Intense Deformation Luminescence from Sintered Sr$_3$Al$_2$O$_6$: Eu

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Sr$_3$Al$_2$O$_6$: Eu 燃結体からの強い変形ルミネセンス

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We have investigated the deformation luminescence (DL) phenomena in sintered Sr$_3$Al$_2$O$_6$: Eu. The DL from sintered Sr$_3$Al$_2$O$_6$: Eu was clearly visible to the naked eye in the atmosphere, and was produced owing to the physical processes induced during deformation. The DL was sensitive to stress and was observed below the pressure of 10 MPa. There is no report on the DL of sintered ceramic, the DL phenomenon of sintered ceramic is first reported first to our knowledge. The DL intensity of sintered Sr$_3$Al$_2$O$_6$: Eu decreased on repetitive application of stress, but it was completely recovered by irradiation with ultraviolet light. The DL intensity was recovered by not only ultraviolet light but also visible light. It is suggested that Sr$_3$Al$_2$O$_6$: Eu is a suitable DL material, which shows repeated DL with undiminished intensity. We think that the DL mechanism arises from the movement of dislocations or heat and recombination between electrons and holes released from these traps associated with doped Eu$^{2+}$ centers.

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1. Introduction

It is well known that light emission phenomena are induced by deformation or fracture of solids, such as SiO$_2$, sugar, rocks, alkali halide, II–VI compounds, and polymer crystals. In deformation luminescence (DL), it is produced during deformation of solids, where no fracture is required. DL is exhibited in single crystals of x- or y-irradiated alkali halides, Mn doped ZnS, and alkaline earth oxides. There is no report on the deformation luminescence of sintered ceramic to our knowledge. It is thought that DL may be produced by, e.g., the mechanical or electrostatic interaction of dislocations with defect centers, or thermal excitation in the stressed regions of solids.

DL phenomena have many potentially important applications, such as a self-indicating method, nondestructive testing like acoustic emission, damage sensors, and the visualization of stress distribution. Furthermore, finding a suitable DL material which will show repeated DL with undiminished intensity is the current challenge in this field.

Recently, we found and investigated the luminescence phenomena in the composite material consisted of Sr$_3$Al$_2$O$_6$: Eu powder and epoxy resin. The luminescence characteristics of only Sr$_3$Al$_2$O$_6$: Eu is needed to clear the luminescence mechanism of the composite material. Further, there is no report on the deformation luminescence of sintered ceramic to our knowledge. In the present study, we report on the deformation luminescence phenomena in sintered Sr$_3$Al$_2$O$_6$ and Eu doped Sr$_3$Al$_2$O$_6$ samples, and consider the nature of the luminescence mechanism.

2. Experimental procedures

Sintered Sr$_3$Al$_2$O$_6$ and Eu doped Sr$_3$Al$_2$O$_6$ samples were prepared from α-Al$_2$O$_3$ (purity 99.99%, High Purity Chemical), SrCO$_3$ (99.9%, Kanto Chemical), Eu$_2$O$_3$ (99.95%, Kanto Chemical) and H$_3$BO$_3$ (99.99%, Aldrich Chemical) powders. These powders were weighed in the normal composition of Sr$_3$Al$_2$O$_6$ and Sr$_3$Al$_2$O$_6$: Eu (0.5 mol%), and H$_3$BO$_3$ was added 20 mol% as a flux. They were mixed, pressed and sintered at 1300°C for 4 h in a reducing atmosphere (Ar+5%H$_2$). The Sr$_3$Al$_2$O$_6$: Eu sample size was 4 x 1 x 20 mm. The samples were applied pressure with an autograph (Oriented RTC-1310A). The samples were irradiated by ultraviolet (UV) light (UVP UVL-56), whose wavelength was 366 nm, for three min before thermoluminescence was measured by a spectrophotofluorometer (Hitachi F-3010).

We measured the luminescence intensity until the sample was fractured. The luminescence intensity change is shown in Fig. 1(a), and the luminescence intensity behavior is shown in Fig. 1(b). The stress increased linearly and was kept at 33 MPa. The luminescence intensity of the sample was observed below 10 MPa and linearly increased with the stress. The luminescence intensity gradually decreased when the stress was kept at 33 MPa. This result is consistent with the results of X-ray irradiated KCl: Cu and ZnS: Mn crystals.

We measured the luminescence intensity until the sintered Sr$_3$Al$_2$O$_6$: Eu was fractured. The luminescence intensity change is shown in Fig. 2. The luminescence intensity increased almost linearly with stress until around 50 MPa and developed the tendency to be saturated below 70 MPa, but the luminescence intensity again increased above 70 MPa. The luminescence intensity drastically increased and was too large to measure it, when the sample was fractured around 80 MPa. At the fracture of many materials, a large peak of luminescence intensity is always observed. This fact may be due to an electric discharge between the differently charged rupture surfaces. It is indicated that the luminescence intensity drastically increased and was too large to measure it, when the sample was fractured around 80 MPa. At the fracture of many materials, a large peak of luminescence intensity is always observed. This fact may be due to an electric discharge between the differently charged rupture surfaces.
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The luminescence intensity of the sample strongly depended on stress, and there was large difference between deformation and fracture luminescence in the Sr₃Al₂O₆ : Eu. The deformation luminescence phenomenon of the sample, where no fracture was required, was observed first to our knowledge.

We have already reported that the luminescence intensity of the composites made by epoxy resin is recovered by ultraviolet light irradiation, and we investigated the influence of UV irradiation on the luminescence intensity of the sample. The result is shown in Fig. 3. The luminescence intensity drastically decreased by the repetitive application of stress, and became stable at about 20%. After that, the sample was irradiated with UV light for three min, and the luminescence intensity recovered completely. Furthermore, we measured the excitation and emission spectra of the sample. The spectra are shown in Fig. 4. The excitation spectrum had a peak from 320 to 440 nm with a maximum at 371 nm. This means that visible light or sunlight also excites the sintered Sr₃Al₂O₆ : Eu sample. On the other hand, the emission spectrum had a peak from 450 to 600 nm with a maximum at 510 nm. It is thought that the doped Eu²⁺ ions act as luminescence centers, because the emission spectrum from the 4f⁷→4f⁵5f transition of Eu²⁺ ions is from 400 to...
process can be represented as follows;\textsuperscript{17,18)}

\[ L + C \rightarrow L^* \rightarrow L + h\nu \]

Chandra reported that in x- or y-irradiated alkali halide crystals, the dislocations bend between pinning points and interact with the nearby F-centers during elastic deformation. Subsequently, they may capture F-center electrons and transfer them to holes, whereby luminescence may occur.\textsuperscript{17)}

From the recovery phenomenon of the luminescence intensity, we thought that the sintered Sr\textsubscript{3}Al\textsubscript{2}O\textsubscript{6}:Eu sample had energy levels that trap excited electrons or holes like F-centers. We measured the thermoluminescence glow curve of the Sr\textsubscript{3}Al\textsubscript{2}O\textsubscript{6}:Eu irradiated with UV in order to confirm that the sample had trapped excited electrons or holes. The glow curve is shown in Fig. 5. The thermoluminescence intensity drastically increased with the temperature, and was sensitive to temperature. The glow curve indicated a peak at 80°C, proving evidence for the existence of the traps.

Ishihara et al. assumed that the excitation of doped rare-earth ions in BaAl\textsubscript{2}Si\textsubscript{2}O\textsubscript{8} is due to the photons emitted from the fracture of BaAl\textsubscript{2}Si\textsubscript{2}O\textsubscript{8}, because they observed that BaAl\textsubscript{2}Si\textsubscript{2}O\textsubscript{8} without intentional dopants also emits white light when it is fractured.\textsuperscript{27)} Williams et al. demonstrated that dislocation induced excitonic transitions adjacent to vacancy clusters produce luminescence in single crystals of MgO, CaO and SrO in a temperature range from 80 to 300 K.\textsuperscript{16)} Chapman et al. proposed a thermal excitation mechanism and reported that most of plastic deformation energy is released as heat in a variety of glasses and crystalline quartz.\textsuperscript{18)} In our case, since the deformation luminescence from the Sr\textsubscript{3}Al\textsubscript{2}O\textsubscript{6} without Eu was not observed and the luminescence of the Sr\textsubscript{3}Al\textsubscript{2}O\textsubscript{6}:Eu sample was sensitive to temperature, we think that the movement of dislocations (D) or heat (H) excites carriers (C) from the filled traps (T\textsuperscript{*}) and the subsequent recombination of the electrons and holes in luminescence centers (L), which is doped Eu\textsuperscript{2+}, give rise to the deformation luminescence. This process can be represented as follows;\textsuperscript{17,18)}

\[ D \text{ or } H + T^* \rightarrow D \text{ or } H + T + C \]

\[ L + C \rightarrow L^* \rightarrow L + h\nu \]

4. Conclusions

We have investigated the deformation luminescence phenomena in the sintered Sr\textsubscript{3}Al\textsubscript{2}O\textsubscript{6}:Eu. The deformation luminescence intensity strongly depended on stress, and there was large difference between the deformation and fracture luminescence. The deformation luminescence phenomenon in the Sr\textsubscript{3}Al\textsubscript{2}O\textsubscript{6}:Eu, where no fracture was required, is observed first to our knowledge. The luminescence intensity drastically decreased by the repetitive application of stress, after that, the Sr\textsubscript{3}Al\textsubscript{2}O\textsubscript{6}:Eu was irradiated with ultraviolet light, and the luminescence intensity recovered completely. We think that the movement of dislocations or heat excita carriers from the filled traps and the subsequent recombination of the electrons and holes in luminescence centers, which is doped Eu\textsuperscript{2+}, give rise to the deformation luminescence. Industrially Sr\textsubscript{3}Al\textsubscript{2}O\textsubscript{6}:Eu could have used as a new type fluorescence material reacting to stress.

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References