

## Synthesis of Defects in Irradiated Quartz

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Glow curves of the natural quartz irradiated by  $\gamma$ -rays were observed for various doses and each glow peak was resolved into three component peaks, B<sub>1</sub>, B<sub>2</sub> and C. The glow peaks caused by the diffusion of impurities in the condition of 1000°C were compared with these peaks and the nature of defect responsible for each peak was determined. The defects for the B<sub>1</sub> peak were associated with the Al-defect, the defects for the B<sub>2</sub> peak were due to the disturbed-network in the vicinity of Li and the defects for the D peak were due to oxygen vacancy. Moreover, the interaction of these defects was discussed from the result of variation of the area of glow curves for various doses.

The radiation-induced defects in quartz has been studied by several groups of workers in recent years. Nevertheless, since quartz contains various impurities and is complicated in structure, much difficulty has been encountered in speculating the role which these impurities play. The visible absorption bands, the A<sub>1</sub> and the A<sub>2</sub> bands,<sup>1)</sup> have been shown from a combination of optical and E. S. R. measurements to be related to an Al ion substituted for silicon with an associated interstitial lithium ion, and the ultraviolet bands, the C and the E bands,<sup>2)</sup> have been suggested from the optical study of neutron irradiated quartz to be associated with the displacement of oxygen ion from its lattice site. The sensitivity of optical absorption was low, i. e. dose range of  $1 \times 10^6$  R, and its spectra showed no sharp bands, so that the detailed radiation effects of quartz was generally poorly understood in the case of irradiation doses of below  $1 \times 10^6$  R. On the other hand, the intensity of thermoluminescence shows the extremely high sensitivity to irradiation doses, and glow curve of  $\gamma$ -ray irradiated quartz can be recorded for the absorbed doses to  $1 \times 10^3$  R or less<sup>3)</sup>. The present investigation was undertaken to explore the defect structure in quartz, utilizing this advantage.

Samples for this experiment were grains obtained by crushing a clear single crystal of Brazilian quartz and then were sieved to obtain the grain size of 100 × 200 mesh. The sample was irradiated by <sup>60</sup>Co  $\gamma$ -rays ( $1 \times 10^3$  R/min) with various doses and its glow curve was recorded at the heating rate of about 75°C/min until the temperature reached 450°C from the room temperature. The natural glow curves for the sample used in this measurement showed the broad glow maximum at about 245°C (B<sub>2</sub> peak). The height of the B<sub>2</sub> peak increased linearly with dose to  $1 \times 10^4$  R, but on further irradiation, saturation occurred in  $8 \times 10^4$  R. For the dose of  $2 \times 10^5$  R the new glow peak could be observed at 185°C (B<sub>1</sub> peak) as well-defined one. This peak grew rapidly with dose, having a maximum for the dose

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of  $6 \times 10^6$  R, and then decreased on further irradiation. Moreover, for above  $4 \times 10^5$  R glow curve showed growth of broad glow maximum at  $340^\circ\text{C}$  (D peak), being linear to  $9 \times 10^6$  R at least. The peak position of its glow maximum shifted toward the higher temperature with the increase of irradiation dose, so that the peak position came to  $360^\circ\text{C}$  for  $9 \times 10^6$  R. After exposure to  $9 \times 10^6$  R, the glow curve showed the peaks  $B_1$  and D in the comparable intensity, being the well-defined peak for the former and the broad one for the latter. The dose dependence of each glow peak ( $B_1, B_2, D$ ) for plates or other Brazilian quartz grains, yielded the same result as this sample. One of the most effective methods of investigating thermoluminescence in natural quartz is to observe the glow curves resulting from the samples prepared with various impurities, that is to obtain the relation between the glow peak and the impurity into crystal. Li and Al were diffused into the quartz grains for this purpose. This technique was to anneal at  $1000^\circ\text{C}$  for 1 hour, after vacuum evaporation of the impurities. The glow curves from prepared samples were recorded, after irradiation with  $1 \times 10^4$  R, to observe the effects of adding impurities. As the results, the glow curve from the sample diffused with Al plus Li exhibited the prominent peak at  $B_1$  peak position, and the peak of low intensity at  $B_2$  peak position, and in the sample diffused with only Li both of them were of comparable intensities. Also, the glow curve for single impurity of Al showed the broad intense glow peak at the D peak position and very small double peak at the region of  $150^\circ\text{C}$  (A peak).

The area under the glow curve i. e., the integrated thermoluminescence as a

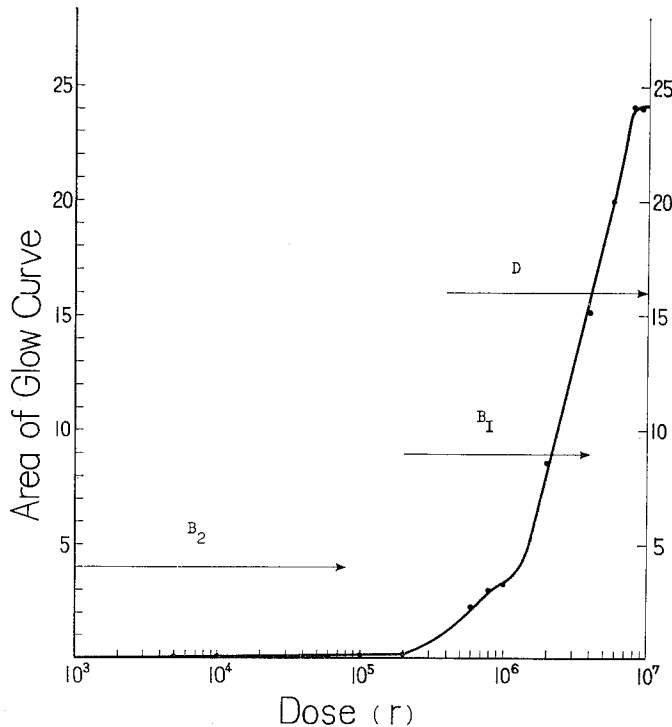


Fig. 1. Variation of area of glow curves for various doses.

function of the absorbed doses of the samples is shown in Fig. 1. Two inflection points on which the area increases rapidly can be noted in the regions of  $2 \times 10^5$  R, and  $1 \times 10^6$  R, and the former is the dose level corresponding to the growth of the  $B_1$  peak, the latter is that of the D peak. If there are several types of trapping imperfection, the glow curve will consist of a corresponding number of glow peaks. If the number of imperfection is constant, the area of glow curve will increase with the doses and come to saturation. Accordingly, the enhancements of the new peaks at the two points indicate that the defect formation resulting from gamma irradiation occurs in quartz crystal. Ditchburn *et al.*<sup>4)</sup> have shown that the U. V. bands continue to increase with increasing neutron dose, but saturate when the radiation employed is x-rays. They proposed, therefore, that ionizing radiation, such as x-rays or  $\gamma$ -rays, does not produce defects in quartz which is a highly covalent structure. On the basis of the above results obtained through the advantage of thermoluminescent high sensitivity, it seemed reasonable to assume that the imperfections in natural quartz play a prominent role in defects formation when sample is exposed to  $\gamma$ -rays.

The growth of the  $B_2$  peak which occurs at the doses below  $2 \times 10^5$  R is contributed by the imperfection presents in the original crystal. From the results of the effects of adding Li, it seems reasonable to conclude that the defects responsible for this peak are due to the disturbed-network which has non-bridging oxygen in the vicinity of the Li. The  $B_1$  peak was enhanced by the simultaneous adding of Al and Li. Therefore, it appears that this peak is associated with the Al-defects, which are responsible for the color of smoky quartz. In the experiments on the variation of glow curve with dose the  $B_1$  peak was enhanced after the saturation of the  $B_1$  peak. In view of this fact, the most reasonable conclusion is that the neutral lithium resulting from electronic effects of  $\gamma$ -rays migrates into crystal and is attracted to the substitutional Al which has a non-bridging oxygen nearby and forms the Al-defect consequently.

The growth of the D peak arose when the quartz was irradiated with the  $\gamma$ -rays of high dose level, or was diffused only with Al as impurity. The former results from the scission of Si-O bond and the rearrangement by the  $\gamma$ -irradiation, the latter being due to the generation of oxygen vacancy by the incorporation of Al in high temperature. Yokota<sup>5)</sup> has suggested that fused quartz prepared in a reducing condition shows the broad glow maximum at the temperature position of the D peak and the defect responsible for it is due to oxygen vacancy. It is considered that the shifts of the D peak is caused by a continuous distribution of oxygen vacancy-interstitial separation. The glow curves for samples irradiated with the doses above  $8 \times 10^6$  R showed the rapid decrease of the  $B_1$  peak and the increase of the D peak so that the area of the glow curve came to be constant. On the basis of these data, it seems that the defects responsible for the two peaks exist in the same lattice site disturbed by the substitutional Al and the enhancement of the D peak results from the destruction of the defect for the  $B_1$  peak.

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