Letters

Effect of transition metal ion impurities on the thermoluminescence of alumina

In view of their promising application as laser material, α-Al_2O_3 crystals have been studied thoroughly by solid state researchers by subjecting them to ionizing radiations. The radiation-induced defects in this system were attributed [1–7] to either trapped hole centres or electron traps involving the impurities, but no definite model could be established. In a previous paper [8], we concluded from thermoluminescence (TL) measurements the existence of two groups of TL traps in X-irradiated α-Al_2O_3, and a distribution of trapped holes (0^-, 0^0) stabilized by trace impurities such as Cr, Ti, was made responsible for the TL phenomena of this system. In this communication, the results on the TL of X-irradiated α-Al_2O_3 powders doped with transition metal ion impurities (Cr, Ti and V) are presented, and these support the above views.

Extrapure (Sarabhai Merck Chemicals Ltd, India) anhydrous alumina powder (α-Al_2O_3) has been used in this investigation. For the purpose of doping, the alumina powder was thoroughly mixed with the transition metal oxides (AnalaR Cr_2O_3, TiO_2 and V_2O_5) in the proportion 1:0.0005 by weight and ground to 200 mesh size and was then sintered at 1400° C in air in a globar furnace for 10 h by placing it in a covered platinum crucible. After sintering, the crucible was taken out of the furnace and quenched to room temperature (27° C) by blowing cold air for about 5 min; heat-treatments for all the samples were same. An undoped alumina sample was also sintered and quenched in an identical fashion for the sake of comparison. All the sintered samples became hard and were again ground to 200 mesh size and used in TL studies. The samples were packed in a brass sample-well (0.5 cm diameter, 0.05 cm depth) and X-irradiated in darkness by using a II POH-I(USSR) X-ray unit with Cu-target being operated at 30 kV, 10 mA. The irradiated powders were then heated in vacuum (10^{-3} mm Hg) at a constant rate (28° C min^{-1}) and the TL outputs were recorded by a 1P28 RCA photomultiplier tube in conjunction with an electrometer amplifier (ECIL EA 812) and a millivolt recorder. The temperature was recorded in a similar millivolt recorder.

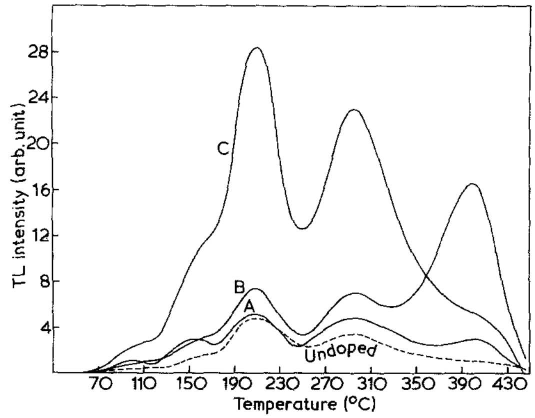

Figure 1 TL glow curves of undoped and doped α-Al_2O_3 powders X-irradiated (30 kV, 10 mA, Cu-target, 15 min) at room temperature. A, B and C stand for the samples doped with vanadium, chromium and titanium, respectively.

Fig. 1 shows the TL glow curves of sintered α-Al_2O_3 powders both undoped and doped with Cr, Ti and V; the glow peaks are at 104, 158, 210, 296 and 400° C. All the doped samples emitted greater TL outputs than the undoped one; no change in glow peak position was noticed except for the prominent development of the glow peak at 400° C with every dopant. This glow peak superceeded other glow peaks in intensity for doping with chromium and the TL output was maximum for the sample doped with titanium. It is clear that all the glow peaks are solely controlled by the impurities. Dependence of the TL outputs of the samples on X-ray dose was studied by recording the glow curves after different periods of X-ray exposure. Fig. 2 represents the characteristic nature of variation in intensity of all the glow peaks of the samples with dose. It was interesting to note that all the glow peaks of each sample attained the saturation value after 10 min of X-ray exposure (sample to target distance being 4 cm).

The basic structure (rhombohedral) of corundum belongs to space group D_{3d}^6; aluminium ions (Al^{3+}) occupy two out of three octahedral interstices along the *c*-axis sharing equilateral triangles of O^{2-} between them and every alternate cation site is vacant, which acts as a void in the lattice. It is known [9] that Schottky disorder is the most

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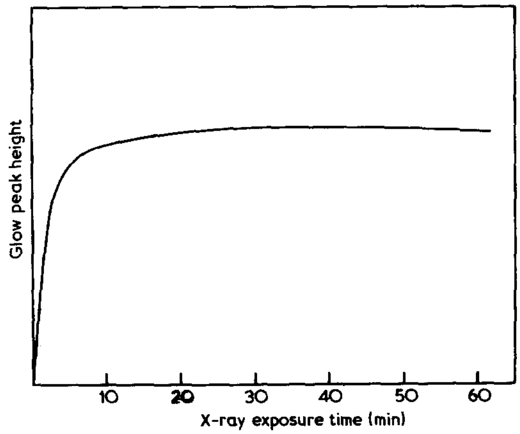

Figure 2 Characteristic nature of variation of the glow peak height of each glow peak with time of X-irradiation (30 kV, 10 mA, Cu-target).

dominant type of disorder in α-Al_2O_3 and the assumption that cation impurity species will occupy the lattice sites substitutionally is quite reasonable. In the α-Al_2O_3 lattice, chromium remains mostly in the trivalent state (Cr^{3+}) and vanadium is predominantly trivalent with a small concentration of V^{4+} [10]. Incorporation of the aliovalent titanium (Ti^{4+}), unlike the other two impurities, produces a large number of cation vacancies in the lattice for charge compensation.

During X-irradiation, electrons are removed from anions (O^{2-}) and trapped holes (O^- and O^0) are formed. The possible traps for the liberated electrons are anion vacancies and the impurities in their highest oxidation states. Considering the results (Fig. 1) on the TL of both doped and undoped α-Al_2O_3, the traps responsible for the TL peaks in both cases are found to be similar in nature. All the glow peaks increased to different extents depending upon the dopants and no preferential behaviour was observed for any individual or group of TL peaks that can be related to the corresponding impurity. The increase of TL outputs in the doped samples can be distinguished from the natural expected increase due to the increase of concentration of impurity centres, by their presence in the form Cr^{4+}; Ti^{4+} and V^{4+} produce additional cation vacancies which help in the formation of more stabilized trapped holes during X-irradiation. These features indicate that the impurities, depending upon their nature and concentration, play important roles in the TL phenomena of this system. The nature of growth of the glow peaks with dose (Fig. 2) shows a linear increase followed by saturation after 10 min X-ray exposure and supports the above views.

Thus, it is concluded that the TL phenomena in α-Al_2O_3 is, in general, controlled by trace impurities which act as catalysts in the production of intrinsic lattice defects, and the stabilization of the trapped holes (O^- or O^0) takes place either at these impurity centres or at defect lattice sites.

References

1. J. K. RIEKE and F. DANIELS, *J. Phys. Chem.* **61** (1957) 629.
2. A. F. GABRYSH, H. EYRING, V. LEFEBRE and M. D. EVANS, *J. Appl. Phys.* **33** (1962) 3389.
3. T. MARUYAMA and Y. MATSUDA, *J. Phys. Soc. Japan* **9** (1964) 1096.
4. J. M. RUSIN and J. I. MUELLER, *Amer. Ceram. Soc. Bull.* **52** (1973) 708.
5. R. A. HUNT and R. H. SCHULER, *Phys. Rev.* **89** (1953) 664.
6. P. W. LEVY, *ibid* **123** (1961) 1226.
7. I. S. RADCHENKO, *Sov. Phys. Solid State* **12** (1971) 2635.
8. D. R. RAO and B. N. DAS, *J. Mater. Sci.* **14** (1979) 19.
9. S. K. MAHAPATRA and F. A. KROEGER, *J. Amer. Ceram. Soc.* **61** (1978) 106.
10. J. LAMBE and C. KIKUCHI, *Phys. Rev.* **118** (1960) 71.

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