Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 38S (2012) S581–S584

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Elastico-mechanoluminescence properties of Pr^{3+}-doped $BaTiO_3$–$CaTiO_3$ diphase ceramics with water resistance behavior

Jun-Cheng Zhang, Mianmian Tang, Xusheng Wang *, Yanxia Li, Xi Yao

Functional Materials Research Laboratory, Tongji University, 1239 Siping Road, Shanghai 200092, PR China

Abstract

The mechanoluminescence (ML) properties of Pr^{3+}-doped $BaTiO_3$–$CaTiO_3$ diphase ceramics in different stressed conditions have been investigated. The results indicate that this ML belongs to elastico-ML (EML) and possesses the advantages of intense emission, non-destruction, repeatability of luminescence, and linear relation between the luminescence intensity and the stress. This EML is considered to have a piezoelectric origin. Furthermore, this material shows superior water resistance property.

Keywords: A. Powders: solid state reaction; C. Optical properties; D. Perovskites; E. Sensors

1. Introduction

Mechanoluminescence (ML) materials are a type of phosphors which emit light when a form of mechanical energy is applied [1,2]. While the luminescence intensity of this ML material is proportional to the stress energy in the elastic region, it is called elastico-ML (EML) material [3]. The advantages of non-destruction and the accurate proportion relation between the luminescence intensity and the stress are promising for the practical application in artificial skin, sensing stress distribution, self-diagnosis systems, mechano-optical stress sensors, and stress imaging devices [4–6]. Therefore, many researchers have devoted their efforts to search and research high-luminance EML materials [4–10]. However, very few materials possess EML property and high EML intensity at the same time. So far, only two kinds of ML materials, $ZnS:Mn^{2+}$ [5] and $SrAl_2O_4:Eu^{2+}$ [6], have been found to have strong enough luminescence. Recently, Pr^{3+}-doped $BaTiO_3$–$CaTiO_3$ ceramics near the solubility limit [11] has been found to show intense ML which could be directly observed by naked eye. After that, we found that more intensive ML could be obtained in the diphase region. It is considered a promising candidate of EML materials. However, there is no report to confirm whether such ML is EML or not. In the present study, the ML properties of Pr^{3+}-doped $BaTiO_3$–$CaTiO_3$ diphase ceramics are investigated in detail. This ML is verified to be EML and the possible EML mechanism is discussed. Moreover, its superior water resistant property is presented.

2. Experimental

Pr^{3+}-doped $BaTiO_3$–$CaTiO_3$ ceramics according to a stoichiometric composition of $(Ba_{1-x}Ca_x)_{0.998}Pr_{0.002}TiO_3$ (where $x = 0$, 0.2, 0.23, 0.25, 0.3, 0.35, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 0.92, or 1, hereafter denoted as $Ba_{1-x}Ca_xTiO_3$:Pr for simplicity) were synthesized using the solid-state reaction method. Raw materials of $BaCO_3$, $CaCO_3$, Pr_6O_{11}, and TiO_2 (≥99.9%) were mixed thoroughly and prefired at 900 °C for 4 h in air, then remixed. Finally, they were sintered at 1400 °C for 4 h in an oxygen atmosphere.

The structural characterization was analyzed by an X-ray diffractometer (XRD, D8 Advance, Bruker AXS GmbH) spectroscopy and a scanning electron microscope (SEM, JSM-5510, JEOL). Photoluminescence (PL) spectrum was measured using a fluorescence spectrometer (LS-55, Perkin-Elmer). Thermoluminescence (TL) curve was obtained on a thermoluminescence-meter (FJ427A1, Beijing Nuclear Instrument Factory).

To evaluate the ML properties, 1.00 g of ceramic powder was mixed with 4.00 g of optical epoxy resin to form a

---

* Corresponding author. Tel.: +86 21 65980544; fax: +86 21 65985179.
E-mail address: xs-wang@tongji.edu.cn (X. Wang).

0272-8842/$36.00 © 2011 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2011.05.102

composite disk with 25 mm diameter and 15 mm thickness. The ML intensity was measured by a photon-counting system that consisted of a photomultiplier tube (R649, Hamamatsu Photonics K.K.) and a photocounter (C3866, Hamamatsu Photonics K.K.) controlled by a computer. Compressive stress was applied on the composite disk with an universal testing machine (WDW-20, Jadarason Co. Ltd.).

To verify the water resistance, the powder samples were immersed in distilled water for 0.5, 1, 5, 10, and 30 days, and then the mixtures were dried at 50 °C for 2 h to evaporate the water completely. The crystal structures and luminescent properties of the examined samples were investigated by means of XRD, PL and ML. All measurements except TL spectra were performed at room temperature.

3. Results and discussion

Powder XRD analysis has revealed that $Ba_{1-x}Ca_xTiO_3$:Pr ceramics are pure tetragonal phase for $x \leq 0.23$ and pure orthorhombic phase for $x > 0.90$. Whereas in the range of $x = 0.25$–0.90, the ceramics exist a diphase coexistence of the tetragonal $Ba_{0.77}Ca_{0.23}TiO_3$:Pr and the orthorhombic $Ba_{0.1}Ca_{0.9}TiO_3$:Pr [11,12]. Our recent results have shown that there is little ML in the pure tetragonal phase and orthorhombic phase. Strong ML only occurs in diphase region. The ML intensities of the samples with $x = 0.50$–0.70 are higher than that near the solubility limit where $x = 0.30$ [13]. Furthermore, ML from $Ba_{1-x}Ca_xTiO_3$:Pr diphase ceramics comes from the $^1D_2$–$^3H_4$ transition of Pr^{3+} in $Ba_{0.1}Ca_{0.9}TiO_3$:Pr because of almost no PL in $Ba_{0.77}Ca_{0.23}TiO_3$:Pr [11,12], and there is little ML in $Ba_{0.77}Ca_{0.23}TiO_3$:Pr. Therefore, the strong interactions between two phases seem to act as an important factor in creating ML feature. Considering that all of the diphase ceramic samples have the similar ML performances, hereafter, the $Ba_{0.4}Ca_{0.6}TiO_3$:Pr sample is selected to show the ML properties.

To investigate the ML phenomenon, a compressive load up to a maximal value of 1000 N with a rate of 3 mm/min is applied on the samples. Fig. 1 shows the load dependence of the ML intensity. The ML intensity is linearly proportional to the magnitude of the applied stress, showing the highest intensity at the maximal load value. It indicates that ML from $Ba_{1-x}Ca_xTiO_3$:Pr diphase ceramics is EML.

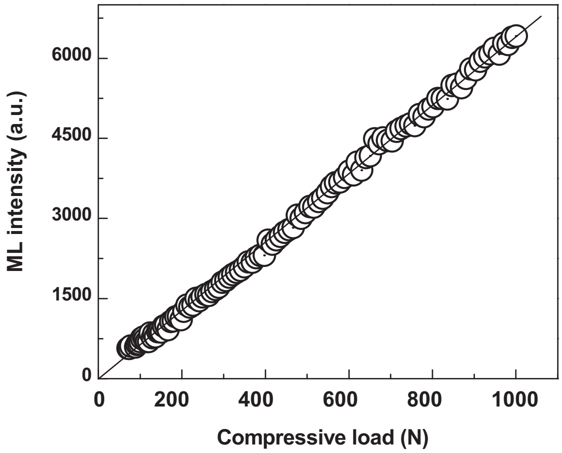

Fig. 1. Load dependence of ML intensity for the $Ba_{0.4}Ca_{0.6}TiO_3$:Pr composite disk.

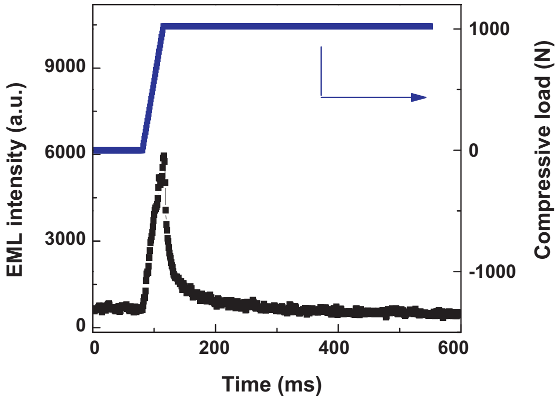

Fig. 2. Typical EML behavior of $Ba_{0.4}Ca_{0.6}TiO_3$:Pr sample during the application of force (1000 N).

Figs. 2 and 3 show the EML behaviors of $Ba_{0.4}Ca_{0.6}TiO_3$:Pr sample when it is applied different kinds of compressive loads. As shown in Fig. 2, it emits red light immediately when the force is applied. However, when the force is kept, the light is attenuated rapidly. It indicates that EML occurs only when the applied force changes. Fig. 3 shows the EML behavior when the compressive load is reapplied. It is significant that the EML intensity decreases with the stressed times, and in each cycle, the EML intensity still linearly changes with the increase or the decrease of the applied mechanical load, showing a ML peak at the peak load.

Fig. 4 shows the dependence of the ML intensity on a repetitive pressure and the effect of UV light irradiation. The ML intensity decreases drastically by applied repetitive stresses, and the ML intensity becomes relatively stable at about 19%. After that, the sample is irradiated UV light (365 nm) for 5 min, and the ML intensity recovers completely. The damage on these samples is very small after repetitive mechanical experimental. It points out the repeatability of EML.

The above-mentioned EML properties of $Ba_{1-x}Ca_xTiO_3$:Pr diphase ceramics are similar with the EML behavior of the materials reported previously, ZnS:Mn^{2+} [5], $SrAl_2O_4$:Eu^{2+}

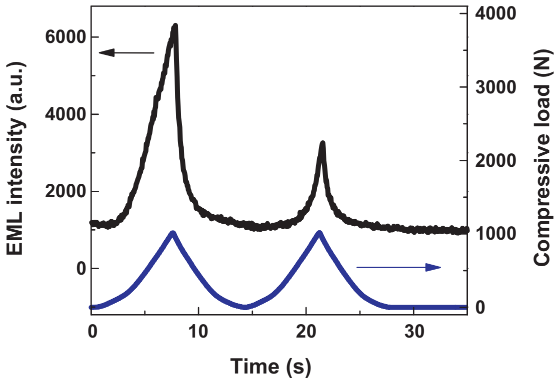

Fig. 3. The EML behavior of $Ba_{0.4}Ca_{0.6}TiO_3$:Pr sample when reapplying a stress.

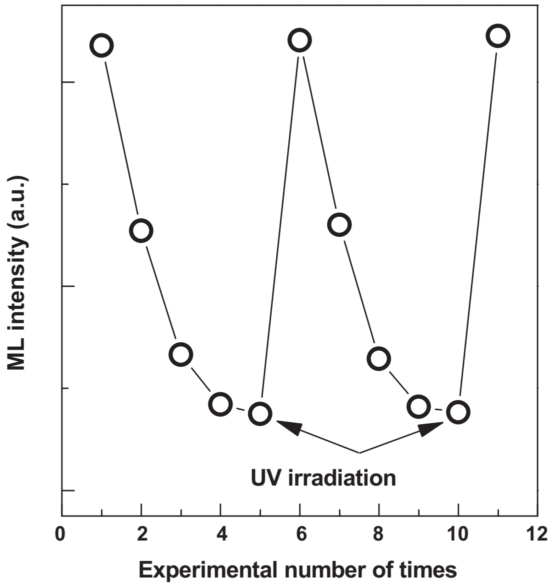

Fig. 4. Dependence of ML intensity of $Ba_{0.4}Ca_{0.6}TiO_3$:Pr sample on repetitive pressures of 1000 N and effect of UV light irradiation. The excitation wavelength is 365 nm and the irradiation time is 5 min.

[14,15], $SrAl_2O_4:Ce^{3+}$ [8], and $Ca_2Al_2SiO_7:Ce^{3+}$ [7], in which the EML origin has been considered to be the trapped carrier excitation, i.e. the carriers trapped at lattice defects are excited by lattice deformation and the luminescence is occurred by the recombination between the carriers and the doped luminescent centers [7,8,15,16]. According to the recovery phenomenon, the $Ba_{1-x}Ca_xTiO_3$:Pr diphase ceramics are thought to also have trap energy levels which can be filled by UV light irradiation, just as other EML materials. To confirm the assumption, the TL glow curves of different $Ba_{1-x}Ca_xTiO_3$:Pr ceramics ($x = 0.2$, 0.5, 0.6, 0.7, and 0.92) with ultraviolet light irradiation are investigated. Among them, samples $Ba_{0.8}Ca_{0.2}TiO_3$:Pr and $Ba_{0.08}Ca_{0.92}TiO_3$:Pr are selected to keep the pure phase. As shown in Fig. 5, there really exist trap energy levels which can be filled by UV light irradiation in the diphase ceramics. Except the sample with $x = 0.2$ without TL peak, the other samples have only one TL peak at around 38 °C above the room temperature. With the increase of the Ca content, the TL peak intensities gradually increase. The trapping center responsible for this TL glow peak has been ascribed to be the positively charged $[Pr_{Ca}]^0$ defect in $CaTiO_3:Pr^{3+}$ [17]. Furthermore, there is little ML in $Ba_{0.1}Ca_{0.9}TiO_3$:Pr sample although its TL intensity is maximal. This fact confirms the conjecture of strong interaction between two phases to induce EML.

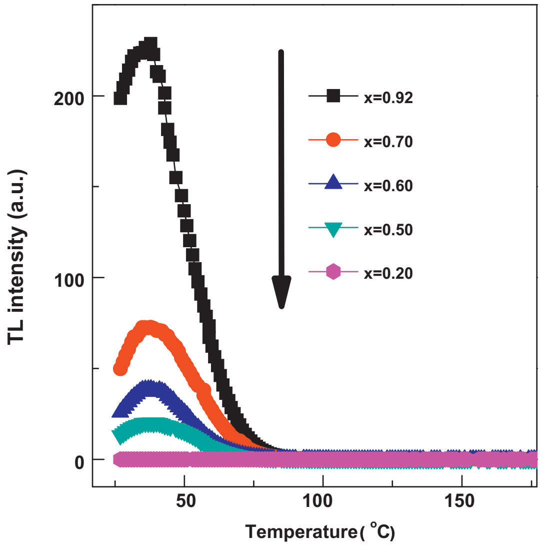

Fig. 5. Thermoluminescence glow curves at a heating rate of 1 °C/s of $Ba_{1-x}Ca_xTiO_3$:Pr ceramics ($x = 0.2$, 0.5, 0.6, 0.7, and 0.92) after 5 min irradiation at 365 nm.

Which kind of interaction do the two phases depend on to excite the carriers trapped in $Ba_{0.1}Ca_{0.9}TiO_3$:Pr phase? The results of our previous reports provide us a clue that $Ba_{0.77}Ca_{0.23}TiO_3$:Pr is a good piezoelectric, even with higher piezoelectric coefficient than $BaTiO_3$:Pr [11,12,18]. Moreover, the SEM pictures of diphase ceramics have exhibited that the smaller $Ba_{0.1}Ca_{0.9}TiO_3$:Pr grains disperse relatively equably in the larger $Ba_{0.77}Ca_{0.23}TiO_3$:Pr grains [12], forming a series of piezoelectric/phosphor/piezoelectric sandwich structures in three dimensions [19]. Therefore, it will be a reasonable assumption that this EML has a piezoelectric origin. When the mechanical pressure is applied, an electric field will be applied on the phosphor due to the piezoelectric effect. The electric field will induce the release of carriers trapped in $Ba_{0.1}Ca_{0.9}TiO_3$:Pr phosphor, and then the luminescence is occurred by the recombination between the carriers and the doped Pr^{3+} ions, which has been detailedly discussed in another article [13].

We have known that this diphase material has the excellent EML properties, which could be employed in various applications for sensing stress in subjects, just as the above mentioned EML materials $ZnS:Mn^{2+}$ and $SrAl_2O_4:Eu^{2+}$. However, the luminescence intensity of $SrAl_2O_4:Eu^{2+}$ disappears rapidly when it is immersed in water due to hydrolysis, which poses a particularly serious problem for its application in aqueous environments [10,20]. Therefore, it is necessary for an EML material with superior water resistance property.

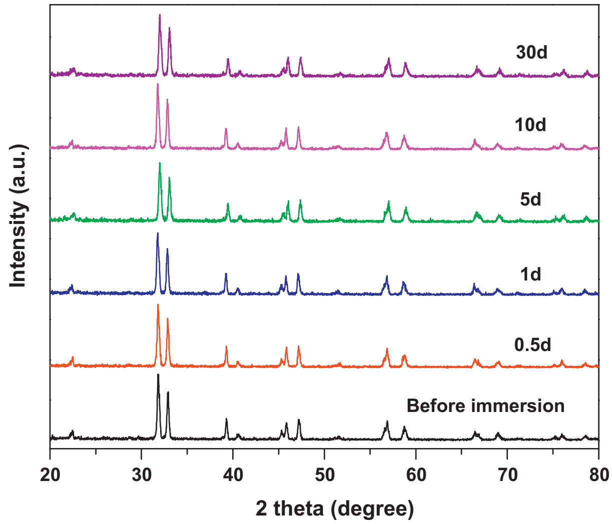

Fig. 6. XRD patterns of $Ba_{0.4}Ca_{0.6}TiO_3$:Pr sample with various immersion time.

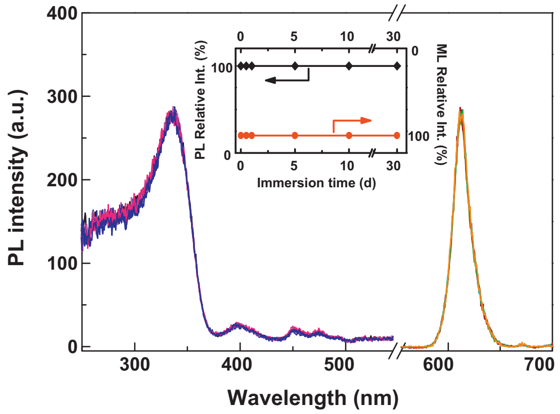

Fig. 7. Excitation and emission spectra of $Ba_{0.4}Ca_{0.6}TiO_3$:Pr sample with various immersion time. The inset is the dependence of relative PL and ML intensities on immersion time.

Fig. 6 shows the XRD patterns of $Ba_{0.4}Ca_{0.6}TiO_3$:Pr sample at different water immersion time. There is no change in the peak positions and intensities even after 30 days immersion, indicating that the crystalline structure remains the same after water treatment. The PL spectra of $Ba_{0.4}Ca_{0.6}TiO_3$:Pr sample after water immersion are shown in Fig. 7. The inset shows the immersion time dependence of the relative PL and ML intensities. All the samples maintain the same PL and ML intensities as those before immersion. The results clearly indicate its superior water resistance property.

4. Conclusion

ML properties of Pr^{3+}-doped $BaTiO_3$–$CaTiO_3$ diphase ceramics in different stressed conditions have been investigated. ML from this material belongs to EML and possesses the advantages of intense emission, non-destruction, repeatability of luminescence, and linear relation between the luminescence intensity and stress. This EML is considered to have a piezoelectric origin. Furthermore, the superior water resistance property is useful for the application in aqueous environments.

Acknowledgements

This work was supported by the Natural Science Foundation of China (No. 50932007), Scientific and Technical Innovation Program of Shanghai (No. 08JC1419100) and Specialized Research Fund for the Doctoral Program of Higher Education (Nos. 20070247010 and 20090072120034).

References

[1] A.J. Walton, Triboluminescence, Advances in Physics 26 (1977) 887–948.

[2] B.P. Chandra, Luminescence induced by moving dislocations in crystals, Radiation Effects and Defects in Solids 138 (1996) 119–137.

[3] B.P. Chandra, Mechanoluminescence, in: D.R. Vij (Ed.), Luminescence of Solids, Plenum Press, New York, 1998, pp. 361–389.

[4] C.N. Xu, T. Watanabe, M. Akiyama, X.G. Zheng, Direct view of stress distribution in solid by mechanoluminescence, Applied Physics Letters 74 (1999) 2414–2416.

[5] C.N. Xu, T. Watanabe, M. Akiyama, X.G. Zheng, Artificial skin to sense mechanical stress by visible light emission, Applied Physics Letters 74 (1999) 1236–1238.

[6] C.N. Xu, X.G. Zheng, M. Akiyama, K. Nonaka, T. Watanabe, Dynamic visualization of stress distribution by mechanoluminescence image, Applied Physics Letters 76 (2000) 179–181.

[7] M. Akiyama, C.N. Xu, H. Matsui, K. Nonaka, T. Watanabe, Recovery phenomenon of mechanoluminescence from $Ca_2Al_2SiO_7$:Ce by irradiation with ultraviolet light, Applied Physics Letters 75 (1999) 2548–2550.

[8] H. Zhang, H. Yamada, N. Terasaki, C.N. Xu, Ultraviolet mechanoluminescence from $SrAl_2O_4$:Ce and $SrAl_2O_4$:Ce,Ho, Applied Physics Letters 91 (2007), 081905.1–081905.3.

[9] H. Zhang, H. Yamada, N. Terasaki, C.N. Xu, Stress-induced mechanoluminescence in $SrCaMgSi_2O_7$:Eu, Electrochemical and Solid-State Letters 10 (2007) J129–J131.

[10] L. Zhang, H. Yamada, Y. Imai, C.N. Xu, Observation of elasticoluminescence from $Ca_2Al_2SiO_7:Eu^{2+}$ and its water resistance behavior, Journal of The Electrochemical Society 155 (2008) J63–J65.

[11] X. Wang, C.N. Xu, H. Yamada, K. Nishikubo, X.G. Zheng, Electro-mechano-optical conversions in Pr^{3+}-doped $BaTiO_3$–$CaTiO_3$ ceramics, Advanced Materials 17 (2005) 1254–1258.

[12] X. Wang, H. Yamada, K. Nishikubo, C.N. Xu, Electrostrictive properties of Pr-doped $BaTiO_3$–$CaTiO_3$ ceramics, Japanese Journal of Applied Physics 45 (2006) 813–816.

[13] J.C. Zhang, X. Wang, X. Yao, C.N. Xu, H. Yamada, Strong elastico-mechanoluminescence in diphase $(Ba,Ca)TiO_3:Pr^{3+}$ with self-assembled sandwich architectures, Journal of The Electrochemical Society 157 (2010) G269–G273.

[14] M. Akiyama, C.N. Xu, K. Nonaka, T. Watanabe, Intense visible light emission from $Sr_3Al_2O_6$:Eu, Dy, Applied Physics Letters 73 (1998) 3046–3048.

[15] M. Akiyama, C.N. Xu, Y. Liu, K. Nonaka, T. Watanabe, Influence of Eu, Dy co-doped strontium aluminate composition on mechanoluminescence intensity, Journal of Luminescence 97 (2002) 13–18.

[16] H. Yamada, H. Kusaba, C.N. Xu, Anisotropic lattice behavior in elasticoluminescent material $SrAl_2O_4:Eu^{2+}$, Applied Physics Letters 92 (2008), 101909.1–101909.3.

[17] P. Boutinaud, E. Pinel, R. Mahiou, Luminescence and afterglow in $CaTiO_3:Pr^{3+}$ films deposited by spray pyrolysis, Optical Materials 30 (2008) 1033–1038.

[18] X. Wang, H. Yamada, C.N. Xu, Large electrostriction near the solubility limit in $BaTiO_3$–$CaTiO_3$ ceramics, Applied Physics Letters 86 (2005), 022905.1–022905.3.

[19] J.C. Zhang, X. Wang, X. Yao, C.N. Xu, H. Yamada, Studies on ac electroluminescence device made of $BaTiO_3$–$CaTiO_3:Pr^{3+}$ diphase ceramics, Applied Physics Express 3 (2010), 022601.1–022601.3.

[20] Y. Imai, R. Momoda, Y. Adachi, K. Nishikubo, Y. Kaida, H. Yamada, C.N. Xu, Water-resistant surface-coating on europium-doped strontium aluminate nanoparticles, Journal of The Electrochemical Society 154 (2007) J77–J80.