

Properties of Combustion Synthesized $\text{SnO}_2:\text{Eu}^{3+}$ Phosphors

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Abstract

A novel ceramic synthesis technique, combustion synthesis, is explored to produce an orange-emitting $\text{SnO}_2:\text{Eu}^{3+}$ phosphors. This technique involves a reaction of metal salts with a citric acid as an organic fuel. The variation of the ratio of citric acid to metal introduces change in reaction temperature and atmosphere of the combustion reaction, which in turn influences crystallinity and luminescence properties of the final products significantly. And the heat treatment of the as-synthesized product improved the CL intensity of the products. Especially, the sample treated at above 1100 °C shows an orange-emission, which is attributed to the formation of single phase and well-crystallized $\text{SnO}_2:\text{Eu}$ in rutile structure.

1. Introduction

Recently, a novel combustion synthesis technique has been of interest and attractive for phosphor synthesis because of its success in producing fine, multi-component, crystalline and homogeneous ceramic at relatively low temperature and with reduced processing time [1, 2]. The process involves an exothermic reaction between metal salt as an oxidizer and an organic fuel, such as urea ($\text{CH}_4\text{N}_2\text{O}$), carbonylhydrazide ($\text{CH}_6\text{N}_4\text{O}$), glycine ($\text{C}_2\text{H}_5\text{NO}_2$) and citric acid ($\text{C}_6\text{H}_8\text{O}_7$). In general, a good fuel should react non-violently and produce non-toxic gases, and act as a chelating material for metal cations. Especially, uniform mixing and prevention of selective precipitation of the components in the stock solutions prior to the reaction are required to obtain homogeneous and crystalline multi-component luminescent oxide powders, because the combustion reaction is completed within a few seconds. Consequently, the selection of an appropriate fuel for the system under this study is very important for the combustion method [3]. Among known fuels, the citric acid has demonstrated the versatility of combustion synthesis methods by the successful preparation of a large number of single-phase, well-crystallized and multi-component oxides [4].

Especially, the citric acid serves two principal purposes : first, complexes with metal cations are formed, and second, it acts as a fuel for the combustion reaction. This work attempts to produce the orange-emitting $\text{SnO}_2:\text{Eu}^{3+}$ phosphor with high brightness with a combustion process using a citric acid as a fuel. The goal in this study is to identify and obtain a better understanding of the significant processing parameters in the combustion synthesis of luminescent $\text{SnO}_2:\text{Eu}$.

2. Results and Discussion

Figure 1 outlines the steps required for the synthesis of $\text{SnO}_2:\text{Eu}$ phosphor. The combustion synthesis of $\text{SnO}_2:\text{Eu}$ phosphor was initiated by the preparation of polymeric precursors using an aqueous tin citrate solution prepared from $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and citric acid. The polymeric precursors were calcined in two steps, initially at 300 °C for 6 hr to promote pyrolysis and then at 900 ~ 1300 °C for 4 hr to allow complete

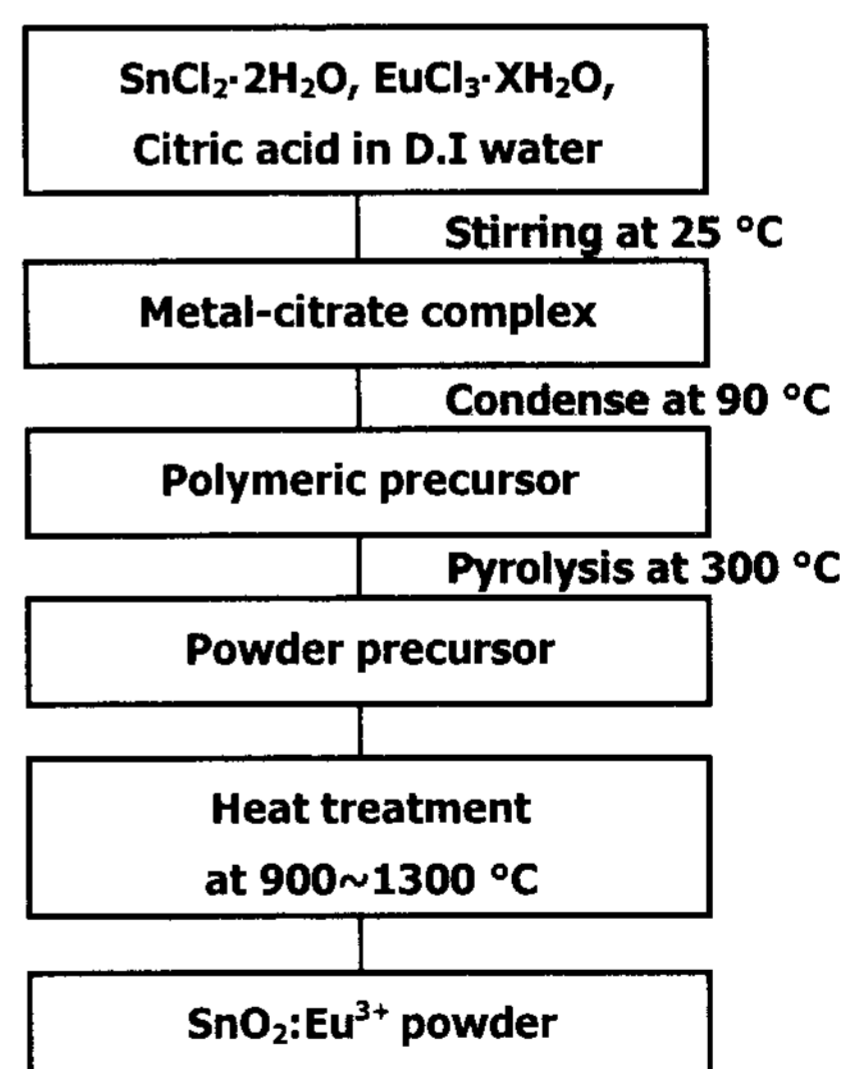


Figure 1 Flowchart of $\text{SnO}_2:\text{Eu}^{3+}$ preparation by combustion synthesis.

oxidization of the organic powder precursor and to promote the crystallization of the SnO₂:Eu phase.

As shown in Fig. 2, the as-pyrolyzed products with the combustion reaction show an unusual morphology, i.e., forming a porous and foamy network due to rapid release of gaseous by-products during the combustion reaction.

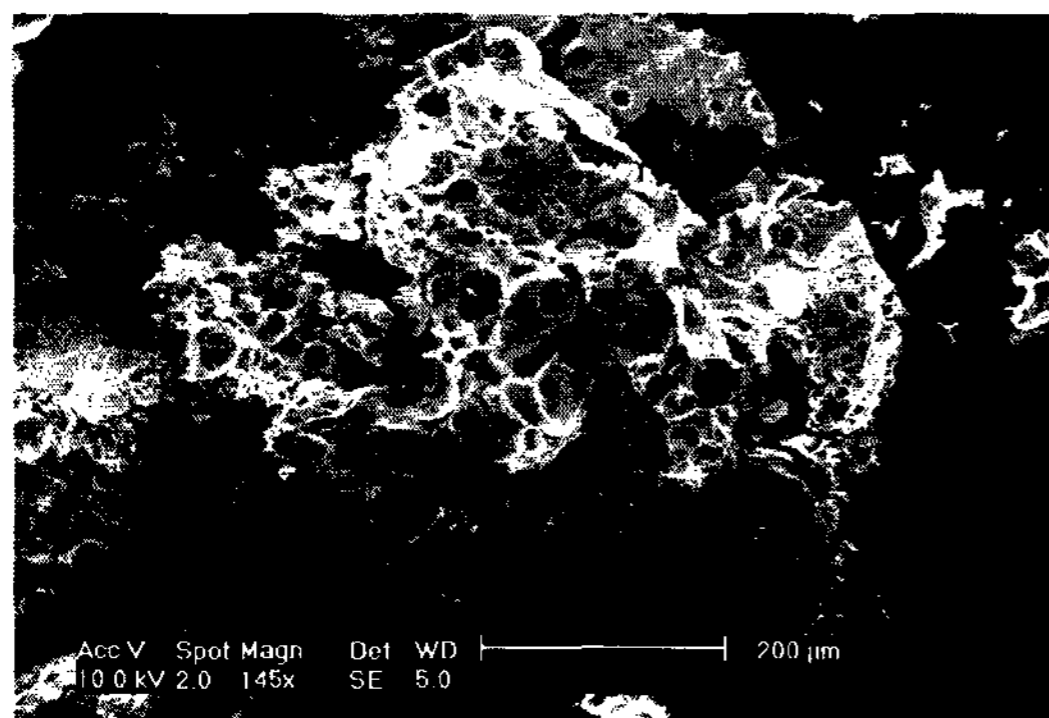


Figure 2 SEM micrograph of as-pyrolyzed SnO₂:Eu products by the combustion reaction.

The differential scanning calorimetry (DSC) (a) and thermogravimetric (TG) (b) curves are shown in Fig. 3 for the polymeric precursors. The drastic weight loss around 170 °C indicates that self-propagating combustion occurs during decomposition of the precursors. The combustion arises from an exothermic anionic oxidation-reduction reaction between the citrate and nitrate ions. The other weight losses at higher temperatures from 300 to 800 °C were

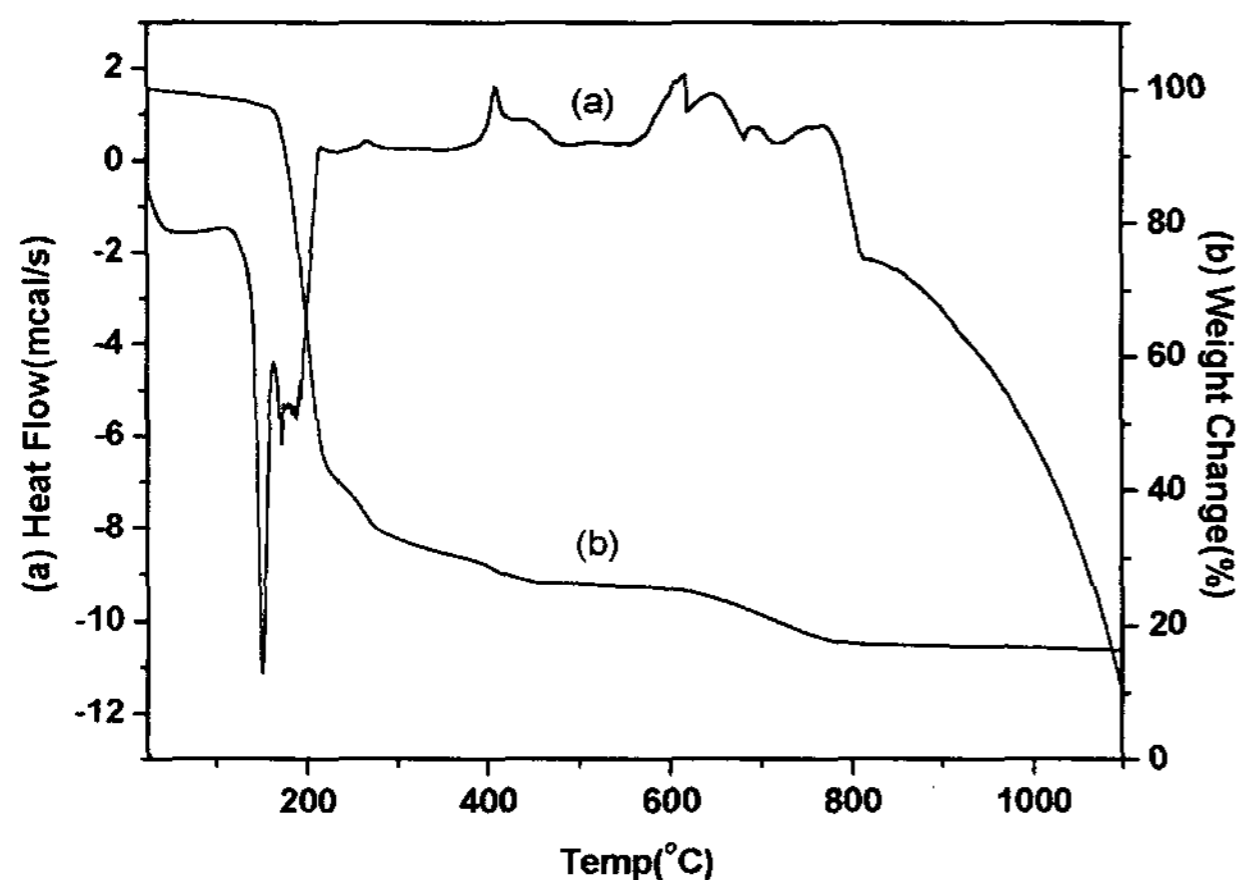


Figure 3 DSC/TG curves for polymeric precursors.

observed corresponding to the burning of residual organic components.

Figure 4 shows XRD spectra of samples synthesized by combustion reaction. X-ray peaks of SnO₂:Eu powder precursor just after pyrolysis is given in Fig. 4(a), which shows the diffraction patterns of a single phase and crystallized SnO₂:Eu oxides in rutile structure even before heat-treated. However, luminescence of SnO₂:Eu precursor produced by the combustion reaction was not observed due to the weak crystallinity and incomplete decomposition of organics by the instantaneous exothermic reaction during the combustion reaction. After subsequent heat treatment at 1200 °C for 4 hr, the spectra of heat-treated powders showed the better crystallinity than that of the precursors (Fig. 4(b)).

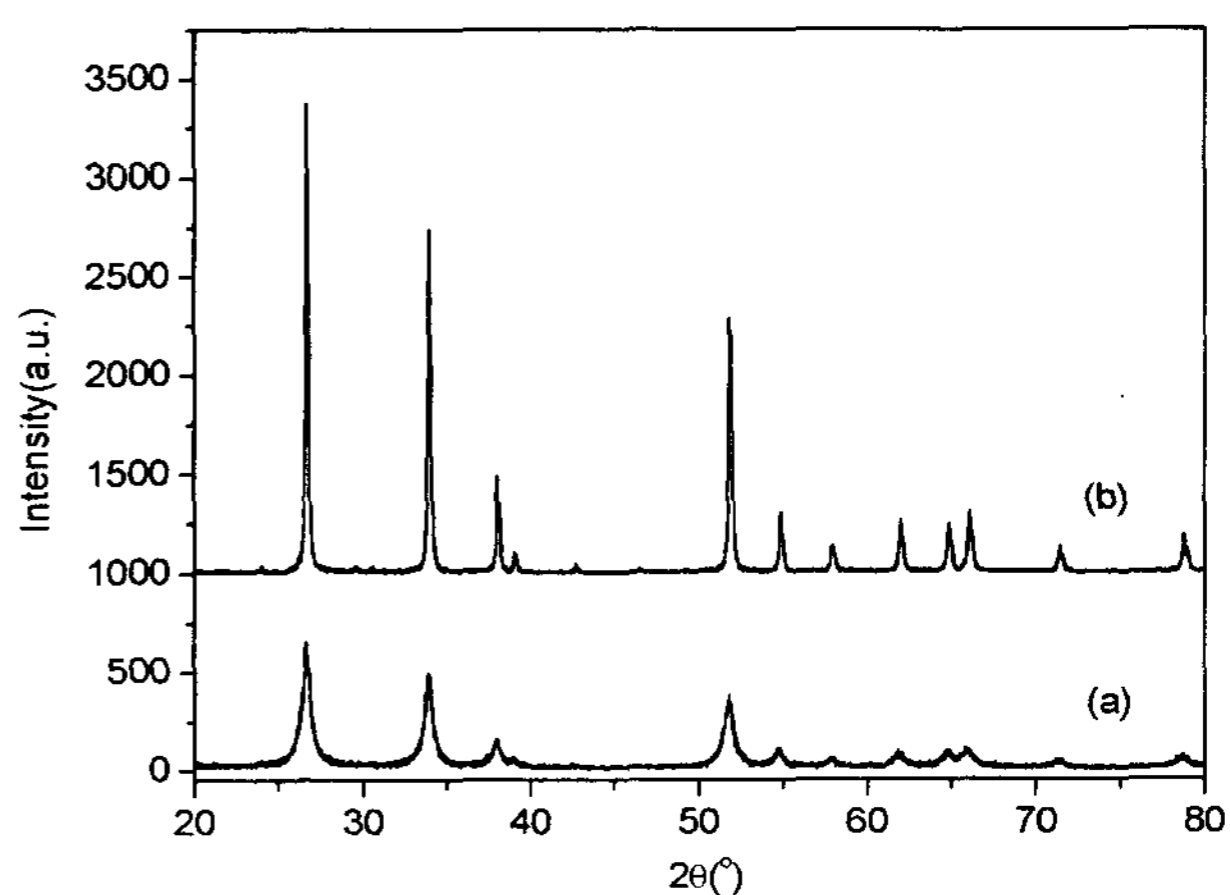


Figure 4 XRD curves of SnO₂:Eu powder heated at (a) 300 °C (powder precursor) and (b) 1200 °C.

Figure 5 shows the SEM micrographs of the combustion synthesized SnO₂:Eu phosphor powders with ratio of citric acid/metal followed by subsequent heat treatment at 1200 °C for 4 hr. There have been several reports on the effects of fuel/metal ratio in combustion reactions to produce fine ceramics [5-7]. As shown in Fig. 5, the particle size of combustion synthesized SnO₂:Eu noticeably increased with the amounts of citric acid. This is most likely due to the decrease in reaction temperature associated with higher fuel/metal ratios, which causes the slow formation of SnO₂:Eu phase thereby developing the particle growth of SnO₂:Eu phosphor [8, 9].

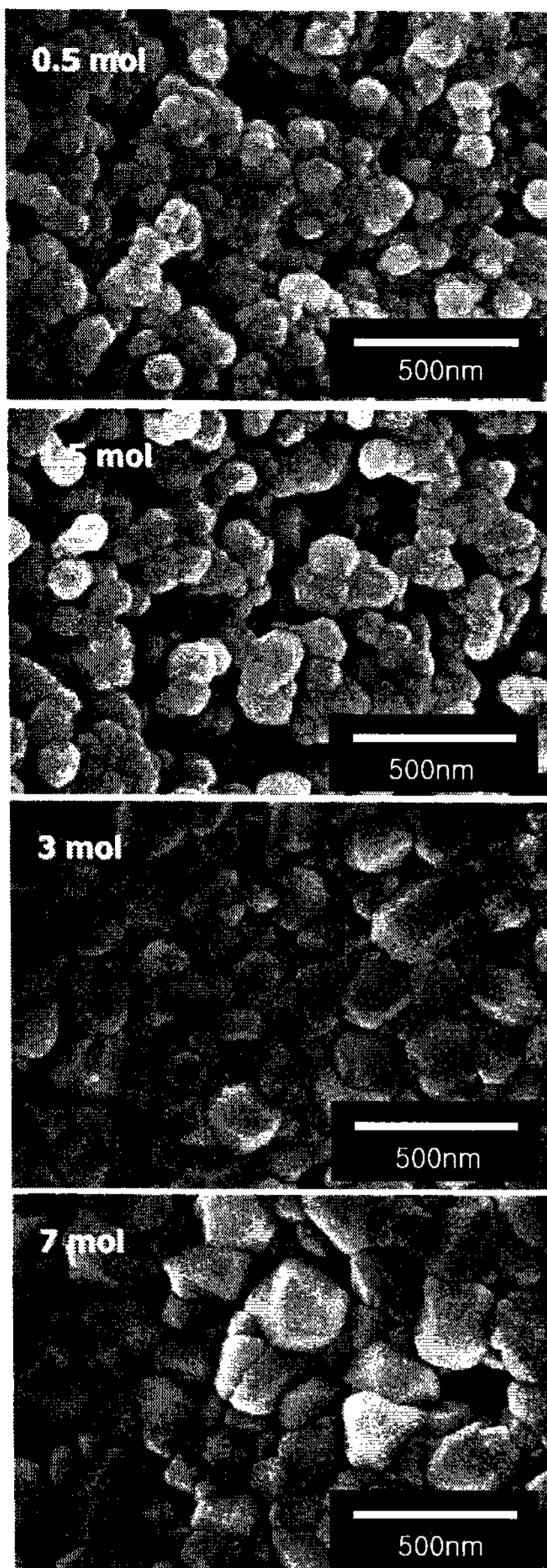


Figure 5 SEM micrographs of the combustion synthesized $\text{SnO}_2:\text{Eu}^{3+}$ phosphor powders with ratio of citric acid/metal.

Figure 6 shows the Cathodoluminescence (CL) of the combustion synthesized $\text{SnO}_2:\text{Eu}$ phosphor with varying the ratio of citric acid/metal followed by subsequent heat treatment at 1200°C for 4 hr. As shown in Fig. 6, the CL of $\text{SnO}_2:\text{Eu}$ with ratio of citric acid/metal shows drastic difference. As the amount of fuel used for the combustion reaction increased up to 1.5 mol, the light output of the resultant powders also increased. In the cases of fuel richer than 1.5 mol,

However, the CL decreased abruptly. It is reported that the use of excessive amount of citric acid may make the atmosphere of reaction more reductive one [10]. From the results of SEM and CL measurement, it is shown that the more reductive atmosphere is formed and the reaction temperature is lowered in the case of fuel richer than 1.5 mol, which deteriorates the crystallinity of $\text{SnO}_2:\text{Eu}$ phase. Consequently, it is found that the luminescence efficiency of the combustion synthesized $\text{SnO}_2:\text{Eu}$ phosphor has very sensitive dependence on its crystallinity. More experiments to know exact reasons for this phenomenon are being carried out.

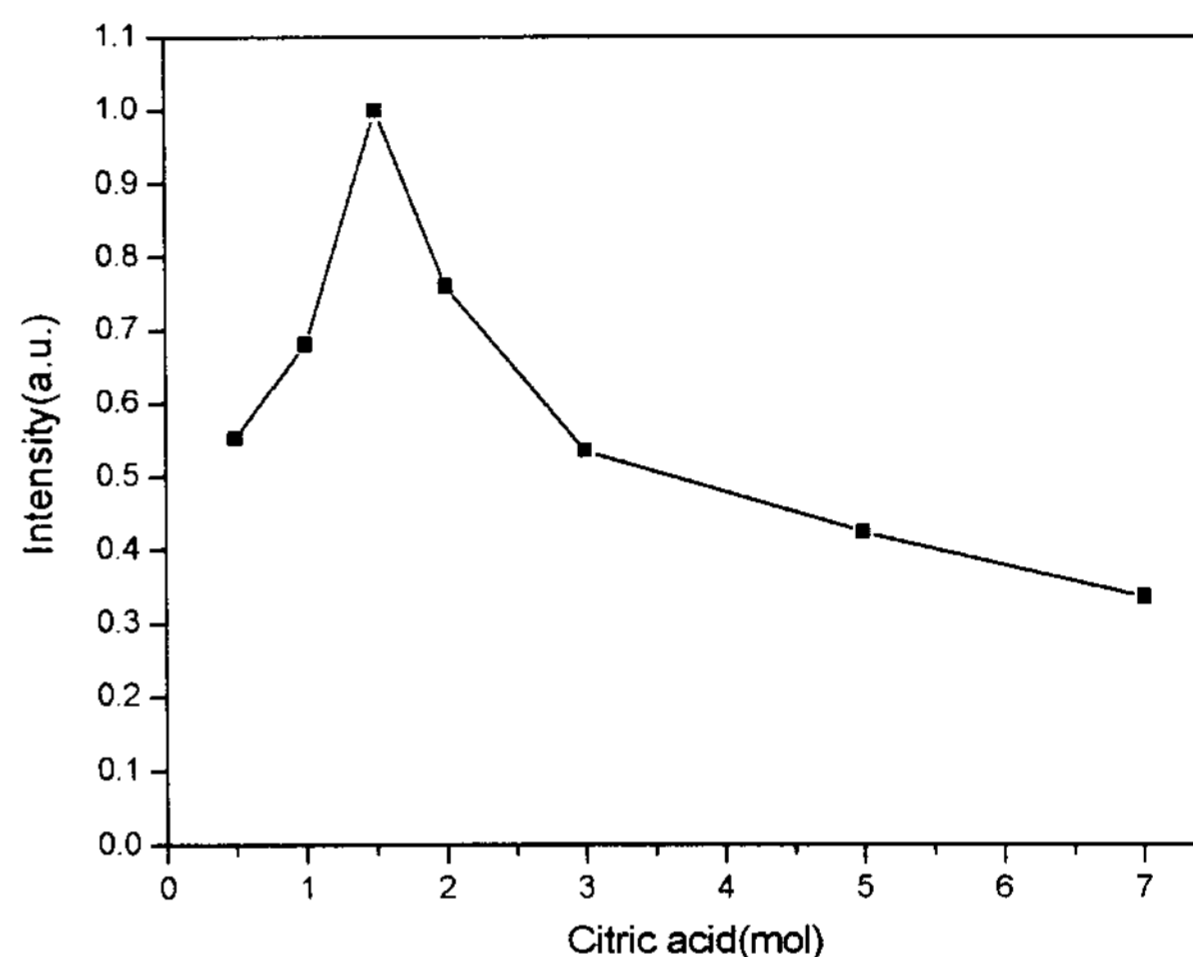


Figure 6 CL of the combustion synthesized $\text{SnO}_2:\text{Eu}^{3+}$ phosphor powders with varying the ratio of citric acid/metal.

3. References

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