\text{CaZn}_{0.99}\text{Mn}_{0.01}\text{OS}$ and $\text{Ca}_{0.97}\text{Li}_{0.06}\text{Zn}_{0.99}\text{Mn}_{0.01}\text{OS}$ compared with the database of CaZnOS .

3. Results and Discussion

Figure 1 shows the XRD patterns of $\text{CaZn}_{0.99}\text{Mn}_{0.01}\text{OS}$ and $\text{Ca}_{0.97}\text{Li}_{0.06}\text{Zn}_{0.99}\text{Mn}_{0.01}\text{OS}$. No impurity phases were identified in $\text{Ca}_{0.97}\text{Li}_{0.06}\text{Zn}_{0.99}\text{Mn}_{0.01}\text{OS}$, regardless of the Mn^{2+} and Li^{+} ions doping, this XRD pattern agrees well with the CaZnOS standard pattern (PDF 01-072-3547), indicating that single CaZnOS phase has been synthesized. Instead, a small amount of ZnS impurity can be still found in $\text{CaZn}_{0.99}\text{Mn}_{0.01}\text{OS}$. The crystallinity of CaZnOS was much lower in the case of $\text{CaZn}_{0.99}\text{Mn}_{0.01}\text{OS}$, the scale of which was five times enlarged in intensity. Meanwhile, the diffraction peaks of $\text{Ca}_{0.97}\text{Li}_{0.06}\text{Zn}_{0.99}\text{Mn}_{0.01}\text{OS}$ have shifted to high angle slightly, confirming that Li^{+} has been co-doped in CaZnOS by the substitution of Ca ions, the ionic radius for Li^{+} (0.76 Å, CN = 6) is smaller compared with Ca^{2+} (1.00 Å, CN = 6). In addition, if compared with $\text{CaZn}_{0.99}\text{Mn}_{0.01}\text{OS}$, the intensities of two main diffraction peaks of $\text{Ca}_{0.97}\text{Li}_{0.06}\text{Zn}_{0.99}\text{Mn}_{0.01}\text{OS}$ increased obviously, the predominant peak was located at 31.34° ; the other strong one was located at 15.52° , they could be assigned to lattice planes (004) and (002), respectively. To analyze the preferred-orientation property, an intensity factor was defined as the ratio of the peak intensity for the diffraction peaks. For instance, the peak located at 48.45° could be ascribed to the lattice plane (110). By co-doping of Li^{+} , the factor $I(004)/I(110)$ significantly increased from 0.65 to 29.83. It illustrated that the $\text{Ca}_{0.97}\text{Li}_{0.06}\text{Zn}_{0.99}\text{Mn}_{0.01}\text{OS}$ exhibited the c -axis oriented direction.

The morphology and the size of the samples were examined by SEM, as shown in Figs. 2(a)–2(d), corresponding to

Fig. 2. The SEM images of $\text{CaZn}_{0.99}\text{Mn}_{0.01}\text{OS}$ ((a) and (b)) and $\text{Ca}_{0.97}\text{Li}_{0.06}\text{Zn}_{0.99}\text{Mn}_{0.01}\text{OS}$ ((c) and (d)).

$\text{CaZn}_{0.99}\text{Mn}_{0.01}\text{OS}$ and $\text{Ca}_{0.97}\text{Li}_{0.06}\text{Zn}_{0.99}\text{Mn}_{0.01}\text{OS}$, respectively. In Figs. 2(a) and 2(b) for sample $\text{CaZn}_{0.99}\text{Mn}_{0.01}\text{OS}$, it could be seen that the round-like particles are smaller in size (less than $10\ \mu\text{m}$). On the other hand, particles of $\text{Ca}_{0.97}\text{Li}_{0.06}\text{Zn}_{0.99}\text{Mn}_{0.01}\text{OS}$ were larger and well crystallized (Fig. 2(c)). As shown in Fig. 2(d), it possessed a beautiful tabular hexagonal structure with plate-like morphology, the particle spread to about $40\ \mu\text{m}$ in diameter. It could be attributed to the active role of Li_2CO_3 . Such a plate-like morphology were corresponding to the crystal growth in a - and b -axis, which was also consistent with the c -axis oriented direction of XRD results. The relatively larger amount of Li_2CO_3 (6 mol%) acted as a strong solvent and exhibited a high ionic diffusion rate in reaction process, Li_2CO_3 of low melting point (723°C) hindered the crystal growth of CaZnOS in c -axis and promoted the crystal growth in a - and b -planes.

Actually, the above results were associated with special layered structure of CaZnOS as shown in Fig. 3. The structure of CaZnOS is noncentrosymmetric and it has the space group $P6_3mc$. This noncentrosymmetric structure contains two puckered hexagonal layers of similar topology of compositions CaO and ZnS , and one Zn atom is tetrahedrally coordinated by three S atoms, which form part of a ZnS puckered layer, and one O atom in a neighboring CaO layer. The structure also shows that the Zn atom presumably competes

Fig. 3. Crystal structure of CaZnOS .

Fig. 4. The photo-excitation and emission spectra of $\text{CaZn}_{0.99}\text{Mn}_{0.01}\text{OS}$ and $\text{Ca}_{0.97}\text{Li}_{0.06}\text{Zn}_{0.99}\text{Mn}_{0.01}\text{OS}$.

against Ca atom for the oxide ion, resulting in the ZnS_3O coordination.¹³ The particles of CaZnOS:Mn,Li were able to grow into a plate-like shape which should be attributed to its unique layered structure.

The photo-excitation and emission spectra of $\text{CaZn}_{0.99}\text{Mn}_{0.01}\text{OS}$ and $\text{Ca}_{0.97}\text{Li}_{0.06}\text{Zn}_{0.99}\text{Mn}_{0.01}\text{OS}$ are illustrated in Fig. 4. The excitation spectra of both phosphors showed very similar bands. The main excitation peaks were both located at 285 nm and the small shoulder peaks around 345 nm were observed, they could be ascribed to the host lattice absorption and the absorption of Mn^{2+} ions, respectively. As shown in Fig. 4, Mn^{2+} showed a relatively weak absorption in the excitation band, because Mn^{2+} belonged to the d-d transition, which was spin and parity forbidden, the absorption band of Mn^{2+} was expected to be weak. On the contrary, the host lattice absorption was rather strong in the excitation spectrum. Upon excitation on 285 nm, the sample exhibited an intense red luminescence centered at 614 nm, this peak could be ascribed to the transition between $^4\text{T}_1 \rightarrow ^6\text{A}_1$ levels of Mn^{2+} .¹⁴ In addition, it is worth mentioning that the PL intensity of phosphor by Li^+ co-doped is much weaker than that of single doping one $\text{CaZn}_{0.99}\text{Mn}_{0.01}\text{OS}$, which may be due to the fact that the certain amount of defects have been generated by Li^+ doping in the phosphor lattice, leading to the degrade PL efficiency.

Figure 5 shows the ML curves of $\text{Ca}_{0.97}\text{Li}_{0.06}\text{Zn}_{0.99}\text{Mn}_{0.01}\text{OS}$ compared with $\text{CaZn}_{0.99}\text{Mn}_{0.01}\text{OS}$ by compressive load up to 800 N, and the inset figures show the ML distribution images of the corresponding composite pellets. The background intensities have been subtracted in this figure for the ML comparison. As shown in Fig. 5, ML intensity increased with increasing applied load, and the $\text{Ca}_{0.97}\text{Li}_{0.06}\text{Zn}_{0.99}\text{Mn}_{0.01}\text{OS}$ showed stronger intensity growth trend. The ML intensity of $\text{Ca}_{0.97}\text{Li}_{0.06}\text{Zn}_{0.99}\text{Mn}_{0.01}\text{OS}$ was four times higher compared with $\text{CaZn}_{0.99}\text{Mn}_{0.01}\text{OS}$ when compressive

Fig. 5. The ML response induced by compressive load and ML images of $\text{CaZn}_{0.99}\text{Mn}_{0.01}\text{OS}$ and $\text{Ca}_{0.97}\text{Li}_{0.06}\text{Zn}_{0.99}\text{Mn}_{0.01}\text{OS}$.

load reached 800 N. It confirmed that ML intensity had been greatly enhanced by Li^+ doping. Meanwhile, the compressive ML image from $\text{CaZn}_{0.99}\text{Mn}_{0.01}\text{OS}$ showed red emission only at the two points of contact position. On the contrary, the ML image of $\text{Ca}_{0.97}\text{Li}_{0.06}\text{Zn}_{0.99}\text{Mn}_{0.01}\text{OS}$ showed a distribution of red emission in the whole ML pellet area, which was associated with stress distribution. These differences in ML images were confirmed by naked eyes. It is clear that doped Li^+ has not only improved the ML intensity, but it also makes $\text{CaZn}_{0.99}\text{Mn}_{0.01}\text{OS}$ more suitable for ML devices application.

4. Conclusion

In summary, we have synthesized ML phosphors CaZnOS:Mn and CaZnOS:Mn,Li , and investigated their crystal structure and luminescence properties. The results have revealed that particles of CaZnOS:Mn,Li exhibited *c*-axis orientation morphology with the smooth surface and plate-like particles caused by low melting Li_2CO_3 . Furthermore, the ML enhancement of CaZnOS:Mn,Li has been achieved compared with CaZnOS:Mn . The mechanism may be ascribed to the polar noncentrosymmetric structure of CaZnOS and the increase of traps caused by Li^+ doping. CaZnOS:Mn,Li phosphor could be prospective to use in smart-skin, self-diagnosis systems and mechanical-optical sensors.

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