Sol–gel synthesis and photoluminescence of $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3 : \text{Pr}^{3+}$ phosphors

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Abstract. $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3 : \text{Pr}^{3+}$ phosphors have been synthesized by sol–gel and solid state methods, with $x = 1/300, 2/300, 3/300, 4/300, 5/300, 6/300, 7/300$, respectively. Powder X-ray diffraction (XRD), UV-visible absorption spectra, photoluminescent spectra (PL), and scanning electron microscopy (SEM) images are used to characterize the powder samples. The inverse absorption at 610 nm appearing in the UV-visible absorption spectra is due to the $^1D_2 \rightarrow ^3H_4$ characteristic emission of Pr^{3+} . Changes in the emission spectra at 610 nm were agreed with those in UV-visible absorption spectra. The strongest red excitation obtained from $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3 : \text{Pr}^{3+}$ ($x = 4/300$) and $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3 : \text{Pr}^{3+}$ ($x = 5/300$) possesses the strongest emission at 610 nm, similar to the intensities of $\text{Ca}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3 : \text{Pr}^{3+}$ ($x = 3/300, 4/300, 6/300$), which may be corresponded to the cell parameters of $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3 : \text{Pr}^{3+}$.

Keywords. Perovskite; luminescence; calcium titanate phosphor; sol–gel synthesis.

1. Introduction

The ideal perovskite, ABO_3 , is a corner-sharing cubic network of BO_6 octahedra with A cations occupying the 12 coordinate position between 8 BO_6 octahedra. Recently, structurally disordered ABO_3 perovskites, such as some titanates: SrTiO_3 (Pontes *et al* 2003a), CaTiO_3 (Pontes *et al* 2003b), BaTiO_3 (Pontes *et al* 2003c), PbTiO_3 , zirconates: SrZrO_3 (Longo *et al* 2007), $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (Silva *et al* 2005) and barium zirconate titanate, $\text{Ba}(\text{Zr}, \text{Ti})\text{O}_3$ (Anicete-Santos *et al* 2005; Cavalcante *et al* 2007) have been investigated in several papers, due to their optic properties at room temperature. These papers have reported diverse theories about the wide-band visible emission observed in titanate which belongs to a universal ‘green-luminescence’, a characteristic property of practically all self-activated ABO_3 perovskites titanates (Jastrabik *et al* 2003). It is suggested that the mechanisms include self-trapped excitons, recombination of electron and whole polarons, and a charge transfer vibronic exciton (Vikhnin *et al* 2001), donor–acceptor recombination (Yamaichi *et al* 1988) and transitions in MeO_6 complexes. The structural order–disorder degree in the lattice, the preparation method and thermal treatment conditions are the main factors which influence the photoluminescent (PL) emission band in ABO_3 perovskites (Souza *et al* 2005).

$\text{Ca}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ is a solid solution of CaTiO_3 and CaZrO_3 . Previous work illustrates perovskite solid solutions $(A'A''\dots)(B'B''\dots)\text{O}_3$ which are very attractive in

many electronic applications because of their structural diversity as well as important physical properties, such as ferroelectric, dielectric, photophysical, photocatalytic and magneto resistance properties (Blasse and Corson 1973; Bode and Van Dosterhout 1975; Patwe *et al* 2005, 2006; Achary *et al* 2006). In this form, the effect of substitution of Ti by Zr in some ABO_3 perovskites like CaTiO_3 (Cavalcante *et al* 2006), BaTiO_3 (Zhai *et al* 2004) and PbTiO_3 has been studied in detail to promote improvements in the dielectric properties of these materials.

In this work, CaTiO_3 doped with 0.2 mol % Pr^{3+} was used as host. Because its CIE colour coordinate is $x = 0.680$ and $y = 0.311$, which is very close to ideal red emission material (Diallo *et al* 2001). Recently, it has been reported that both Pr^{3+} doped SrTiO_3 and CaTiO_3 showed red emission at 612 nm (Okamoto *et al* 1999; Park *et al* 2003). The substitution of Ti^{4+} by Zr^{4+} was investigated to further evaluate the influence of Zr^{4+} concentration on $\text{CaTiO}_3 : \text{Pr}^{3+}$.

As far as we know, previous work had focused on perovskite solid solutions $(A'A''\dots)(B'B''\dots)\text{O}_3$. In this paper, $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3 : \text{Pr}^{3+}$ were synthesized by sol–gel and solid state methods, and the influence of low doping concentration of Zr^{4+} on luminescent intensities were investigated.

2. Experimental

2.1 Synthesis of $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3 : \text{Pr}^{3+}$ powders

The powder samples of $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3 : \text{Pr}^{3+}$ ($x = 1/300, 2/300, 3/300, 4/300, 5/300, 6/300, 7/300$) were synthe-

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sized by the following method. CaCO_3 , $\text{Ti}(\text{OC}_4\text{H}_9)_4$, $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4$, and $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were used as the starting materials. A certain quantity of $\text{Ti}(\text{OC}_4\text{H}_9)_4$ was dissolved in absolute alcohol, agitated for 30 min, to obtain solution A. The stoichiometric amounts of CaCO_3 were dissolved in HNO_3 , $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4$ and 0.2 mol % $\text{Pr}(\text{NO}_3)_3$ and H_2O were mixed to form solution B. Then solution A was dropped slowly in solution B with vigorous agitation, followed by further stirring for 3 h, then we got the yellowish sol C. Twelve h later, C turned into gel in air, then the gel was put into the oven at 80°C . When the gel dried, mulling was done. The resulting mixture was calcined at 800°C for 5 h in muffle roaster. Subsequently, the obtained $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3:\text{Pr}^{3+}$ powders were milled again.

2.2 Characterizations

The crystal phases of the prepared samples were identified by a Rigaku D/max-rB diffractometer equipped with a Cu anode in a 2θ range from 0.6° – 6° using a Nova 1000 analyser. UV-vis absorption spectra of dry pressed disk samples were obtained on a Lambda-900 UV-vis spectrophotometer and BaSO_4 was used as a reference standard. The morphology and particle size of the as-prepared powders were characterized by scanning electron microscopy (SEM) (JEOL, Model JEM-1230). The fluorescence excitation and emission spectra were obtained on a Perkin-Elmer RF-5301 spectrophotometer.

3. Results and discussion

Figure 1 presents the XRD patterns of $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3:\text{Pr}^{3+}$ powders with $x = 1/300, 2/300, 3/300, 4/300, 5/300,$

Figure 1. XRD patterns of $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3:\text{Pr}^{3+}$ powders, with $x = 1/300, 2/300, 3/300, 4/300, 5/300, 6/300, 7/300$.

$6/300, 7/300$, respectively. These diffraction peaks are in good agreement with the standard Joint Committee on Powder Diffraction Standards (JCPDS) card No. 22-0153, which is assigned to perovskite- CaTiO_3 , the pure orthorhombic phase of CaTiO_3 with lattice parameters $a = 5.4405 \text{ \AA}$, $b = 7.6436 \text{ \AA}$ and $c = 5.3812 \text{ \AA}$. It belongs to $Pnma$ (62) space group. No obvious impurity peaks were observed in the XRD patterns, indicating that zirconium had been doped in $\text{CaTiO}_3:\text{Pr}^{3+}$.

Figure 2 shows (a) UV-vis absorption spectra of $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3:\text{Pr}^{3+}$ with $x = 1/300, 2/300, 3/300$ and (b) UV-vis absorption spectra of $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3:\text{Pr}^{3+}$ with $x = 4/300, 5/300, 6/300, 7/300$. The inverse absorption at 610 nm appearing in the UV-visible absorption spectra is due to the $^1D_2 \rightarrow ^3H_4$ characteristic emission of Pr^{3+} . It can be seen from the spectra that $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3:\text{Pr}^{3+}$ ($x = 5/300$) possesses the strongest red emission.

The variation in PL intensity may result from the change of defect state on the surface (Meng *et al* 1995).

Figure 2. (a) UV-vis absorption spectra of $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3:\text{Pr}^{3+}$ with $x = 1/300, 2/300, 3/300$ and (b) UV-vis absorption spectra of $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3:\text{Pr}^{3+}$ with $x = 4/300, 5/300, 6/300, 7/300$.

The smaller the grain size, the greater the number of the d -surface states and thus of the localized sensitizing centres, so that the recombination via self-trapped excitations is enhanced. Finally, the emission band increases in intensity with decreasing grain size. The SEM images of $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3:\text{Pr}^{3+}$, with $x = 1/300, 5/300, 7/300$ are shown in figure 3. It can be seen from the images that both a and b products mainly consist of solid micron crystalline structures, which exist with some conglomeration among the crystalline grain for the high temperature

Figure 3. SEM images of $\text{Ca}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3:\text{Pr}^{3+}$ with (a) $x = 3/300$, (b) $x = 5/300$ and (c) $x = 7/300$.

800°C of thermal decomposition. The typical crystalline grain of $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3:\text{Pr}^{3+}$ ($x = 3/300$) (M) is estimated to be around 0.2 μm and $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3:\text{Pr}^{3+}$ ($x = 5/300$) (N) is estimated to be around 0.1 μm . The grain size of $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3:\text{Pr}^{3+}$ ($x = 7/300$) (O) is bigger than M and N because of conglomeration. From the previous theory, we can conclude that the luminescent intensity of N is much better than O, but little better than M.

Figure 4 represents the excitation spectra of $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3:\text{Pr}^{3+}$ powder samples, monitoring at 610 nm. The changes of the samples were very regular. The main excitation peaks' location of all the samples were close to each other, and the intensity of these peaks increased up to $x = 5/300$, then began to decrease. The present studies illustrate that the excitation of the samples results from the mother structural absorbance. So these main excitation peaks at about 323 nm was attributed to a direct recombination of a conduction electron in Ti 3d orbital and a hole in O 2p valence band. The peaks at about 370 nm agree with the $4f \rightarrow 5d$ transition of Pr^{3+} . In addition, there were three weaker peaks, at about 458 nm, 478 nm, and 496 nm, rooting in the excitation of $4f \rightarrow 4f$ of Pr^{3+} , and in agreement with the transition from ground state to $^3P_2, ^3P_1, ^3P_0$ state of Pr^{3+} , respectively (Jia *et al* 2003).

In this work, the A sites were not substituted, so any change in excitation spectra should be ascribed to the change of B. For $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3$, the Ti^{4+} sites of the bulk centre are partially substituted by Zr^{4+} . Since the ionic radius of Zr^{4+} (0.79 Å) is bigger than that of Ti^{4+} (0.68 Å), the $[\text{BO}_6]$ octahedral will be distorted by bending, which affects the O–O distances while preserving a uniform distribution of the B–O distances.

Figure 4. Excitation spectra of $\text{Ca}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3:\text{Pr}^{3+}$ with $x = 1/300, 2/300, 3/300, 4/300, 5/300, 6/300, 7/300$, monitoring at 613 nm.

Figure 5. Emission spectra of $\text{Ca}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3:\text{Pr}^{3+}$ (a) $x = 1/300$, (b) $x = 2/300$, (c) $x = 3/300$, (d) $x = 4/300$, (e) $x = 5/300$, (f) $x = 6/300$, and (g) $x = 7/300$, pumped at 325 nm.

Figure 6. Relationship between luminescent intensities and Zr^{4+} doping concentration, x .

The photoluminescence emission spectra have been widely used to investigate the efficiency of charge carrier trapping, immigration and transfer (Yamashita *et al* 1997). Figure 5 shows the PL emission spectra of $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3:\text{Pr}^{3+}$ powder samples, pumped at 325 nm. All the samples have approximately the same shape. The main emission peak at 610 nm was in agreement with the $^1D_2 \rightarrow ^3H_4$ characteristic emission of Pr^{3+} . With addition of zirconium, the red luminescence intensity increased up to $x = 5/300$. And then, the red emission dropped down. It

could be observed that the intensity of $x = 3/300$, $4/300$, $6/300$ were close to $x = 5/300$. This phenomenon is shown in figure 6.

The luminescent procedure of $\text{CaTiO}_3:\text{Pr}^{3+}$ can be described briefly as follows: Ti–O band absorbed excited energy through charge transfer mechanism; subsequently, the energy of excited state was transferred to luminescent centre Pr^{3+} ; then the $^1D_2 \rightarrow ^3H_4$ transition of Pr^{3+} exhibits red emission (Diallo *et al* 2001). So the luminescent intensity should be connected with these three procedures. The lattice distortion will influence this procedure.

4. Conclusions

In summary, the solid solution Zr^{4+} -doped $\text{CaTiO}_3:\text{Pr}^{3+}$, with different concentrations of Zr^{4+} , were synthesized successfully by sol–gel and solid state reaction methods. Pr^{3+} doped $(A'A''\dots)(B'B''\dots)\text{O}_3$ solid solutions are a very interesting system, not only for applications in display technologies but also for luminescence physics. In this work, strong red emission from 1D_2 at 610 nm was obtained in $\text{CaTi}_{1-x}\text{Zr}_x\text{O}_3:\text{Pr}^{3+}$ ($x = 5/300$). Because of the mismatch of Zr^{4+} and Ti^{4+} , the lattice was distorted. Thus, the excitation spectra show slight and regular changes.

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