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Short communication

Red emission in Pr doped $CaBi_4Ti_4O_{15}$ ferroelectric ceramics

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ABSTRACT

In this paper, Pr doped $CaBi_4Ti_4O_{15}$ ceramics were prepared by a traditional solid state method. Crystal structure and morphologies of the ceramics were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The photoluminescence properties of the samples were investigated by a spectrofluorometer. Three excitation bands are located at wide range of wavelength, which are 300–430 nm, 440–510 nm and 550–570 nm respectively. Upon the excitation of 494 nm light, the samples shows an emission peak centered at 614 nm, corresponding to $^1D_2 \rightarrow {}^3H_4$ transition. A 614 nm red emission excited under the wave with long wavelength of Pr doped $CaBi_4Ti_4O_{15}$ makes it useful in the white LEDs. In addition, it is an intrinsic ferroelectric and piezoelectric material; the enhanced ferroelectric properties were obtained by Pr doping. As a multifunctional materials, Pr doped $CaBi_4Ti_4O_{15}$ may be useful in white LEDs, sensor, and optical-electro integration.

1. Introduction

Aurivillius bismuth layered-structure ferroelectrics (BLSFs) are generally expressed as $Bi_2A_{m-1}B_mO_{3m+3} = (Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, where A is a large 12-coordinate cation and B is a small 6-coordinate cation with a d^0 electron configuration [1]; A can be mono-, di-, or tri-valent ions or a mixture of them, B represents tetra-, penta-, or hexa-valent ions, and the subscripts m and m-1 are the numbers of oxygen octahedron and pseudo-perovskite units in the pseudo-perovskite layers, respectively. The crystal structure of BLSFs consists of pseudo-perovskite layers, which interleave bismuth oxide $(Bi_2O_2)^{2+}$ layers along the *c*-axis. Since the 1960s, the series of BLSFs have attracted many attentions for their potential applications in ferroelectric and piezoelectric device. It was found that the ferroelectric and piezoelectric properties of BLSFs can be greatly enhanced by doping with rare earth elements [2,3]. As important luminous centers; rare earths are doped in many host materials to design a large number of luminescent materials [4]. However, the luminescence properties of these rare earth elements in the BLSFs are nearly ignored.

In the past decades, Pr is doped in many host materials for various luminescent applications. Among which, Pr doped pervoskite-type compounds $CaTiO_3$ [5], $SrTiO_3$ [6], $BaTiO_3$ [7], $(Ca,Sr)TiO_3$ [8], $(Ca,Ba)TiO_3$ [9] and $(Ca,Sr,Ba)TiO_3$ [10] have been studied intensively as red phosphor materials for potential flat-panel display, field-emission display (FED). Interestingly, in some Pr doped ferroelectric pervoskite-type compounds, several new optical and electrical properties were observed [8,9,11]. It is known that Bi^{3+} ion can be used as both a sensitizer and activator to develop phosphors for various luminescent applications [12,13]. Recently, it was reported that Pr, Nd, Eu, and Er doped layered pervoskite-type $Bi_4Ti_3O_{12}$ exhibit excellent photoluminescence properties [14–18]. However, there are few reports about Pr doped other BLSFs compounds such as $CaBi_4Ti_4O_{15}$, $SrBi_4Ti_4O_{15}$ and $BaBi_4Ti_4O_{15}$. So it is of interest and significance to study photoluminescent properties of rare earth doped these BLSFs.

In this work, $CaBi_4Ti_4O_{15}$ pervoskite-type compound being chosen as host materials, a series of different concentrations of Pr doped $CaBi_4Ti_4O_{15}$ (CBT_Pr) ceramics were synthesized. The photoluminescent properties of the samples were reported. To the best of our knowledge, this is the first report of Pr activator in $CaBi_4Ti_4O_{15}$ host. It is found that the CBT_Pr samples Exhibit 614 nm emission at room temperature. The strongest excitation band of the samples is located at blue regions; which covers the emission wavelength of commercial blue light-emitting diode (LED) chips, meaning that Pr doped $CaBi_4Ti_4O_{15}$ may be used as environmental friendly phosphors for the application of white LEDs. Additionally, $CaBi_4Ti_4O_{15}$ is an intrinsic ferroelectric and piezoelectric material. As a multifunctional material, Pr doped $CaBi_4Ti_4O_{15}$ may be useful in white LEDs, sensor and optical-electro integration.

2. Experimental

$CaBi_4Ti_4O_{15} + x$ mol.% Pr (CBT_Pr_*x*) ceramics were prepared by the solid-state reaction method. Bi_2O_3 (99.5%), TiO_2 (99.99%), Pr_6O_{11} (99.99%), and $CaCO_3$ (99.99%) as starting materials were weighed and ground finely in an agate mortar according to the

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appropriate stoichiometric ratio. Next, the homogeneous mixture dried and calcined at 850 °C for 2 h in an alumina crucible. After calcination, the ground powders, added with 10 wt.% polyvinyl alcohol (PVA) binder, were pressed into disk-shaped pellets at 100 MPa and ball-milled powders were pressed into disks of 10 mm in diameter and about 2 mm in thickness. Finally samples sintered at temperatures of 1180 °C for 4 h in a sealed alumina crucible. The crystal structure was identified by a X-ray diffractometer (XRD; D8 Advance, Bruker AXS GmbH) with Cu K_ radiation ($\lambda = 0.154056$ nm), tube voltage 40 mV, tube current 40 mA, and scanning speed 6°/min. The photoluminescence (PL) spectra at room temperature were recorded using a spectrofluorometer (LS-55, PerkinElmer). The polarization-electric field (P-E) hysteresis loops were measured by a precision ferroelectric analyzer (Premier II, Radiant Technologies Inc., Albuquerque, NM).

3. Results and discussions

Fig. 1 shows the XRD patterns of CBT_Pr_*x* ceramics with $x = 0.5$, 1, 1.5 and 2 mol.%. The XRD patterns of the samples are well consistent with JCPDS 52-1640 [$CaBi_4Ti_4O_{15}$]. The CBT_Pr_*x* ceramics does not show any evidence of the formation of praseodymium oxide or associated compounds that contain $CaTiO_3$ or $Bi_4Ti_3O_{12}$. This observation indicates all the CBT_Pr_*x* samples are single bismuth layered structure with no apparent secondary phase. In $CaBi_4Ti_4O_{15}$ unit cell, 1/2 Bi^{3+} cations are in $(Bi_2O_2)^{2+}$ layer, 1/2 Bi^{3+} cations and all Ca^{2+} disperse in the A sites, and Ti^{4+} cations occupy the B sites. The radius of Pr^{3+} (1.14 Å) ion is much larger than that of Ti^{4+} (0.68 Å), but similar to that of Bi^{3+} (1.03 Å) or Ca^{2+} (1.07 Å) irons. It was confirmed the bismuth layer is very strong that Bi^{3+} cations in it are hard to be substituted [19,20], So in the case of CBT_Pr, Pr^{3+} ions may enter the A sites of the pseudo-perovskite block for substituting the Bi^{3+} or Ca^{2+} irons and form a solid solution. Previous reports also showed that Pr ions are easy to occupy the A sites of other BLSFs [21,22].

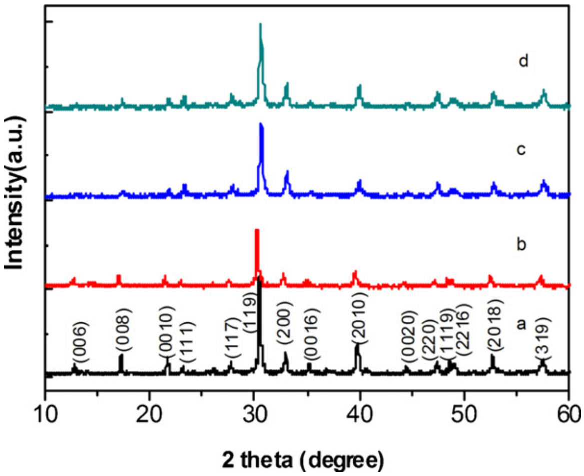

Fig. 1. XRD patterns of CBT_Pr_*x* (a: $x = 0.5$, b: $x = 1$, c: $x = 1.5$ and d: $x = 2$) sintered at 1180 °C.

SEM images of CBT_Pr_*x* ceramics with $x = 0.5$, 1, 1.5 and 2 mol.% are shown in Fig. 2. It can be seen from the SEM micrographs that all the ceramic samples are dense and have similar plate-like morphology, which is the typical morphology of BLSFs, further proved that the praseodymium ions in the CBT_Pr do not form minority phases or segregate from the interior grain but dissolve into the $CaBi_4Ti_4O_{15}$ host lattice.

Photoluminescence excitation spectra (PLES) of CBT_Pr_*x* ceramics with $x = 0.5$, 1, 1.5 and 2 mol.% are shown in Fig. 3. It can be seen that the excitation band covers several broad wavelength bands which are 300–430 nm, 440–510 nm and 550–570 nm. The PLES exhibits strong excitation band ranging from 440 nm to 510 nm, which are due to the f–f transitions from the $^3H_4$ ground state to the ^3P_J ($J = 0$, 1, 2) excited states of Pr^{3+}, the intense sharp

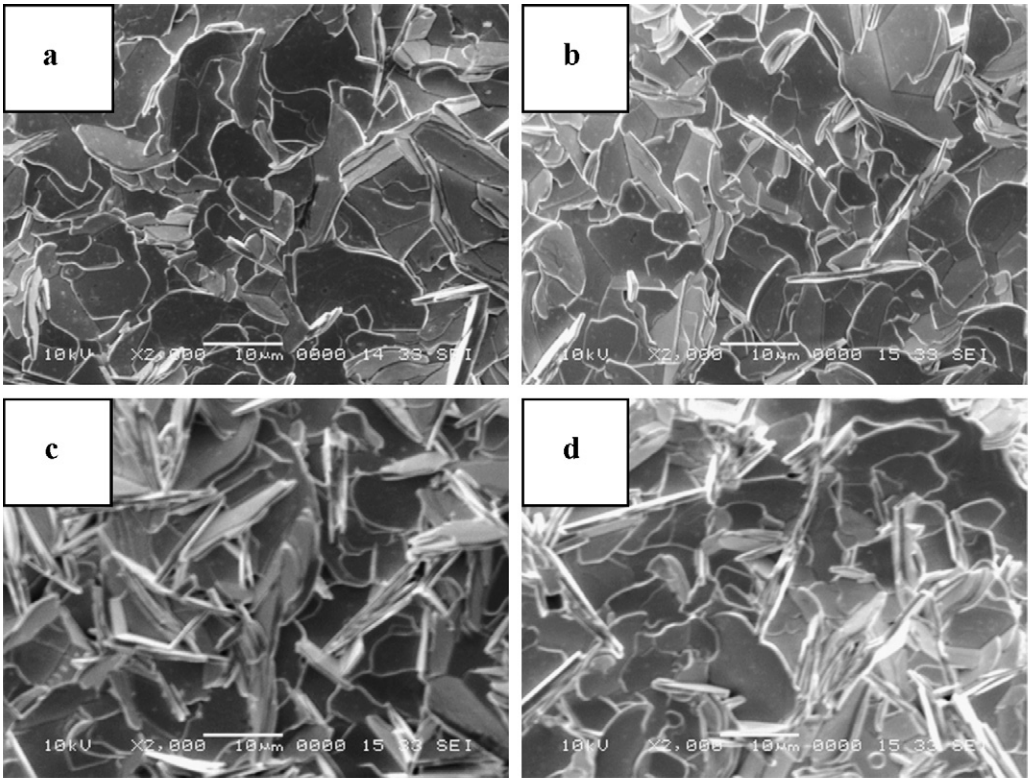

Fig. 2. SEM images of CBT_Pr_*x* (a: $x = 0.5$, b: $x = 1$, c: $x = 1.5$ and d: $x = 2$) sintered at 1180 °C.