Optical Materials 35 (2013) 520–525

Contents lists available at SciVerse ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Can divalent ions co-doping strategy make $Lu_{0.8}Sc_{0.2}BO_3$:Ce scintillation materials perform better?

Yuntao Wu [a,*], Guohao Ren [a,*], Dongzhou Ding [a], Guoqing Zhang [b,a], Shanshan Shang [c,a], Dandan Sun [a], Shangke Pan [a]

[a] Shanghai Institute of Ceramics, Chinese Academy of Sciences, No. 215 Chengbei Road, Jiading, Shanghai 201800, China
[b] Faculty of Material Science and Chemistry, China University of Geosciences, Hubei 430074, China
[c] College of Materials Science, China Jiliang University, Zhejiang 310018, China

ARTICLE INFO

Article history:
Received 5 August 2012
Received in revised form 28 August 2012
Accepted 7 October 2012
Available online 2 November 2012

Keywords:
Scintillation
Co-doping
Valence state
Point defect

ABSTRACT

The $Lu_{0.8}Sc_{0.2}BO_3$ polycrystalline powders doped with 1 at%Ce^{3+} and co-doped with Ca^{2+}, Mg^{2+}, or Sr^{2+} with varying concentration were fabricated by conventional solid-state reaction method. We applied X-ray diffraction, optical diffuse reflectance spectrum, luminescent spectra under UV and X-ray excitation, fluorescence decay time and X-ray absorption near edge spectroscopy to study the effects of divalent ions co-doping on the $Lu_{0.8}Sc_{0.2}BO_3$:Ce scintillation materials. Through experiments, the influence of divalent ions co-doping strategy on scintillation efficiency and the action mechanism were revealed.

1. Introduction

$LuBO_3$:Ce was regarded as a high-figure-of-merit scintillator, due to its high density (~7 g/cm^3), high light yield (over 20,000 ph/MeV), and fast decay time (~30 ns) [1–3]. However, its complex phase transformation behavior [4–6] makes it hard to obtain bulk single crystal directly from melt. Recently, the phase transformation of $LuBO_3$ was successfully prevented by Sc^{3+} admixture [7]. Resultant Czochalski-grown Ce-doped lutetium scandium orthoborate single crystals appeared promising scintillators for γ-ray detection [8–10].

Many efforts have been devoted to optimizing its scintillation performance, such as cerium concentration optimization [11], cerium oxide state tuning [12,13] and Pr^{3+} co-doping [14]. Beside, in fact, co-doping optically inactive ion is another effective strategy. In the past ten years, it has tended to be an efficient tool to improve scintillation characteristics of a plenty of inorganic scintillators. By adopting suitable optically inactive co-doping ions, the concentration of traps theoretically can be effectively reduced and in turn accelerate the energy transfer to activator ions [15,16]. This deduction was confirmed by a large number of experimental results. For instance, co-doping trivalent ion La^{3+} [17] or Gd^{3+} [18] could successfully suppress the intrinsic traps in $PbWO_4$ and accelerate its mean time of scintillation decays. The other trivalent ions co-doping strategy for $PbWO_4$ were also applied but the results were not ideal, such as Pr^{3+} [19], Tb^{3+} [20] or Sm^{3+} [21] co-doping. Besides, as for the orthosilicate system, co-doping Ca^{2+} ions could make Lu_2SiO_5:Ce scintillator show higher light yield and faster time response [22]; the tetravalent Zr, Hf and Ge co-doping optimize the light yield and energy resolution of Gd_2SiO_5:Ce scintillator [23]. With respect to the aluminate system, the concentration of point defects in crystals, such as $Lu_3Al_5O_{12}$ [24], $YAlO_3$:Ce [25] and $Lu_{1-x}Y_xAlO_3$:Ce [26], can be efficiently eliminated or reduced by co-doping Zr^{4+} ions because of the charge compensation effect. Nevertheless, co-doping strategy did not always show the positive side [27,28]. Due to the complexity of co-doping optically inactive ions behavior, the optimization effect is hard to apply mechanically to different inorganic scintillators, even for the same system.

Our previous work showed that there was negative influence of isovalent ions Ga^{3+} co-doping on the scintillation efficiency of $Lu_{0.8}Sc_{0.2}BO_3$:Ce [29]. The successful attempt of Ca^{2+} co-doping in LSO:Ce [22] with further improvement of light yield and decay time, although its effect mechanism is still at issue, strongly motivates us to investigate the effects of divalent ions co-doping such as Ca^{2+}, Mg^{2+} and Sr^{2+} in $Lu_{0.8}Sc_{0.2}BO_3$:Ce system. Specifically, we will present our results discussing the influence of divalent ions co-doping on the phase purity, optical properties, cerium valence state and scintillation efficiency.

2. Experimental

The $Lu_{0.8}Sc_{0.2}BO_3$ polycrystalline powder samples, doped with 1 at% Ce^{3+} concentration and co-doped with 0.5 at.%, 1 at.%, 3 at.%

---

[*] Corresponding authors. Tel.: +86 21 69987740; fax: +86 21 59927184 (G. Ren).
E-mail addresses: wyt@mail.sic.ac.cn (Y. Wu), rgh@mail.sic.ac.cn (G. Ren).

0925-3467/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.optmat.2012.10.005

and 5 at.% divalent ions such as Ca^{2+}, Mg^{2+} or Sr^{2+} have been prepared by using high-temperature solid-state reaction method. The reactants include 4 N purity Lu_2O_3, Sc_2O_3, CeO_2, CaO (MgO or $SrCO_3$) and H_3BO_3. Stoichiometric amounts of starting materials were weighed except for H_3BO_3 which was 5 wt% rich due to vaporization loss in high-temperature synthesis. The pulverous mixtures were ground in an agate mortar, pressed into wafers with the same dimension about $\varnothing 25 \times 0.5$ mm^3. Subsequently the wafers were calcined at 1200 °C in carbon condition for 10 h and gradually cooled down to room temperature. The carbon condition is that the sufficient amount of carbon powder and samples were placed in a hermetical alumina crucible without contact.

The phase identification of the polycrystalline powder were determined by Rigaku D\max-2550 V (scanning rate = 2.4deg/min at 40 kV and 50 mA) where Cu Kα was used as incident X-ray. Optical diffuse reflectance, photoluminescence emission (PL) and excitation (PLE) spectra and fluorescence decay curves were recorded on the Perkin–Elmer Lambda 1050 UV/VIS/NIR spectrometer, Perkin–Elmer LS50B and FLS-920 spectrofluorometer, respectively. The X-ray excited luminescence spectra were conducted on an X-ray Excited Luminescence Spectrometer, assembled at Shanghai Institute of Ceramics.

X-ray absorption near edge structure (XANES) spectroscopes of divalent ions co-doping $Lu_{0.8}Sc_{0.2}BO_3$:Ce powders were recorded at Shanghai Synchrotron Radiation Facility (SSRF), on a wiggler based beamline BL14W1. Measurements were collected at room temperature, at the Ce L_{III}-edge (5723 eV), in the fluorescence mode due to the low content of cerium in the polycrystalline powders by using Si (1 1 1) double crystal monochromator. The XANES spectra were recorded in two regions: (1) from 5650 to 5720 eV (pre-edge) every 0.5 eV with 5 s accumulation time per point; (2) from 5720 to 5850 eV (XANES), every 0.5 eV with 8 s accumulation time per point. The divalent ions co-doping $Lu_{0.8}Sc_{0.2}BO_3$:Ce polycrystalline powder were coated on the transparent tape for XANES spectra measurements. The XANES spectra of Ce^{4+} and Ce^{3+} reference samples were recorded at the XAFS station of Beijing Synchrotron Radiation Facility (BSRF) and the specific measurement can be found in Ref. [30]. All the spectra were normalized in the same way using Athena software [31].

3. Results and discussions

The phase purities of Me^{2+}, and Ce^{3+} co-doped $Lu_{0.8}Sc_{0.2}BO_3$ (M = Ca, Mg, Sr) samples are identified. Their XRD patterns are presented in Fig. 1. All diffraction peaks of each sample can be well assigned to a calcite phase structure with the characteristic diffraction peaks of lutetium orthoborate ($LuBO_3$, PDF$^{\#}$72-1053) just with accordant movement to higher angle. Except the phases mentioned above, no other phases, such as Sc_2O_3, MgO, CaO, or SrO, can be found.

Fig. 2 shows the optical diffuse reflectance spectra of Me^{2+}, and Ce^{3+} co-doped $Lu_{0.8}Sc_{0.2}BO_3$ (Me = Ca, Mg, Sr) pre-growth polycrystalline powders. In comparision to $Lu_{0.8}Sc_{0.2}BO_3$:Ce, the absorption strengths of all co-doped samples significantly increase in the region of 200–370 nm. Specifically, the broad band absorption within 200–300 nm, being assigned to the charge transfer transition between Ce^{4+} and O^{2-} [10], becomes stronger after divalent ions co-doping. It indicates that the Ce^{4+} content in the co-doped samples increases with increasing codopant concentration. It is reasonable because when the divalent ions sit at original trivalent sites (Lu^{3+} or Sc^{3+}), in order to compensate the missing positive charge, it may introduce addition Ce^{4+}. By way of illustration, the defect equillibrium equation is listed as follows:

$$2\mathrm{Lu(Sc)}^{\times}_{\mathrm{Lu(Sc)}^{3+}} \rightarrow \mathrm{Me}'_{\mathrm{Lu(Sc)}^{3+}} + \mathrm{Ce}^{\cdot}_{\mathrm{Lu(Sc)}^{3+}} \quad (\mathrm{Me} = \mathrm{Ca, Mg, Sr}) \qquad (1)$$

The cross, apostrophe and dot notation represent neutral, negative (−1) and positive (+1) charged, respectively.

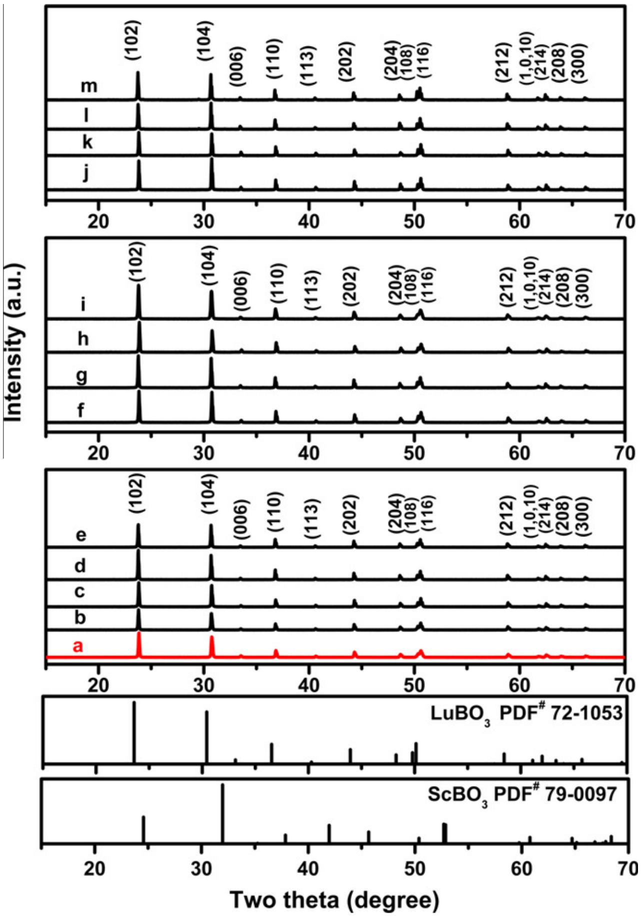

Fig. 1. The XRD patterns of $Lu_{0.8}Sc_{0.2}BO_3$:Ce polycrystalline powders co-doped with: none (a), 0.5 at.%Ca (b), 1 at.%Ca (c), 3 at.%Ca (d), 5 at.%Ca (e), 0.5 at.%Mg (f), 1 at.%Mg (g), 3 at.%Mg (h), 5 at.%Mg (i), 0.5 at.%Sr (j), 1 at.%Sr (k), 3 at.%Sr (l), 5 at.%Sr (m).

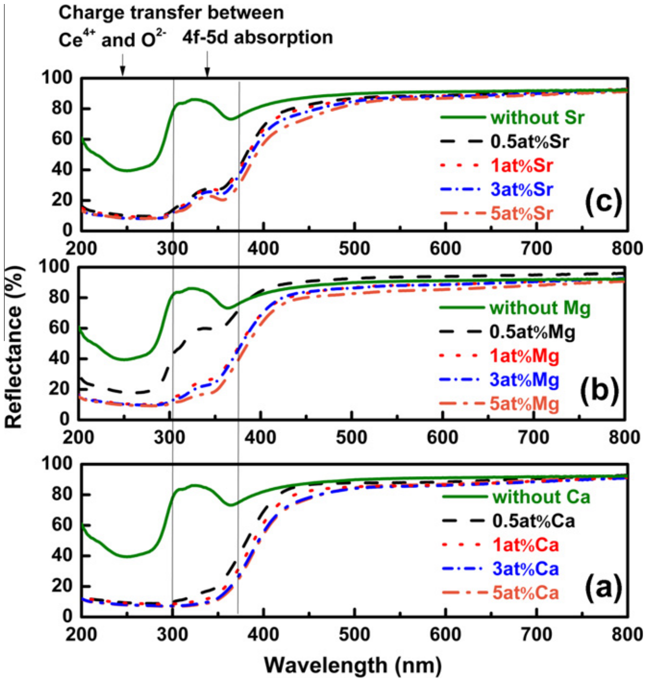

Fig. 2. The optical diffuse reflectance spectra of $Lu_{0.8}Sc_{0.2}BO_3$:Ce polycrystalline powder co-doped with: Ca^{2+} (a), Mg^{2+} (b), Sr^{2+} (c).