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Optical absorption and thermoluminescence of bismuth-doped NaCl single crystals irradiated with X-rays

M. R. SEN, A. V. KRISHNA RAO, K. V. RAO
Department of Physics, Indian Institute of Technology, Kharagpur 721302, India

The optical absorption in the wavelength range 200 to 800 nm of Bi-doped NaCl single crystals (0.08 and 1.3 mol %) before and after X-ray irradiation for different times, has been measured. The partial thermal bleaching characteristics of NaCl : Bi (1.3 mol %) irradiated for one hour have been studied. The thermoluminescence (TL) curves of the doped samples irradiated for one hour have been recorded. These measurements indicate conversion of Bi^{3+} to Bi^{2+} in the doped samples with X-ray irradiation; however, when NaCl : Bi (1.3 mol %) is X-ray irradiated for larger times than one hour, Bi^{+} and Bi^{0} seem to be formed also. An attempt is made to understand the results of the present investigations.

1. Introduction

A study of the colour centre phenomena in pure and doped alkali halides irradiated with ionizing radiations like X-rays yielded valuable information regarding the defect-controlled properties of these solids [1, 2]. Considerable work on the effect of doping alkali halides with a monovalent or a divalent impurity on their physical properties has been reported in the literature [3, 4]. However the data on doping these materials with trivalent ions is very meagre. Recently the effect of doping bismuth in minute concentrations (few ppm) into various alkali halides on some of their physical properties like optical absorption, electrical conductivity, etc. was investigated [5, 6]. Radhakrishna and Srinivasa Setty [6] showed that bismuth can exist in a divalent/trivalent form or in both valency states in these crystals depending on how the crystals were grown and also how they were heated. It is our interest to report in this paper the data of our investigations on the optical absorption and thermoluminescence of Bi-doped NaCl single crystals irradiated with X-rays and attempt an understanding of the defect processes in them. The bismuth concentrations are 0.08 and 1.3 mol %. Results of our detailed studies on the dielectric properties of these solids have already been reported [7].

2. Experimental methods

Bi-doped NaCl crystals were grown by the Kyropulus method by taking the required proportions of NaCl and $BiCl_3$ and cooling the crystal to room temperature slowly. No specific heat treatment was carried out on the samples. X-ray diffraction studies indicated that in samples with larger Bi-doping, there are present specks of a precipitated bismuth salt; these measurements indicated that traces of such specks formed beyond 0.3 mol % of Bi-doping. We have concentrated on measurements in NaCl : Bi crystals with two dopings: (i) 0.08 mol % Bi-doping in which precipitation of bismuth salt has not occurred and (ii) 1.3 mol % in which considerable bismuth salt precipitation has taken place.

Samples were cut from boules, then ground and optically polished. The final dimensions of the samples were about 1.5 cm × 1.5 cm × 0.1 cm.

X-ray irradiation of the crystals was carried out at room temperature using 35 kV, 10 mA from a Philips Norelco unit keeping the sample at a distance of 2 cm from the window of the tube. The

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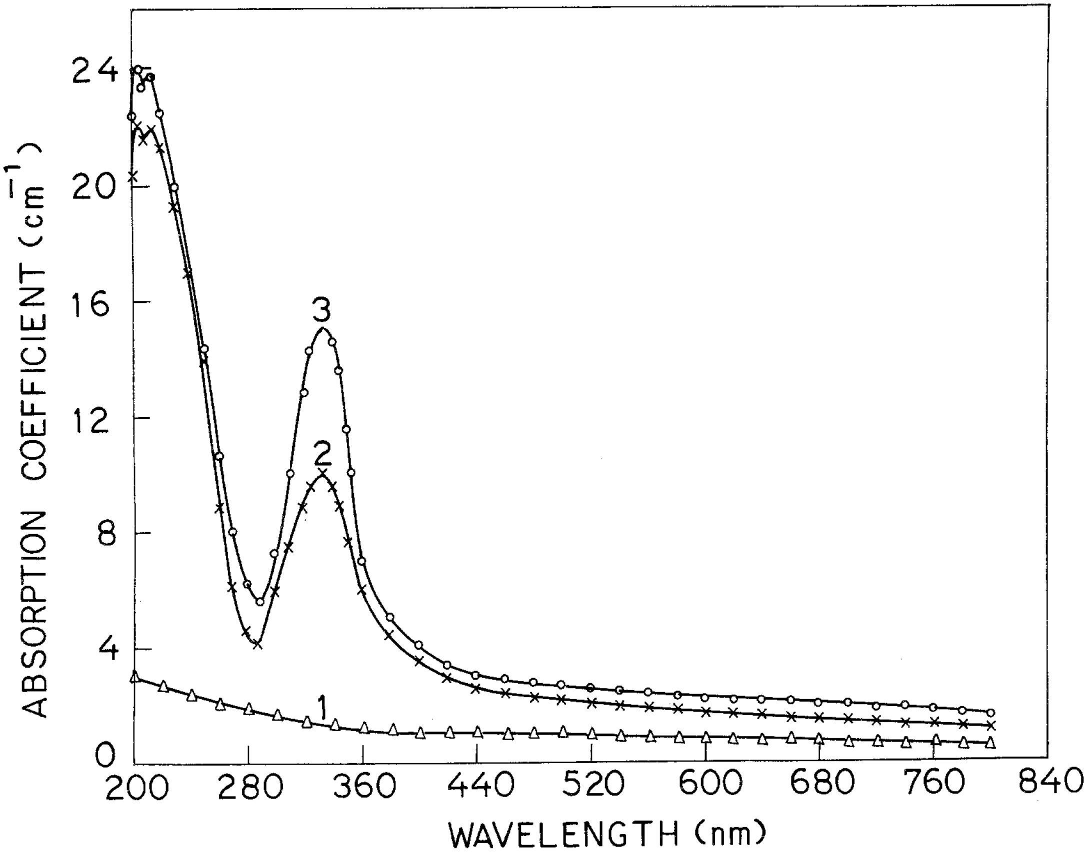


Figure 1 Optical absorption at 30° C as a function of wavelength for undoped and Bi-doped NaCl single crystals. Curve 1, undoped NaCl, curve 2, NaCl : Bi (0.08 mol%) and curve 3, NaCl : Bi (1.3 mol%).

samples were always irradiated on one side for half of the mentioned time and the remaining half on the other side.

Optical absorption measurements were taken on a Beckman model 26 Spectrophotometer (with a resolution of 0.2 nm) in the range 200 to 800 nm. Thermoluminescence glow peaks were recorded with an Esterline-Angus recorder using a conventional set-up [8]. The accuracy in measurement of the absorption coefficient, α, is 0.05 cm^{-1} and in temperature measurement of TL is 2° C. Measurements on at least three samples of each concentration have been carried out and the absorption and TL curves are reproducible to the accuracy mentioned.

3. Results

Fig. 1 presents the optical absorption at room temperature ($\approx$ 30° C) of undoped and Bi-doped NaCl crystals. Bi-doped samples exhibit absorption bands at 334 and 205 nm, the latter band showing two subpeaks. The absorption in the two bands at 334 and 205 nm increases with bismuth concentration.

Figs. 2a and b show the optical absorption of NaCl : Bi (0.08 and 1.3 mol%) irradiated with X-rays for different times. We find that in NaCl : Bi (0.08 mol%) the absorption in the band at 205 nm is decreased and that in 334 nm gradually increased with time of irradiation (X-ray dosage); also the *F* band at 465 nm (in NaCl) is present and it increases up to one hour of irradiation. The absorption data for NaCl : Bi (0.08 mol%) for 3 h X-ray irradiation were not shown in Fig. 2a as the changes in absorption were small and this graph would be practically the same as that for 2 h X-ray irradiation. For larger times of irradiation, the *F* band is reduced giving rise to the *M* band at 725 nm.

The absorption band at 205 nm is reduced with X-ray dosage in NaCl : Bi (1.3 mol%); however the band at 334 nm and the *F* band of NaCl initially increase up to one hour of X-ray irradiation beyond which the absorption in these bands decreases. Also the *M* band of NaCl grows beyond one hour of irradiation.

Plotting the absorption coefficient values at the

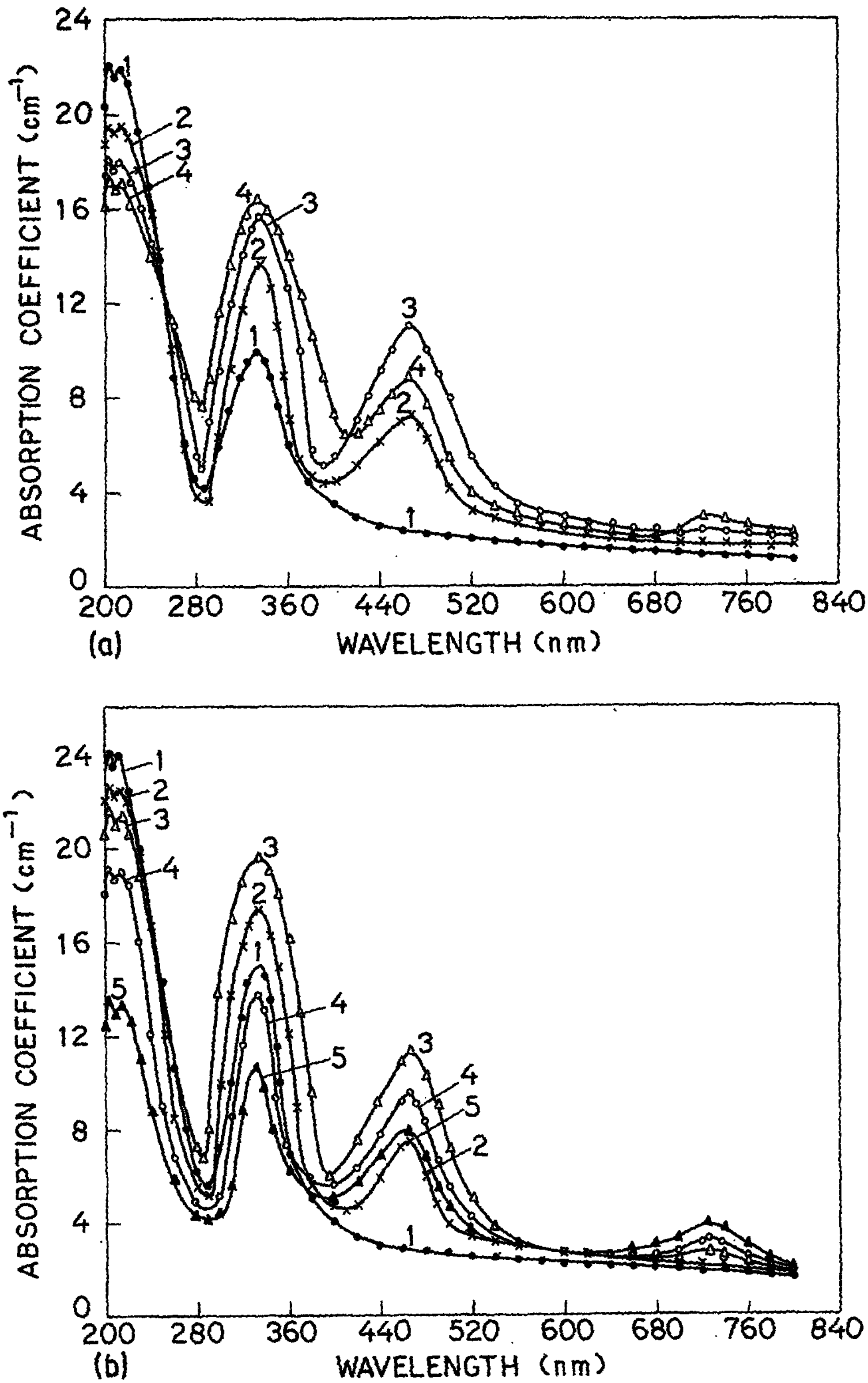
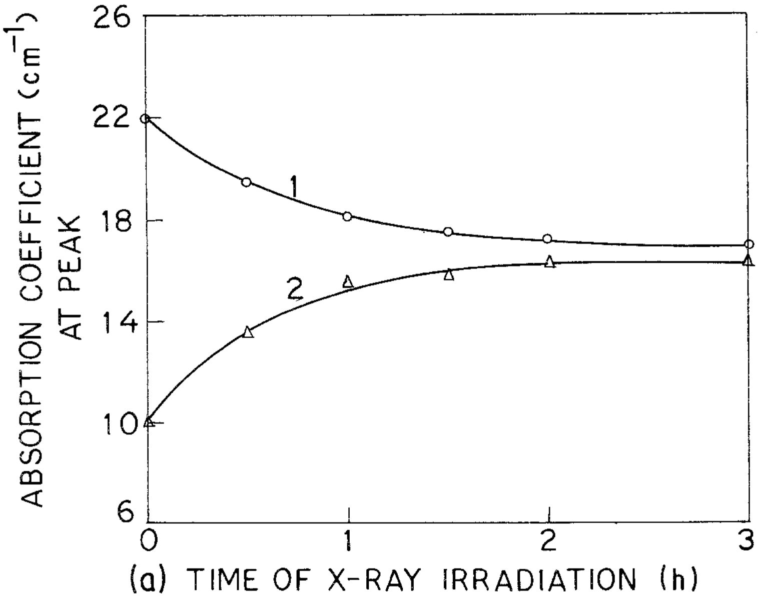


Figure 2 (a) Optical absorption at 30° C as a function of wavelength for NaCl:Bi (0.08 mol%) for different times of X-ray irradiation. Curve 1, unirradiated, curve 2, 0.5 h, curve 3, 1 h, and curve 4, 2 h. (b) Optical absorption at 30° C as a function of wavelength for NaCl:Bi (1.3 mol%) for different times of X-ray irradiation. Curve 1, unirradiated, curve 2, 0.5 h, curve 3, 1 h, curve 4, 2 h and curve 5, 3 h.



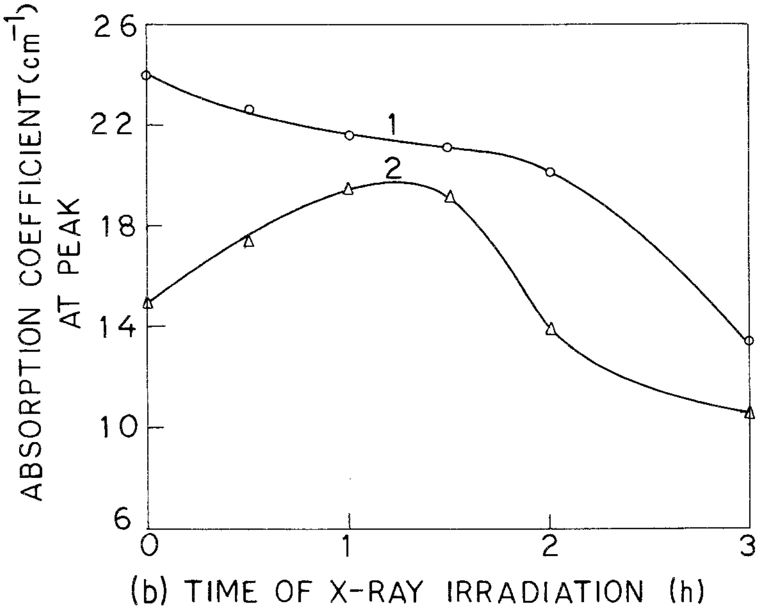


Figure 3 (a) Absorption coefficient at the peak of the bands as a function of time of X-ray irradiation for NaCl:Bi (0.08 mol%). Curve 1, 205 nm and curve 2, 334 nm. (b) Absorption coefficient at the peak of the bands as a function of time of X-ray irradiation for NaCl:Bi (1.3 mol%). Curve 1, 205 nm and curve 2, 334 nm.

peak of the bands at 205 and 334 nm as a function of time of X-ray irradiation, the graphs shown in Figs. 3a and b are obtained for NaCl:Bi (0.08 and 1.3 mol%, respectively). The absorption band at 205 nm in NaCl:Bi (0.08 mol%) gradually decreases and the one at 334 nm increases with X-ray dose. However, in NaCl:Bi (1.3 mol%), the band at 205 nm decreases slowly up to two hours of X-ray irradiation; for larger times, the decrease in this band is more. The absorption band at 334 nm increases in the initial stages of colouration but decreases at larger times of irradiation. Thus it is found that NaCl doped with a larger concentration of bismuth exhibits different behaviour in regard to the absorption bands at 205 and 334 nm with a X-ray dose compared to that with a low concentration of bismuth.

The partial thermal bleaching characteristics of NaCl:Bi (1.3 mol%) irradiated with X-rays for one hour are given in Fig. 4. The samples were heated to a particular temperature 90° C (or 180 and 300° C); later the samples were slowly cooled to room temperature where the absorption measurements were always taken. The absorption band at 205 nm increases and that in 334 and 465 nm (*F* band of NaCl) decrease with the increase in temperature of bleaching. The *M* band at 725 nm in NaCl observed in the doped sample disappears

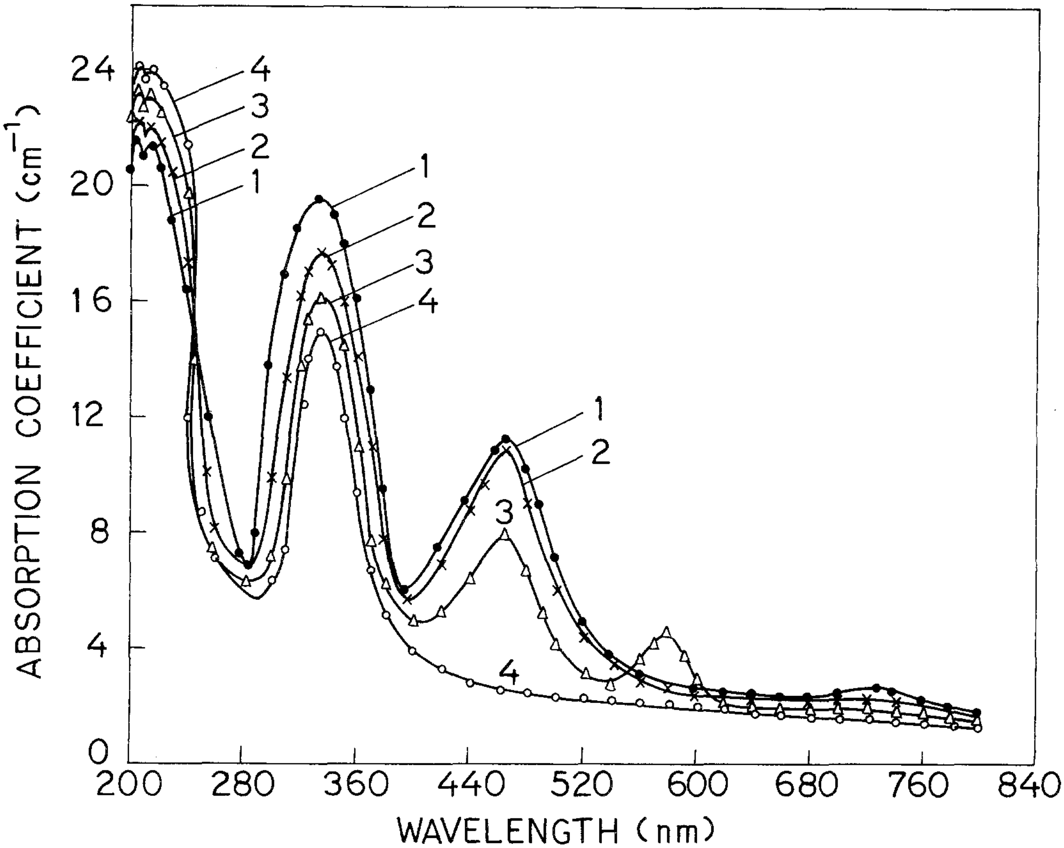


Figure 4 Partial thermal bleaching characteristics of the absorption band in NaCl:Bi (1.3 mol%) X-ray irradiated for 1 h. Curve 1, 1 h X-ray irradiated, curve 2, bleached at 90° C, curve 3, bleached at 180° C and curve 4, bleached at 300° C.

at higher temperatures of bleaching. It can also be noticed that when this sample is heated to 180° C, an absorption band at 580 nm is obtained. The crystal practically comes back to its condition before irradiation when it is heated to a temperature of 300° C.

Fig. 5 presents the thermoluminescence (TL) curves of the doped samples X-ray irradiated for one hour. The undoped NaCl crystal gives TL peaks at 77 and 240° C. The low temperature TL peak is shifted to higher temperatures with Bi-doping whereas the high temperature peak is shifted to low temperatures; also the TL light output in the two peaks seems to be reduced compared to that in undoped NaCl. In NaCl:Bi (1.3 mol%) an additional feeble TL peak at 124° C is noticed.

4. Discussion

The comparatively low values for the absorption coefficient exhibited by undoped NaCl crystals indicate that the crystals grown in the laboratory are of moderately high quality; the estimated intrinsic defect concentration (like vacancies, etc.) is of the order of 10^{15} cm^{-3} [9]. The absorption bands at 334 and 205 nm observed in Bi-doped NaCl are ascribed to Bi^{2+} and Bi^{3+}, respectively [7, 6]. These earlier workers reported that the 205 nm was formed in NaCl doped with few ppm of bismuth where the samples were irradiated at liquid nitrogen temperatures. However our results indicate that this band can be formed when X-ray irradiation is done at room temperature in NaCl samples doped with a much larger concentration of bismuth.

X-ray irradiation and alkali halides is known to produce electrons and holes. The electrons seem to be trapped at Bi^{3+} converting them into Bi^{2+}. Thus we find the reduction of the 205 nm band and the increase in the 334 nm band with X-ray irradiation in Bi-doped NaCl. The present measurements point out that in NaCl:Bi (1.3 mol%), this $Bi^{3+} \rightarrow Bi^{2+}$ conversion occurs up to about one hour of irradiation beyond which it is likely that these complexes

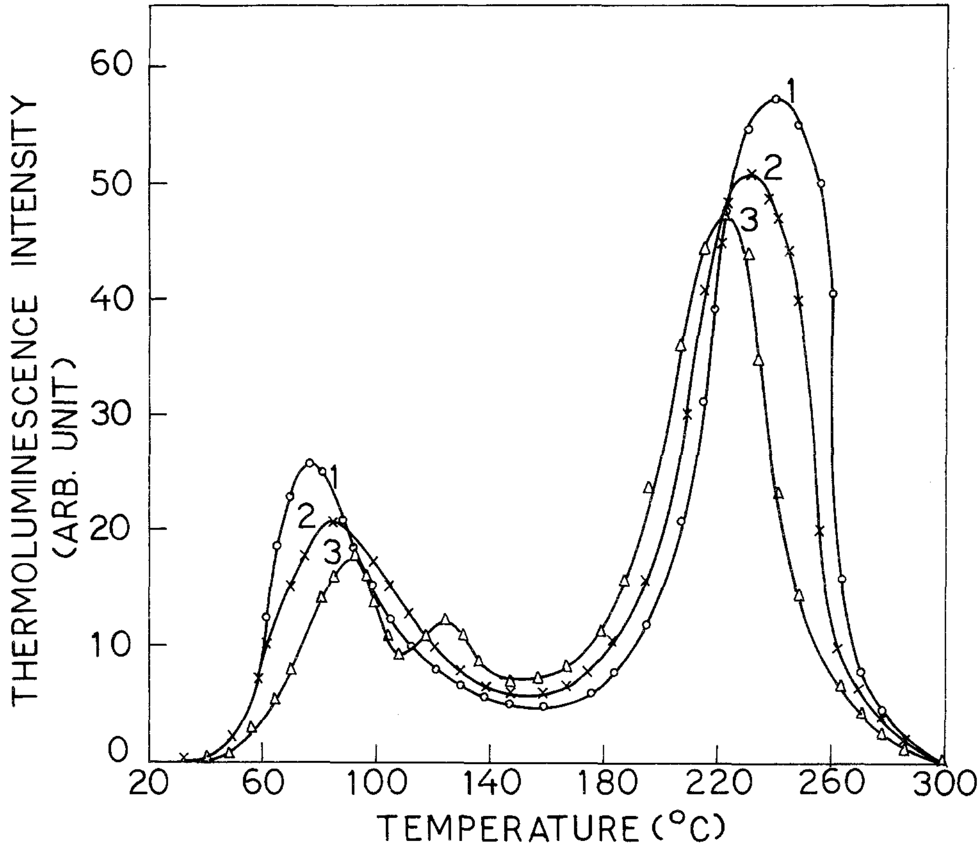


Figure 5 Thermoluminescence for undoped and Bi-doped NaCl, X-ray irradiated for 1 h. Curve 1, undoped NaCl, curve 2, NaCl:Bi (0.08 mol%) and curve 3, NaCl:Bi (1.3 mol%).

may be further reduced to still lower valency states of bismuth (e.g. Bi^+ and Bi^0); the absorption bands of these seem not to lie in this wavelength range.

It may be mentioned here that the *F*-centre concentration produced in Bi-doped NaCl crystals is about 20% less than in undoped NaCl for the same X-ray dosage (data not presented) indicating that bismuth doping adversely affects the formation of *F*-centres in NaCl crystals. The changes in *F* and *M* absorption bands in these doped samples – observed in the present work – can be understood with the usual ideas pertaining to them [3].

Interestingly we find from the partial thermal bleaching experiments carried out on NaCl:Bi (1.3 mol%) X-ray irradiated for one hour, that Bi^{2+} can be converted into Bi^{3+} by heating. The absorption band observed at 580 nm in these samples bleached at 180° C seems to be connected with *F*-aggregate centres (*R* centres) [10].

It is generally believed [11] that in NaCl, the low temperature glow peak is due to an intrinsic process, namely the destruction of *F*-centres whereas the high temperature glow peak at 240° C is presumed to be due to the destruction of *F*-aggregate centres. Our results indicate minor changes in both TL light output as well as in TL peak temperatures in Bi-doped NaCl; the slight change in peak temperatures may be associated with lattice distortion of NaCl caused by the dopant [7].

Further work, in progress now, to detect the possible formation of Bi^+ and Bi^0 (in these doped crystals) by other methods using scanning electron microscope and the spectral characteristics of thermoluminescence, etc. it is hoped, will throw more light on the defect processes taking place in these solids.

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