Morphological, structural and photoluminescence properties of sol-gel synthesized strontium titanate ($SrTiO_3$:Pr,Al) nanophosphors

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Abstract
Luminescent phosphors of Pr^{3+}-doped $MTiO_3$ (Ca, Sr, Ba) has been reported being superior to those of the type Y_2O_3:Eu^{3+}. However, as one of the tricolour, red phosphors with efficient afterglow property are still deficient. Therefore, improving the luminescence property and afterglow performance of red phosphors becomes an important task. In order to address these issues, Al^{3+} co-doped, Pr^{3+}-doped $SrTiO_3$, red nano phosphors were fabricated through sol-gel process, using acetic acid and ethylene glycol (EG) as additives. The photoluminescence, crystallinity and particle morphology of persistent phosphors were investigated by using luminescence spectrometer, X-ray diffractometer (XRD) and scanning electron microscopy (SEM), respectively. The results showed that the acetic acid to ethylene glycol mole ratio significantly affect the morphological, structural and photoluminescence properties of the nanostructures. The SEM micrograph depicts spherical and regular shaped structures with sizes in nano ranges confirmed by SEM and XRD measurements. The same XRD patterns display pure and well-crystalline $SrTiO_3$ with cubic structure. Photoluminescence spectra revealed broad dominant emission from the $^1D_2 \rightarrow$ $^3H_4$ transition of Pr^{3+} at about 615 nm. The preparation parameters were found to affect significantly the luminescence intensity and afterglow property of the $SrTiO_3$:Pr;Al red phosphors. It is found that the addition of Al leads to the enhancement of red fluorescence and phosphorescence at 615nm originating from $^1D_2$-$^3H_4$ transition of Pr^{3+}, following the increase of the lifetime for the $^1D_2$ state.

Keywords: Morphology; Phosphors; Luminescence; Sol-gel; $SrTiO_3$; Long Afterglow

1. Introduction

Long-lasting phosphorescences (LLP) have attracted considerable attention in the recent half-century. Since the green and blue emitting LLP phenomena of Eu2+- doped alkaline-earth aluminates were first reported in 1996 by Matsuzawa et al. [1], the oxide LLP materials have been studied extensively and developed rapidly to replace the traditional sulfide afterglow materials. At present, the most efficient LLP materials are still based on alkaline-earth aluminates such as $SrAl_2O_4$:Eu^{2+}, Dy^{3+} (green), $CaAl_2O_4$:Eu^{2+}, Nd^{3+} (blue), especially $SrAl_2O_4$:Eu^{2+}, Dy^{3+}, whose afterglow time can last over 20hr and has already shown its great commercial value [1]. However, as one of the tricolour, red LLP phosphors with efficient afterglow property are still deficient. Until now, none of the reported red LLP phosphors has met the requirement for commercial use [2-4]. As a result, the multicoloured application of LLP materials has been greatly restricted. Therefore, improving the afterglow performance of red LLP phosphors becomes an urgent task. Perovskite-type praseodymium-doped $SrTiO_3$:Pr^{3+} is a potential red phosphor, its dominant emission from the $^1D_2 \rightarrow ^3H_4$ transition of Pr^{3+} (at about 615 nm), makes it an “ideal red phosphor” for various display applications. In particular, doping of $SrTiO_3$ with Pr is known to result in red luminescence. Although the luminescence of $SrTiO_3$:Pr^{3+} itself is rather weak, co-doping of the samples with oxides of group-III elements (Al, B, Ga, In) enhances luminescent efficiency up to 200 times [5,9,10]. Recently, many other methods, such as sol–gel [6], hydrothermal [7] and auto-combustion syntheses [5], have been used to prepare $SrTiO_3$ of different sizes and morphologies. $SrTiO_3$:Pr^{3+} phosphors can be prepared by a varies methods such as solid-state reaction, sol–gel [8], the solvothermal method and etc, the influence of different synthesis methods on the particle size, morphology, structural and the luminescent properties of $SrTiO_3$:Pr^{3+}. The Pr^{3+} ions act as activator whilst the addition of Al^{3+} ions acts as sensitizers. The Pr^{3+} ions emit the radiation to improve the luminescence properties, Al^{3+} ions help energy transfer to Pr^{3+} ions in $SrTiO_3$ lattice. In this study, $SrTiO_3$:Pr;Al nanophosphors are synthesized by sol-gel process CH_3COOH to adjust the pH of the system. The gel was converted to strontium titanate ($SrTiO_3$) by drying and calcinations, which is one of the most technologically important in dielectric ceramics.

2. Experiment

Al^{3+} co-doped, Pr^{3+}-doped $SrTiO_3$ red phosphors powders were synthesised at low temperatures by the sol-gel process. The starting materials used, were strontium acetate ($Sr(CH_3COO)_2$), praseodymium nitrate ($Pr(NO_3)_3.6H_2O$), aluminium nitrate($Al(NO_3)_3.9H_2O$), and tetra-n-butyl titanate($Ti(OC_4H_9)_4$ with 99.9% purity. To investigate the effect of $Pr^{3+}$and Al^{3+} on the structural and PL properties of $SrTiO_3$: Pr^{3+} the doping concentration of Pr and Al were fixed at 1 a% of Sr component which is the optimized amount to obtain the good red phosphor. The solutions were prepared at room temperature by dissolving ($Sr(CH_3COO)_2$), ($Pr(NO_3)_3.6H_2O$), ($Al(NO_3)_3.9H_2O$), into ($Ti(OC_4H_9)_4$ and then CH_3COOH as a chelating agent. Different volumes of Ethylene glycol (0, 2, 4, 8, 12 ml) were added drop wise while continuously stirred until 3.5 pH value were reached and the solution formed a thick gel. The gel solution were dried at room temperature (for about 7-14 days), residual solvent was removed by drying the gel solution in oven 80^0C for 2h. The heat treatment was carried out in two stages: initial heating at 400^0C for 2h, followed soon thereafter by heating at 700^0C for 2 h to crystallize on the furnace. Finally the powder was crushed into a fine powder. The crystal structures of the particles were studied by an x-ray diffraction (Bruker D8 diffractometer, Bruker Corporation of Germany, operating at 40 kV and 40 mA, and using Cu K_α = 1.5406 Å). The morphologies of particles were investigated using Shimadzu model ZU SSX – 550 Superscan scanning electron microscope (SEM), coupled with an energy dispersive x-ray spectrometer (EDS). Photoluminescence measurement was performed at room temperature on a Cary Eclipse fluorescence spectrophotometer (Model: LS 55) with a built-in 150 W xenon lamp as the excitation source and a grating to select a suitable wavelength for excitation.

3. Results

3.1 Morphology and XRD analysis

A representative XRD patterns recorded for the $SrTiO_3$:Pr,Al compositions is shown in Figure 1. The results of x-ray phase analysis of as-synthesized by sol-gel process demonstrated that the diffraction peak positions and the relative intensities of the prepared sample well-indexed relative to those of the standard cubic crystal structure of $SrTiO_3$ (JCPDS 84–0444). The presence of dopant and co-dopant do not affect the structural properties of the phosphors. Figures 2 (a) and (b) depict SEM images of the surface morphologies of the ground $SrTiO_3$:Pr^{3+} and $SrTiO_3$:Pr,Al phosphors synthesized using sol-gel process. The SEM micrograph depicts mixture of spherical and regular shaped structures with straight edges. The sizes of the spherical shaped particles are clearly in nano ranges. The straight edges confirm the high crystalline structures confirm by the by XRD measurements. It was observed that the different volume of the ethylene glycol ions have an effect on the morphology of the samples.

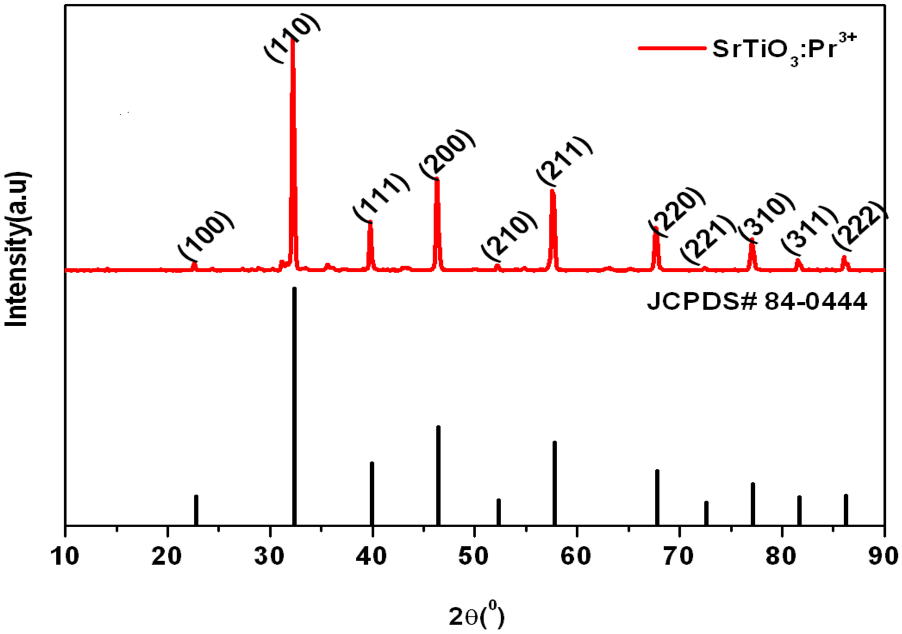
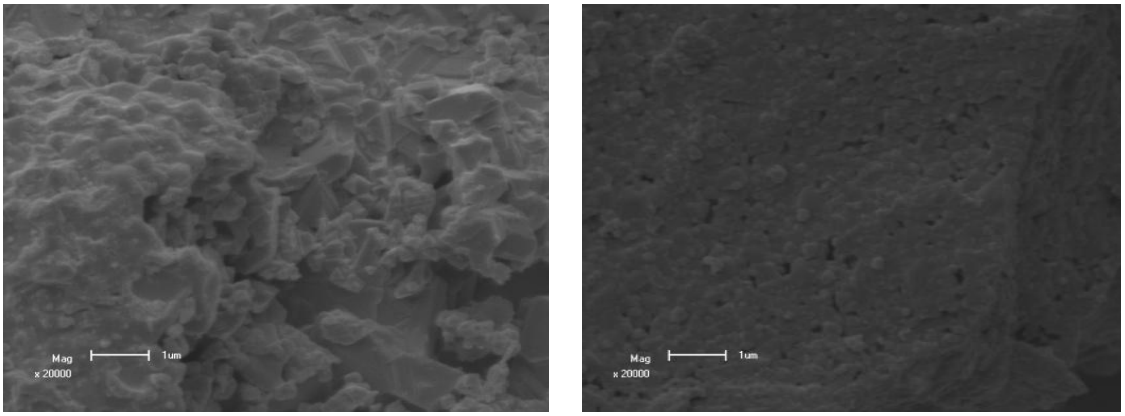


Figure 1 A representative XRD pattern of SrTiO$_3$:Pr^{3+} with different volume of (CH$_3$O)$_2$, all the peaks revealed SrTiO$_3$ a cubic lattice (JCPDS# 84-0444)



(a) **(b)**

Figure 2 SEM image of SrTiO$_3$:Pr^{3+} (a) and SrTiO$_3$:Pr,Al (b) at 2000X magnification.

3.2 Optical analysis

Fig. 3(a) shows the excitation spectrum of SrTiO$_3$:Pr^{3+},Al^{3+} phosphor powders prepared by sol-gel process. The excitation spectrum display a broad band, corresponding well to the absorption edge of the titanate group at wavelength below 340nm, which indicates that the emission in Fig. 3(b) results from energy transfer from the titanate group to the excited states of praseodymium ions. The absence of the weaker 4f absorption demonstrates its low absorption cross section and the forbidden characteristic of the 4f transitions. Furthermore, the 4f excitation is rather inefficient, relative to that of the titanate groups. Photoluminescence (PL) spectra were measured within the wavelength range 450 to 800 nm under nitrogen laser. The PL spectrum has three peaks, the highest intensity was observed for the peak at λ = 613 nm, the emission spectra show the peaks mainly at λ = 490 to be of blue emission, λ = 530 of a green emission [10-14] and 613 nm of a red emission respectively when excited at 325 nm excitation wavelength. The emission peaks are from transitions of Pr^{3+} the ($^{1}D_{2}$ state to the $^{3}H_{4}$ state and belong to the characteristic emission of Pr^{3+} and Al^{3+} ions added to the starting material enhanced the red emission from SrTiO$_3$:Pr^{3+} ($^{1}D_{2}$–$^{3}H_{4}$ emission of Pr^{3+}). A broader excitation spectra was observed at λ = 331nm when emitted with 615nm emission wavelength. The material under UV shows a red colour and the PL results clearly confirm that the material synthesis exhibit red luminescence properties.

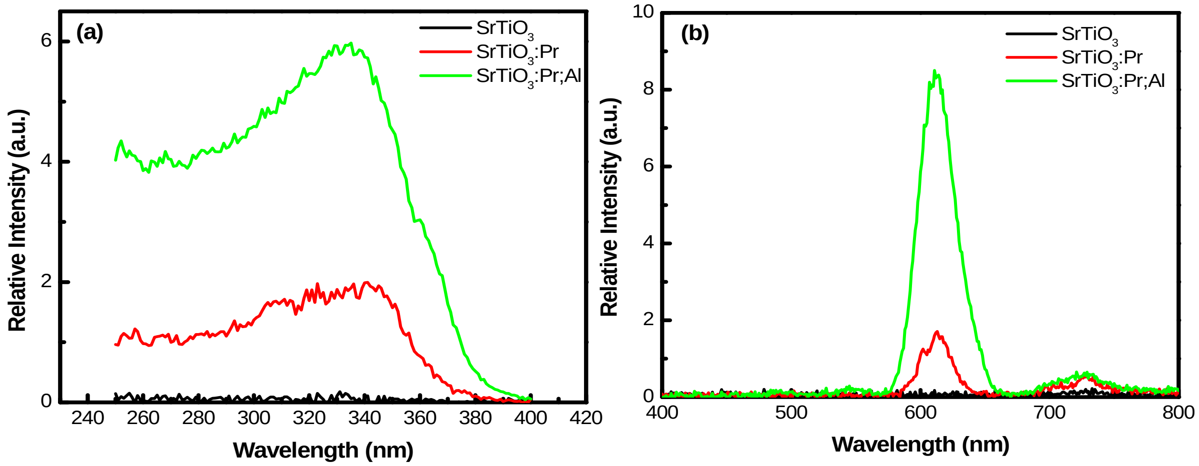


Figure 3 (a) excitation and emission spectra of undoped, Pr^{3+} -doped and Al^{3+} co-doped SrTiO$_3$ phosphors

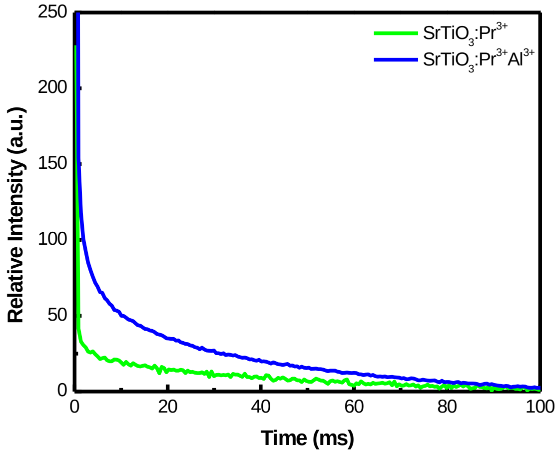


Figure 4 Red emission decay curves of Pr doped and Al co-doped for SrTiO$_3$ phosphor powders at 325 excitation wavelengths.

Figure 4 shows comparative curves of Pr-doped and Al co-doped SrTiO$_3$ and all the samples showed some decay property when the powders were efficiently excited by UV light. The results indicate that the initial luminescence intensity and decay time of phosphors is enhanced when Al ions are present.

4. Conclusion

$SrTiO_3$**:**Pr^{3+},Al^{3+} phosphor which is promising material for further researches and applications as the red-emitting one for white light emitting diodes was successfully synthesized by the sol-gel method. The XRD results implied that the phosphor has a cubic structure. The Al^{3+} ions were observed to have a great effect in luminescence properties of the host material ($SrTiO_3$), the PL results show that $SrTiO_3$**:**Pr**,**Al emits higher intensities than undoped $SrTiO_3$ and doped $SrTiO_3$. The SEM reveals that the addition of varies ethylene glycol and the annealing temperatures has significant impact on the morphology, crystalline structure and the particle size of the samples. The obtained $SrTiO_3$ powders are in nanoscale range with regular morphology when doped and co-doped viewed at a high magnification.

Acknowledgement

The financial support of the National Research Foundation (NRF) and the University of the Free State are acknowledged.

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