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Luminescence Properties of Fe^{3+} and Ce^{3+} Co-doped γ-$LiAlO_2$

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Abstract: Fe^{3+}, Ce^{3+} co-doped $LiAlO_2$ samples were successfully prepared by solid-state reaction method. The XRD and the SEM results showed that tetragonal γ-$LiAlO_2$ with diameter less than 10 μm was obtained. It was found firstly that the luminescence intensity of γ-$LiAlO_2$: Fe^{3+} is enhanced greatly by introducing a small amount of Ce^{3+} ions. The Ce^{3+} plays a role as sensitizer in host lattice, resulting in the enhancement of deep red emission of Fe^{3+} ions. The improved phosphor might be widely applied to agricultural film and fluorescent lamps relating to plant growth.

Key words: phosphor; luminescence; efficiency; co-doped

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1 Introduction

The compound $LiAlO_2$ has three known possible configuration, namely, α-$LiAlO_2$, the low temperature (400 ℃) form; β-$LiAlO_2$, the intermediate temperature (400 ~ 800 ℃) form; γ-$LiAlO_2$ which presents the most stable form at high temperature (>1 000 ℃). It is well known that the γ-$LiAlO_2$ is a latent substitute for reproducing tritium in a nuclear fusion reactor due to its chemical and thermal stability as well as less radiation damage property[1,2]. More interestedly, the γ-$LiAlO_2$ doped with Fe^{3+} emits in the deep red region under ultra-violet excitation, rendering it suitable for artificial plant illumination phosphor blends. The light centered at about 730 nm is optimum for controlling satisfactory plant growth and flowering[3,4]. It makes prominent sense that the phosphor is applied in artificial illumination applications or agricultural film[5] as light conversion agent.

The preparation and luminescent properties of γ-$LiAlO_2$: Fe^{3+} had been reported in some references[6~8]. However, the luminescence efficiency of Fe^{3+}-doped γ-$LiAlO_2$ phosphor is not the best. In the past approximate thirty years, the luminescence has hardly been improved. In this work, Fe^{3+} and Ce^{3+} co-doped γ-$LiAlO_2$ phosphors are successfully prepared with various Ce^{3+} concentrations. It was firstly found that by introducing suitable content of Ce^{3+} ions into γ-$LiAlO_2$: Fe^{3+}, the luminescence efficiency is remarkably enhanced.

2 Experiments

The reagents were all of analytical grade. The

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starting materials were $FeCl_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, CeO_2, Li_2CO_3 and HNO_3. First the $LiNO_3$ and $Ce(NO_3)_3$ were obtained by dissolving CeO_2 and Li_2CO_3 into H_2O_2 and HNO_3 solution. Then according to the chemical composition of $LiAlO_2$: Fe^{3+}, Ce^{3+}, appropriate quantities of nitrates and $FeCl_3 \cdot 6H_2O$ were dissolved into deionized water. The mole fraction of Fe^{3+} was fixed at 1%, while the mole fraction of Ce^{3+} varied from 0 to 3%. The mixed solutions were put into a muffle furnace and fired at 400 ℃ for 2 h. During this process the solutions gradually turned into solid and decomposed into well mixed oxides. The mixtures were grounded and fired at 800 ℃ and 1 200 ℃ for 10 h, respectively. After cooled to room temperature, the white powders were obtained ultimately.

The prepared powders were characterized by X-ray diffraction (XRD) on Rigaku D/max-A diffractometer equipped with graphite monochromatized Cu Kα(λ = 0.154 06 nm) radiation in the 2θ ranges of 10° to 80°. The morphology of products was observed by scanning electron microscopy (SEM, JSM-5600LV, JEOL, JAPAN). The PL spectra were measured using a spectrometer (FLS920, EDINBURGH) at room temperature.

3 Results and Discussion

The XRD patterns of samples were shown in Fig. 1, which clearly indicates that the samples are pure $LiAlO_2$ phase and a small amount of Fe^{3+} and Ce^{3+} did not change the host structure. Fig. 2 shows the SEM pattern, the $LiAlO_2$ products consist of almost entire sphere-like particles with the diameters less than 10 μm, and the particles show well-defined crystals of $LiAlO_2$. The optical properties of luminescent materials are frequently affected by the preparation method[9~12]. It has been well known that the particle with spherical shape and fine size is helpful to improve the efficiency of luminescence. The morphology and particle size of the samples are improved better than that reported previously[8]. It might be due to the intimate mixing of reactants in preparation process. Fig. 3 shows the excitation and emission spectra of $LiAlO_2$: 1% Fe^{3+} without Ce^{3+} doping and co-doped with 1.5% Ce^{3+}, respectively. As can be seen that the excitation spectra have a strong band at 265 nm followed by a weak band at 391 nm and a broad band of medium intensity at 446 nm. The excitation intensity of the $LiAlO_2$: 1% Fe^{3+}, 1.5% Ce^{3+} are also enhanced more than that of the $LiAlO_2$: 1% Fe^{3+}. The emission intensity at 742 nm for the $LiAlO_2$: 1% Fe^{3+}, 1.5% Ce^{3+} powders is near two times stronger than that of $LiAlO_2$: 1% Fe^{3+} powders. Fig. 4 shows that the

Fig. 1 The XRD spectra of samples obtained at 1 200 ℃: (a) γ-$LiAlO_2$: 1% Fe^{3+}, 1.5% Ce^{3+} and (b) γ-$LiAlO_2$: 1% Fe^{3+}.

Fig. 2 SEM of γ-$LiAlO_2$: Fe^{3+}, Ce^{3+} phosphors prepared by solid-state reaction method

Fig. 3 Excitation and emission spectra of γ-$LiAlO_2$: 1% Fe^{3+}, 1.5% Ce^{3+} phosphors by monitoring emission at 742 nm and under excitation of 265 nm at room temperature, respectively.

Fig. 4　The intensity of the samples varied with different Ce^{3+} mole fraction (a) 0%, (b) 0.5%, (c) 1.5%, (d) 3%.

luminescence intensity varied with different concentration of Ce^{3+}. It was found that at the molefraction of 1.5% Ce^{3+}, the luminescence intensity reaches to the maximum. However, when the concentration is up to 3%, the luminescence intensity decreased. In the emission and excitation spectra, the peaks positions have no shift.

The excitation peaking at 265 nm can be assigned to the $O^{2-} \rightarrow Fe^{3+}$ charge transfer band[7]. The excitation band centered at 391 nm can be explained by using the Tanabe-Sugano diagram[13], which shows that the absorption of Fe^{3+} ions from the ground state to the ^4E_g state leads to the excitation bands centered at 391 nm. This is similar to that of the band centered at 446 nm (Fig. 3). Seen from excitation spectra, the position peaking at 391 nm does not change in the crystal field, which could attribute to the excited ^4E_g, $^4A_{1g}(^4G)$ state paralleling to the ground state in the Tanabe-Sugano diagram.

For the excitation bands peaking at 391 and 446 nm, the excitation bands intensities of the $LiAlO_2$: 1% Fe^{3+}, 1.5% Ce^{3+} were enhanced. The Ce^{3+} plays the important role of sensitizing the Fe^{3+} ions. The $Ce^{3+} \rightarrow Fe^{3+}$ energy transfer can be expected to occur in $LiAlO_2$ using the Dexter's theory of energy transfer[14]. The schematic energy levels of Ce^{3+} and Fe^{3+} are drawn in Fig. 5. According to Fig. 5, the energy difference between the lower energy level (28 336 cm^{-1}) of 5d excited state and that of the ground state of Ce^{3+} is a match for the largest excitation (25 575 cm^{-1}) of Fe^{3+}. So the 4f electron of Ce^{3+} is excited into the high energy level (37 736 cm^{-1}) under UV at 265 nm, and then relaxes to the lower energy level, where the excitation energy of Ce^{3+} transfers to Fe^{3+} in the form of radiationless decay. On the other hand, for the emission band centered at 742 nm under excitation of 265 nm, the emission intensity of the samples with the concentration of Ce^{3+} from without Ce^{3+} to 1.5% gradually increased. However, the intensity of the samples with the concentration of Ce^{3+} from 1.5% Ce^{3+} to 3% decreased. It can be explained as follows: in the host lattice, the Fe^{3+} substitutes for Li^+ proved by EPR spectra of Fe^{3+} ions as reported[7], and the Ce^{3+} ions were assumed to substitute for Li^+ ions or to be interstitial ions. The doped Ce^{3+} ions might make the lattice site symmetry reduced, leading to increasing the probability of the $O^{2-} \rightarrow Fe^{3+}$ charge transfer. While the charge transfer band transferred the more absorbed energy to the emitting levels. Consequently, the luminescence efficiency of Fe^{3+} is improved greatly (see Fig. 4). However, as the concentration of the Ce^{3+} increases from 1.5% to 3%, the probability of transfer energy $Fe^{3+} \rightarrow Ce^{3+}$ gradually increases. While the probability of transfer energy between Ce^{3+} and Ce^{3+} also increases. Finally, the $Ce^{3+} \rightarrow Ce^{3+}$ energy transfer will reach to the quench trap position and the results cause the luminescence efficiency to decrease.

Fig. 5　Schematic energy levels of Ce^{3+} ions and Fe^{3+} ions in γ-$LiAlO_2$: (a) Fe^{3+}; (b) Ce^{3+} ions.

4　Conclusion

In summary, the Ce^{3+}, Fe^{3+} co-doped $LiAlO_2$ were successfully prepared by solid-state reaction

method. The relation between Ce^{3+}-doped concentration and the PL properties of samples was investigated. When the Ce^{3+}-doped concentration is up to 1.5%, the emission intensity of Fe^{3+} ions reaches to the maximum. It is inferred that Ce^{3+} plays a role as sensitizer in host lattice. The work might be helpful for further search of agricultural film and artificial plant illumination phosphors.

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Fe^{3+}、Ce^{3+} 共掺杂 γ-$LiAlO_2$ 的发光性质

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摘要： 采用不同于传统固相反应法的制备方法合成了 Fe,Ce 共掺杂 γ-$LiAlO_2$。通过 XRD 和 SEM 分析表明，采用这种方法能够成功获得尺寸小于 10 μm 的四方相结构 γ-$LiAlO_2$ 荧光粉。从 γ-$LiAlO_2$: Fe,Ce 的激发和发射光谱可以看出，通过引入少量的铈离子，我们首先发现了铈离子掺杂对样品的发光效率有明显的影响。并且随着铈离子浓度的增加，其发光效率也出现规律性的变化，而且发射光谱在 Ce 离子摩尔分数达到 1.5% 的

情况下发光效率最强,当 Ce 离子摩尔分数达到 3% 时,发光效率明显下降。这种高效的荧光粉作为转光剂应用于人工植物照明和农用转光膜具有积极的意义。

关　键　词: 荧光体; 发光; 效率; 共掺杂

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