

Sol-gel composition synthesis and double-color luminescence of Pr^{3+} activated $(\text{Ca}_x\text{Sr}_{1-x})\text{TiO}_3$ ceramics

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$\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3: \text{Pr}^{3+}$ ceramics have been synthesized from the solid-state calcination of sol-gel composed precursors through the hydrolysis and polycondensation process of tert-n-butyl titanate ($\text{Ti}(\text{OC}_4\text{H}_9)_4$), whose phase composition and microstructure are characterized with XRD and SEM. The photoluminescent behaviors have been compared with the different host composition (molecular ratio of Sr, Ca). Especially these $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3: \text{Pr}^{3+}$ ceramic samples present double-color luminescence in visible region, blue emission (450 ~ 500 nm) and red one (centered in 611 nm) under the excitation of 320 nm. With the content of Ca, the intensity of red emission is enhanced while it is decreased for blue emission.

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1. Introduction

The investigation on the luminescence properties of the rare earth ions activated phosphors such as metal oxide, oxysalts and various semiconductor materials is strongly motivated for their potential applications in optoelectronics devices and flat panel displays [1-2]. Among the development of semiconductor ceramics with photoactive properties such as photoluminescence, electroluminescence, or non-linear optics may lead to new optoelectronic devices with superior performance [3, 4]. During the past decades, the luminescence of several types of semiconductor compounds have been extensively studied in ceramic samples or crystals doped with rare-earth ions such as Eu^{3+} , Nd^{3+} , Er^{3+} in the fields of optoelectronics [5, 6]. As we know, some divalent metal (Pb, Ba) titanates belong the important functional ceramics materials such as piezoelectricity, electrooptics, semiconductor etc [7-9]. In the recent years, the research has begun to pay more attention to the optical properties, especially photoluminescence properties for these compounds doped with some photoactive central species because these perovskite-structure materials are attractive as host matrices for rare earth doping, which can be suggested for integrated light-emission devices, field

emission displays (FEDs), and all-solid compact laser devices operating in the blue-green region [10-14]. Beside this, several authors tried to substitute different metal ions (A or B) in these ABO_3 type lattice structure by using the similarity of physical properties [15-17]. The main discussion on the nature of the photoluminescence for these titanates may be related to the disordered structure in their ABO_3 materials. It needs to refer that the room temperature photoluminescence behavior of amorphous titanate-type compounds doped rare earth ions, i.e. Pr^{3+} , has also been studied for its abundant luminescent behavior which strongly depends on the composition of titanates [18-21]. The characteristic luminescence of Pr^{3+} can show different color derived from matchable transition of energy levels. For example, $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ is the solid solution of CaTiO_3 and SrTiO_3 has shown several compositional phase transformations. Changes in the emission spectra were observed in different phases. The blue emission at 491 nm from $^3\text{P}_0$ state was found quite strong in the tetragonal phase, and was thermally quenched in the orthorhombic phases. The intensity of the red luminescence from $^1\text{D}_2$ increases with increasing content of calcium [22, 23].

In this paper, we report the preparation of $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3: \text{Pr}^{3+}$ luminescent ceramics with sol-gel

composed precursors. We observed the double color luminescence of Pr^{3+} in the mixed alkali earth titanate host and the intensities of the two emission bands show the dependence on the molar ratio of Ca^{2+} and Sr^{2+} .

2. Experimental section

2.1 Sol-gel assisted solid state synthesis of $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3: \text{Pr}^{3+}$ ceramics ($x = 0, 0.1, 0.2, 0.3, 0.35, 0.4, 0.5, 0.7, 0.8, 1.0$)

CaCO_3 , SrCO_3 , Pr_4O_{11} and $\text{Ti}(\text{OC}_4\text{H}_9)_4$ were used as the starting materials and CaCO_3 , SrCO_3 , Pr_4O_{11} are firstly converted to their nitrates by concentrated nitric acid. A certain amount of mixed calcium and strontium nitrates (total 2 mmol) with different molar ratio was dissolved in water, after string 30 minutes, the stoichiometric ratio $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ dissolved in H_2O were mixed. Then the absolute alcohol of tetra-n-butyl titanate (2 mmol) was dropped slowly in the above mixed nitrates solution with vigorous agitation for 3 hours, light-yellow sol was obtained and dried in an oven at 80°C to age as gel after twelve hours. Finally the resulting gel precursor was calcined at 800°C for 5 h in muffle roaster.

2.2 Characterization

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° to 6° . temperature, using a Nova 1000 analyzer. 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 fluorescence excitation and emission spectra were obtained on a Perkin-Elmer RS-5301 spectrophotometer. The morphology and particle size of the as-prepared powders were characterized by scanning electron microscopy (SEM) (JEOL, Model JEM-1230).

3. Results and discussion

The XRD patterns for $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3: \text{Pr}^{3+}$ with different molar ratio of $\text{Ca}^{2+}/\text{Sr}^{2+}$ are shown in Fig. 1 (a) and (b), respectively. Both of these XRD patterns are very consistent with JCPDS (35-0734), showing that the sample has a single phase in the orthorhombic system with space group Pnma. Deduced from the XRD data, the samples are well-crystallized without any hybrid phase, and this also

suggests that the doped Pr^{3+} ions uniformly enter into crystal lattice of $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ to form solid state solution. The average crystallite size can be estimated from the full width at half maximum of the diffraction peak by the Scherrer equation [13, 14]. From the estimated data, these phosphors are found in the range of 66 – 230 nm. Besides, it can be seen these phosphors possess well crystalline state for that the existence of some XRD peaks besides around 40° and 46.5° , respectively, suggesting the structural order [15]. As already known, the system $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$ has several phases at room temperature depending on its composition ($\text{Sr}^{2+}/\text{Ca}^{2+}$ molar ratio): cubic (Pm3m), tetragonal (I4/mcm), orthorhombic (Bmmb), and orthorhombic (Pnma). But the volume and shape of unit cells between different phases are very small and the non-cubic phases deviate slightly from the cubic phase [22, 23]. From the XRD patterns, it can be also observed that there does not exist apparent distinction for different compoision of $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3$.

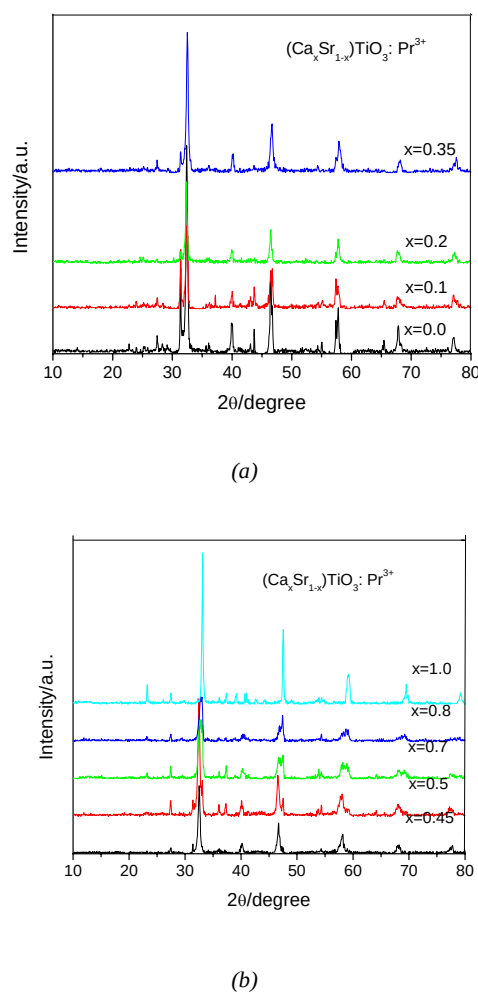


Fig. 1. XRD patterns of $(\text{Ca}_x\text{Sr}_{1-x})\text{TiO}_3: 0.02\text{Pr}^{3+}$ ceramics: $x = 0, 0.1, 0.2, 0.35$ (a); $x = 0.45, 0.5, 0.7, 0.8, 1.0$.

Selected scanning electron microscopy (SEM) for $\text{CaTiO}_3: 0.02\text{Pr}^{3+}$ (a) $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3: 0.02\text{Pr}^{3+}$ (b) and $\text{SrTiO}_3: 0.02\text{Pr}^{3+}$ (c) are shown in Fig. 2. There exist some conglomeration phenomena in the SEM micrograph for the solid state thermal decomposition at 800°C . They show similar morphology and little difference in particle size. The particle size for these samples are around 100 nm, corresponding to the data from the XRD estimation. SEM image of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3: 0.02\text{Pr}^{3+}$ seems not same regular as that of pure host CaTiO_3 and SrTiO_3 , which reveals the alkali earth metal ions with different ion radius have influence on the crystal growth process. This is not beneficial for the formation of uniform microstructure.

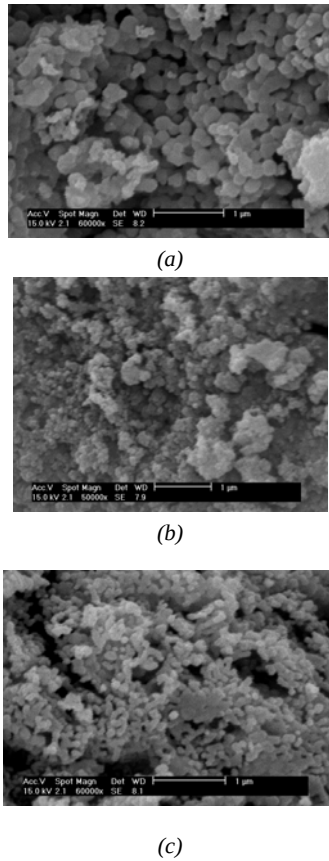


Fig. 2. Selected SEM image of $\text{CaTiO}_3: 0.02\text{Pr}^{3+}$, $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3: 0.02\text{Pr}^{3+}$, $\text{SrTiO}_3: 0.02\text{Pr}^{3+}$.

Fig. 3 shows the selected UV-vis diffuse reflectance absorption spectra of $(\text{Ca}_x\text{Sr}_{1-x})\text{TiO}_3: \text{Pr}^{3+}$, which shows the similar absorption feature for the similar host composition of TiO_6^{8-} . The dominant absorption bands exist in the range of 300 – 400 nm ultraviolet region with maximum absorption centered in 325-350 nm. This takes agreement with the excitation spectra (Fig. 4). These phosphors show apparent broad excitation bands from $4f^5$ transitions in the narrow wavelength ultraviolet spectral bands (250 ~ 400 nm), while the very weak excitation peaks appear in the long wavelength (around 400 nm) region corresponding to the $f \rightarrow f$ transition absorption of Pr^{3+} . The two absorption peaks at around 360 and 315 nm, split from $4f5d$ state can be observed. TiO_6^{8-} with an

empty d shell can show a broad band absorption belonging to charge transfer excited state which electrons are promoted from bonding orbitals (in the ground state) to antibonding orbitals (in the excited state) and have moved from oxygen ligands to the central metal ions.

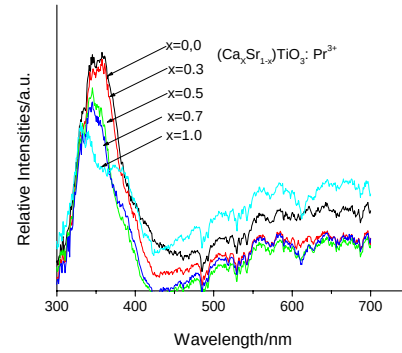
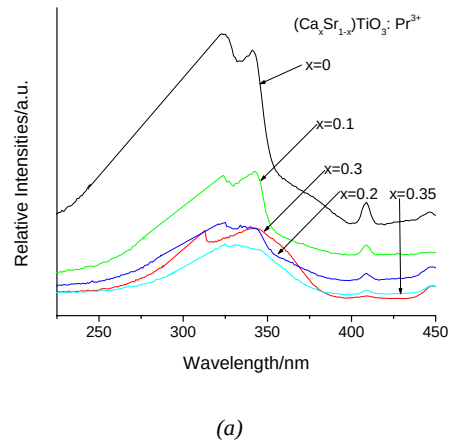
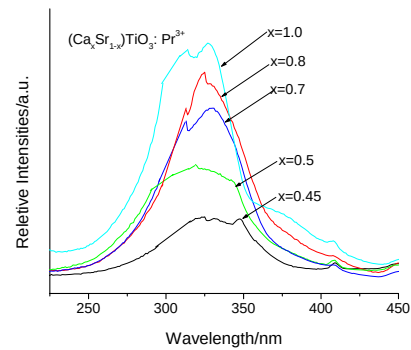


Fig. 3. Selected UV-vis diffuse reflectance absorption spectra of $(\text{Ca}_x\text{Sr}_{1-x})\text{TiO}_3: \text{Pr}^{3+}$.

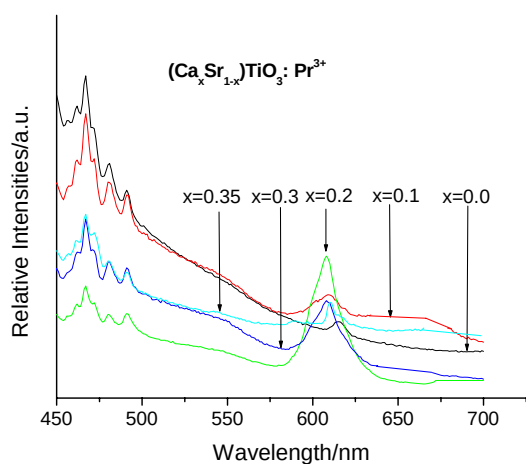


(a)

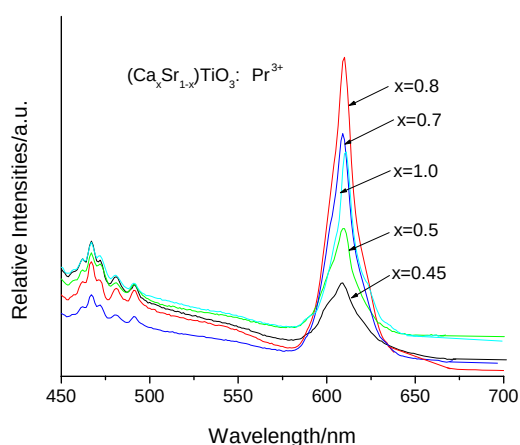


(b)

Fig. 4. Excitation spectra of $(\text{Ca}_x\text{Sr}_{1-x})\text{TiO}_3: \text{Pr}^{3+}$: (a) $x = 0, 0.1, 0.2, 0.3, 0.35$; (b) $x = 0.45, 0.5, 0.7, 0.8, 1.0$.



(a)



(b)

Fig. 5. Emission spectra of $(\text{Ca}_x\text{Sr}_{1-x})\text{TiO}_3:\text{Pr}^{3+}$: (a) $x = 0, 0.1, 0.2, 0.3, 0.35$; (b) $x = 0.45, 0.5, 0.7, 0.8, 1.0$.

The corresponding emission spectra for these phosphors show a similar feature, presenting a strong broad emission band (about 50 nm range) in the range of 585 ~ 635 nm with a maximum peak at 611 nm for the $\text{Ca}_x\text{Sr}_{1-x}\text{TiO}_3:\text{Pr}^{3+}$ phosphors. These emission bands originate from the characteristic $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transition of Pr^{3+} . The luminescence of Pr^{3+} has only a single series of spectra, which was ascribed to the praseodymium ions at the alkaline-earth site by comparison of ionic sizes. The characteristic luminescence of these phosphors is determined by the electronic structure of the doped Pr^{3+} , while the width and the relative intensity of the spectra frequently depend on the crystal symmetry of the host matrix. Besides a red emission peaks near 611 nm, there

exists some blue emission bands at the range of 450 to 500 nm. With adding calcium, the red luminescence intensity increased. The blue emission peak at first is getting stronger with increasing the content of Ca, and reaches the intensity comparable as the red emission peak at 611 nm. After then, the blue emission drops down rapidly and become very weak. Compared the excitation and emission intensities for different Sr-Ca molar ratio of matrix, it can be observed that different host composition has no influence on the luminescent bands except for little distinction of luminescent intensities. Sr and Ca ions act as the counter ion to balance the electron for the octahedron framework (ABO_3 type) of $(\text{TiO}_6)^{8-}$, and the different ion radius for the two ions may affect the lattice structure of ABO_3 . Subsequently the energy absorption of TiO_6^{8-} may be influenced, resulting in the luminescence of Pr^{3+} . Of course, the influence is very little.

4. Conclusions

In summary, $\text{Ca}_x\text{Sr}_{1-x}\text{O}_3:\text{Pr}^{3+}$ luminescent ceramics are synthesized through the sol-gel composition of precursors. Both XRD and SEM indicate that these products show the similar microstructure in spite of little distinction of crystal phase. Both diffuse reflectance absorption and excitation spectra show that there exist broad CT absorption bands in ultraviolet region which is favorable for the energy transfer and luminescence of Pr^{3+} . The corresponding emission spectra exhibit a red emission with maximum peak of 611 nm originated from the characteristic $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transition of Pr^{3+} and weak blue emission bands at the range of 450 to 500 nm.

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