Luminescence of submicrometer $Sr_xCa_{1-x}TiO_3$: Pr^{3+}, Al^{3+} ceramic phosphors by sol-gel composition of hybrid precursors

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Rare earth coordination polymers with ortho hydroxylbenzoic acid (OHBA) were used as the precursors of luminescent species, composed with polyethylene glycol (PEG) to achieve hybrid dispersing media and other functional components to modify the composition and pH value. The resulting multicomponent hybrid precursors were assembled by a sol-gel process of tert-n-butyl titanate ($Ti(OC_4H_9)_4$) and further thermally decomposed to obtain a series of rare earth oxysalts ceramic phosphors: $Sr_xCa_{1-x}TiO_3$: Pr^{3+}, Al^{3+} ceramic phosphors. Both XRD and SEM indicated the particle sizes were in the submicrometer range of 100 ~ 300 nm. Photoluminescence for $Sr_xCa_{1-x}TiO_3$: Pr^{3+}, Al^{3+} was compared with the different component of host (molecular ratio of Sr, Ca). These phosphors presented a broad excitation band in the visible blue-violet region with the maximum excitation peak at 445 nm and a wide emission band with a maximum peak at 619 nm. Furthermore, the introduction of Al^{3+} can sensitize the luminescence of Pr^{3+}.

1. Introduction

The investigation of luminescent properties of the rare earth elements hosted in several crystalline matrices such as metal oxides, oxysalts, metal–organic compounds and variety of semiconductor materials is strongly motivated because of their applications in optoelectronics devices and flat panel displays [1]. Among the development of semiconductor ceramics, materials with active optical properties such as photoluminescence (PL), electroluminescence, cathode-luminescence, non-linear optical or electro-optical properties may lead to new optoelectronic devices with superior performance [2]. During the past decades, the luminescence of several types of semiconductor compounds have been extensively studied in ceramic samples or single crystals doped with rare-earth ions such as Eu^{3+}, Nd^{3+}, Er^{3+}, due to their potential optoelectronic applications [3]. Alkali-earth metal titanates belong to the important functional ceramics materials such as piezoelectricity, elctrooptics, semiconductor etc [4, 5]. Lately, the study 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 photoactive rare earth ions doping which can be expected to have great applications in integrated light-emission devices, field emission displays (FEDs), and all-solid compact laser devices operating in the blue-green region and positive temperature coefficient (PTC) resistors [6-8]. Beside this, some work has tried to substitute different metal ions (A or B) in these ABO_3 type la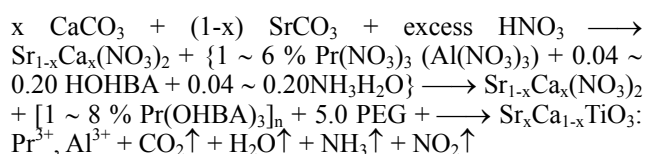ttice structure by using the similarity of physical properties [9,10]. The main discussion one the nature of the photoluminescence for these titanates may be related to the disordered structure in their ABO_3 materials. It is worthy pointing out that the room temperature photoluminescence behavior of amorphous titanate-type compounds doped rare earth ions, i.e. Pr^{3+}, has not yet been extensively studied except for some fragmentary work although they have great potential applications in optical display and energy conversion. On the other hand, Al^{3+} has been found to enhance the luminescence of Pr^{3+} in titanate phosphors [11, 12].

In this paper, a modified sol-gel synthesis technology was afforded to prepare ceramics phosphors: $Sr_xCa_{1-x}Ti_yZr_{1-y}O_3$:$Pr^{3+}$, Al^{3+}. Lanthanide coordination polymers and poly ethyl glycol (PEG) were introduced in the course of sol-gel (hydrolysis and polycondensation) process of tetra-n-butyl titanate as titanate source, resulting in multicomponent hybrid precursors. The room-temperature photoluminescence for these phosphors were discussed in detail.

2. Experimental section

0.2 g $SrCO_3$ (2 mmol) was dissolved with excess concentrated nitric acid to convert into strontium nitrates completely. Then an appropriate amount of ortho hydroxylbenzoic acid (HOHBA) was dissolved in a little of ethanol solution, whose *p*H value was adjusted to about 6.5, then $Pr(NO_3)_3 \cdot 6H_2O$ solution was added of which the molar ratio of HOHBA: Pr^{3+} was 3.2. Different amounts of aqueous solutions of calcium nitrate were added into the above mixed solutions, stirring by introducing PEG and

tetra-n-butyl titanate (2 mmol). After heating and stirring, light-yellow sol was obtained and dried in an oven to age as gel. The hybrid precursors were calcinated in a resistance stove for 5 hours at 800 ℃, light yellow solid powders were achieved. For Sr$_{1-x}$Ca$_x$TiO$_3$: 0.03 Pr^{3+}, x = 0.6, 0.75, 0.8, 0.9 and 1.0. For SrTiO$_3$: Pr^{3+}, Al^{3+}, the doping concentration of Pr^{3+} and Al^{3+} is 0.03, Pr^{3+}: Al^{3+} = 4:1, 3:2, 1:1 and 1:3. The typical procedure for the synthesis is represented in the following:

x CaCO$_3$ + (1-x) SrCO$_3$ + excess HNO$_3$ $\longrightarrow$ Sr$_{1-x}$Ca$_x$(NO$_3$)$_2$ + {1 ~ 6 % Pr(NO$_3$)$_3$ (Al(NO$_3$)$_3$) + 0.04 ~ 0.20 HOHBA + 0.04 ~ 0.20NH$_3$H$_2$O} $\longrightarrow$ Sr$_{1-x}$Ca$_x$(NO$_3$)$_2$ + [1 ~ 8 % Pr(OHBA)$_3$]$_n$ + 5.0 PEG + $\longrightarrow$ Sr$_x$Ca$_{1-x}$TiO$_3$: Pr^{3+}, Al^{3+} + CO$_2\uparrow$ + H$_2$O$\uparrow$ + NH$_3\uparrow$ + NO$_2\uparrow$

The particle size was characterized by means of X-ray diffraction (XRD, Bruke, D8-Advance, 40 kV and 20 mA, CuKα) and scanning electronic microscopy (SEM, Philps XL-30). Excitation and emission spectra at room temperature were determined with a Perkin-Elmer LS-55 model fluorophotometer (excitation slit width = 10 nm, emission width = 2.5 nm).

3. Results and discussion

The representative XRD patterns for Sr$_{0.25}$Ca$_{0.75}$TiO$_3$: 0.015Pr^{3+} and SrTi$_{0.25}$Zr$_{0.75}$O$_3$: 0.015Pr^{3+}, 0.015Al^{3+} are shown in Fig. 1 (A) and (B), respectively. Both of XRD patterns show that the resultant product of Sr$_{0.25}$Ca$_{0.75}$TiO$_3$: 0.015Pr^{3+} and SrTi$_{0.25}$Zr$_{0.75}$O$_3$: 0.015Pr^{3+}, 0.015Al^{3+} were indexed to crystallize in the orthorhombic system with space group Pnma for high thermolysis temperature, in agreement with JCPDS (35-0734). The average crystallite size was 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 67 – 244 nm size. 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, indicating the structural order [15].
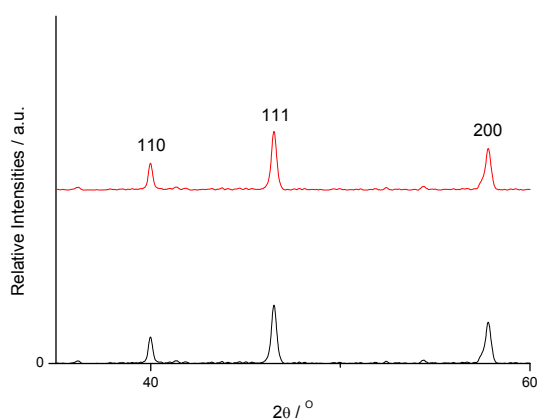
Resulted scanning electron microscopy (SEM) for Sr$_{0.5}$Ca$_{0.5}$TiO$_3$: 0.015Pr^{3+} (A) and SrTi$_{0.25}$Zr$_{0.75}$O$_3$: 0.015Pr^{3+}, 0.015Al^{3+} (B) phosphors are shown in Fig. 2. There exist some conglomeration phenomena in the SEM micrograph for the high temperature of thermal decomposition. It can be predicted approximately that both the two samples possess crystal particle size more than 100 ~ 300 nm, which takes agreement with the data from the XRD estimation. Rare earth coordination polymers of ortho hydroxylbenzoic acid have an infinite chain-like polymeric structure [16], together with organic polymer, polyethylene glycol (PEG) were combined as a dispersing medium to form the hybrid precursor with interpenetrating polymeric network template [17]. So the particle sizes of these phosphors can be controlled and determined by the hybrid precursors. Therefore, this preparation technique connects the assembly of hybrid material with the synthesis of solid-state phosphors, which can be expected to be a candidate for the synthesis of other luminescent materials based on rare earth oxysalts.
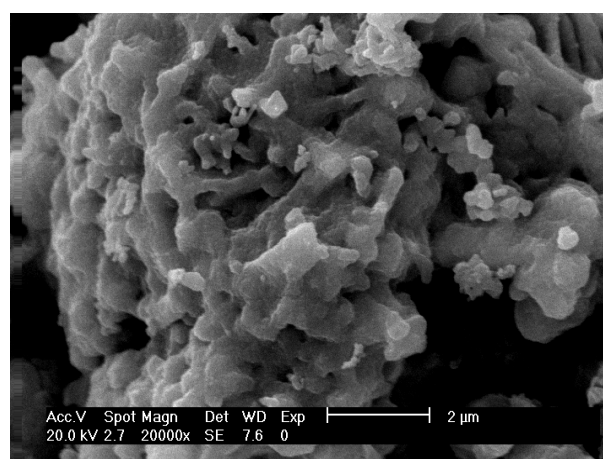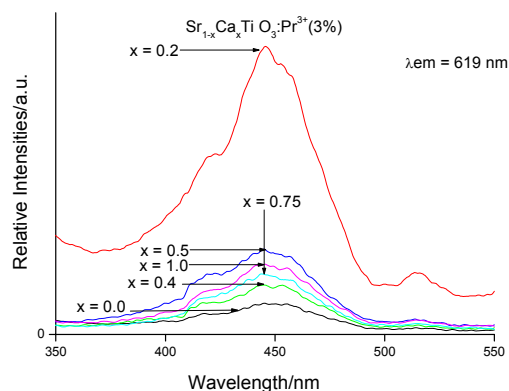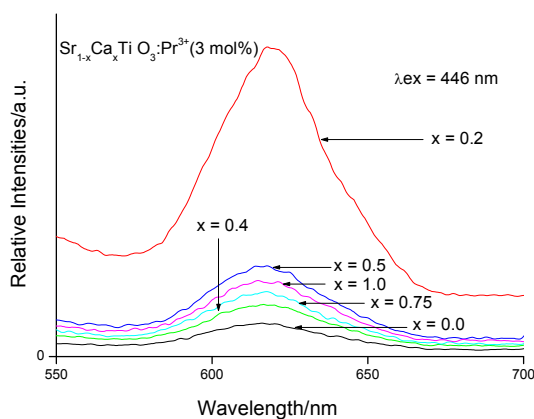

a
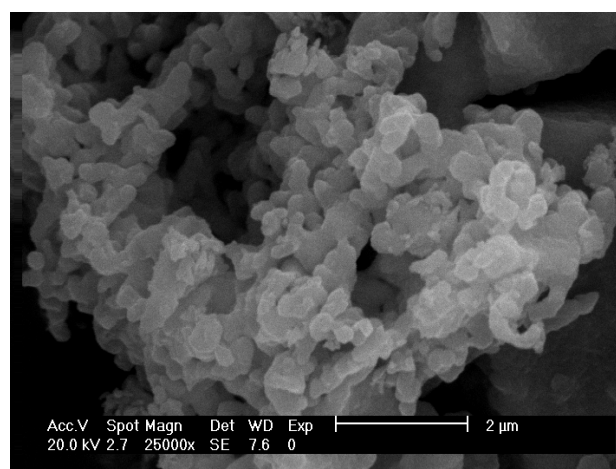
b

Fig. 2. Representative SEM of Sr$_{0.25}$Ca$_{0.25}$TiO$_3$: 0.015Pr^{3+} (A) and SrTi$_{0.25}$Zr$_{0.25}$O$_3$: 0.015Pr^{3+}, 0.015Al^{3+} (B)

Fig. 1. Representative XRD patterns of Sr$_{0.25}$Ca$_{0.25}$TiO$_3$: 0.015Pr^{3+} (A) and SrTi$_{0.25}$Zr$_{0.25}$O$_3$: 0.015Pr^{3+}, 0.015Al^{3+} (B)
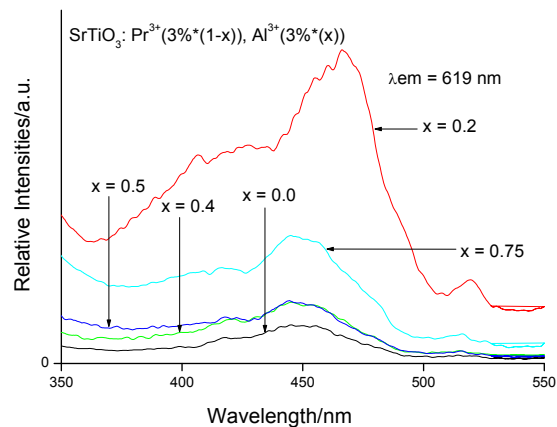
a

b

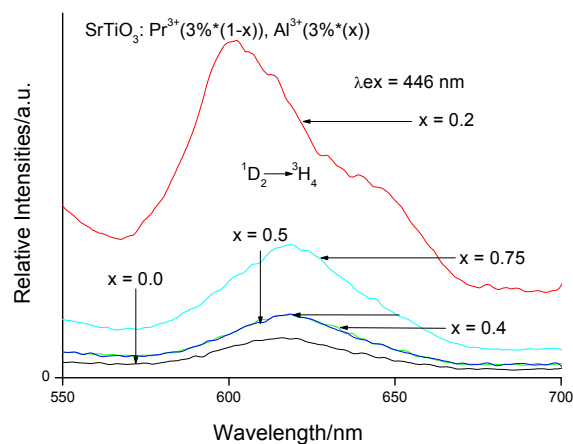*Fig. 3. Excitation spectra (A) and emission spectra (B) of Sr₁₋ₓCaₓTiO₃ doped with 3 mol % Pr³⁺*

Fig. 3 presents the excitation and emission spectra for $Sr_{1-x}Ca_xTiO_3$ doping 3 mol % Pr^{3+} with different host composition of Sr − Ca ratio. These phosphors show no apparent excitation in the narrow wavelength ultraviolet spectral bands (200 ~ 330 nm), while they exhibit distinct excitation bands in the long wavelength ultraviolet-visible region (330 ~ 500 nm), especially a strong excitation peak in blue-purple visible region with a maximum excitation peak around 446 nm for $SrTiO_3$: Pr^{3+}. These wide excitation spectral bands are ascribed to the f → f transition absorption. The fact of strong excitation bands in visible region has a special significance as regards the expectation to realize the conversation of visible light. The corresponding emission spectra for these two series of phosphors show a similar feature, presenting a strong broad emission band (about 50 nm range) in the range of 580 ~ 630 nm with a maximum peak at 619 nm for the $SrTiO_3$: Pr^{3+} phosphors. These emission bands originate from the characteristic $^1D_2 \rightarrow ^3H_4$ 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 [8]. 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 [8]. It is worthy pointing out that these phosphors present excitations in the blue-purple light range and emission in red light range, which can achieve light conversion in visible religion.

Compared the excitation and emission intensities for different Sr-Ca 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. Among $Sr_{0.80}Ca_{0.20}TiO_3$: 3 mol % Pr^{3+} presents the strongest luminescence. Sr and Ca ions act as the counter ion to balance the electron for the octahedron framework (ABO_3 type) of (TiO_3^{2-}), and the different ion radius for the two ions may affect the lattice structure of ABO_3. Subsequently the energy absorption of TiO_3^{2-} may be influenced, resulting in the luminescence of Pr^{3+}. Of course, the influence is very little.

a

b

Fig. 4. Excitation spectra (A) and emission spectra (B) of Sr₁₋ₓCaₓTiO₃ doped with Pr³⁺ and Al³⁺

When Al^{3+} was introduced to replace some ratio of Pr^{3+}, it can be found that both excitation and emission intensities of the phosphors with doped Al^{3+} are stronger than that $SrTiO_3$: Pr^{3+} without Al^{3+}, suggesting that Al^{3+} can enhance the excitation intensity (as shown in Fig. 4). The luminescent process may be due to the interaction between Al^{3+} and Pr^{3+} ions. Al^{3+} absorbs the excitation radiation and then transfers the absorbed energy to Pr^{3+}, resulting in the emission of Pr^{3+} [11].

In summary, multicomponent inorganic/organic hybrid polymeric precursors were composed by means of the in-situ sol-gel process and subsequently $Sr_xCa_{1-x}Ti_yZr_{1-y}O_3$:$Pr^{3+}$, Al^{3+} phosphors were synthesized. SEM indicates that the particle sizes are in the range of $100 \sim 300$ nm. The excitation spectra show that there exist no apparent bands in ultraviolet region except for a band in violet-blue region with maximum peak of 445 nm. The corresponding emission spectra exhibit a broad band in red region with maximum peak of 619 nm, originated from the characteristic $^1D_2 \rightarrow {}^3H_4$ transition of Pr^{3+}. These phosphors bear both excitation and emission in visible region, which can be expected to have potential application in visible light conversion.

Acknowledgements

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