Development of highly sensitive mechanoluminescent sensor aiming at small strain measurement*

Yuki Fujio^{†,††}, Chao-Nan Xu^{†,‡,§,§§}, Maiko Nishibori[¶], Yasutake Teraoka[¶],
 Kazutaka Kamitani^{||}, Nao Terasaki[†] and Naohiro Ueno^{**}

[†]Measurement Solution Research Center

National Institute of Advanced Industrial Science and Technology
 Saga 841-0052, Japan

[‡]International Institute for Carbon-Neutral Energy Research (WPI-I² CNER)
 Kyushu University, Fukuoka 819-0395, Japan

[§]Interdisciplinary Graduate School of Engineering Sciences
 Kyushu University, Fukuoka 816-8580, Japan

[¶]Faculty of Engineering Sciences
 Kyushu University, Fukuoka 816-8580, Japan

^{||}Research Center for Synchrotron Light Applications
 Kyushu University, Fukuoka 816-8580, Japan

^{**}Graduate School of Science and Engineering
 Saga University, Saga 840-8502, Japan

^{††}yuki-fujio@aist.go.jp

^{§§}cn-xu@aist.go.jp

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This paper was focused on the elasticoluminescence (ELS) characteristics, especially a response to small strain (below 1000 μ st), of mechanoluminescence (ML) sensor using strontium aluminate doped with small amount of europium ($\text{SrAl}_2\text{O}_4\text{:Eu}$) synthesized by different methods. By using nitrate decomposition method as a synthetic method of $\text{SrAl}_2\text{O}_4\text{:Eu}$, the response to small strain of the ML sensor was enhanced in comparison with using a conventional solid-state reaction method. Based on SEM observation and thermoluminescence (ThL) measurement, we proposed a hypothesis that the sensing characteristic of small strain affect the plate-like shape of $\text{SrAl}_2\text{O}_4\text{:Eu}$ grain and/or shallower carrier trap levels formed by nitrate decomposition method.

Keywords: Mechanoluminescence; $\text{SrAl}_2\text{O}_4\text{:Eu}$; small strain measurement.

1. Introduction

A mechanoluminescence (ML) sensor using composite film prepared by using elasticoluminescence (ELS) material and flexible polymeric material is one of the promising candidates for health monitoring of various constructions, such as bridge, building, chemical plant, and social infrastructure, as well as an effective tool to check a risk and residual life of products.^{1–11} The sensing characteristics of ML sensor are mainly affected by the optical and structural properties of ELS material, e.g., emission intensity, emission wavelength, and anisotropic deformation.^{3,12–14} Among various ELS materials reported, strontium aluminate doped with small amount of europium ($\text{SrAl}_2\text{O}_4\text{:Eu}$, SAOE) has been reported to give much stronger green light emission (about 520 nm), which can be easily seen by our naked eye.^{2,12,15}

So far, there have been numerous reports regarding the improvement in ELS characteristics of a composite material consisting of SAOE powder and polymeric material. For example, Xu *et al.* have achieved that the ELS intensity was dramatically enhanced by controlling the amount of Sr vacancy and crystal structure.^{3,12} Subsequently Sohn *et al.* have reported to improve the ELS intensity by tuning the amount of dopant Eu ion.¹⁶ However, these reports were focused on the ELS intensity toward much larger stress (or strain), and as far as we know, there are few reports of a response to relatively small stress (or strain). This is a highly preferable characteristic in view of the actual application of the sensor to structural health monitoring and check tool of product. Such a highly sensitive response to a small mechanical stimulation, such as compression, tension, friction, and vibration, is strongly required to commercialize an ML sensor.

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In the present study, the ML sensor utilizing SAOE films synthesized by different methods were fabricated and their ELS characteristics were examined, aiming at the development of highly sensitive detection of a small strain (below $1000\ \mu\text{st}$). After optimizing a synthetic method of SAOE powder, the influential factors for small strain response of the fabricated ML sensor were also investigated and discussed here.

2. Experimental Procedure

2.1. Preparation of $\text{SrAl}_2\text{O}_4\text{:Eu}$

The sensing materials of SAOE were synthesized by a conventional solid-state reaction method and a nitrate decomposition method. The solid-state reaction method has been commonly used as a method for manufacturing $\text{SrAl}_2\text{O}_4\text{:Eu}$. In this study, the commercial SrCO_3 (Kanto Chemical Co., Inc., Japan), $\alpha\text{-Al}_2\text{O}_3$, and Eu_2O_3 (Kojundo Chemical Laboratory Co., Ltd., Japan) were weighed precisely to the molar ratios of $\text{Sr}_{0.97}\text{Al}_2\text{O}_4\text{:Eu}_{0.03}$, and mixed together by means of ball-milling method (using a planetary ball-mill, Pulverisette 7, Fritsch, Germany) in ethanol solution ($10\ \text{cm}^3$) at 600 rpm for 2 h using zirconia balls (3 mm in diameter). The resulting suspension was stirred and dried simultaneously to obtain a precursor of SAOE. In the nitrate decomposition method, the corresponding metal nitrates ($\text{Sr}(\text{NO}_3)_2$ and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$: Kanto Chemical Co., Inc., Japan; $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$: Kojundo Chemical Laboratory Co., Ltd., Japan) were dissolved in distilled water. The aqueous solution was mixed well by ultra-sonication for 1 h, and then vigorously stirred on a hot-plate stirrer and evaporated to dryness in an atmospheric air. The precursors obtained from different methods were calcined at 800°C for 1 h in air and sintered subsequently at 1350°C for 4 h in 5% H_2/Ar atmosphere. The SAOE powders synthesized by solid-state reaction method and nitrate decomposition method are denoted by SS-SAOE and ND-SAOE, respectively.

Each of the synthesized SAOE powders was thoroughly mixed with epoxy resin to prepare SAOE pastes. The SAOE films (ML sensor) were fabricated by means of a screen printing technique using each resulting SAOE paste. The thickness of SAOE films was controlled to be approximately $30\ \mu\text{m}$.

2.2. Evaluation of ML sensor

The ELS characteristics of the fabricated SAOE films were evaluated under a laboratory-built ELS evaluation system in a dark room at room temperature, as reported elsewhere.^{6,8,17} The ELS evaluation system is made up of metal test piece (SUS631, $200 \times 20 \times 0.5\ \text{mm}$) attached with an SAOE film ($10 \times 10\ \text{mm}$) and a commercial strain gage (Kyowa Electronic Instruments Co., Ltd., Japan), a CCD camera, material testing machine (MTS 810, MTS Systems Co., US),

Fig. 1. The schematic illustration of laboratory-built ELS evaluation system.

and a computer, as shown in Fig. 1. The applied tensile load and loading speed were controlled to be approximately $1000\ \mu\text{st}$ of strain and $1000\ \mu\text{st/s}$ of strain rate, respectively. For quantitative and reproducible measurement, the SAOE film was once irradiated by ultraviolet light (UV, $365\ \text{nm}$, $0.7\ \text{mW/cm}^2$) for 1 min and kept under dark condition for 1 min. The ELS intensities were estimated from the ELS images.

2.3. Material characterizations

The crystal structure of the synthesized powders was determined by means of X-ray diffraction (XRD, RINT2000, Rigaku Co., Japan) analysis. The $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\ \text{\AA}$) and $2.00^\circ/\text{min}$ angle step were used for all measurements. Morphology of the synthesized powders was observed by a field-emission scanning electron microscope (FE-SEM, JSM-7001F, JEOL Ltd., Japan). To determine the oxidation state of Eu in the samples, X-ray absorption near edge spectroscopy (XANES) was performed at beamline (BL06) in the SAGA Light Source (SAGA-LS), Japan, which has a storage ring operating energy of $1.4\ \text{GeV}$. Eu L_3 -edge XANES spectra of the synthesized samples and reference compounds were measured under transmission mode by using pelletized mixtures ($10\ \text{mm}\phi \times 0.5\ \text{mm}'$) of the synthesized SAOE and boron nitride powders (BN, Kojundo Chemical Laboratory Co., Ltd., Japan). The incident intensity (I_0) and the transmitted intensity (I) through the sample were monitored using $50\%\text{He} + 50\%\text{N}_2$ and $15\%\text{Ar} + 85\%\text{N}_2$ filled ionization chambers, respectively. The obtained XANES spectra were compared with two reference spectra (Eu_2O_3 and EuS) using Athena software.^{18,19}

The emission and excitation spectra of photoluminescence (PL) for the synthesized SAOE powders were measured via a spectrofluorometer (FP-6600, JASCO Co., Japan). The thermoluminescence (ThL) glow curve measurements were performed by means of a special system consisting of a spectrofluorometer (FP-6500, JASCO Co., Japan) and a heating/freezing stage (Linkam Scientific Instruments Ltd., UK). After deexcitation process, which a metal holder loaded with weighed amount of SAOE powder ($200\ \text{mg}$) was heated up to 300°C to release all carriers trapped in defect inside SrAl_2O_4 matrix, the SAOE powder was exposed to UV light for 5 min and waited for 1 min at room temperature, and then

the ThL glow curve was recorded when it was heated up to 300°C at the heating rate of 30°C/min.

3. Results and Discussion

Figure 2(a) shows XRD patterns of the synthesized SAOE powders after sintering at 1350°C in 5% H_2/Ar atmosphere. To calibrate the obtained XRD patterns and confirm the diffraction peak shift, a standard reference CeO_2 powder (SRM 674a, NIST) was mixed with each of the synthesized SAOE powders. As a result, both SAOE powders were in excellent agreement with the diffraction pattern of monoclinic SrAl_2O_4 (PDF no. 01-074-0794 in ICDD), and no impurity phase was observed. Figure 2(b) depicts the enlarged XRD patterns in the 2θ range of 26–34°. It can be seen that all diffraction

(a)

(b)

Fig. 2. (a) XRD patterns of $\text{SrAl}_2\text{O}_4:\text{Eu}$ powders synthesized by solid-state reaction and nitrate decomposition methods as well as standard PDF data for SrAl_2O_4 (01-074-0794), and (b) enlarged XRD patterns of the synthesized samples.

Fig. 3. Emission spectra under 365 nm excitation wavelength and excitation spectra under 520 nm emission wavelength for the synthesized SAOE powder samples.

peaks of both SAOE powders coincide completely, although the peak intensities of ND-SAOE are higher than those of SS-SAOE. This indicates that the SS-SAOE and ND-SAOE powders formed a same SrAl_2O_4 matrix, whereas the crystallinity of ND-SAOE is higher than that of SS-SAOE.

The PL emission and excitation spectra for the synthesized SAOE powders were investigated via a spectrofluorometer and compared in Fig. 3. As a result, ND-SAOE powder was found to exhibit higher excitation efficiency in the range of 400–500 nm compared to SS-SAOE. Such a high excitation efficiency in visible region is a practical advantage as a ML sensor. On the other hand, the peak positions of emission spectra for both SAOE powders are almost same, which is centered at approximately 520 nm, although those PL intensities are a bit different. This suggests that PL from both synthesized SAOE powders can be attributed to the transition of electrons in Eu^{2+} ions from the excited state $4f^65d^1$ to the ground state of $4f^7$.

To investigate the oxidation state of Eu doped in SrAl_2O_4 matrix, Eu L_3 -edge XANES spectra for the synthesized SAOE powders were measured using synchrotron radiation at SAGA-LS. XANES measurement using synchrotron radiation helps in identifying an oxidation state of infinitesimal amount of dopant element. Figure 4 displays the XANES spectra of the synthesized SAOE samples and the reference compounds. The reference samples (EuS and Eu_2O_3) gave only a peak at around 6973 and 6981 eV, respectively. The resonance for Eu^{2+} is approximately 8 eV below the Eu^{3+} edge, which is good agreement with previous reports.^{20,21} The XANES spectra of both SAOE powders have only a peak which centered at approximately 6973 eV. Thus, it can be concluded that Eu ion doped in SrAl_2O_4 matrix for both synthesized SAOE powders exists as a divalent ion (Eu^{2+}).

The ELS characteristics of the fabricated ML sensors utilizing SS-SAOE and ND-SAOE films prepared by solid-state reaction method and nitrate decomposition method, respectively, were investigated under laboratory-built ELS evaluation

Fig. 4. Eu L_3 -edge XANES spectra of the synthesized SAOE powders as well as EuS and Eu_2O_3 used as reference materials.

system. Figure 5 shows dependence of the ELS intensity of the ML sensors utilizing SS-SAOE and ND-SAOE films on strain obtained from the strain gage attached to the back side of SUS631. It can be seen that the ML sensor utilizing SS-SAOE film responds from approximately $300 \mu\text{st}$ of strain, and the ELS intensity increases with increase in strain in the examined range of $300\text{--}1000 \mu\text{st}$. Meanwhile, ND-SAOE film was found to respond to below $200 \mu\text{st}$ of strain and the ELS intensity in the range of $200\text{--}1000 \mu\text{st}$ is larger compared to that of SS-SAOE film. Such a highly sensitive response to small strain was confirmed to maintain over the examined 1000 cycles. Undoubtedly, the use of nitrate decomposition method as a synthesis of SAOE seems to be a very promising solution for improvement in the characteristic of small strain response for ML sensor.

To investigate the reasons for such an improvement in the ELS characteristic, the morphology observation and carrier

Fig. 5. Dependence of ELS intensity on strain for the ML sensors utilizing either SS-SAOE or ND-SAOE films.

(a)

(b)

Fig. 6. Representative SEM images of (a) SS-SAOE and (b) ND-SAOE powders after sintering 1350°C in $5\%\text{H}_2/\text{Ar}$ atmosphere.

trap level analysis for both SAOE powders were carried out by means of SEM observation and ThL measurement, respectively. Figure 6 shows the representative SEM images of the SS-SAOE and ND-SAOE powders. It is seen that the rounded SS-SAOE particles agglomerate, forming sub-micrometer sized SAOE particles. While, ND-SAOE particles also agglomerate, but forming much larger particles (several $10 \mu\text{m}$). The particle shape of ND-SAOE forms plate-like and the grain boundary between primary particles is clearly seen. The size of ND-SAOE particle is larger than that of SS-SAOE particle even after sintering at same temperature. This is maybe due to a nanosized precursor in nitrate decomposition method, in other words, the much larger SAOE particle is suggested as the cause of lower melting temperature of precursor synthesized from metal nitrates. Thus, we can speculate that the improved small strain responsive ELS characteristics of ML sensor may be a result of specific shape (plate-like shape) of SAOE secondary particle formed by a nitrate decomposition method.

The mechanism of emitting light from ELS material is considered that the emission of the carriers trapped in defects.

Fig. 7. Thermoluminescence glow curves for SS-SAOE and ND-SAOE powders recorded at a heating rate of 30°C/min.

Considering this carrier trapping model, the trapped carrier analysis is very important for explaining the reason for improved small strain responsive characteristics of ML sensor. Thus, the trapped carrier analysis was investigated via ThL glow curve measurement. All of ThL glow curve measurements were carried out using a heating rate of 30°C/min after deexcitation and excitation processes. The obtained ThL glow curves for both synthesized powders are shown in Fig. 7. As can be seen from Fig. 7, both SAOE powders gave two distinct peaks in ThL glow curves. The peaks are located at around 68°C and 136°C in the case of SS-SAOE, and around 48°C and 125°C in the case of ND-SAOE. The position of both peaks for ND-SAOE is lower than that of SS-SAOE, that is to say ND-SAOE has shallower trapped level than SS-SAOE. From this result, it is indicated that the carriers trapped in defects of ND-SAOE is easy to be released by smaller thermal energy as well as smaller mechanical energy compared to SS-SAOE. Thus, the two possible mechanism of small strain response of the ML sensor using SAOE film can be proposed on the basis of the aforementioned results and considerations. This specific characteristic may be caused by a plate-like shape as well as much larger sized SAOE particle formed by a lower melting temperature of precursor, and/or shallower trapped levels, which is easy to release the trapped carrier. However, the investigation of most effective factor for small strain response should be investigated further.

4. Conclusion

The ELS characteristics, especially a small strain response, of the ML sensor using SAOE films synthesized by different method were examined. The ML sensor utilizing SAOE film synthesized by a nitrate decomposition method showed sensitive response to small strain (below 200 μm) compared to a conventional solid-state reaction method. Both SAOE materials show same crystal structure and the doped Eu ions in SrAl_2O_4 matrix exist as same divalent. It was revealed via

SEM observation and ThL glow curve measurement that such a sensitive response to small strain is caused by a plate-like SAOE particle and/or shallower trapped levels formed by a nitrate decomposition method.

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References

- ¹C. N. Xu, T. Watanabe, M. Akiyama and X. G. Zheng, Artificial skin to sense mechanical stress by visible light emission, *Appl. Phys. Lett.* **74**, 1236 (1999).
- ²C. N. Xu, T. Watanabe, M. Akiyama and X. G. Zheng, Direct view of stress distribution in solid by mechanoluminescence, *Appl. Phys. Lett.* **74**, 2414 (1999).
- ³C. N. Xu, *Encyclopedia of Smart Materials*, ed. M. Schwartz, Vol. 1 (John Wiley & Sons Inc., New York, 2002), pp. 190–201.
- ⁴J. S. Kim, Y. N. Kwon and K. S. Sohn, Dynamic visualization of crack propagation and bridging stress using the mechanoluminescence of $\text{SrAl}_2\text{O}_4\text{:}(\text{Eu,Dy,Nd})$, *Acta Mater.* **51**, 6437 (2003).
- ⁵J. S. Kim, Y. N. Kwon, N. Shin and K. S. Sohn, Mechanoluminescent $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$ phosphor for use in visualization of quasidynamic crack propagation, *Appl. Phys. Lett.* **90**, 241916 (2007).
- ⁶C. Li, C. N. Xu, L. Zhang, H. Yamada and Y. Imai, Dynamic visualization of stress distribution on metal by mechanoluminescence images, *J. Vis.* **11**(4), 329 (2008).
- ⁷D. Ono, C. N. Xu, C. Li and N. Bu, Visualization of internal defect of a pipe using mechanoluminescent sensor, *J. Jpn. Soc. Exp. Mech.* **10**, 152 (2010).
- ⁸C. Li, C. N. Xu, Y. Imai and N. Bu, Real-time visualisation of the Portevin-Le Chatelier effect with mechanoluminescent-sensing film, *Strain* **47**, 483 (2011).
- ⁹N. Terasaki, C. N. Xu, C. Li, L. Zhang, C. Li, D. Ono, M. Tsubai, Y. Adachi, Y. Imai, N. Ueno and T. Shinokawa, Visualization of active crack on bridge in use by mechanoluminescent sensor, *Proc. SPIE*, Vol. 8348, (2012), pp. 83482D-1–D-6.
- ¹⁰S. Guo, C. N. Xu, D. Ono, C. Li, Y. Sakata and S. Watanabe, Visualization of the fatigue crack for pressure vessel by mechanoluminescent sensor, *2012 IEEE Sensors Applications Symp. Proc.* (2012), pp. 212–216.
- ¹¹N. Ueno, C. N. Xu and S. Watanabe, Fatigue crack detection of CFRP composite pressure vessel using mechanoluminescent sensor, *Proc. IEEE SENSORS 2013* (2013), pp. 1851–1854.

- ¹²C. N. Xu, H. Yamada, X. Wang and X. G. Zheng, Strong elastoluminescence from monoclinic-structure SrAl_2O_4 , *Appl. Phys. Lett.* **84**, 3040 (2004).
- ¹³H. Zhang, H. Yamada, N. Terasaki and C. N. Xu, Ultraviolet mechanoluminescence from $\text{SrAl}_2\text{O}_4\text{:Ce}$ and $\text{SrAl}_2\text{O}_4\text{:Ce,Ho}$, *Appl. Phys. Lett.* **91**, 081905 (2007).
- ¹⁴H. Yamada, H. Kusaba and C. N. Xu, Anisotropic lattice behavior in elasticoluminescent material $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$, *Appl. Phys. Lett.* **92**, 101909 (2008).
- ¹⁵C. N. Xu, X. G. Zheng, M. Akiyama, K. Nonaka and T. Watanabe, Dynamic visualization of stress distribution by mechanoluminescence image, *Appl. Phys. Lett.* **76**, 179 (2000).
- ¹⁶K. S. Sohn, S. Y. Seo, Y. N. Kwon and H. D. Park, Direct observation of crack tip stress field using the mechanoluminescence of $\text{SrAl}_2\text{O}_4\text{:}(\text{Eu,Dy,Nd})$, *J. Am. Ceram. Soc.* **85**, 712 (2002).
- ¹⁷Y. Fujio, C. N. Xu, N. Terasaki and N. Ueno, Influence of organic solvent treatment on elasticoluminescent property of europium-doped strontium aluminates, *J. Lumin.* **148**, 89 (2014).
- ¹⁸M. Newville, IFEFFIT: Interactive EXAFS analysis and FEFF fitting, *J. Synchrotron Radiat.* **8**, 322 (2001).
- ¹⁹B. Ravel and M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT, *J. Synchrotron Radiat.* **12**, 537 (2005).
- ²⁰K. Korthout, K. Van den Eeckhout, J. Botterman, S. Nikitenko, D. Poelman and P. F. Smet, Luminescence and X-ray absorption measurements of persistent $\text{SrAl}_2\text{O}_4\text{:Eu,Dy}$ powders: Evidence for valence state changes, *Phys. Rev. B* **84**, 085140 (2011).
- ²¹N. M. Souza-Neto, J. Zhao, E. E. Alp, G. Shen, S. V. Sinogeikin, G. Lapertot and D. Haskel, Reentrant valence transition in EuO at high pressures: Beyond the bond-valence model, *Phys. Rev. Lett.* **109**, 026403 (2012).