Preparation and Optical Properties of AlF₃: Cr³⁺ Phosphor

Min Cai, Xinyan Yao and Shiqing Man*

School of physics and electronic information, Yunnan normal university University, Kunming, Yunnan, 650500, China

*Corresponding author e-mail: sqman_ynnu@163.com, 734802877@qq.com, 446794682@qq.com

Abstract. Cr³⁺ doped AlF₃ phosphors were synthesized via a facile solid state reaction method. XRD results showed that the prepared samples are single-phase. In the emission spectrum of AlF₃:Cr³⁺ powders, there is one sharp line emission located at 695 nm, which is arisen from 2E→4A₂ transition of Cr³⁺ in AlF₃ lattice. The excitation spectrum of AlF₃:Cr³⁺ powders monitored at 695 nm emission have two excitation bands of 500~600 nm and 380~450 nm. At room temperature, the fluorescence decay of Cr³⁺ ions in AlF₃ have been measured and the fluorescence decay curve have been reported.

1. Introduction

Inorganic materials with special morphologies have been attracting more and more attention owing to their potential in fundamental studies and technological applications [1–3]. Fluorides have attracted great interest for their low phonon energy and optical transparency over a wide wavelength range [4–6]. Fluorides doped with rare earths (RE) are very attractive materials for optical applications because they combine high-quantum efficiency with favorable chemical and mechanical properties [7, 8]. Furthermore, fluorides possess good thermal and environmental stability [9, 10].

Cr is a transition metal with an electronic configuration of 3d⁵4s¹, which becomes Cr³⁺ when it loses two electrons of the 3d layer and one electron of the 4s layer. On the basis of electronic structure, the unfilled 3d³ electronic shell of the Cr³⁺ ion splits into a number of low-lying energy levels, among which photon transitions can arise generating luminescent emission [11, 12]. Cr³⁺ doped materials are preferred because they possess wide absorptions, broadband emissions, high QE, and a good match with commercial blue or red LED chips [13]. The emission properties of Cr³⁺ can be significantly tuned from a narrow R-line (²E→²A₂ transition) emission to a broadband (⁴T₂→⁴A₂ transition) emission by varying the crystal field which has a high sensitivity of local surroundings [14].

In this work, we have prepared Cr³⁺ doped AlF₃ fluorescent materials by a large number of experiments, and analyzed their XRD patterns. The detailed spectra and its lifetimes were reported. It indicates that AlF₃:Cr³⁺ phosphor has the potential value of developing LED optoelectronic devices.

2. Experimental

Powder samples of AlF₃:Cr³⁺ were prepared by the solid-state reaction method. The starting materials were AlF₃·3H₂O(99%), Cr(NO₃)₃(99%) and NH₄F(99.99%). In order to prevent AlF₃·3H₂O hydrolyzing to Al₂O₃ at high temperature, firstly heat AlF₃ to 300℃ in vacuum for three hours to obtain anhydrous AlF₃. Stoichiometric amounts of the starting materials were thoroughly mixed and ground together by
an agate mortar, then placed in a corundum crucible and calcined at 960°C for 3h in N₂ protective atmosphere.

The X-ray diffraction (XRD) patterns of the samples were recorded on a (Rigaku Ultra IV, Japan) X-ray diffractometer using Cu Kα radiation ranging (λ = 1.5418 Å) with 10–80° at step rate of 0.02°. The room-temperature photoluminescence (PL) emission and PL excitation (PLE) spectra were recorded on an Edinburgh FS5 spectrometer with a 150W continuous-wave Xenon lamp as the excitation source. The decay curves were obtained by Edinburgh FS5 spectrometer using pulsed Xenon lamp as an excitation source.

3. Results and Discussion

The XRD patterns of the AlF₃:0.5%Cr³⁺ is presented in Fig. 1. The patterns can well match the standard card of PDF#044-0231 (AlF₃) selected from the international database for material structures. No impurity diffraction peaks were detected, which indicates that there was no obvious influence of the dopants on the crystalline structure of the host.

![Figure 1. XRD patterns of AlF₃:0.5%Cr³⁺ phosphors.](image)

The excitation spectra of AlF₃:0.5%Cr³⁺ at room temperature is shown in Fig. 2. As seen, sample has two excitation bands of 500~600 nm and 380~450 nm. The excitation band of 500~600 nm is attributed to the ⁴A₂g(F)→⁴T₂g(F) transition of Cr³⁺, and the excitation of 380~450 nm is attributed to the ⁴A₂g(F)→⁴T₁g(F) transition of Cr³⁺. Thus, AlF₃:Cr³⁺ phosphor may have great potentials in spectroscopy applications.

Fig. 3 shows the emission spectrum of the AlF₃:0.5%Cr³⁺ sample under 407 nm excitation. It can be observed that the emission band has a sharp peak at 695 nm which could be attributed to the ²E→⁴A₂ transition of Cr³⁺ to generate the R line. The appearance of the R line also demonstrates that the doped ions are in a relatively strong crystal field.

![Figure 2. Excitation intensity of AlF₃:0.5%Cr³⁺ under 695 nm emission](image)
Figure 3. Emission intensity of AlF$_3$:0.5%Cr$^{3+}$ excited at 407 nm

The RT fluorescent decay curves of the $^2$E$\rightarrow$$^4$A$_2$ transition of AlF$_3$:0.5%Cr$^{3+}$ phosphor under the excitation of 407 nm is shown in Fig. 4. The corresponding luminescent decay curves can be well fitted using a single exponential function: $I(t) = I_0 \exp(-t/\tau)$. On the basis of this fitting results, we can calculate the lifetime for the samples is 2.926 ms for AlF$_3$:0.5%Cr$^{3+}$.

Figure 4. Luminescence decay curves of AlF$_3$:0.5%Cr$^{3+}$

4. Conclusion
In conclusion, AlF$_3$:Cr$^{3+}$ phosphors have been synthesized by solid state reaction. XRD and luminescence results suggest that Cr$^{3+}$ have been doped into AlF$_3$ host lattices successfully. When excited at 407 nm, the R line emissions corresponding to the $^2$E$\rightarrow$$^4$A$_2$ transitions of Cr$^{3+}$ observed. The room temperature decay curves of $^2$E$\rightarrow$$^4$A$_2$ transitions of AlF$_3$:Cr$^{3+}$ was measured and luminescence lifetime of 2.926 ms was given out. The strong red emission of AlF$_3$:Cr$^{3+}$ phosphors suggests that these nanoparticles might have potential applications for LED, solid-state lasers and spectrometer calibration.
Acknowledgments
This work was supported by the National Natural Science Foundation of China (21661036).

References
[1] P. Alivisatos, The use of nanocrystals in biological detection [J]. Nature biotechnology, 2004, 22(1): 47.
[2] J. Zhou, Z. Liu, F. Li, Upconversion nanophosphors for small-animal imaging [J]. Chemical Society Reviews, 2012, 41(3): 1323-1349.
[3] X. Yu, M. Li, M. Xie, Dopant-controlled synthesis of water-soluble hexagonal NaYF4 nanorods with efficient upconversion fluorescence for multicolor bioimaging [J]. Nano Research, 2010, 3(1): 51-60.
[4] C. Li, J. Yang, P. Yang, Hydrothermal synthesis of lanthanide fluorides LnF3 (Ln= La to Lu) nano-/microcrystals with multiformal structures and morphologies [J]. Chemistry of Materials, 2008, 20(13): 4317-4326.
[5] C. Li, Z. Quan, J. Yang, Highly uniform and monodisperse β-NaYF4: Ln3+ (Ln= Eu, Tb, Yb/Er, and Yb/Tm) hexagonal microprism crystals: hydrothermal synthesis and luminescent properties [J]. Inorganic chemistry, 2007, 46(16): 6329-6337.
[6] Y. Jin, W. Qin, J. Zhang, Preparation and optical properties of SrF2: Eu3+ nanospheres [J]. Journal of Fluorine Chemistry, 2008, 129(6): 515-518.
[7] G. Lakshminarayana, J. Qiu, Photoluminescence of Pr3+, Sm3+ and Dy3+-doped SiO2–Al2O3–BaF2–GdF3 glasses [J]. Journal of Alloys and Compounds, 2009, 476(1-2): 470-476.
[8] G. Lakshminarayana, J. Qiu, Photoluminescence of Pr3+, Sm3+ and Dy3+: SiO2–Al2O3–LiF–GdF3 glass ceramics and Sm3+, Dy3+: GeO2–B2O3–ZnO–LaF3 glasses [J]. Physica B: Condensed Matter, 2009, 404(8-11): 1169-1180.
[9] M. Leblanc, V. Maisonneuve, A. Tressaud, Crystal chemistry and selected physical properties of inorganic fluorides and oxide-fluorides [J]. Chemical reviews, 2014, 115(2): 1191-1254.
[10] P.D. Belsare, C.P. Joshi, S.V. Moharil, One step synthesis of complex fluoride powders for solid-state lasers [J]. Journal of Alloys and Compounds, 2008, 464(1-2): 296-300.
[11] H. Mi, Y. Huang, Z. Lin, Cr3+-doped CaMgSi2O6 crystal: a promising tunable laser and ultrashort laser crystal [J]. Cryst Eng Comm, 2014, 16(5): 763-765.
[12] P. Wagenblast, R. Ell, U. Morgner, Diode-pumped 10-fs Cr3+: LiCAF laser [J]. Optics letters, 2003, 28(18): 1713-1715.
[13] B. Malysa, A. Meijerink, T. Jüstel, Temperature dependent Cr3+ photoluminescence in garnets of the type X3Sc2Ga3O12 (X= Lu, Y, Gd, La) [J]. Journal of Luminescence, 2018, 202: 523-531.
[14] B. Henderson, G.F. Imbusch, Optical spectroscopy of inorganic solids [M]. Oxford University Press, 2006.