JOURNAL OF MATERIALS SCIENCE 25 (1990) 1545-1547

ESR study for a TSEE peak in X-irradiated $Li_2B_4O_7$: AgCl crystallized glass

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Thermally stimulated exoelectron emission (TSEE) from X-irradiated crystallized glass of $Li_2B_4O_7$ doped with 0.03 mol% AgCl showed a conspicuous peak at 155° C, which is absent in an undoped sample. ESR analysis of the samples revealed that Ag^0 atoms which had been formed by X-irradiation are responsible for the 155° C TSEE peak.

1. Introduction

Lithium diborate ($Li_2B_4O_7$) is widely used as a material for radiation dosimetry, because its effective atomic number (7.3) is very close to that of human tissue (7.4). We have previously measured TSEE of $Li_2B_4O_7$ as well as other borate compounds and found that the sintered or microcrystallized samples such as crystallized glasses showed remarkable peaks compared with those amorphous samples [1, 2]. It is also known that the samples doped with some activators such as silver or copper ions usually show much higher thermoluminescence (TL) peaks compared with undoped ones [3]. These TL peaks with activators have been used in practice for radiation dosimetry [4].

It is the purpose of this report to investigate the role of silver ions in the TSEE of X-irradiated $Li_2B_4O_7$ crystallized glass by using the ESR spectra measured stepwise for the same sample annealed at higher temperatures. For the sake of comparison TL spectra were measured simultaneously. The results are discussed along with those for an undoped sample.

2. Experimental procedure

Reagent grade $Li_2B_4O_7$ powder (99.99% purity) was obtained from Furuuchi Chemical Company. The main impurities in this material were found by X-ray fluorescence analysis to be Fe 10 p.p.m. and Pb 6 p.p.m. by weight. No other heavy metals or alkali earth ions were detected.

Reagent grade AgCl (0.03 mol %) was dissolved in methanol solution and well mixed into the $Li_2B_4O_7$ powder. The mixture was first dried in air by heating to 250° C for 1 h and then melted in a platinum crucible at 950° C for 2 h followed by rapid cooling to room temperature (RT) in order to make a transparent glass. An undoped $Li_2B_4O_7$ glass was also made by the same method. It should be mentioned that the melting point of $Li_2B_4O_7$ is 917° C. The glasses were then polished into 1 mm thick plates and heated again to 600° C for several hours. It has been reported that many nuclei develop during this heating period [4]. The glass plates were subsequently heated at 910° C for 1.5 h and cooled slowly to RT. The microcrystals developed completely during this heating process. In order to take ESR spectra, these crystallized glasses were crushed in an agate crucible into fine powders. However, the results were the same as those obtained for a chip of crystallized glass. This indicates that the crystallized glass is composed of fine microcrystals, with random crystalline axes. The density of these crystallized glasses was about 2.1 $g\,cm^{-1}$.

X-ray irradiation was performed at room temperature with a tungsten target source operated at 35 kV and 10 mA. It was possible to carry out the X-irradiation from the outside of the TSEE apparatus if it was required to keep the samples untouched [5].

Simultaneous measurements of TSEE and TL were performed using the apparatus described elsewhere [5]. The heating rate for the measurements was 20° C min^{-1}.

ESR spectra of the samples were measured by using a Varian X-band E-104B apparatus at room temperature. Before taking the measurements, the X-irradiated samples were heated stepwise to several temperatures and again cooled to room temperature. With these procedures it may be possible to compare the TSEE and TL with ESR spectra.

3. Results

3.1. TSEE and TL spectra

Fig. 1 shows the simultaneously measured TSEE (full line) and TL (broken line) for a $Li_2B_4O_7$: AgCl (0.03 mol %) sample X-irradiated at RT for 30 min in vacuum of about 10^{-4} Pa of the apparatus, which allows the measurements to be made *in situ*. It is seen from the figure that there are remarkable TSEE and TL peaks at about 155° C. TSEE peaks are also observed at about 75, 230 and 300° C and only an extra TL peak is observed at about 95° C.

Fig. 2 shows the corresponding data for an undoped $Li_2B_4O_7$ sample measured under the same conditions as in Fig. 1. The result shows that if we disregard the relative heights of the peaks, they are essentially at the same temperatures as those in Fig. 1, except the

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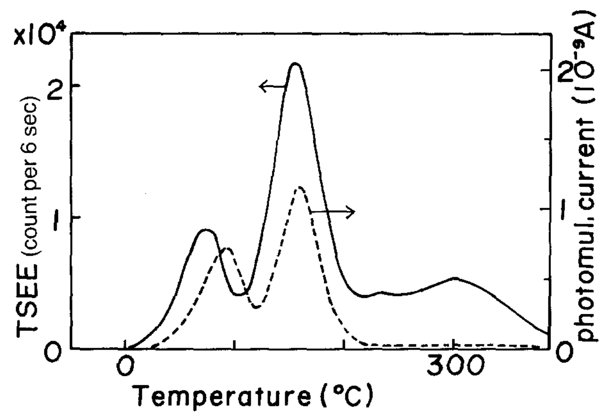

Figure 1 Simultaneous measurement for TSEE (full curve) and TL (broken curve) for a $Li_2B_4O_7$: AgCl (0.03 mol %) sample X-irradiated at room temperature.

remarkable difference that no TSEE peak is observed at about 155° C.

3.2. ESR spectra

Fig. 3 shows the ESR spectra for the undoped $Li_2B_4O_7$ sample measured stepwise at the temperatures indicated for 5 min and each time quickly cooled to room temperature to take the spectrum. The spectra changed gradually by the successive heating and decayed away completely at 300° C. By the heating process around 190° C, the familiar "five-line-plus-a-shoulder" spectrum due to BOHC (boron–oxygen–hole–trapped–centre [6]), whose g-values are about $g_1 = 2.00$, $g_2 = 2.01$ and $g_3 = 2.03$, was observed. Some signals decayed by the heating at 100° C and some others at 210° C suggesting that they are roughly related to the corresponding TSEE peaks. However, no clear change was observed by heating at 150° C although at this temperature a remarkable TL glow peak was observed (see Fig. 2).

Fig. 4 shows the ESR spectra for a $Li_2B_4O_7$: AgCl sample X-irradiated at room temperature and successively heated stepwise to higher temperatures. It is seen that the two complex signals appear pairwise at both sides of the $g = 2.0$ position and a simple signal appears between them. The origin of the pairwise signal is considered to be due to Ag^0 atoms, whose nuclear spin is $I = 1/2$ and isotropic hyperfine coupling constants are $A_0 = -1{,}760$ and $-2{,}022$ MHz, respectively for the two natural isotopes, ^{107}Ag and ^{109}Ag. The observed g-value for the pairwise signal is a little less than $g = 2.00$. This suggests that the signal is due to electron trapped type centres. Although we cannot presently isolate the effect of the two silver isotopes, the mean separation of the signal pair seems to indicate that about 45% of the trapped electron is localized on the Ag^+ ion by taking the Breit–Rabi equation [7] into consideration. In other words, the silver ion may be considered to have a character of 45% of Ag^0 atom and 55% of Ag^+ ion. The complex splitting of the signal may be brought about by the super-hyperfine interaction with the boron and lithium nuclei, although the position of the Ag^+ ion in the crystal is not clear. It may be replaced with a Li^+ ion.

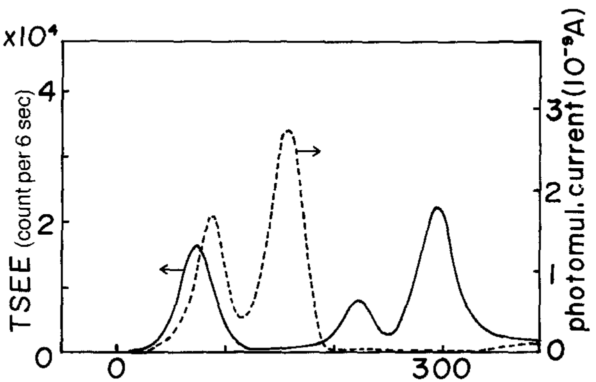

Figure 2 Simultaneous measurement for TSEE (full curve) and TL (broken curve) for an undoped $Li_2B_4O_7$ sample X-irradiated at room temperature.

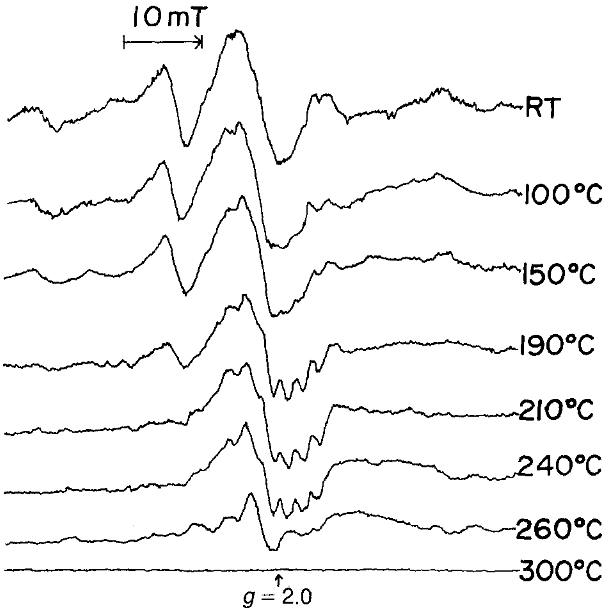

Figure 3 ESR spectra for an X-irradiated $Li_2B_4O_7$ (undoped) sample measured after each successive heating to the indicated temperatures. Measurements were made at room temperature.

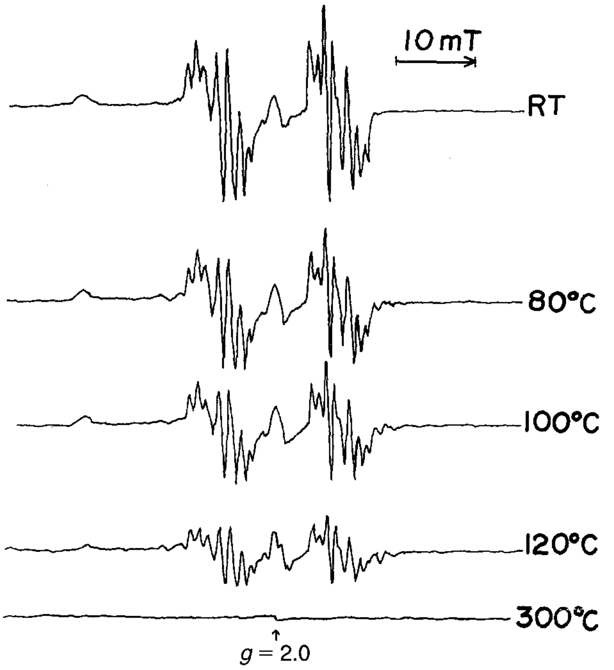

Figure 4 ESR spectra for an X-irradiated $Li_2B_4O_7$: AgCl (0.03 mol %) sample measured after each successive heating to the indicated temperatures. Measurements were made at room temperature.

The simple signal at the centre of the spectra ($g = 2.0$) is considered also to be due to electron trapped centres because it grows slightly by heating to 80° C, where the Ag^0 centres partially decay. In this case, the thermally released electrons from Ag^0 atoms may be trapped to form the $g = 2.0$ centres.

The Ag^0 centres decay most rapidly at 120° C, which is the temperature corresponding to the lower-temperature side slope of the TESS peak at 150° C in AgCl-doped sample. It should be mentioned here that the Cl^- ions (0.03 mol %) doped with Ag^+ ions play almost no role for TSEE and TL. This fact was ascertained by doping 0.03 mol % LiCl in the $Li_2B_4O_7$ sample.

4. Discussion

As has been mentioned in the above, the TSEE and TL peaks observed in $Li_2B_4O_7$ crystallized glass samples doped with and without 0.03 mol % AgCl appeared at the same temperatures. However, there are differences in the intensities of the peaks. The only remarkable difference between the two samples is the appearance of the strong TSEE peak at 155° C in AgCl-doped sample and no TSEE peak in this region in an undoped sample. The similarity of the peak temperatures except the 155° C TSEE peak in the silver-doped sample implies that the origins of them are common to the two samples, although the details are not known yet.

In the following we concentrate our attention on the 155° C TSEE peak, which is well traced by the disappearance of the ESR signal for Ag^0 atoms as shown in Fig. 4.

The correspondence of the temperatures for the decay of the Ag^0 atoms with the TSEE emission leads us to consider the idea that the electrons emitted from the sample surface are those thermally released from the Ag^0 atoms. The exoelectron emission is purely a surface effect, thus those Ag^0 atoms responsible for the TSEE should be located near the surface. In contrast, TL is a phenomenon which belongs to a body effect, and so long as the sample is transparent, light is emitted by the recombination of electrons with holes, some of which are thermally released from the trapped sites and move through the lattice to the others.

As is observed in Figs 1 and 2, TL peaks are observed at 155° C in both samples, though little appreciable change is observed in the ESR spectrum around this temperature for the undoped sample. Therefore, it may be assumed that the trapping centres for holes and electrons relevant to the 155° C TL peak are diamagnetic. They may be in coagulated states. However, the details are still unknown. The reason that the ESR spectrum corresponding to the undoped $Li_2B_4O_7$ sample is not observed with $Li_2B_4O_7 : AgCl$ (0.03 mol %) may be due to much higher sensitivity of the Ag^0 signal (Fig. 4) than those observed in Fig. 3 for the undoped sample. Such corresponding signal produced in silver-doped sample is weak and might be hidden under the Ag^0 spectrum. In any case TL light emission is observed at 155° C in both samples.

The reason why the 150° C-TSEE peak appears only in the silver-doped sample should be ascribed to the destruction of the Ag^0 atoms with the emission of trapped electrons. The motivation for the destruction should be the TL light emitted at the same temperature. The spectral distribution for the TL light has been measured by Kutomi and Takeuchi [8] for undoped $Li_2B_4O_7$ crystallized glass and it was found that a strong peak appears at about 340 nm and a weak one at about 600 nm. On the other hand, it is reported that the Ag^0 atom in a free state absorbs light of wavelength of 338.38 nm due to the $5s(^2S_{1/2}) \rightarrow 5p(^2P_{1/2})$ transition [9]. If it were an ion, interaction with the surrounding ions or the crystal lattice will affect the energy levels. However, we are now considering Ag^0 in the atomic state, which will be little affected by the surroundings. Therefore, there is a high possibility that the TL light at 340 nm will partially be absorbed directly by the Ag^0 atoms and excite them. According to the Maxwell tail theory [10, 11], the electrons at a skin part of the sample are easily released from the surface, according to the Maxwell function $\exp(-E/kT)$. Therefore, in the present case, when the Ag^0 atoms are in the excited state, they release electrons much more easily than when they are in the ground state, because the necessary activation energy to the vacuum level is smaller. This leads to exoelectron emission, i.e. the TSEE peak at 155° C.

As for the other TSEE peaks, we cannot yet give any clear explanation for their origins. We can only assume that they are inherent in the $Li_2B_4O_7$ matrix, and not to the activators, because the peaks appear at the same temperatures in both the silver-doped and undoped samples.

Acknowledgements

Part of this work has been carried out under the Visiting Researcher's Program of the Research Reactor Institute, Kyoto University. The authors are thankful to Dr Y. Kutomi for his help with some of the measurements.

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Received 8 January
and accepted 23 August 1989