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Luminescence Properties of $\text{LiAl}_5\text{O}_8 : \text{Fe}^{3+}$ Phosphor

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Abstract: Iron-activated LiAl_5O_8 is one of red emitting phosphors, exhibiting a broad-band photoluminescence peaked around 675 nm. The component of the matrix and the content of activation ion in $\text{LiAl}_5\text{O}_8 : \text{Fe}^{3+}$ phosphors were studied in this paper. The results shown that, under the monitoring at 673 nm, the ordered phase of excitation spectra indicated that there is a strong absorption band at 284 nm, which is charge transfer band of $\text{Fe}^{3+}-\text{O}^{2-}$. And there is a single emission band at 673 nm emission under 254 nm excitation. And the emission band is slight asymmetry in the direction of longer wavelength, which belongs to ${}^4\text{T}_1({}^4\text{G}) \rightarrow {}^6\text{A}_1({}^6\text{S})$ transition. The luminescent intensity is the strongest when the content ratio of Li_2CO_3 and Al_2O_3 is 0.21. The emission intensity enhances as the content of Fe^{3+} increases. When the content of Fe^{3+} is 0.5%, the luminescent intensity is the strongest. But the luminescent intensity decreases when the content of Fe^{3+} increases over 0.5%.

Key words: red phosphor; $\text{LiAl}_5\text{O}_8 : \text{Fe}^{3+}$; synthesis; photoluminescence

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1 Introduction

The phosphors of aluminate system have advantages of high quantum efficiency, high color rendering, wide excitation range and emitting light on visible range, which has become one of hotspot studies in the field of fluorescence materials^[1-5]. For aluminate phosphors, studies mainly focus on rare earth ions activated blue-green phosphors^[6,7]. However red phosphors, especially deep red phosphors emitting with long wave red light, were reported in literature rarely. LiAl_5O_8 is a good matrix material and it is suitable for transition metal doping to make long wave red emitting phosphors. Our scholars have improved current manufacturing technology to enhance Fe^{3+} ions doping content significantly by wet method pre-treatment and oxygen introduction, to form more luminescence centers and they concluded that emission intensity increases as the treatment temperature increasing within 1 500 °C^[8,9].

In this paper, $\text{LiAl}_5\text{O}_8 : \text{Fe}^{3+}$ was synthesized from Al_2O_3 and Li_2CO_3 as the starting material by high temperature solid-phase process. The component of the matrix and the content of activation ion in $\text{LiAl}_5\text{O}_8 : \text{Fe}^{3+}$ phosphors were studied.

2 Experiments

2.1 Solid-state Synthesis

Analytically pure Al_2O_3 , Li_2CO_3 , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, H_3BO_3 , anhydrous alcohol and chemical pure PEG4000 as raw materials were used. According to different formula, the reagents were weight and put into a ball milling pot. After ball milling for 2 h, the mixture was dried for 5 h and ground. The raw sample was heated at 1 000 °C to 1 500 °C for 1 ~ 5 h. The sample was milled and sifted after cooling.

2.2 Sample Characterization and Analysis

DongNan 98B fluorophotometer was used to measure excitation and emission spectra of the sample. X-ray diffractometer type ARL X'TRA was used

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to detect crystal structure of the sample, with condition of Cu K α line, tube voltage 40 kV, and tube current 100 mA.

3 Results and Discussion

3.1 Excitation and Emission Spectra of Li-Al₅O₈:Fe³⁺

Fig. 1 shows the excitation spectra of iron-activated LiAl₅O₈. Under the monitoring 673 nm, the ordered phase of the excitation spectra indicated that there is a strong absorption band at 284 nm with weak band at 396 nm and 454 nm. Due to width and higher strength on strong band at 284 nm, it isn't Fe³⁺ intracenter transition. As d⁵ ion, electric dipole transition is spin-forbidden and parity-forbidden, so strong band can't migrate. Therefore, first absorption is charge transfer band of Fe³⁺-O²⁻ [10]. Except a dominant role of charge transfer band in Fig. 1, three group of spectral lines are also showed. Pott and McNicol considered that weak absorption of higher wavelength is Fe³⁺ intracenter transition, that is, the band at 396 nm is attributed to the transition ⁶A₁(⁶S) - ⁴A₁ and ⁴E(⁴D), the band at 454 nm and 586 nm to the transition ⁶A₁(⁶S) - ⁴T₂(⁴D) and ⁶A₁(⁶S) - ⁴T₂(⁴G). The different width of 396 nm and 586 nm absorption shows that the second band is around superposition of 402 nm and 550 nm [11].

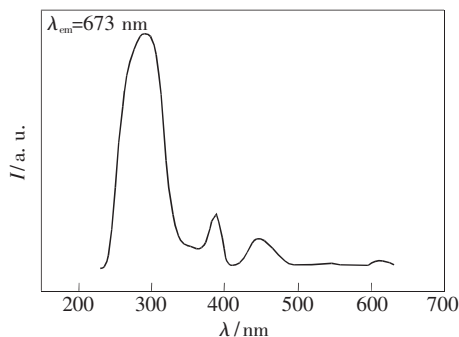


Fig. 1 Excitation spectra of LiAl₅O₈:Fe³⁺

So, in the Fe³⁺ compounds, we usually observe two or three transition: the broad band both of ⁶A_{1g}-⁴T_{1g} and ⁶A_{1g}-⁴T_{2g}, one narrow band of ⁶A_{1g}-⁴E_{1g} + ⁴A_{1g}(⁴G).

As shown in Fig. 2 the emission spectra of the ordered phase sample shows that there is a single emission band peaked at 673 nm under 254 nm exci-

tation. And the emission band is slight asymmetry in the direction of longer wavelength, which indicates that the second band superimposed around 700 nm and zero phonon line does not be found. The emission belongs to ⁴T₁(⁴G) - ⁶A₁(⁶S) transition.

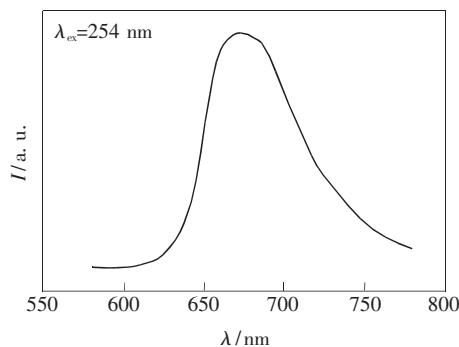


Fig. 2 Emission spectra of LiAl₅O₈:Fe³⁺

Literature reported that there are three luminescence centers at excitation and emission spectra of iron-activated LiAl₅O₈ red phosphor. The strong emission band at 673 nm is due to Fe³⁺ transition in tetrahedron, while weak emission band at 700 nm is the result of Fe³⁺ transition in octahedron. The emission band at 604 nm and its related excitation peak is attributed to defect center of Fe³⁺-V_O, which can be further confirmed by the lack of charge transfer band.

The excitation spectra of disorder phase is the same as the order phase. However, the peak value of emission spectra in disorder phase at 673 nm doesn't appear and the peak value at 700 nm transfers to 725 nm (due to weak crystal field), and the emission intensity decreases, because Fe³⁺ occupies higher symmetry position, leading to Fe³⁺ emission intensity reduces.

3.2 Effect of Different Li₂CO₃/Al₂O₃ Ratio on Luminescent Properties

Synthesis of aluminate luminescent material Li-Al₅O₈:Fe³⁺ needs high temperature treatment in order to generate corresponding matrix lattice, so different ratio of Li₂CO₃/Al₂O₃ impacts on phase composition.

Fig. 3 shows the diffraction patterns of the samples with different Li₂CO₃/Al₂O₃ ratio heated at 1400 °C for 4 h. Under the same calcination tem-

perature and the same calcination time , the ratio of $\text{Li}_2\text{CO}_3/\text{Al}_2\text{O}_3$ is in the range of 0.18 ~ 0.22 and crystallinity changes little. While the ratio of Li/Al is less than 0.2 , Al_2O_3 phase does not appear in XRD patterns. The reason is due to a slow process of Li^+ and Fe^{3+} ions diffused into $\gamma\text{-Al}_2\text{O}_3$ forming $\text{Li-Al}_5\text{O}_8:\text{Fe}^{3+}$, which generates one unreacted central kernel and this unreacted kernel is not bounded by correct composing component of fluorescence materials.

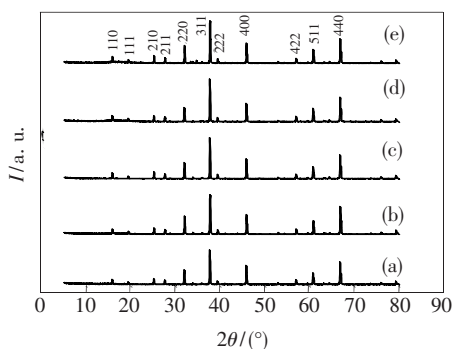


Fig. 3 XRD patterns of $\text{LiAl}_5\text{O}_8:\text{Fe}^{3+}$ with different ratio of $\text{Li}_2\text{CO}_3/\text{Al}_2\text{O}_3$ (mol) : (a) 0.18 , (b) 0.19 , (c) 0.20 , (d) 0.21 , (e) 0.22.

The emission intensity of the samples with different $\text{Li}_2\text{CO}_3/\text{Al}_2\text{O}_3$ ratio heated at 1400 °C for 4 h is shown in Fig. 4. It can be seen that light luminance is the highest when the ratio of Li/Al is 0.21. That is due to Li_2O has little volatilization at 1200 °C , which is the decomposition product of Li_2CO_3 . So , final phase of LiAl_5O_8 is approximate to stoichiometric ratio when Li_2CO_3 is a little excessive.

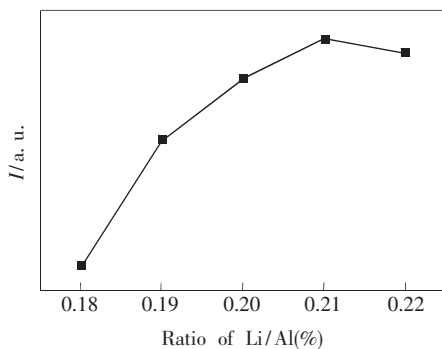


Fig. 4 The relationship between luminous intensity and of $\text{Li}_2\text{CO}_3/\text{Al}_2\text{O}_3$ ratio (mol)

3.2 The Effect of Fe^{3+} Content on the Luminescence Intensity

The amounts of activators have a great effect on

luminescence intensity. In general , the less the added amount , the less the constructive luminescent centers , the lower the luminescent intensity and luminous brightness. When the amount of activator is over a value , the concentration quenching can appear.

Fig. 5 shows the changes of the luminescence intensity of $\text{LiAl}_5\text{O}_8:\text{Fe}^{3+}$ emission peak with the Fe^{3+} under 245 nm excitation.

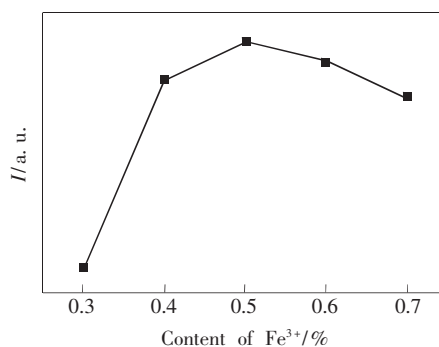


Fig. 5 The relationship between emission intensities of Fe^{3+} and content of Fe^{3+} in $\text{LiAl}_5\text{O}_8:\text{Fe}^{3+}$

It is found that luminescence intensity enhances with increasing Fe^{3+} content. When Fe^{3+} content is 0.5% , the luminescence intensity reaches maximum. Subsequently , the intensity become low with further increasing Fe^{3+} content.

4 Conclusion

1. Under the monitoring 673 nm , the excitation spectra of ordered phase indicate that there is a strong absorption band at 284 nm , which is charge transfer band of $\text{Fe}^{3+}-\text{O}^{2-}$. And there is a single emission band peaked at 673 nm under excitation of 254 nm. The emission band is slight asymmetry in the direction of longer wavelength , which belongs to ${}^4\text{T}_1({}^4\text{G})-{}^6\text{A}_1({}^6\text{S})$ transition.

2. Luminescent intensity is the strongest when the molar ratio of Li_2CO_3 and Al_2O_3 is 0.21.

3. Luminescence intensity is enhanced at 673 nm with increasing Fe^{3+} ion content. When Fe^{3+} ion content is 0.5% , the luminescence intensity reaches maximum.

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$\text{LiAl}_5\text{O}_8:\text{Fe}^{3+}$ 发光粉的发光性能

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摘要: Fe^{3+} 激活的铝酸锂是深红色发射的红色荧光粉, 其发射的峰值波长为 675 nm, 呈现出少有的纯正的深红色发光。本文对 $\text{LiAl}_5\text{O}_8:\text{Fe}^{3+}$ 荧光粉的基质组成和激活剂浓度进行了研究。结果表明: Fe^{3+} 掺杂 LiAl_5O_8 的激发光谱, 在 $\lambda_{\text{em}} = 673$ nm 的波长监测下, 有序相的激发光谱在 284 nm 处有强吸收带, 为 $\text{Fe}^{3+}-\text{O}^{2-}$ 电荷迁移带; 激发波长 $\lambda_{\text{ex}} = 254$ nm 的有序相样品的发射波长峰值为 673 nm, 并伴随一个在长波方向轻微不对称得, 发射是属于 ${}^4\text{T}_1({}^4\text{G}) \rightarrow {}^6\text{A}_1({}^6\text{S})$ 的跃迁。当原料 Li_2CO_3 与 Al_2O_3 的量的比为 0.21 时, 样品的发光强度最好; 样品的发光强度随激活剂 Fe^{3+} 的浓度的增加而提高, 当浓度达到 0.5% 时, 发光强度达到最大值, 超过 0.5% 时呈现出浓度猝灭效应。

关键词: 红色荧光粉; $\text{LiAl}_5\text{O}_8:\text{Fe}^{3+}$; 合成; 光致发光

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