Technical Paper

Thermoluminescence of Lithium Borate Activated by Manganese or Other Elements

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The present investigation has been carried out to examine preparing conditions which have an effect upon the thermoluminescence of manganese-activated lithium tetraborate, and to match the spectral distribution of thermoluminescence, when activated with other elements than manganese, coincide to that of the highest sensitivity of a photomultiplier. In this work the samples were prepared by the solid-state reaction between lithium carbonate and ammonium tetraborate. The mixing ratio of matrix, firing condition and activator concentration were examined as preparing factors affecting thermoluminescence characteristics.

From results obtained it was found that thermoluminescent intensity depended on a small deviation around stoichiometric ratio of the matrix, and that as the firing temperature rised up to the melting point the higher intensity was obtained, while rapid cooling gave a good result. Activation with copper, silver and gallium gave fair luminescent characteristics.

1 Introduction

Lithium tetraborate phosphors activated by manganese were prepared by a method of preventing the glassification during their calcination and the effect of preparing conditions their thermoluminescence were discussed. Activation by other elements than manganese was carried out and the results were discussed from the viewpoint of practical uses for thermoluminescent dosimetry.

Lithium tetraborate activated by divalent manganese for thermoluminescent dosimetry (TLD) was studied by Schulman19 and thereafter several researches 19-21 were reported. From these results it was found that the phosphor had several advantages over lithium fluoride which is now applied to TLD, while some disadvantages, such as low sensitivity, influence of preparing conditions upon the glow curve and the fluctuations of sensitivity from batch to batch, were observed. We prepared this phosphor by a different method from that published19, that is, we prepared it without melting and obtained phosphors with a good reproducibility which were more sensitive than the ones previously obtained. On the other hand, we prepared phosphors activated by other elements than manganese in order to shift the spectral distribution of thermoluminescence (TL) to shorter wavelengths, which increases the sensitivity of TLD.

2 Experimental

Preparation of phosphors: Purified lithium carbonate and ammonium tetraborate were mixed and aqueous solution of manganese chloride or sulfate was added.

![Fig. 1 Apparatus measuring the thermoluminescence](image)

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to the mixture. After drying it was fired at 850°C for 2 hours in a platinum crucible. Fired product was lightly crushed, sieved and used for measurement of thermoluminescence.

Measurement of thermoluminescence: The sample was exposed for 30 min. to ca. 1.3 kCi 60Co source and its TL was measured after one day by the apparatus shown in Fig. 1. The photomultiplier used was RCA-1P21 and filter was Matsuda Filter IRQ-80. Measuring dish was made from aluminum, its diameter and depth being 10 mm and 3 mm respectively. Rate of increasing temperature was about 40°C/min.

3 Experimental Results and Discussion

Crystal structures of the fired products were shown in Fig. 2 and coincided with those published by Hummel. When heated above the melting point (917°C), they showed no X-ray patterns. However, they recrystallized after annealed.

Fig. 2 X-ray diffraction patterns of phosphor and reference

Glow curves had a single peak at ca. 240°C for the phosphor activated by manganese, but immediately after the exposure to γ-ray they had another peak at about 110°C, which diminished after several hours at room temperature. The temperature of about 240°C at which the peak appeared was varied with the changes of manganese concentration, mixing ratio of matrix, firing temperature and other preparing conditions. When activated by some rare earth or uranium ions, the emission which is characteristic to those ions was observed under ultraviolet excitation, while TL was faint. The glow curves were almost the same with each other. As an example, a glow curve of phosphor activated by terbium is shown in Fig. 3, while one activated by copper or silver has a glow curve shown in Fig. 4. When activated by copper a main peak of glow curve shifted to lower temperature and the area under glow curve was smaller than activated by manganese. In this case a blue emission was
observed under ultraviolet excitation. When silver was used as an activator, characteristics of TL was almost the same as in the case of copper. As shown in Fig. 5, however, a glow peak became broader with the increase of amounts of the activator. When activated by copper or silver, the color of TL was white and the total area under glow curve was about one third as compared with that for the phosphor activated by manganese.

Some parameters of preparation affecting the intensity of TL were tested for the phosphors activated by manganese. Better results were obtained with a raw material of ammonium tetraborate than one of boron trioxide. As for temperatures, optimal one was about 150°C for the dried mixed paste of host materials and activator salt. The result is explained by the fact that when dried at lower temperatures the mixture was agglomerated to make its removal from the bowl difficult, which caused the fluctuation of batch composition and also of thermoluminescent output.

The effects of the firing temperature, composition of host, and activator concentration on the thermoluminescent output are shown in Fig. 6, 8 and 9. As shown in Fig. 6 the light output increased with the rise of firing temperature till the melting temperature of lithium borate (917°C). The glow curves of phosphors fired at temperatures between 500°C and 850°C are shown in Fig. 7. The form of glow curves changed by the firing temperature below 750°C, as is seen in the figure, i.e., the glow peaks shifted to higher temperature with the increase of firing temperature, while the form was almost the same for firing temperature above 750°C. Although the product which was fired above 920°C and glassified showed a faint TL, the TL became stronger by annealing it at 850°C for 1 hour. To clarify the effect of the cooling rate from firing temperature upon the thermoluminescent output the fired product was cooled by putting it in liquid nitrogen. The obtained results showed that the thermoluminescent output was larger than that cooled in air, as shown by a point marked as (●) in Fig. 6. The effect of composition of the matrix compound upon the thermoluminescent output is shown in Fig. 8. When lithium and borate ratio was varied...
around a stoichiometric one (2:1), the output decreased with the decrease of the amount of borate composition, and the glow peak shifted to lower temperature with it, being independent of amounts of manganese concentration. That is, the thermoluminescent output was larger on the side of smaller amount of lithium composition than stoichiometric ratio. The output was maximum between 0.01 and 0.03 wt% of manganese concentration and decreased with the increase of its concentration, the result being shown in Fig. 9. With the increase of manganese concentration the glow peak shifted to higher temperature, which was independent of the composition of host materials. The effect of additives to the manganese-activated phosphor upon TL was not observed with the exception of gallium compound which shifted the glow peak to 200°C with the addition of 0.05 wt% and made the glow curve narrower.

The maximum fluctuation of thermoluminescent output was 12% during the whole course of experiments described above.

From the obtained result it would be concluded that traps for TL are present in the nonstoichiometric lithium borate matrix and TL is emitted from these traps via manganese activator. The preparation of lithium borate phosphors activated by manganese is not difficult, but the preparing conditions, especially the firing condition must be well controlled.

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4) C. R. Wilson, J.R. Cameron, ibid, p. 161 (U. S. AEC 1968).