$$3SiO(G) + 3C(S) + 2N_2(G) = Si_3N_4(S) + 3CO(G) \quad (3)$$

The result shown in Fig. 1 means that excess carbon might be an essential component to give more chances for oxygen reduction from silicon monoxide vapour.

Table II shows typical weight loss and variation of total silicon in nitriding reaction. Silicon was not responsible for the total weight loss of 5 to 9% in the heat-treatment at 1000° C, in which silicon nitride was not formed. On heating, a small amount of silicon was lost, presumably in the form of silicon monoxide. The results in Table II and Fig. 1 indicated that at low C/silica ratio (2 to 10), considerable amounts of silica and silicon monoxide remained unreacted after heating at 1400° C for 5 h.

Figs. 2 and 3 show X-ray diffraction patterns and micrographs of typical reaction products, respectively. The X-ray diffraction patterns indicated that lower nitrogen content powder products contained residual unreacted silica (arrow) and a small amount of Si_2ON_2. On the other hand, high nitrogen powders gave sharper diffraction lines of α silicon nitride than low nitrogen content ones. The shape of the powder product after reaction was different from that of raw silica powder, which had a granular shape with irregular surfaces, i.e. initial-stage reaction products with a lower nitrogen content, were rather fibrous in shape and small in size, and the shape of the products gradually changed from fibrous to granular with increasing nitrogen content. This behaviour might be evidence that the vapour-phase reaction had occurred during the silicon nitride formation process. The grains of the final product with a high nitrogen content were in the shape of hexagonal columns.

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On the thermoluminescence of X-ray irradiated polycrystalline Al_2O_3 powder

Ceramics are of utmost importance in advanced technology and hence the studies of their properties are of great interest. Attempts have been made to understand the effect of radiation on ceramics, especially on Al_2O_3 in various forms, e.g. single crystals, flakes, powders. More recently, attempts have been made to use ceramics as radiation dosimeters by utilizing their thermoluminescence output. Thermoluminescence is generally used in studying the electron and hole traps in solids and also in understanding the radiative recombinations and related electronic processes. The thermoluminescence of γ-irradiated α-Al_2O_3 crystals has been studied by several workers [1-5] and the main glow peaks are well known. The coloration induced in single crystals of corundum (Al_2O_3) by X-rays has been investigated by Hunt *et al.* [6] and that induced by γ-rays has been studied by Levy [7]. The electronic processes in α-Al_2O_3 crystals are now well understood. However, sufficient information about the effect of X-rays on polycrystalline Al_2O_3 powder is absent from the literature. Rieke *et al.* [8] studied the thermoluminescence of γ-irradiated Al_2O_3 powder and, more recently, Galli [9] has investigated the defects produced in the reactor-irradiated polycrystalline α-Al_2O_3 by E.P.R. measurement. Ziniker *et al.* [5] and Buckman [10] have proposed the potential use of α-Al_2O_3 crystals as a thermoluminescent dosimeter for X-rays. But to the best of the author's knowledge, no work has been reported on the possibility of using polycrystalline Al_2O_3 powder as X-ray dosimetry material. The purpose of this work is to investigate the thermoluminescent output of polycrystalline Al_2O_3 powder.

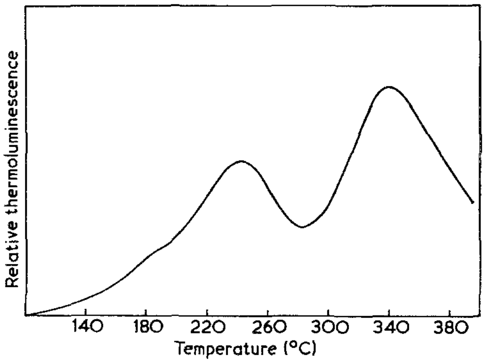

Figure 1 Thermoluminescence glow curve of polycrystalline Al_2O_3 powder, irradiated with X-rays (Mo-target, 20 kV, 5 mA, 30 min). Heating rate 28° C min^{-1}.

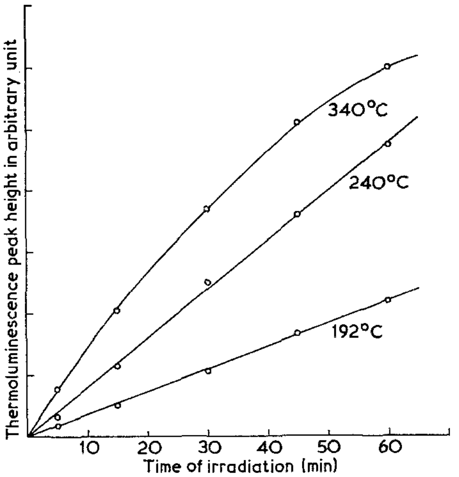

Figure 2 Growth of the three glow peaks (at 192, 240 and 340° C) with time of X-ray irradiation (Mo-target, 20 kV, 5 mA).

White polycrystalline Al_2O_3 powder (BDH Analar grade) was ground uniformly to 200 mesh size and was packed in a brass sample-well 0.5 cm diameter and 0.05 cm depth. It was X-irradiated in darkness for $\frac{1}{2}$ h using a Machlette Tube (Mo-target, 20 kV, 5 mA) at room temperature (30° C). On irradiation the white powder became light pink in colour. The irradiated powder was then heated in vacuum (10^{-3} mm of Hg) at a constant rate (28° C min^{-1}) from room temperature (30° C) to 400° C and the strong thermoluminescence output was conveniently recorded by a 1P28 RCA photomultiplier tube in conjunction with an electrometer amplifier (ECIL EA 812) and a mV recorder. The temperature was recorded in a similar mV recorder.

Fig. 1 shows a typical thermoluminescent glow curve of the polycrystalline Al_2O_3 powder. The glow curve consists of three broad overlapping peaks (at 192, 240 and 340° C), each of which corresponds to a particular type of trap. Each trap is emptied of its captured electron as the rising temperature provides the necessary energy. Considering the difference in heating rate, the glow peak temperatures appear to be identical with those reported by Rieke *et al.* [8]. The methods of calculating the activation energy (E) and frequency factor (S or $S'n_0$) have been reviewed by Ziniker *et al.* [5] and Shalgaonkar *et al.* [11]. More recently, Rao [12] has proposed an easier method of analysing overlapping glow peak pattern to evaluate the E and S or $S'n_0$ values. Following Rao's [12] method, the activation energies of the glow peaks (at 192, 240 and 340° C) are found to be 0.80, 1.26 and 1.18 eV respectively and the corresponding frequency factors are 2.93×10^7, 5.69×10^{10}, and 7.35×10^7 sec^{-1}. The last two peaks (at 240 and 340° C) followed second order kinetics while the first glow peak (192° C) followed those of the first order. Fig. 2 represents the growth of the three glow peak heights with time of irradiation. It is clear that the 340° C peak tends to saturate earlier than the other two peaks. The result of cyclic irradiation is also interesting. The irradiated sample was annealed thermally at 350° C for 10 min and was then re-irradiated at room temperature with the same dosage. In this case, the thermoluminescence output was exactly the same as that of the sample irradiated only once. The thermoluminescent emissions for all peaks were observed to be red in colour.

Present work shows that the thermoluminescent glow emissions are caused by the recombination of three kinds of trapped electrons. The results of cyclic irradiation prove that no additional lattice defects are created by X-rays. As additional lattice defects are usually stable up to temperatures higher than that used in the annealing procedure (350° C), the defect concentration in the annealed sample would be higher than that in the unannealed sample, if they were actually created, and would give rise to a greater thermoluminescence output. However, the outputs were exactly the same in both samples; therefore, only electron-hole pairs are created by X-ray irradiation of Al_2O_3 powder. The oxygen ions become singly or doubly ionized and the electrons released from these will be trapped by either the impurity ions (e.g. R^{3+}) or anion vacancies. Therefore, following X-ray irradiation, the formation of F-centres, O$^-$ ions, neutral oxygen atoms and R^{2+} ions are evident. The probability of the electrons being captured by R^{3+} ions or anion vacancies will be determined by the ratio of their concentrations. As the glow emission was the same colour for all peaks, it can be concluded that a single recombination site for the trapped electrons exists and that this may be attributed to either an O$^-$ ion or a neutral oxygen atom. The growth curves of the three peaks (Fig. 2) shows that the 340°C peak saturates earlier than the other two peaks. This may be attributed to the substitutional impurities present as it is well established that the glow peak caused by substitutional impurities in ionic solids saturates earlier than other glow peaks and it is quite reasonable to assume that minute traces of impurities such as Fe and Cr occupy substitutional positions in the Al$_2$O$_3$ lattice. This result agrees with that reported by Maruyama *et al.* [13]. The first two glow peaks (at 192 and 240°C) must, therefore, be due to the recombinations of electrons, trapped at various energy levels of anion vacancies, with the O$^-$ ion or neutral oxygen atom. Further work is in progress to identify the kind of F-centres responsible for the first two glow peaks and will be communicated shortly.

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Dielectric behaviour and morphology of polyvinylidene fluoride

Polyvinylidene fluoride (PVDF) exists in three crystalline forms [1] and previous work [2-9] has shown the existence of three relaxations α, β and γ. The α relaxation (occurring at the highest temperature for a fixed frequency) has been shown to be associated with crystalline regions [7-9], the β with amorphous regions and the γ with local motion in amorphous regions. Yano [7] found that the magnitude of the α relaxation loss peak and the relaxation times increased with increasing lamellar thickness (although only a narrow range from about 160 to 220 Å was quoted) and assigned this relaxation to chain motion within the lamellae. However, the magnitude of the α relaxation for specimens preferentially oriented with their chain axes perpendicular to the applied field was found (surprisingly) to be lower than that for isotropic specimens. Since the dipole moment of PVDF is approximately perpendicular to the chain axis, such specimens would be expected to give a greater relaxation magnitude than an isotropic one if chain motion occurs within the lamellae [10, 11]. Kakutani [8] found a possible anisotropy in the size of the α loss peaks for an oriented specimen as compared with an isotropic one, but the data were complicated by a change in crystalline form from α to β on drawing and by lack of resolution of the α peak. Previous work [11, 12] of ours on polychlorotrifluoroethylene (PCTFE) has shown that the α relaxation arose mainly in the interior of the lamellae with little contribution from chain folds. We have extended this work to study the effects of orientation on the α (and β) relaxation in PVDF and have also made