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Optical absorption and thermoluminescence of barytes single crystals irradiated with γ-rays

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

The optical absorption in the wavelength region 200 to 800 nm of barytes single crystals before and after γ-ray irradiation for different times has been measured. The thermoluminescence (TL) of the irradiated crystals has also been studied. γ-ray irradiation produces absorption bands at 590 and 370 nm possibly due to Ba^+ and $(SO_4)^-$ centres, respectively. Partial thermal bleaching experiments carried out on these absorption bands show that the absorption in both bands gradually decreases up to 200° C beyond which it falls rapidly. The γ-ray irradiated barytes exhibits TL peaks at 90, 180 and 208° C. An attempt is made to understand the results.

1. Introduction

The formation of colour centres in alkali halide crystals by ionizing radiations and the properties of the colour centres thus formed have been extensively studied [1, 2] yielding valuable information regarding the defect-controlled properties of these solids. Such studies are being extended to other materials. Barytes are naturally available single crystals of $BaSO_4$. The thermoluminescence (TL) of powdered barytes irradiated with γ-rays was studied by Gupta *et al.* [3] TL and ESR measurements on γ-ray and pile-irradiated natural barytes were carried out by Gupta *et al.* [4] who showed that pile-irradiation (i.e. neutron irradiation) produces high temperature TL peaks compared to those obtained with γ-ray irradiation. It has been reported by Prokic [5] that the development of different TL peaks in annealed and γ-ray irradiated barytes crystals depends on the γ-ray dosage. Morimoto *et al.* [6] suggested from their studies that each of the barium and sulphate ions associates with itself one absorbed water molecule. Interestingly, the optical absorption of X-ray or γ-ray irradiated barytes seems not to have been reported until now. It is the aim of this paper to present the data of our detailed studies on optical absorption and thermoluminescence of naturally available, transparent barytes single crystals irradiated with high doses of γ-rays, or X-rays.

2. Experimental methods

The barytes crystals used in the present investigations are obtained from Geologists' Syndicate, India. Samples were prepared from originally available big lumps and these were moderately transparent; the final dimensions of the samples are about 1 cm × 1 cm × 0.1 cm.

X-ray irradiation of the samples was carried out at room temperature using 35 kV, 15 mA from a Norelco unit keeping the samples at a distance of 2 cm from the window of the tube. The samples are always irradiated on one side for half of the mentioned time and the remaining half time on the other side. γ-ray irradiation was carried out with a Co^{60} source of 10^3 Curie strength giving a dose of 80 kilorads h^{-1}.

Optical absorption measurements were taken in the wavelength region 200 to 800 nm using a Beckman 26 spectrophotometer. The accuracy in measurement of absorption coefficient α is 0.05 cm^{-1}. Thermoluminescence glow peaks were recorded with an Esterline–Angus recorder using a conventional set up [7].

3. Results

The optical absorption at room temperature of barytes as a function of wavelength is shown in Fig. 1. We find a weak absorption band with peak at 300 nm; this band is reduced by heating the

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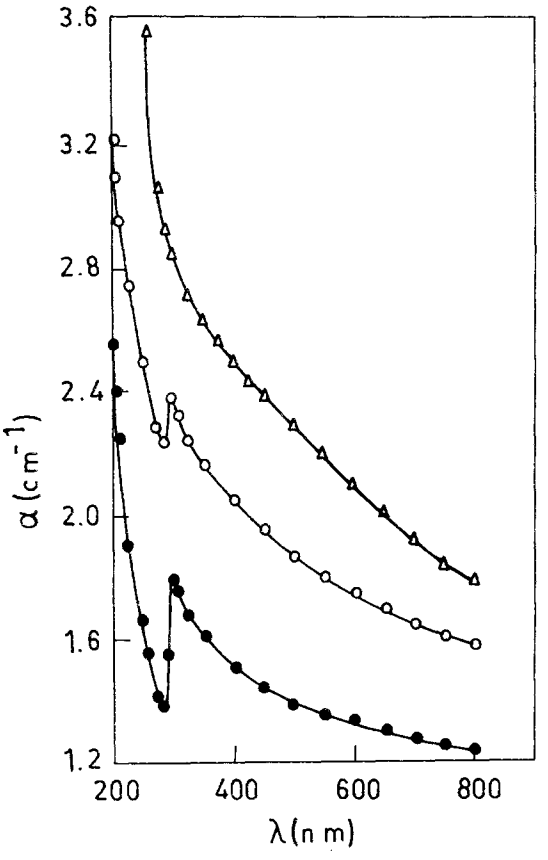

Figure 1 Optical absorption coefficient at 30° C as a function of wavelength for barytes crystals in as-obtained, and heated to different temperatures and cooled to room temperature: • as-obtained; ○ heated to 300° C; △ heated to 400° C.

crystal to 300° C. This band is removed and the background absorption increased when the crystal is heated at 400° C for 30 min (the absorption measurements were always taken at room temperature after cooling the crystals) and this absorption has comparatively large values at low wavelengths.

γ-ray irradiation of barytes crystals does not practically affect the absorption band at 300 nm but produces two bands at 370 and 590 nm; the absorption in these bands increases with γ-ray dosage (Fig. 2). Additionally the absorption in the low wavelength region increases. Similar results are obtained by irradiating the barytes crystals with X-rays; only the absorption in the two bands at 370 and 590 nm is much less. Hence these data are not presented. However the insets in Fig. 2 give the growth characteristics of the absorption bands at 370 and 590 nm for barytes irradiated with γ-rays or by X-rays. Smakula's equation [8] was used for calculating the colour centre concentration; the oscillator strength of the centres responsible for these bands is taken to be unity.

Fig. 3 presents the results of partial thermal bleaching experiments on barytes crystals γ-ray irradiated for 24 h. It is observed that the absorption in the crystals decreases slightly up to 200° C beyond which it decreases rapidly with the temperature of bleaching; the sample seems to regain its original (as obtained) condition when it is heated to 300° C except that in the bleached crystal, the absorption is large at low wavelengths. The data on X-ray irradiated barytes are not given as the behaviour is the same. Insets of Fig. 3 show how the absorption in the two bands is reduced with the temperature of bleaching for barytes crystals irradiated with γ-rays or X-rays.

Fig. 4 gives the thermoluminescence pattern of barytes γ-ray irradiated for 12, 24 and 48 h. It shows TL peaks at 90, 180 and 228° C, larger γ-ray dose simply increasing the TL light output in these peaks. X-ray irradiation of barytes crystals for 2 h is found to give very feeble thermoluminescence.

4. Discussion

Barytes is normally supposed to contain some adsorbed water which seems to be responsible for the absorption band at 300 nm[6]. The present measurements show that such water of adsorption can be reduced by heating the crystal to 300° C and removed at 400° C.

Barytes ($BaSO_4$) lattice is basically made up of Ba^{2+} and $(SO_4)^{2-}$. γ-ray irradiation of barytes probably transfers an electron from $(SO_4)^{2-}$ to Ba^{2+} ions thus forming $(SO_4)^{-}$ and Ba^{+}. In analogy with alkali halides, Ba^{+} can be considered as an electron-trapped centre and $(SO_4)^{-}$ a hole-trapped centre. The absorption bands at 590 and 370 nm observed in γ-ray irradiated as-obtained barytes crystals may be attributed to these electron-trapped and hole-trapped centres, respectively. The formation of similar type of absorption bands in γ-ray irradiated calcite crystals has been earlier reported [9]. The growth curves of these bands (inset of Fig. 2) indicate saturation effects at higher γ-ray dosages. (The 370 nm seems to saturate at still higher γ-ray dosage.) The increase in absorption in the low wavelength region suggests that the concentration of defects in the barytes increases with γ-ray irradiation. The absorption band at 300 nm – apparently due to adsorbed

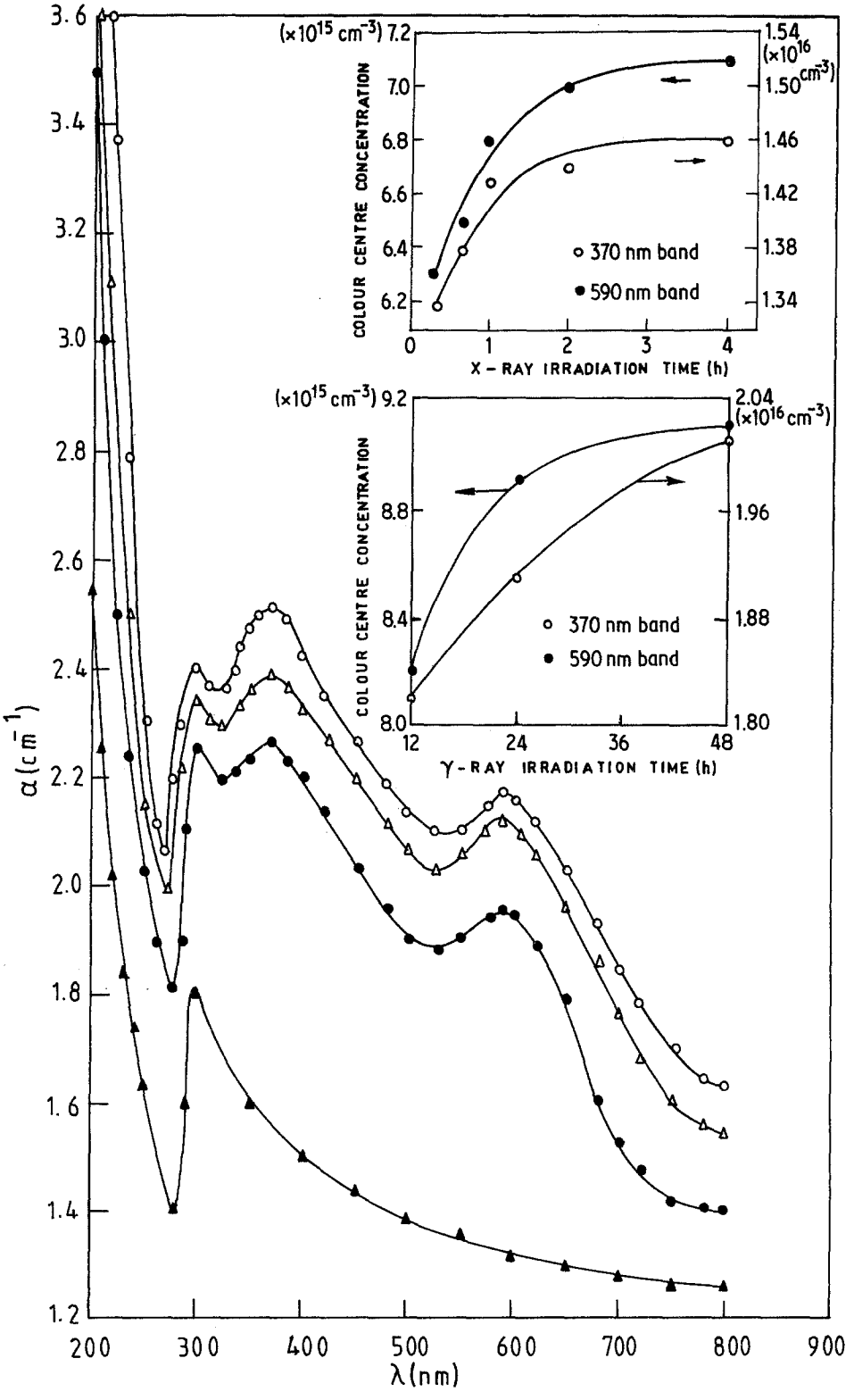

Figure 2 Absorption coefficient at 30° C as a function of wavelength for barytes crystals before and after γ-ray irradiated for different times; ▲ before irradiation; ● γ-ray irradiated for 12 h; △ for 24 h; ○ for 48 h. Insets: Growth characteristics of 370 and 590 nm absorption bands with time of X-ray or γ-ray irradiation.

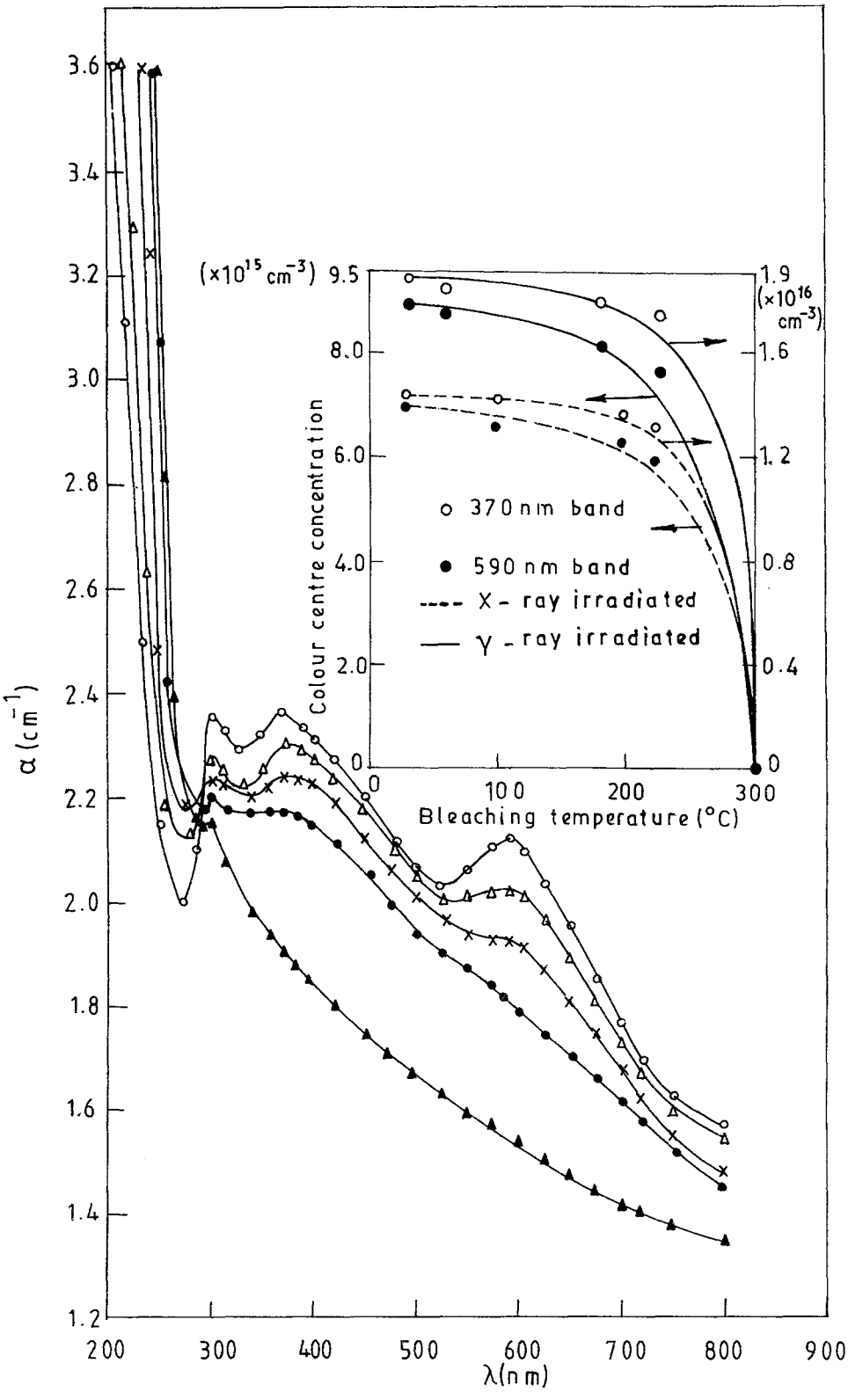

Figure 3 Partial thermal bleaching characteristics of the absorption bands at 370 and 590 nm in γ-ray irradiated (for 24 h) barytes crystals: ○ γ-ray irradiated for 24 h; △ bleached at 100° C; x at 200° C; • at 225° C; ▲ at 300° C. Inset: Colour centre concentration in 370 and 590 nm absorption bands with bleaching temperature in X-ray (2 h) or γ-ray (24 h) irradiated barytes crystals.

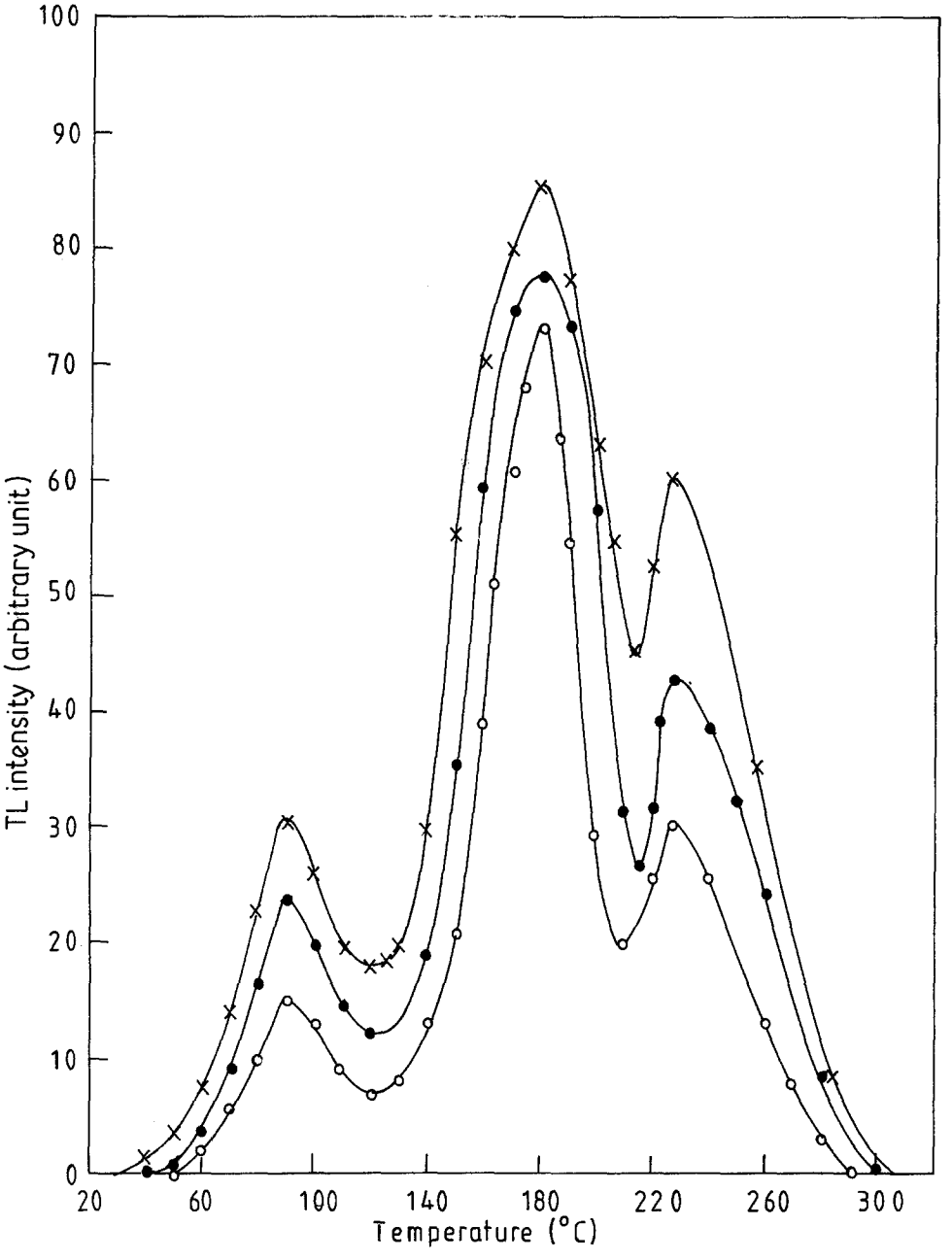

Figure 4 Thermoluminescence curves for barytes crystals γ-ray irradiated for different times: ○ 12 h; ● 24 h; x 48 h.

water – is practically unaffected by γ-ray irradiation. When irradiation of these crystals was carried out with X-rays, it appears that the transfer of electrons from $(SO_4)^{2-}$ to Ba^{2+} becomes less efficient leading to a smaller concentration of these centres, as observed in the present measurements. Our partial thermal bleaching experiments on optical absorption in both X-ray and γ-ray irradiated barytes show that the absorption in these two bands gradually decreases up to 200° C beyond which it falls rapdily. The bleached samples, containing a comparatively larger concentration of defects, exhibit the maximum absorption in the low wavelength region.

Barytes crystals are expected to contain impurities which give rise to traps of different trap depths in the forbidden region. When X-ray or γ-ray irradiated, electrons may be released from the lattice of the material and these electrons may be trapped at impurities forming luminescent cen-

tres. When X-ray irradiated, the shallow traps are likely to be filled with electrons and may be destroyed at room temperature; as such, thermoluminescence has not been exhibited by these X-ray irradiated samples. However, γ-ray irradiation is expected to fill up deep traps with electrons and the destruction of these traps with heating, seem to be responsible fot the TL peaks in γ-ray irradiated barytes.

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