JOURNAL OF MATERIALS SCIENCE 28 (1993) 5133–5137

Thermoluminescence dosimetry in the μGy range of neodymium-doped tellurite–phosphate glass

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Thermoluminescence (TL) of tellurite–phosphate glass of the composition of ($TeO_{2\,0.81}$–$P_2O_{5\,0.19}$) doped with different concentrations of Nd_2O_3 was prepared. The optimum concentration of Nd_2O_3 was experimentally determined as 10^{-3} wt% Nd_2O_3 in this glass. TL showed a single, isolated glow curve which peaked at approximately 498–513 K (depending on the Nd concentration). This peak is very suitable for radiation dosimetry, and obeys second-order kinetics. The TL response against the irradiation dose was found to be linear in the low-dose region (11.2–224.2 μGy), indicating the high sensitivity of our glass samples to low-dose γ rays. Finally, the trap depth was also calculated, using methods concerning the second-order kinetics.

1. Introduction

Thermoluminescence (TL) phenomena of solid-state materials irradiated with ionizing radiation have already found practical applications in the field of radiation dosimetry in the form of thermoluminescent dosimeters (TLDs), but the many phenomena observed to be associated with the TL response are not all well understood [1–7].

The TL behaviour of a phosphor depends on the dose received [8, 9]. In general, each TL glow peak exhibits different phases as the dose varies: linear, supralinear, saturation, and decreasing [10, 12]. Peaks appear (practically above a certain threshold dose), grow and perhaps completely disappear. The above behaviour is a result of a relative number of the appropriate TL traps in the host material, the relative cross-section of filling the traps with electrons (or holes), and the creation and destruction of the traps by irradiation. The luminescence in the glassy state has been reviewed by Rindone [13]. The luminescence of rare-earth ions in glass has been a subject of renewed interest since the advent of the laser, because sharp emission bands occur under proper excitation. Karapetyan [14] has made an extensive luminescence study of rare-earth activated silicate, borate and phosphate glasses of simple composition.

Thermoluminescence in irradiated glasses containing activators has been investigated by several authors [15–17]. Changhong *et al.* [18] studied the temperature dependence and time resolution of luminescence of Ce^{3+}, Tb^{3+} and Tm^{3+} in phosphate glasses in the temperature range 80–300 K. A systematic study of the spectral properties of Ce^{3+}, Tm^{3+} and Tb^{3+} ions at room temperature in different glass hosts has also been studied [19, 20].

Two mechanisms have been proposed to explain the TL process in rare earth (RE)-doped materials. The first proposes that the RE ions act as recombination and luminescence centre: the reduction and oxidation of RE ion during irradiation and thermal readout play a vital role in the overall process. Nambi [21] was the first to suggest this mechanism. The second TL mechanism proposes that the RE impurity ion acts only as a luminescent centre. The valence state of the RE ion is inconsequential in this mechanism, insofar as the RE ion can still accept resonant electromagnetic energy from the donor recombination centre. In this mechanism, which was suggested by Huzimura *et al.* [22], recombination during thermal readout involves only the paramagnetic radicals or defects within the host lattice (e.g. $CaSO_4$) and does not include the rare-earth impurity ion. This mechanism was latter modified by Matthews & Stoebe [23].

The low radiation-dose measurements in the range of μGy to mGy are of great importance for use in radioecology (10^{-2} μGy), personnel dosimetry (10 μGy to a fraction of a Gy), radiotherapy and experimental radiobiology (10^{-3}–10^{2}Gy). In the present work, thermoluminescence of the ($TeO_{2\,0.81}$–$P_2O_{5\,0.19}$): glass system, doped with trivalent Nd^{3+}, has been studied in an attempt to find a TLD glass material sensitive to μGy–mGy radiation doses.

2. Experimental procedure

A series of binary TeO_2–P_2O_5 glasses was prepared

0022–2461

by melting the appropriate mixture of analar TeO_2 and P_2O_5 using open alumina crucibles heated in an electric furnace open to the atmosphere. The mixture was heated first at 250°C for 1 h and then transferred to a second furnace held at 800°C for 45 min. The melts were stirred from time to time. Each melt was cast into a mild steel mould to form glass rods. Then the glasses were annealed at 300°C for 1 h. The glass system of (81 mol% TeO_2–19 mol% P_2O_5) was chosen for TL measurements, due to its high structural stability and lower hygroscopic nature [24, 25]. Nd_2O_3 was added to the above composition with

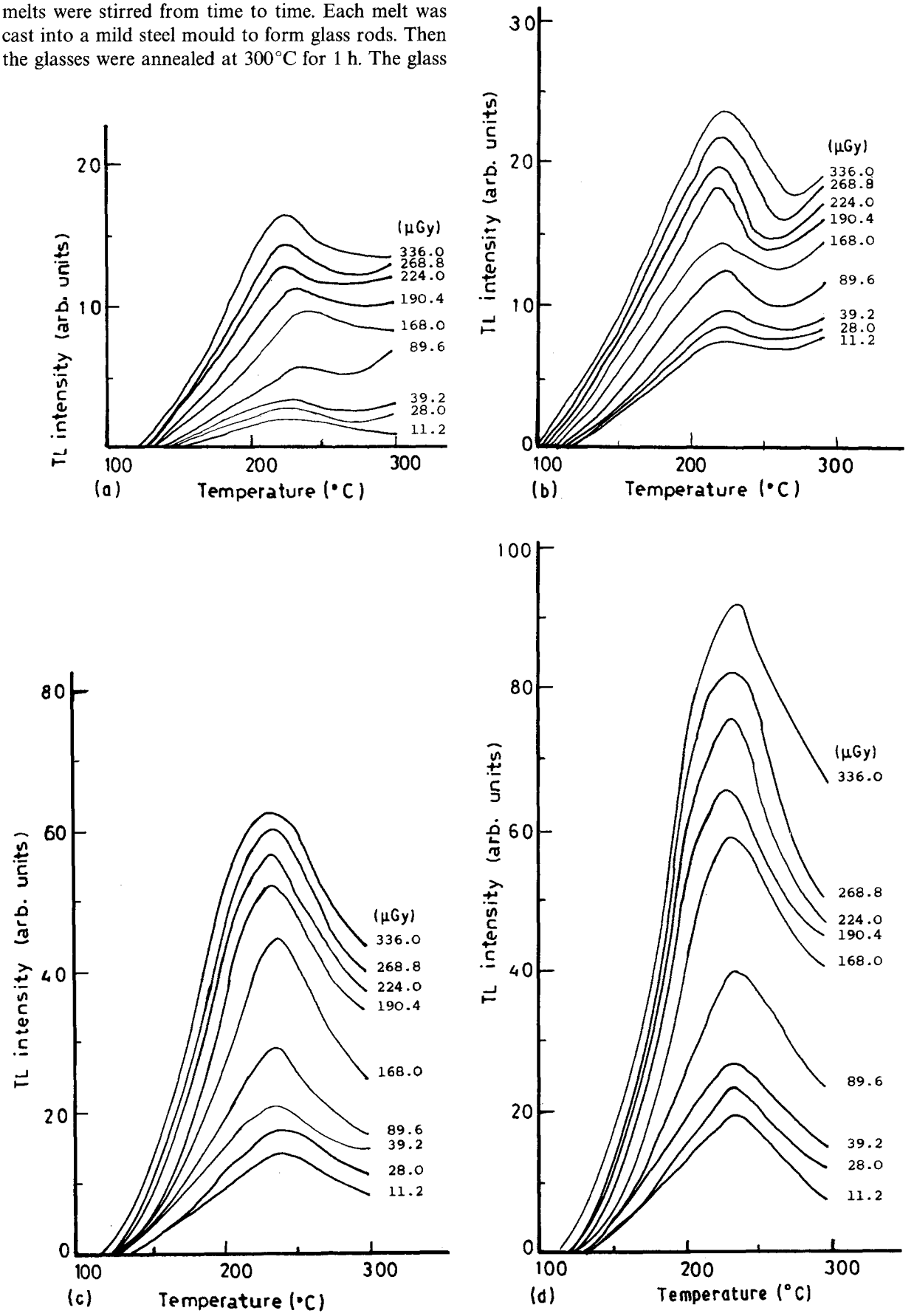

Figure 1 TL glow curves of $TeO_{2_{0.81}}$–$P_2O_{5_{0.19}}$ glass doped with (a) 10^{-4}; (b) 3×10^{-4}; (c) 7×10^{-4}; (d) 10^{-3}; (e) 10^{-2} wt% Nd_2O_3 after exposure to different γ-ray doses.

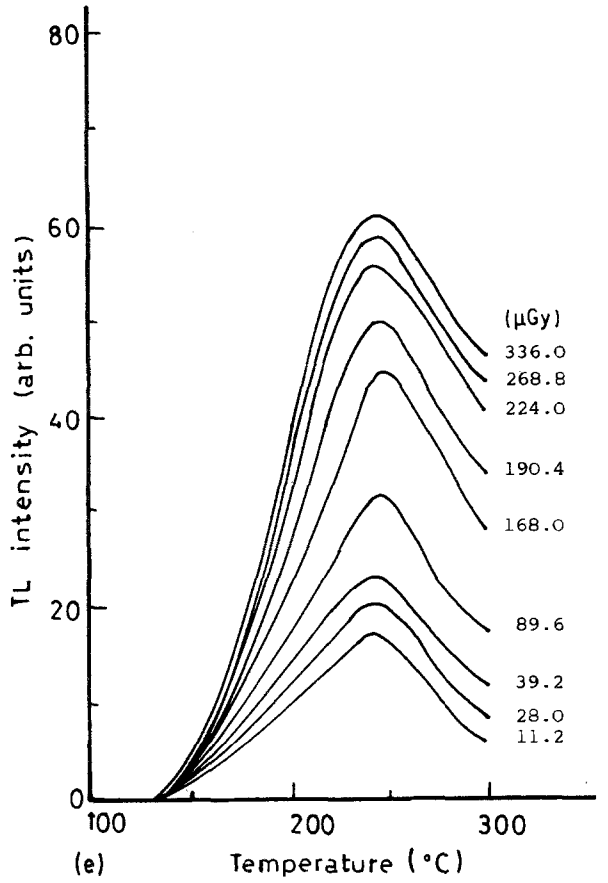

Figure 1 continued.

concentrations varying from 10^{-4}–0.2 wt %. The mixtures were melted at 1000°C for 2 h and then cast in the mild steel mould followed by annealing at 300°C for 1 h.

The samples were irradiated in a ^{60}Co-γ cell at room temperature at a dose rate of 67.2 μGy h^{-1}. The experimental doses were in the range of 11.2–336 μGy.

Thermoluminescence was measured by a TL analyser supplied by Harshaw Chemical Company. The type model 2000 A and B was used. It consists of two separate units: the unit 2000 A thermoluminescent detector and the unit 2000 B automatic integrating picoammeter. The basic function of the detector is to heat the irradiated material using a reproducible controlled temperature cycle and to detect the light emitted from the samples by means of a low noise and high gain photomultiplier which converts the emission from TL materials into a current signal which is amplified, integrated, and displayed.

3. Results and discussion

Tellurite–phosphate glasses with different concentrations of Nd_2O_3 were prepared. The prepared samples were exposed to ^{60}Co γ rays at a dose rate of 67.2 μGy h^{-1} at room temperature. Fig. 1 shows the typical glow curves obtained for samples 1–5, respectively (see Table I). The curves were recorded using a heating rate of 2.5 K s^{-1}. For the dose level and temperature range investigated, only a single isolated glow peak appears at ~ 498–513 K. The shape of the glow peak did not alter significantly with an increased γ-ray dose. The only effect observed is an increase in intensity of the glow peak with dose, due to the increased population of the electron traps. A change in the glow-peak temperature with increasing γ-irradiation exposure was recognised; similar behaviour was observed in a number of glow curve studies on $CaSO_4$–Dy by Mangia *et al.* [26]. This behaviour was explained by assuming that either a multilevel or a continuous distribution of trap depths was associated with the main glow peak, with a single associated frequency factor. This picture coincided with the conclusion of Spurny & Novotny [27] that the most probable environment for a trapped electron or hole is a non-spherically symmetrical cavity which contains a distribution of activation energies.

Fig. 2 shows the dependence of glow curve on the composition of Nd_2O_3 for samples 1–5 after irradiation at 336 μGy. It can be easily seen that the peak response and sensitivity increase with increasing Nd_2O_3 concentrations up to 10^{-3} wt % (curve d), and a further increase in Nd_2O_3 content decreases the glow curve intensity (curve e).

The TL response to ^{60}Co γ rays was investigated. The total charge in nanocoulombs (nc), collected and displayed on the TLD analyser, was noted; this charge is functional to the total investigated area under the full glow curves for the irradiated glass samples. Therefore an attempt was also made to measure the area in cm^2 under the recorded glow curve using a planimeter. The estimated areas were then plotted as a function of irradiation dose, and the results are displayed in Fig. 3. For each sample, an approximately straight line was obtained in the dose range up to 224.2 μGy. Beyond this dose all samples showed saturation except sample d (10^{-3} wt % Nd_2O_3) which exhibited linearity up to 336 μGy.

The changes in peak height with irradiation dose for all glass samples investigated are illustrated in Fig. 4. The peak height increases linearly with the increase

TABLE I Trap depth calculated by different methods [28–33] for $(TeO_{2_{0.81}}–P_2O_{5_{0.19}})$: Nd^{3+} glass doped with variable Nd_2O_3 concentrations

Sample number	Concentration of Nd_2O_3 in $TeO_{2_{0.81}}–P_2O_{5_{0.19}}$ (wt %)	Trap depth (eV)					
		Grossweiner [28]	Lushchik [29]	Halperin & Braner [30]	Chen; first half width [31]	Chen; total width [32]	Mazumdar *et al.* [33]
1	10^{-4}	0.62	0.78	0.64	0.60	0.74	0.66
2	3×10^{-4}	0.63	0.71	0.66	0.61	0.71	0.67
3	7×10^{-4}	0.59	0.55	0.62	0.57	0.59	0.63
4	10^{-3}	0.61	0.64	0.63	0.59	0.61	0.65
5	10^{-2}	0.56	0.53	0.57	0.53	0.57	0.59

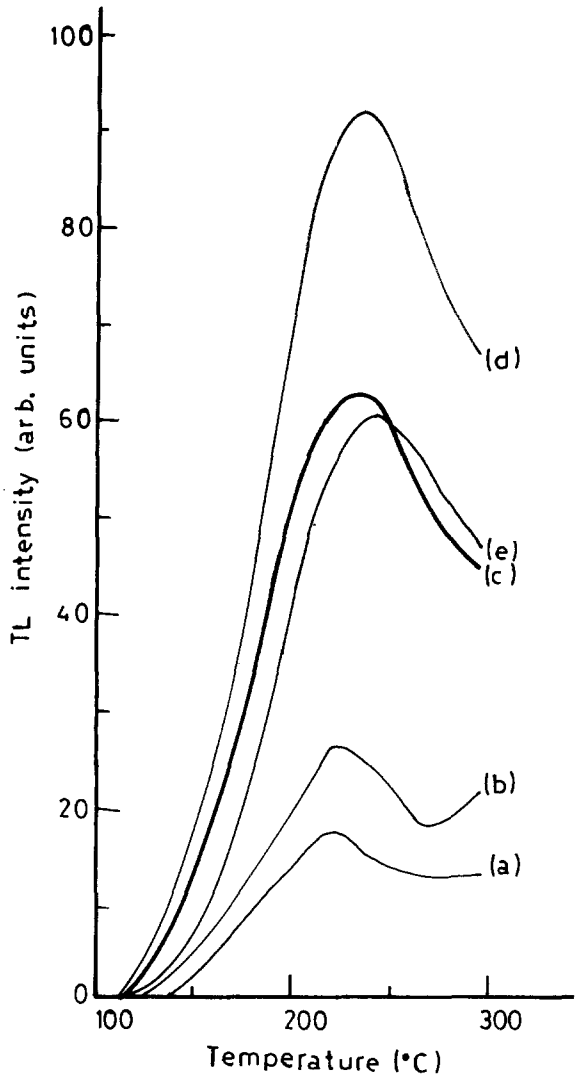

Figure 2 TL glow curves of $TeO_{2_{0.81}}$–$P_2O_{5_{0.19}}$ glass doped with (a) 10^{-4}; (b) 3×10^{-4}; (c) 7×10^{-4}; (d) 10^{-3}; (e) 10^{-2} wt % Nd_2O_3 after exposure to a γ-ray dose of 336 μGy.

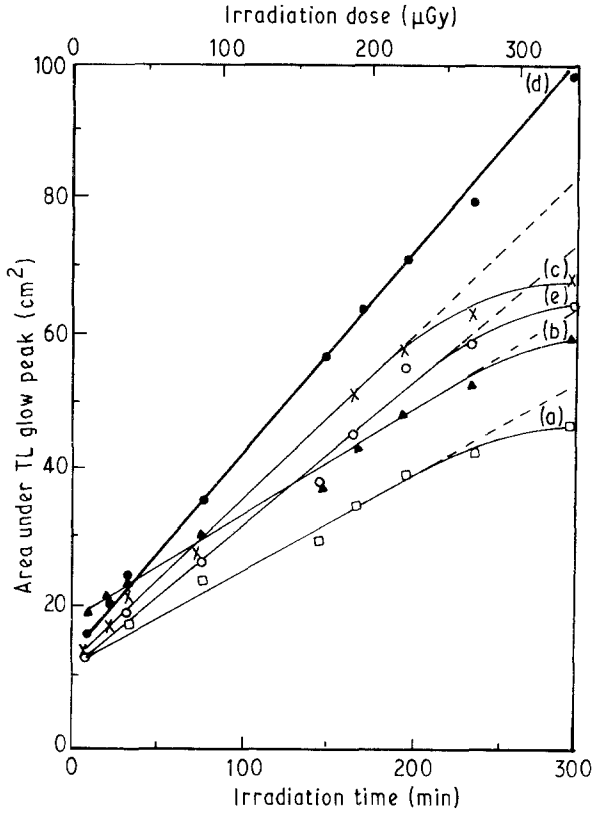

Figure 3 Variation of the area under TL glow curves with γ-irradiation dose for glass samples (a) 10^{-4}; (b) 3×10^{-4}; (c) 7×10^{-4}; (d) 10^{-3}; (e) 10^{-2} wt % Nd_2O_3-doped glass.

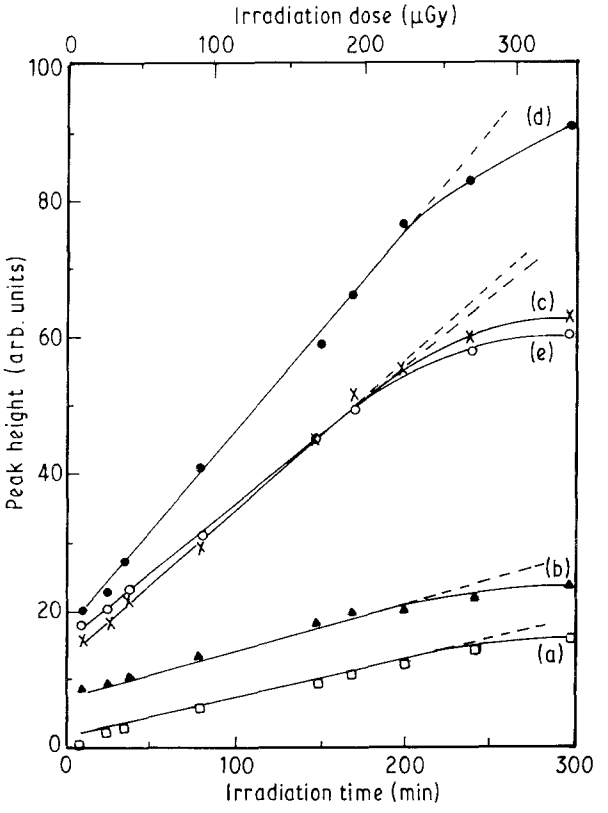

Figure 4 Peak height against γ-irradiation dose for five glass samples: (a) 10^{-4}; (b) 3×10^{-4}; (c) 7×10^{-4}; (d) 10^{-3}; (e) 10^{-2} Nd_2O_3 wt %.

of irradiation dose up to 224.2 μGy, then tends to saturate.

Figs 5 and 6 show the peak height and total thermoluminescence response as a function of Nd_2O_3 concentrations, respectively. From the two figures, it can be easily seen that the peak height and TL response are increased with Nd_2O_3 increase up to 10^{-3} wt %, followed by a slight decrease in peak height and a strong decrease in the total TL response with Nd_2O_3 concentration up to 0.2 wt % in this glass system.

The measured glow curves were analysed to obtain the activation energy for the electron trap state present. The glow-curve-shape methods [28–32], as well as the computerized method [33], concerning either general-order or second-order kinetics were used to calculate the trap parameter. The resulting data are shown in Table I. Apparently the various methods used to estimate trap depth (eV) show some scatter due to the different basic techniques on which these methods were established.

In general, the observed effect of γ irradiation on tellurite–phosphate glasses doped with trivalent Nd^{3+} can be discussed in terms of two main phenomena which operate at the same time for the materials during irradiation. γ rays create trapping centres, the number of which increases with increasing γ dose. They also act as an exciting source, raising electrons from the valence band of the material, which are later trapped in states created either by defects produced by

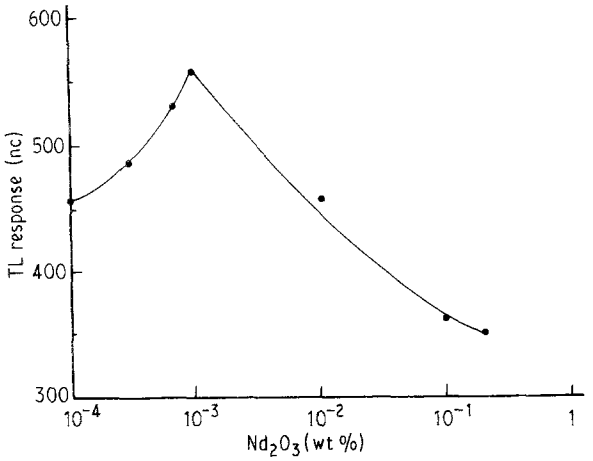

Figure 5 Variation of peak height with Nd_2O_3 (wt %).

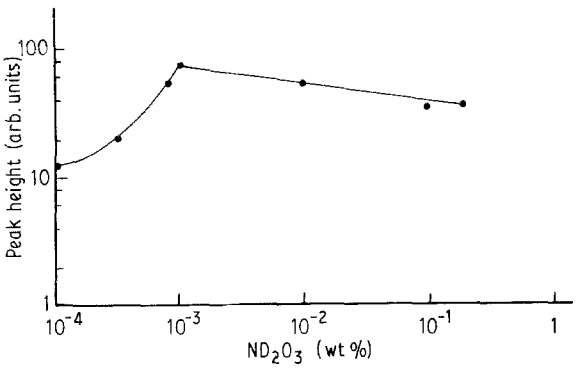

Figure 6 Thermoluminescence response against Nd_2O_3 (wt %).

irradiation, or by Nd^{3+} impurities originally present in the host material. On heating, the trapped electrons will be released and will recombine with holes left in the valence band to give a thermal glow. The increase in the TL response and particularly the intensity of the glow peak with increasing the γ dose from 0 to ~ 224 μGy results from an increased number of excited electrons leading to an increased probability of recombination.

The saturation in intensity of all the measured glow curves for different concentrations of Nd^{3+} above 224 μGy may be caused by new traps created by irradiation at such dose levels. These new unresolved traps may participate in the trapping process affecting (perhaps reducing) the number of electrons originally available for the main trap level.

4. Conclusions

Materials exhibiting a reproducible single glow peak at a reasonably high temperature (498–513 K) are ideal for radiation dosimetry. The sensitivity of our glass samples to the very low γ dose (11.2–224.2 μGy) indicates the great potential benefit of these glass systems to environmental radiation monitoring and personnel dosimetry. However, the glass systems under investigation need more modifications to increase their TL response. Also, research must continue in an effort to find suitable matrices in which rare-earth ions may show improved TL performance.

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Received 17 October 1990
and accepted 2 May 1991