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Thermoluminescence properties of SiO_2: Al, Eu

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Abstract

SiO_2 crystals have been used in lasers, fiber amplifiers, electroluminescence devices and thermoluminescence (TL) dosimeters. However, the emission mechanism of TL has not yet been clearly explained. Recently, it has become possible to obtain amorphous, highly pure, SiO_2 prepared by the sol–gel method. The emission mechanism of TL was investigated using SiO_2 samples doped with Al and/or Eu. Two glow peaks were observed on Al,Eu-codoped samples and Eu-doped samples, but a weak glow peak was done on Al-doped samples. In Al,Eu-codoped samples, the TL spectra contained TL spectra of both Al-doped and Eu-doped samples. These results indicate that Al or Eu substitutes for Si and plays the role of a hole trap and/or electron trap, which contributes to the TL phenomenon. In addition, the trap depth was evaluated from two TL glow peaks (ca. 0.5 and 2 eV). From these results, the emission mechanism of TL was obtained.

Keywords: SiO_2; Thermoluminescence; ESR; Dating

1. Introduction

It has been known that the SiO_2 crystals are useful as a matrix for the element of a thermoluminescence (TL) dosimeter, useful, for example for the TL dating of earthen vessels and lava [1]. Al and Eu, the main impurities in natural SiO_2 crystals, are reported as the origin of blue and red emission on TL phenomena, respectively [2]. However, an open question has been the correlation between TL intensity and the concentrations of Al and Eu [3–18].

Recently, amorphous and highly-pure SiO_2 crystals have been synthesized [19,20] and it has become possible to prepare SiO_2 crystals doped with various impurities.

In this paper, we prepared SiO_2 crystals doped with Al and/or Eu. These impurities have been reported to contribute to the TL in natural SiO_2 crystals. We have investigated the emission mechanism of TL in the doped SiO_2 crystals.

2. Experimental

Various SiO_2 samples doped with Al and/or Eu were prepared as follows. Measured amounts of Al_2O_3 or Eu_2O_3 were homogeneously mixed with acetone and SiO_2 prepared by the sol–gel method (Mitsubishi Chemical Co. Ltd.) and then the mixture was fired at 1573 K for 1–40 h in air. Doping concentrations were selected to obtain the maximum value of ESR and TL intensities, respectively.

Fig. 1 shows the apparatus for measuring TL spectra, which consists of a black box with a projection lamp as heater, optical quartz fiber, spectrometer with multichannel analyzer and intensifier (Hamamatsu Photonics Co. Ltd., PMA-10) and a personal computer for data analysis. The SiO_2 sample irradiated by X-ray (about 0.8 kGy, Cu Kα, 8 keV) was flatly spread on the Ag tray in a black box and then was heated from 298 K to about 680 K by the projection lamp with constant rate of heating. The TL emission was fed to the spectrometer equipped with a multichannel analyzer and intensifier using an optical quartz fiber, and the emission spectrum was taken to a personal computer. The heating rate was controlled by an automatic temperature regulator.

The ESR spectra were measured on the SiO_2 sample irradiated by X-rays (1.5 kGy, Cu Kα, 8 keV) using an X-band ESR spectrometer with a 100 kHz magnetic field modulator and a phase-sensitive detector (JEOR Ltd., JES-FEX1XG).

The crystal structure of the SiO_2 sample was measured, using an X-ray powder diffraction device (Rigaku Co. Ltd., XRD; Cu Kα).

3. Results and discussion

Fig. 2 shows the XRD patterns of various SiO_2 matrices.

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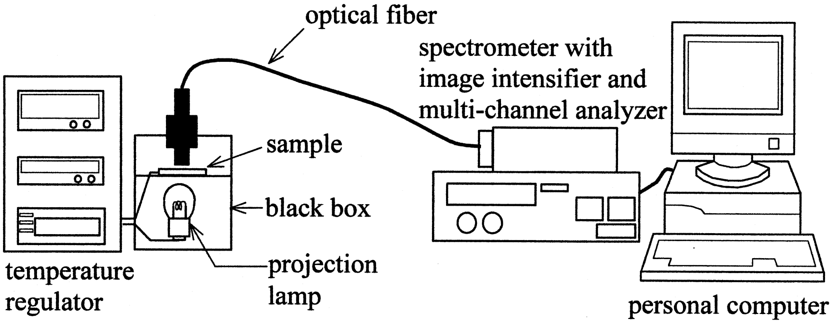

Fig. 1. Apparatus for measuring TL spectra.

From Fig. 2, we deduced that the unfired matrix (a) was amorphous, because of the diffused peak on the XRD pattern. This XRD pattern was not changed on the sample fired for an hour at 823 K prior to the phase transition point from α-quartz (trigonal) to β-quartz (hexagonal) (b). The XRD pattern of the SiO_2 matrix fired for an hour at 1573 K in air (c) and fired for 6 h in the same conditions (d), showed sharp peaks which are assigned to the tridymite structure. The XRD pattern did not change if the firing time was extended more than 6 h at 1573 K in air, so the firing conditions for further investigations were fixed as 6 h at 1573 K in air.

The ESR spectra of various samples after X-ray irradiation are shown in Fig. 3. An E_1' center due to oxygen defects was produced in the SiO_2 matrix (a) [3–5]. On the Al (1 mmol.%)-doped sample (b), an ESR signal appeared near a g-value=2.003. This is assigned to an Al center, which consists of the non-bridging oxygen capturing a hole [21]. The ESR signal of the Eu (1 mmol.%)-doped sample (c) appeared at a slightly larger g-value compared with the Al center. It was found from the temperature dependence of the ESR signal (see Fig. 5) that this signal consists of two signals, one with g=2.003(7) due to a shallow trap (electron trap) and another with g=2.003(4) due to a deep

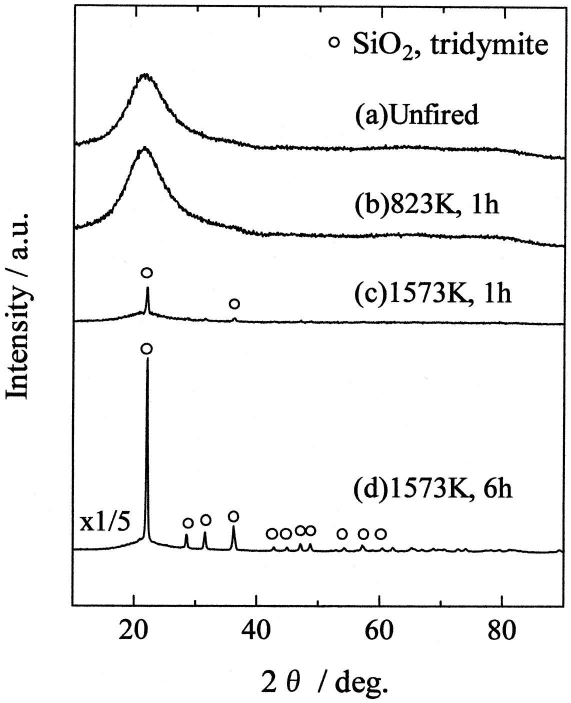

Fig. 2. Room temperature X-ray powder diffraction patterns of various SiO_2 matrices under various firing conditions: (a) the unfired SiO_2 matrix, (b) the SiO_2 matrix fired for an hour at 823 K in air, (c) the SiO_2 matrix fired for an hour at 1573 K in air and (d) the SiO_2 matrix fired for 6 h at 1573 K in air.

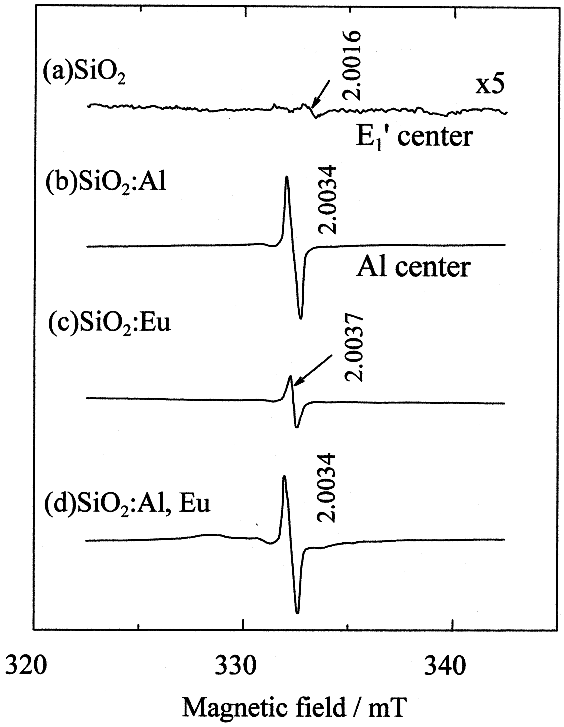

Fig. 3. ESR spectra of various samples after X-ray irradiation: (a) the SiO_2 matrix fired for an hour at 1573 K in air, (b) SiO_2: Al, (c) SiO_2: Eu and (d) SiO_2: Al, Eu.

trap (Eu-related center). The ESR signal of Al (1 mmol.%), Eu (1 mmol.%)-codoped sample (d) was a combination of the signals from both Al-doped and Eu-doped samples.

Fig. 4 shows the TL spectra of the Al (1 mol.%)-doped and Al,Eu-codoped samples. The TL spectrum of the sample doped with Eu was ascribed to f–f transitions of Eu^{3+}, and that of the Al-doped sample was very weak and had a broader peak, which had a maximum value at ca. 450 nm and also contained shorter wavelengths (ca. 450 nm and 475 nm) among the emission peaks of Eu (10 mmol.%)-doped sample. In the Al,Eu-codoped sample, the TL spectrum contained TL spectra of both Al-doped and Eu-doped samples.

The TL glow curves were examined for the sample doped with Al and/or Eu (Fig. 5). The TL glow curve of Al,Eu-codoped and Eu-doped samples had two peaks of ca. 350 K and ca. 500 K, while that of Al-doped sample had a higher temperature peak of ca. 500 K. To elucidate the relationship between the ESR and TL phenomena, the temperature dependence of the ESR was examined and compared with the TL glow curves. ESR signal intensity rapidly decreased at near glow peak temperatures in all samples. ESR signal (g=2.003) in Al-doped samples is observed when a hole is captured to Al substituted for Si, (i.e. Al-center) [21] and this fact is also applied to Eu in Eu-doped samples because a Eu ion substituted for Si is trivalent like Al. From Eu-doped samples, the ESR signal, g=2.003(7), which diminished near 370 K, is ascribed to an electron trap, probably Eu (which charges from Eu^{3+} to Eu^{2+}), and ESR signal, g=2.003(4), which diminished at near 500 K, is ascribed to a Eu-related center like the Al-center. From these facts, it was deduced that Al or Eu substitutes for Si and plays a role of hole trap and/or electron trap, which contributes to the TL phenomenon.

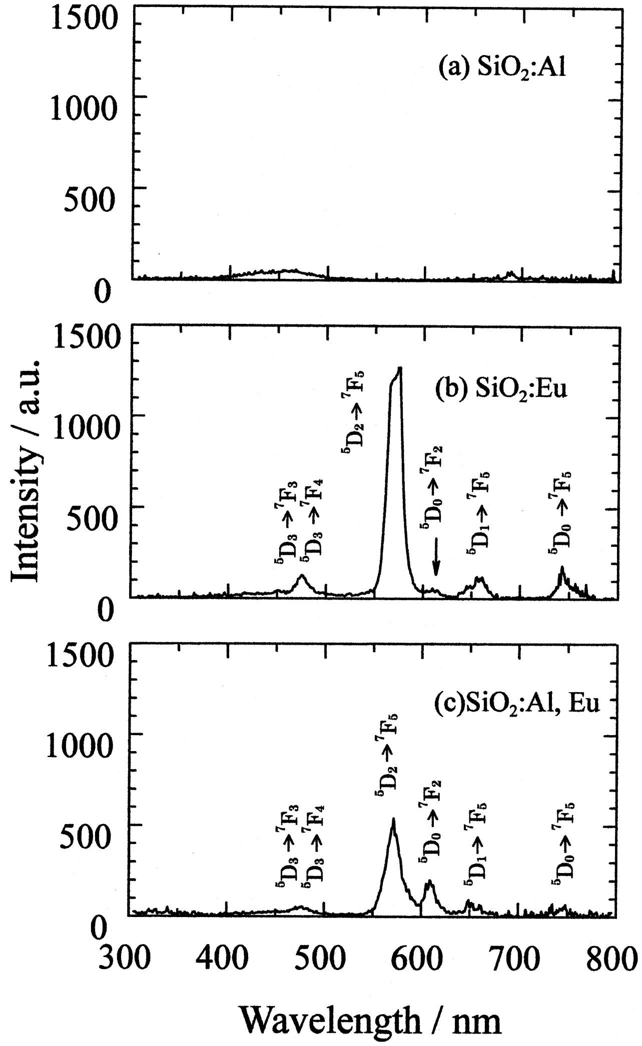

Fig. 4. TL spectrum of (a) SiO$_2$: Al (1 mol.%) and (b) SiO$_2$: Al (1 mmol.%), Eu (1 mmol.%).

The temperature of TL glow peaks measured at various heating rates was analyzed by the Hoogenstraaten method [22] in order to evaluate the trap depth of each glow peak. The trap depth was ca. 0.5 eV and 2 eV for the lower and higher temperature peaks, respectively.

From the above results, the emission mechanism for the Al,Eu-codoped sample was deduced and is shown in Fig. 6. There are two traps, a hole trap and an electron trap. The hole trap is an Al center or Eu-related center with trap depth of ca. 2 eV and the electron trap is probably Eu (from *sn* Eu^{3+} to Eu^{2+} transition), for which the trap depth is ca. 0.5 eV.

An electron and a hole are generated in the sample by X-ray irradiation and those are captured by electron traps and hole traps, respectively. On heating the irradiated sample, the electron is first released from an electron trap and recombines with a hole which exists in the valence band. Eu^{3+} is excited by the surplus energy of recombining the electron and hole, and TL due to f–f transition of Eu^{3+} is observed. On further heating, the hole is released from the hole trap and recombines with a conduction band electron. So the TL due to Eu^{3+} is dominant. From our results, the emission of Al should not be found in natural SiO$_2$ crystals, since the doping concentration in natural SiO$_2$ crystals (20–150 ppm) is less than 1/100 of the Al-doped sample which was analyzed in our investigation.

4. Conclusion

We have deduced that the traps of the Eu-doped sample are electron traps and hole traps, while that of the Al-doped sample are hole traps, as deduced from their ESR signal. The emission mechanisms of Al,Eu-codoped SiO$_2$ crystals have been clarified. The red and blue emissions were ascribed to Eu and both Eu and Al, respectively, from their TL spectra in the separately doped sample. In

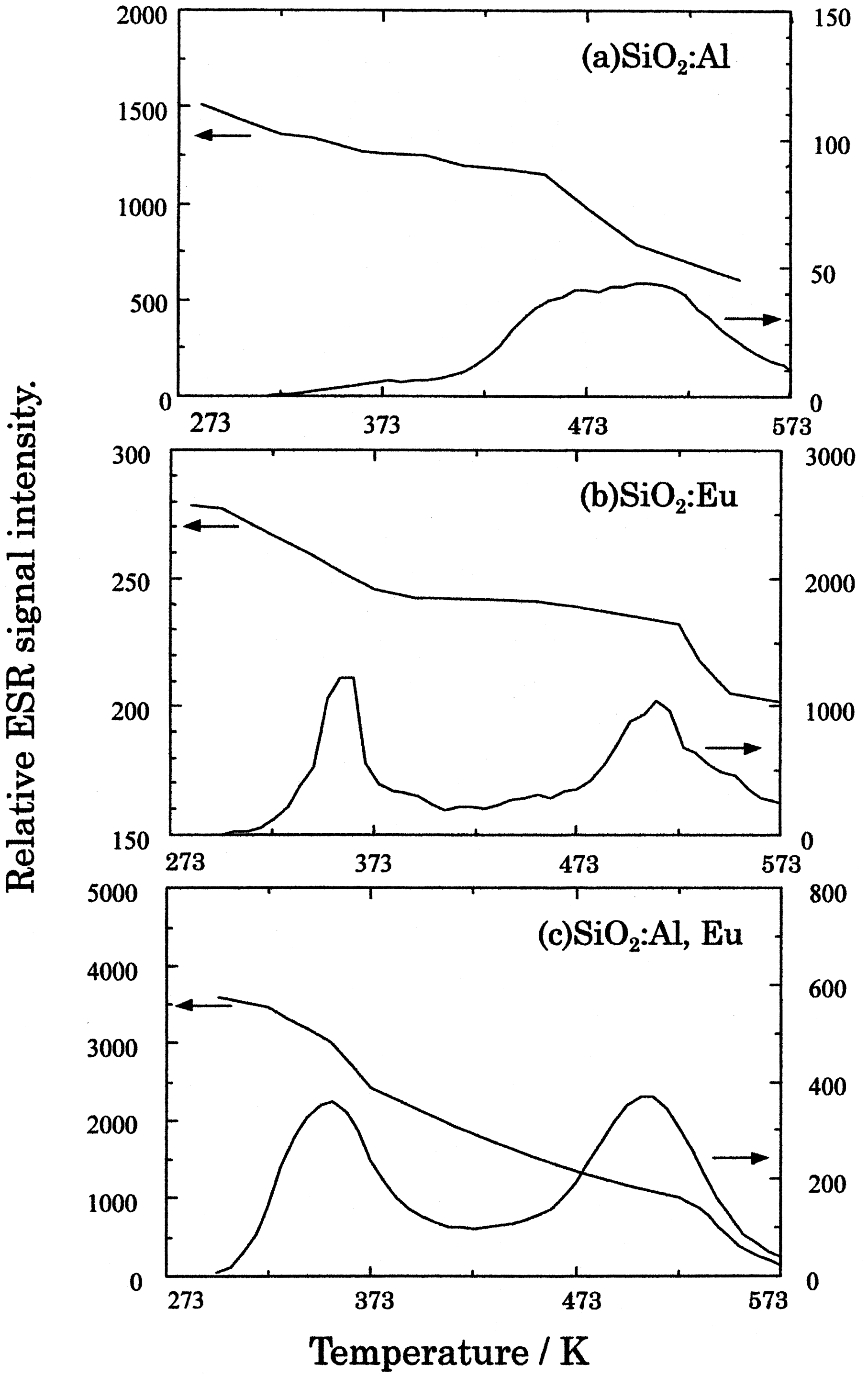

Fig. 5. TL glow curves and the results of ESR measurement with heating after X-ray irradiation of (a) SiO_2: Al, (b) SiO_2: Eu and (c) SiO_2: Al, Eu.

addition, the depth of the hole trap was found to be ca. 2 eV and that of the electron trap ca. 0.5 eV.

For the Al,Eu-codoped sample, the TL intensity was a combination of Al and Eu emission. The weak TL emission due to Al would be undetectable in natural SiO_2 crystals, because it would be concealed by the bright emission due to Eu.

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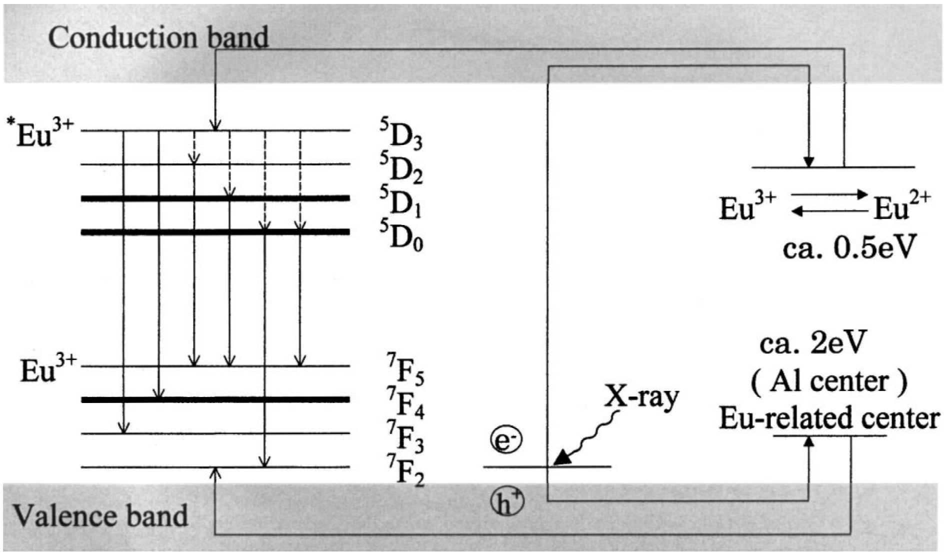

Fig. 6. Energy level diagram of SiO_2: Al, Eu.

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