Journal of Alloys and Compounds 656 (2016) 94–97

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Mechanoluminescence in $(Sr,Ca,Ba)_2SnO_4:Sm^{3+},La^{3+}$ ceramics

Haifeng Zhao, Xiaona Chai, Xusheng Wang*, Yanxia Li, Xi Yao

Key Laboratory of Advanced Civil Engineering Materials of the Ministry of Education, Functional Materials Research Laboratory, Tongji University, Caoan Road 4800, Shanghai 201804, China

ARTICLE INFO

Article history:
Received 7 July 2015
Received in revised form
23 September 2015
Accepted 24 September 2015
Available online 30 September 2015

Keywords:
$(Sr,Ca,Ba)_2SnO_4:La,Sm$
Mechanoluminescence
Thermoluminescence

ABSTRACT

$(Sr,Ca,Ba)_2SnO_4:Sm^{3+},La^{3+}$ phosphors were prepared by traditional solid-state reactions. Based on previous $Sr_2SnO_4:Sm^{3+}$ phosphor, mechanoluminescence (ML) property was greatly enhanced by substitution of Ca^{2+}, Ba^{2+} and codoped of La^{3+}. Among the samples, $(Sr_{0.7}Ca_{0.27}Ba_{0.03})_{1.92}La_{0.06}Sm_{0.02}SnO_4$ showed excellent properties with intense ML and good linearity between the intensity and the load. ML spectrum of $(Sr_{0.7}Ca_{0.27}Ba_{0.03})_{1.92}La_{0.06}Sm_{0.02}SnO_4$ is consistent with the PL spectrum, ascribed to the $^4G_{5/2}$ to ^6H_J (J = 5/2, 7/2, 9/2, and 11/2) transitions of Sm^{3+} ions. Introducing Ca^{2+}, Ba^{2+} and La^{3+} causes more lattice distortion or defects in the crystal grains, indicating traps can be controlled in both trap depth and quantity. Due to the improvement of traps in the system, ML performance is enhanced.

1. Introduction

Mechanoluminescence (ML) is the phenomenon of light emission induced by a mechanical stress such as compression, tension, torsion or friction on solids [1]. To date, ML can be classified into two categories, fractoluminescence (Fracto-L) and deformation luminescence (DL) [1,2]. The latter category (DL) is further divided into plastico-mechanoluminescence (PML) and elastico-mechanoluminescence (EML) according to the type of the deformation involved [2]. Compared with Fracto-L and PML, tremendous advantages of EML such as intense emission, repeatability of luminescence, multicolor, and proportional relationship between luminescence intensity and stress and loading rate [3] make EML materials most promising for stress sensing devices. Research work of Xu etc. about application of EML materials have already proven it. Visualization of stress distribution as the most valuable application by EML, exhibits strong superiority [4]. Additionally, other applications such as photocatalysis as ubiquitous light source [5], ID identification with handwriting [6] and observation of crack propagation [7] show great possibilities on different territories. On the other hand, many researchers have discovered some important ML performances and made meaningful discussion. For example, Chandra etc. discuss systematically the relation between EML and piezoelectricity [8]. And Sohn etc. found above the excitation threshold steady-state ML without decay was ascribed to saturation of traps [9]. These facts provides us strong motivation to develop novel EML materials or optimize existing EML materials and explore related cryptic mechanism.

As the prerequisite for stress sensor application, ML materials should possess prompt response, intense EML, multi-stress sensitivity, and wide measurement range for the dynamic load etc [3]. $SrAl_2O_4:Eu^{2+}$ is almost a perfect EML material for stress sensors because of the intense luminescence. Still, drawbacks like high cost and dissolution in water restrict the extent and depth of application to a certain degree. Up to now, existing ML materials are mostly long-lasting phosphors, such as $SrAl_2O_4$:Eu [4], $BaSi_2O_2N_2$:Eu [10], $CaAl_2Si_2O_8$:Eu [11], (Ca,Ba)TiO_3:Pr [12] etc. Stannate phosphors as promising long-lasting phosphors demonstrated physical and chemical stability and more convenient synthesis process [13,14], some of which, such as $Sr_2SnO_4:Sm^{3+}$, showed EML property though it is poor. For an exact ML material, ML intensity could be enhanced by means of co-doping with suitable rare earth ions, like $SrAl_2O_4$: Eu, Dy better than $SrAl_2O_4$: Eu [7], or substituting partially ions of the host with other ions like $(Sr,Ca)Al_2Si_2O_8$:Eu better than $CaAl_2Si_2O_8$:Eu [11]. In the present work, by partially substituting Sr with Ca and Ba and co-doping with La in Sr_2SnO_4:Sm, we obtain $(Sr_{0.7}Ca_{0.27}Ba_{0.03})_{1.92}SnO_4Sm_{0.02}La_{0.06}$ with better ML performance.

2. Experimental

Sm doped and Sm/La co-doped $(Sr_{1-x-y}Ca_xBa_y)_2SnO_4$ were prepared by a solid-state reaction. The materials are designed on the stoichiometry of $(Sr_{1-x-y}Ca_xBa_y)_{2-z}M_zSnO_4$ (M is Sm or the

* Corresponding author.
E-mail address: xs-wang@tongji.edu.cn (X. Wang).

http://dx.doi.org/10.1016/j.jallcom.2015.09.218
0925-8388/

composite of Sm and La). High-purity raw materials $SrCO_3$ (99.99%), $CaCO_3$ (99.99%), $BaCO_3$ (99.99%), SnO_2 (99.99%), Sm_2O_3 (99.99%) and La_2O_3 (99.99%) were employed as reactants. High-purity starting powders were weighed out accurately, mixed with addition of alcohol, and ground for 1.5 h. After being dried, the mixture was preheated at 900 °C for 4 h in a tube furnace and then was ground again for 1 h. Finally, the mixture was sintered at 1420 °C for 4 h in air atmosphere. In order to examine the ML property, a composite disk 25 mm in diameter and 15 mm in thickness was formed by mixing synthesized powders with an optical epoxy resin. For thermoluminescence (TL) measurements, prepared powder products were pressed into a disk 20 mm in diameter and 3 mm in thickness.

The phases of synthesized powders were identified by an X-ray diffractometer (D/MAX-2550, Rigaku, Japan) using Cu Kα radiation ($\lambda = 1.5418$Å) at 40 kV and 30 mA in the 2θ range from 10° to 80°. The photoluminescence (PL) spectra were investigated by a fluorescence spectrophotometer (F-7000, Hitachi, Japan). ML spectra were carried out by a photon multi-channel analyzer system (QE65000, Ocean Optics, USA). TL curves were recorded by a combining system with the mentioned above fluorescence spectrophotometer and a lab-made temperature-controlling equipment. ML intensity was inspected through a computer system coupling a photomultiplier tube (CR131, Zolix Instruments Co., China) and a photon counter (DCS103, Zolix Instruments Co., China) with compressive stress applied on prepared composite disks with a universal testing machine (WDW-20, Shanghai Jadaronson M&C System Co., China).

3. Results and discussion

Fig. 1 displays X-ray diffraction (XRD) patterns of $(Sr_{0.7}Ca_{0.27}Ba_{0.03})_{1.98}Sm_{0.02}SnO_4$ and $(Sr_{0.7}Ca_{0.27}Ba_{0.03})_{1.92}$ $La_{0.06}Sm_{0.02}SnO_4$. They were meant to be synthesized as a solid solution with pure-phase Sr_2SnO_4. However, from XRD results coexistence of two phases, Sr_2SnO_4 and $Sr_3Sn_2O_7$, came to be the reality. Both Sr_2SnO_4 and $Sr_3Sn_2O_7$ are Ruddlesden-Popper-type phases, consisting of layered corner-shared SnO_6^{-8}. The layer number of corner-shared SnO_6^{-8} is one for Sr_2SnO_4, while it is two for $Sr_3Sn_2O_7$ [15,16]. Neither $Sr_3Sn_2O_7$ nor Sr_2SnO_4 is piezoelectric material [17], notwithstanding their perovskite-like crystal structure and defects generated during sintering in crystal may result in local piezoelectric properties. Although piezoelectricity has not been proved to have an inevitable connection with ML, most researchers devoted to studying ML believe piezoelectricity could be responsible for engenderment of ML [11,12,17]. Via two-phase XRD Rietveld refinement, where the reliability factors, wRp and Rp, are 14.2% and 10.4% respectively, molar concentration fractions of Sr_2SnO_4 and $Sr_3Sn_2O_7$ are 0.636 and 0.364 respectively in $(Sr_{0.7}Ca_{0.27}Ba_{0.03})_{1.98}Sm_{0.02}SnO_4$. Introduce of La contributed very little to crystal change by comparing XRD patterns of $(Sr_{0.7}Ca_{0.27}Ba_{0.03})_{1.98}Sm_{0.02}SnO_4$ and $(Sr_{0.7}Ca_{0.27}Ba_{0.03})_{1.92}$ $La_{0.06}Sm_{0.02}SnO_4$.

Fig. 2 shows ML intensity of composite disks of $Sr_{1.98}Sm_{0.02}SnO_4$, $Sr_{2.98}Sm_{0.02}Sn_2O_7$ and $(Sr_{0.7}Ca_{0.27}Ba_{0.03})_{1.92}La_{0.06}Sm_{0.02}SnO_4$ on applied compression load. With regard to $Sr_{2.98}Sm_{0.02}Sn_2O_7$ and $(Sr_{0.7}Ca_{0.27}Ba_{0.03})_{1.92}La_{0.06}Sm_{0.02}SnO_4$, ML intensity rose with increasing applied load and maximum was achieved at maximum load, demonstrating good linearity of ML intensity. Besides, threshold load was barely found, i.e. their threshold load equaled zero. Favorable ML performance of $(Sr_{0.7}Ca_{0.27}Ba_{0.03})_{1.92}$-$La_{0.06}Sm_{0.02}SnO_4$, good linearity and small threshold load value, makes it a suitable candidate material for stress sensor. However, for $Sr_{1.98}Sm_{0.02}SnO_4$, ML could not be observed until compressive load nearly rose up to the maximum value 1000 N. As above described, doping of Ca, Ba and La ions substituting for Sr ion in

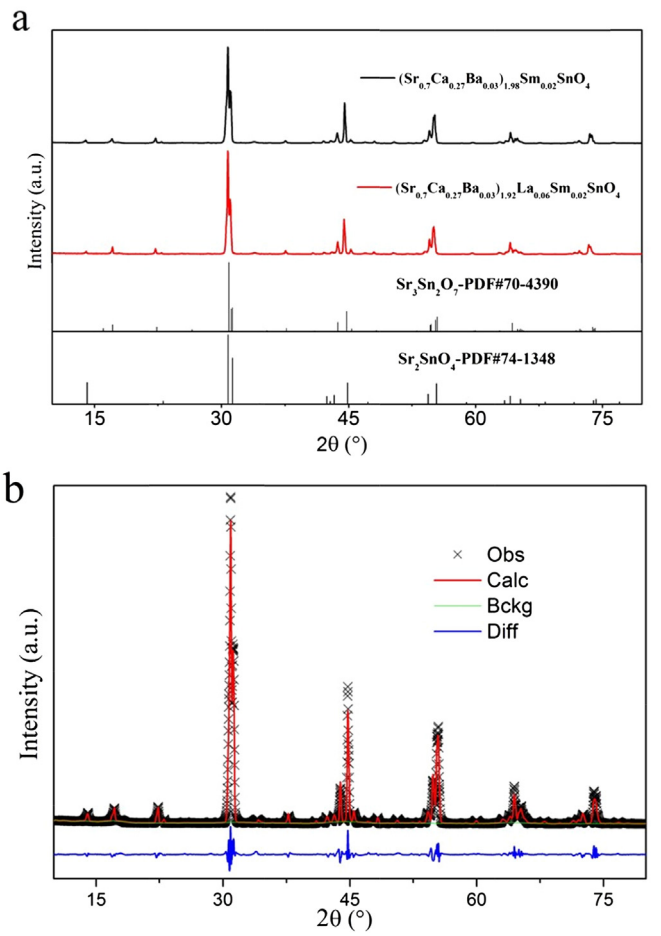

Fig. 1. (a) XRD patterns of $(Sr_{0.7}Ca_{0.27}Ba_{0.03})_{1.98}Sm_{0.02}SnO_4$ (black line) and $(Sr_{0.7}Ca_{0.27}Ba_{0.03})_{1.92}La_{0.06}Sm_{0.02}SnO_4$ (red line). (b) Rietveld refinements for $(Sr_{0.7}Ca_{0.27}Ba_{0.03})_{1.98}Sm_{0.02}SnO_4$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Sr_2SnO_4:Sm brought up an improvement of ML properties. Ca and Ba doping was designed to alter crystal structure of the host material while La doping to play a role positively on trap mechanism,

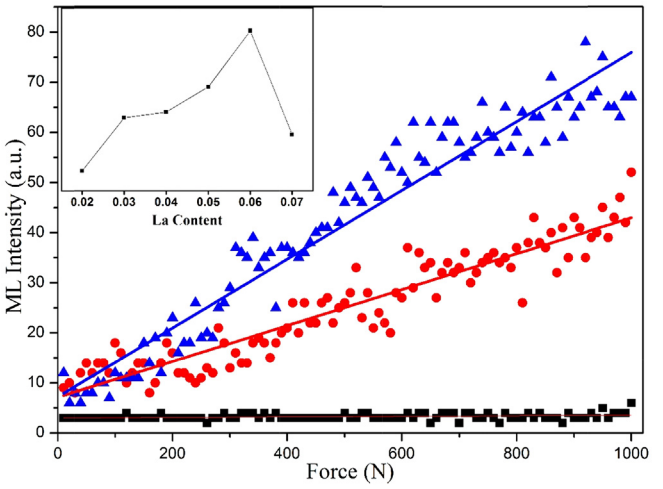

Fig. 2. ML intensity of composite disks of $Sr_{1.98}Sm_{0.02}SnO_4$ (black), $Sr_{2.98}$ $Sm_{0.02}Sn_2O_7$ (red) and $(Sr_{0.7}Ca_{0.27}Ba_{0.03})_{1.92}La_{0.06}Sm_{0.02}SnO_4$ (blue) on applied load under compression. The inset shows dependence of ML intensity at 1000 N on La content for $(Sr_{0.7}Ca_{0.27}Ba_{0.03})_{1.98-x}La_xSm_{0.02}SnO_4$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)