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Effect of LiCl on the crystallization behavior and luminescence of $Y_3Al_5O_{12}$: Tb

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Abstract

The single-phase cubic $Y_3Al_5O_{12}$: 1% Tb sol–gel-derived powders were prepared after firing at 650°C for 2 h when a LiCl flux was used. The addition of the LiCl can increase the crystalline size of the powders at low temperatures. By using the broadening effect of X-ray patterns, the estimated crystalline size of the powder with 20 wt.% LiCl addition fired at 650°C for 2 h was evaluated as 480 Å. Both emission and excitation luminescent spectra of the samples were measured. Emission spectra of the synthesized powders mainly show $^5D_4$–^6F transition under 275 nm excitation. The excitation spectra of The Tb^{3+} ions are different between amorphous and crystalline phase because of the crystal field effect. The excitation spectra also help observing the degree of the crystallinity of the resulting YAG phase.

Keywords: $Y_3Al_5O_{12}$: Tb; LiCl addition; Crystallization; Emission spectrum; Excitation spectrum

1. Introduction

Yttrium-aluminum garnet (YAG, $Y_3Al_5O_{12}$) has a useful structure for applications in optical fields. It is generally used as lase host crystal and phosphors. The synthesis of phase-pure YAG phosphors by conventional solid-state reaction usually requires high temperatures above 1600°C. The improved solid-state reaction process which was associated with flux such as BaF_2 or YF_3 [1,2] can lower the sintering temperature down to 1500°C. Chemical methods have also been developed to lower the synthesis temperatures down to 900°C but the temperatures are not low enough to develop the phosphors on the glass substrate such as indium tin oxide (ITO) [3–6]. In this study, we prepare the flux-added powders by using sol–gel process to lower the synthesis temperature. We also investigate the effect of flux on the phase formation and luminescent properties of $Y_3Al_5O_{12}$: Tb.

2. Experiments

The $Y_3Al_5O_{12}$: Tb starting powders were fabricated from the starting materials of yttrium nitrate, terbium nitrate, and aluminum tri-sec butylate in the mole ratio of 2.97 : 0.03 : 5, dissolved in the mixture of ethylaceto acetate and 2-methoxythanol and the details were described elsewhere [7]. The starting powders without LiCl addition (sample A), with 20 wt.% LiCl (sample B), and 200 wt.% LiCl (sample C) were fired at temperatures from 650°C and 750°C for 2 and 10 h. The high amount of LiCl used in the sample C is for studying the crystallization behavior of the starting powders in the melt.

The phase in the resultant powders were examined by using MAC MXP3 X-ray diffractometer with nickel-filtered Cu K_α radiation 40 kV and 20 mA at a scan rate of 4° min^{-1}. Both emission and excitation luminescent spectra of the samples were measured by using Shimadzu RF-5301 PC photoluminescence spectrometer with xenon lamp.

3. Results and discussion

The X-ray diffraction (XRD) patterns of the sample A treated at 650–950°C for 2 and 10 h are indicated in Fig. 1. The powders show amorphous for 2 and 10 h heat treatment at 750°C and they attain more perfect crystalline at 850°C. the powders become more complete YAG phase at 950°C. The heat treatment times (2 and 10 h) affect the intensities of the XRD patterns at 850°C much more than they do at 950°C (Fig. 1). On the basis of XRD results, it is clear that YAG is the only crystalline phase. The XRD pattern of the sample B

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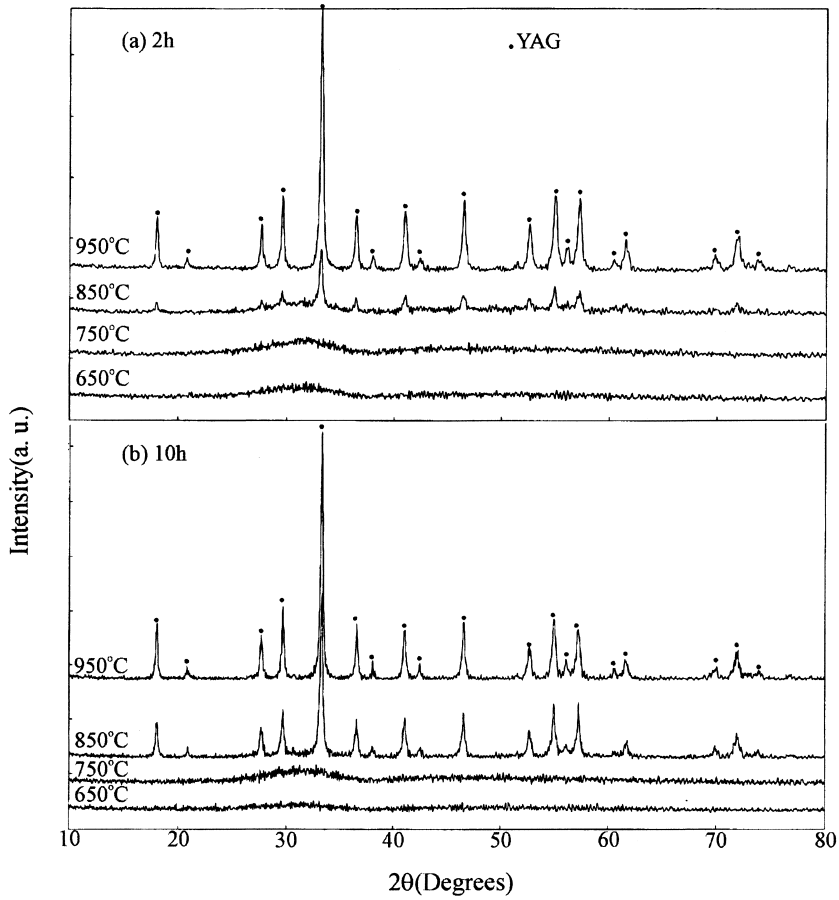

Fig. 1. The XRD patterns of the samples A heat-treated from 650°C to 950°C for (a) 2 h and (b) 10 h.

heated at 650°C for 2 h shows peaks corresponding to YAG phase (Fig. 2(a)). The sample C heated at 650°C has similar XRD pattern to the sample B and also shows pure YAG crystalline phase.

The crystalline size of the powders is dependent on heat treatment time, temperature and amount of LiCl addition. On the basis of XRD broadening effect, crystalline size of the samples can be determined by Scherrer's formula [8]. The evaluated results are listed in Table 1. It indicates that the crystalline sizes of the sample A are all under 100 Å. The 850°C fired sample A does not present much difference in crystalline sizes for different firing times, 2 and 10 h. However, the crystalline size of the 950°C fired sample A depends on firing time. The powders with LiCl almost show larger crystalline size than the powders without LiCl even at lower treatment temperature (650°C and 750°C). The crystallization temperature of the sample with LiCl is lowered to 650°C while that of the sample without LiCl is about at 950°C.

The crystalline size of sample C is about 1.5 times that of sample B at 650°C for 2 h. The crystalline size is over 1000 Å for sample C treated at 750°C for 10 h. The crystalline size obviously depends on the heat treatment time and the amount of LiCl added.

Table 1
The estimated crystalline sizes of the samples A–C by using broadened effect of XRD patterns

Samples	Firing condition		Estimated crystalline size (Å)
	Temperature (°C)	Time (h)	
A	850	2	410
		10	480
	950	2	480
		10	860
B	650	2	480
		10	860
	750	2	600
		10	860
C	650	2	600
		10	860
	750	2	860
		10	>1000

Fig. 3 shows the emission luminescence spectra of the samples A–C heat-treated at 650°C. The spectra are mainly due to the $^5D_4$–^6F transitions of the Tb^{3+} ion, which belong to green region. The emission spectra of the crystalline phases of the samples B and C show Stark levels due to the crystal field [9]. The spectra of the amorphous phases of the

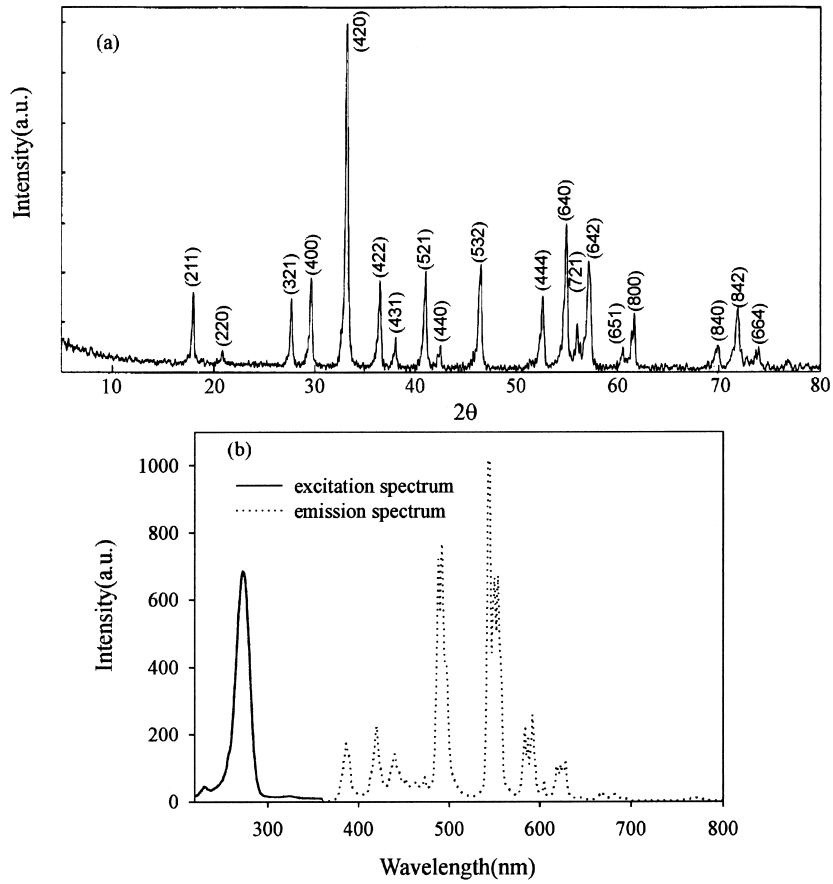

Fig. 2. The X-ray pattern (a), the excitation and emission spectra (b) of sample B heat-treated at 650°C for 2 h. The XRD patterns are indexed by using JCPDS cards 33–40.

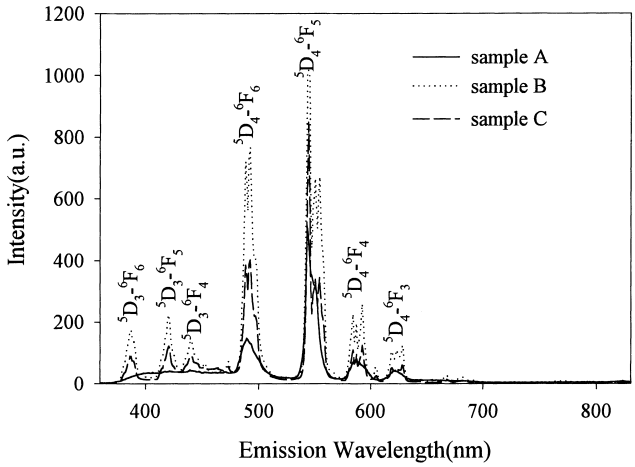

Fig. 3. The emission spectra of the samples A–C heat-treated at 650°C for 2 h. The samples A is under 254 nm excitation while samples B and C are under 275 nm excitation.

sample A are broadened and do not show Stark levels so that there are no crystal field effect on Tb^{3+} ions. However, the emission spectra of the amorphous phase and the crystalline phase show peaks at the same positions. Besides the $^5D_4$–^6F transitions, the $^5D_3$–^6F transitions of the blue region are also observed in the spectra of the samples B and C. Due to the cross-relaxation ($^5D_3(Tb_1)$–$^5D_4(Tb_2)$), the spectral intensity for $^5D_3$–^6F transitions is relatively lower in the crystalline phase. The $^5D_3$–^6F transitions are not obvious in amorphous phase in which there are many shunt path so that the luminescence efficiency of the amorphous powders is low.

We can compare the excitation spectra of sample A heat-treated at various temperatures for 2 and 10 h (Fig. 4(a) and (b)). The samples A heat-treated at 650°C and 750°C show a broadened peak near 254 nm (Fig. 4). This peak splits into three peaks located at 230, 275, and 323 nm after 850°C and 950°C heat-treatment and the phases are also transformed from amorphous to crystalline phase. In Fig. 4, there are two kinds of spectra which can be classified into amorphous phase (254 nm) and crystalline phase (230, 275, and 323 nm) spectra. The spectra of amorphous phase are broader than those of the crystalline phase. We can also observe the degree of crystallinity of YAG phase from the excitation spectra. The excited states of Tb^{3+} ion which belong to 5d orbitals are strongly affected by crystal field in the crystalline phase. Therefore, the 4f–5d transitions [10] show a group of sharp lines in the excitation spectra recorded from 220 to 400 nm of the crystalline phase. In

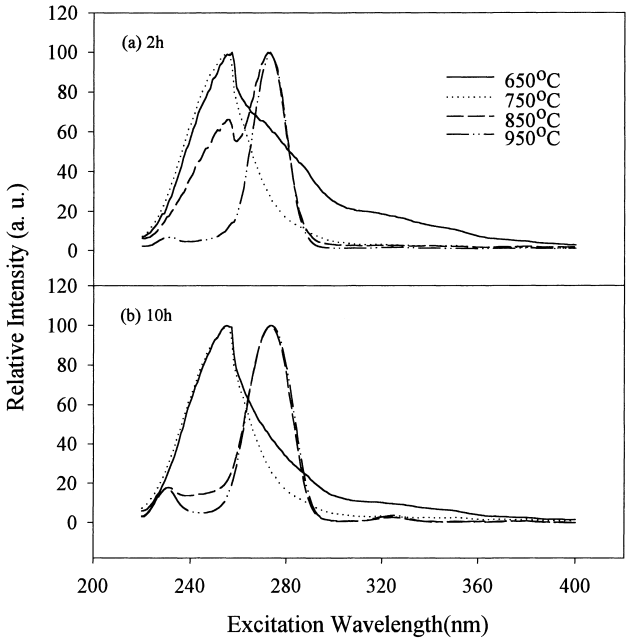

Fig. 4. The excitation spectra of the sample A heat-treated from 650°C to 950°C for (a) 10 h and (b) 2 h. The detected emission wavelength is 544 nm for all samples.

Fig. 4(b) we can find that there are still some degrees of amorphous phase existing in the sample A heated at 850°C for 10 h based on the relatively low intensity of 230 nm peak. However, we cannot detect such small amount of amorphous phase existing in 850°C, 10 h sample A from XRD pattern (Fig. 1(b)). On the other hand, there is no 254 nm amorphous broadened peak in the excitation spectra for the 650°C 2 h treated sample B as shown in Fig. 2(b) which agrees with the XRD result of high purity YAG crystalline phase as shown in Fig. 2(a).

4. Conclusions

We could successfully synthesis a complete YAG crystalline phase at 650°C for 2 h by mixing the sol–gel-derived powder with LiCl. The present synthesis temperature is 300°C lower than that without LiCl. Based on the analysis of the crystalline sizes, we envisage that the LiCl addition could enhance the growth behavior of the YAG crystalline phase.

The emission spectra of the samples fired with LiCl, which are crystalline phase, showing $^5D_4$–^6F transitions and little $^5D_3$–^6F under 275 nm excitation. The peaks show stark levels on $^5D_4$–^6F transitions. The amorphous phase shows only $^5D_4$–^6F transitions and no stark levels are observed. The excitation spectra indicate the 4f–5d absorption of the Tb^{3+} ions. In the excitation spectra, the amorphous phases show a broadened peak at 254 nm and the crystalline phases show three peaks at 230, 275, and 323 nm, respectively. The excitation spectra of the synthesized powders also support the purity of YAG : Tb crystalline phase.

Acknowledgements

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