Thermal behaviour of rare-earth mixed single crystals of neodymium copper oxalate

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Most of the oxalate crystals are insoluble in water and decompose before melting. The gel method[1] is useful for the growth of crystals that decompose at temperatures below their melting point and also for those for which there are no suitable solvents for recrystallization. The method is also efficient for the growth of crystals. Mixed crystals like calcium strontium tartarate[2], ammonium nickel sulphate, potassium nickel sulphate, ammonium alum and potash alum[3] have been grown in silica hydrogel. Here we report the thermal behaviour of single crystals of neodymium copper oxalate grown by gel method.

This acousto-optically important special-type rare-earth mixed single crystal was grown from silica gel (density = 1.03 g cm^{-3}) acidified with oxalic acid. The top solution used was nitrates of neodymium and copper along with nitric acid. Dissolution from the precipitate leads to nucleation to form well-faceted crystals of neodymium copper oxalate. These are characterized by different methods like X-ray, IR, EDAX and thermal methods.

TGA and DTA data of various oxalates have been described in general by Dollimore et al[4-6]. A thermogravimetric plot for neodymium copper oxalate was obtained using a Delta series TGA 7 at a scanning rate of 20°C per min (Figure 1). The crystal begins to lose water molecules at 51.36°C and complete dehydration occurs by 301.36°C in three stages. In the first stage 26 molecules of water are lost between 51.32°C
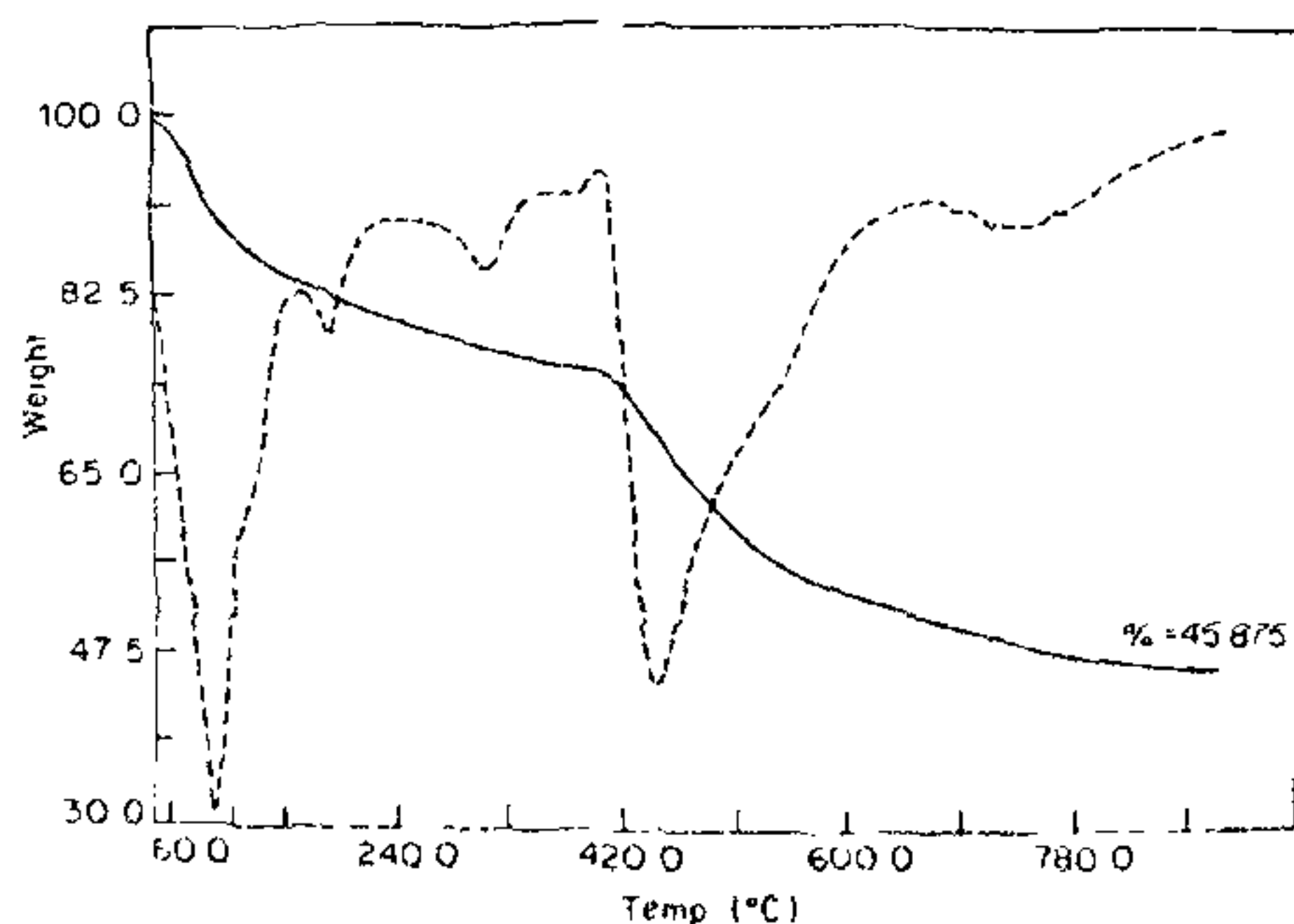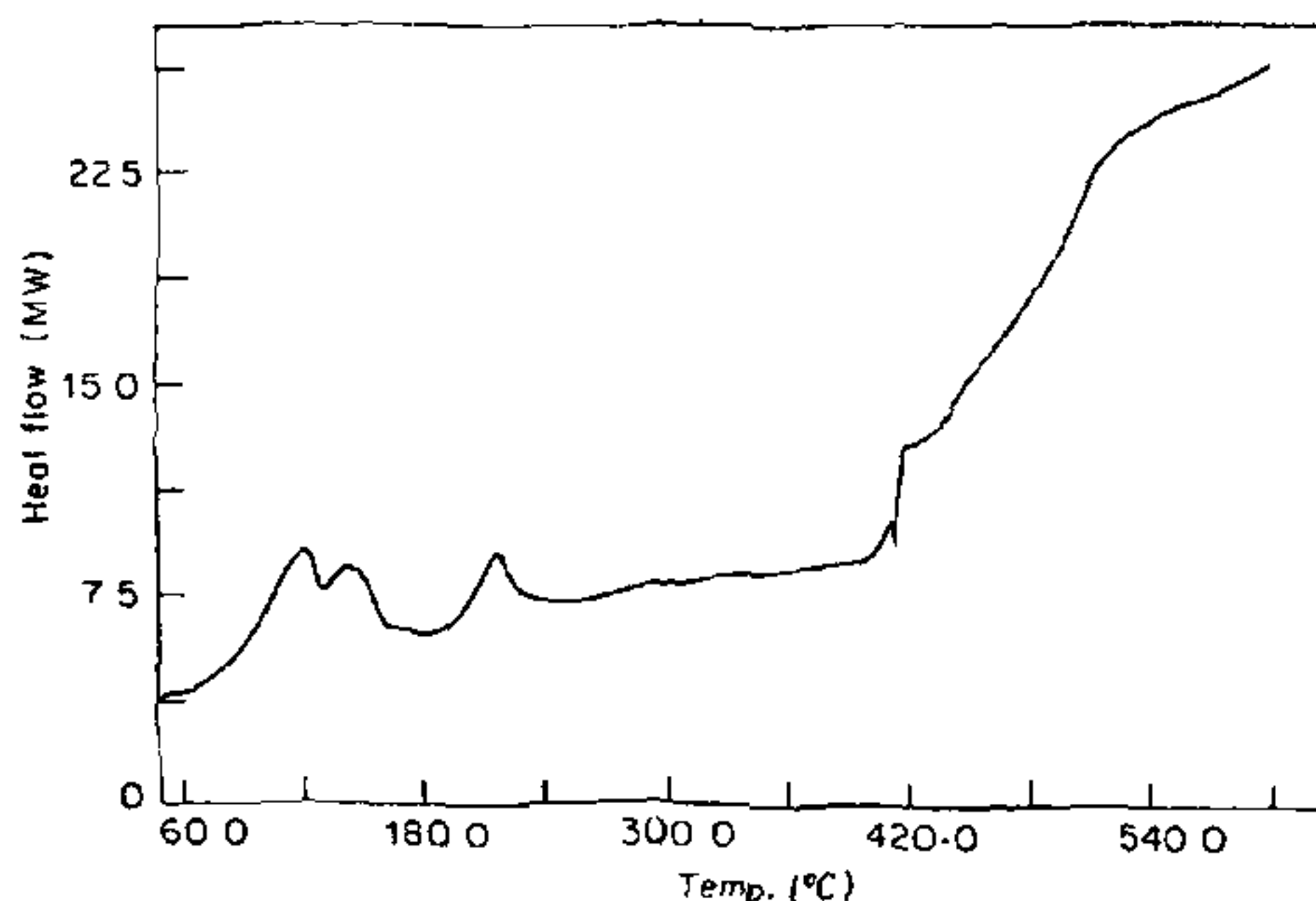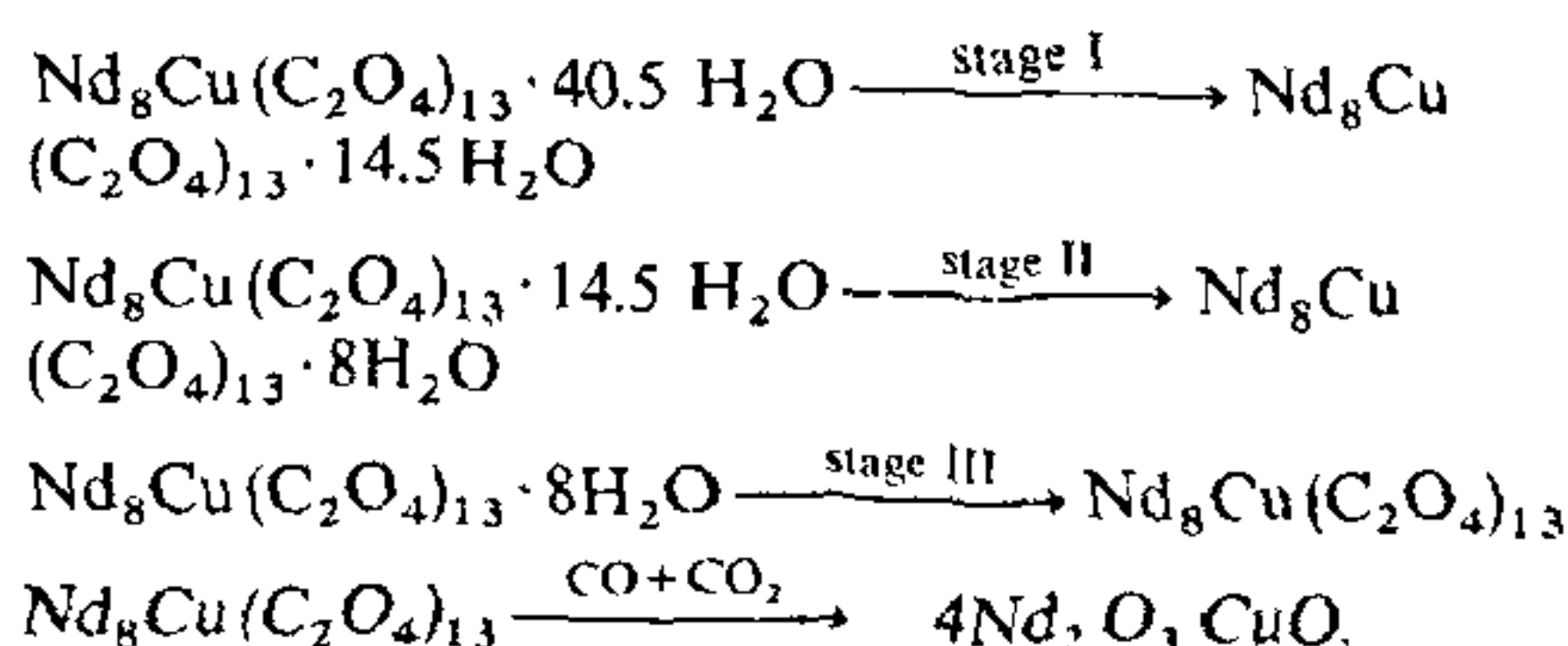

Figure 2. Differential scanning calorimetric plot for neodymium copper oxalate

and 121.36°C. In the second stage 6.5 molecules of water are lost between 121.36°C and 203.18°C. In the third stage, i.e. between 203.18°C and 301.86°C, the remaining molecules of water are lost. In the fourth stage, i.e. between 301.36°C and 870°C, decomposition occurs.

Differential scanning calorimetric analysis was done using a Delta series DSC 7 at a scanning rate of 20°C per min (Figure 2). In the DSC curve six heat flow peaks are seen at 120°C, 140.86°C, 216.52°C, 412.2°C, 420°C and 519.13°C. On the basis of TGA and DSC studies the following tentative mechanisms have been proposed for the thermal conversion.

$$Nd_8Cu(C_2O_4)_{13} \cdot 40.5\ H_2O \xrightarrow{\text{stage I}} Nd_8Cu (C_2O_4)_{13} \cdot 14.5\ H_2O$$

$$Nd_8Cu(C_2O_4)_{13} \cdot 14.5\ H_2O \xrightarrow{\text{stage II}} Nd_8Cu (C_2O_4)_{13} \cdot 8H_2O$$

$$Nd_8Cu(C_2O_4)_{13} \cdot 8H_2O \xrightarrow{\text{stage III}} Nd_8Cu(C_2O_4)_{13}$$

$$Nd_8Cu(C_2O_4)_{13} \xrightarrow{CO+CO_2} 4Nd_2O_3\ CuO.$$

The structural formula proposed for neodymium copper oxalate is $Nd_8Cu(C_2O_4)_{13} \cdot 40.5\ H_2O$. We conclude that the TGA and DSC data support this structural formula. Crystal-structure determination from X-ray diffraction studies is in progress.

Figure 1. Thermogravimetric plot for neodymium copper oxalate

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14%–Efficiency gallium arsenide photo-electrochemical solar cells

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We have achieved 12–14% AM1 solar conversion efficiencies in n-GaAs |KOH–Na$_2$Te/Na$_2$Te$_x$| graphite redox system using the technique of Ru surface modification, which has been shown to reduce the surface recombination velocity and increase the band bending, resulting in enhanced J_{SC} and V_{OC}. Spectral-response studies were used to determine the effective minority carrier-diffusion length which increased from 0.54 μm to 0.66 μm on surface modification.

THE efficiency and electrical properties of photo-electrochemical (PEC) solar cells depend strongly on the nature of the photoelectrode surface. The surface-modification technique[1,2] using transition-metal ions has been shown to be a possible method of improving performance and stability of such cells. In this investigation we show that the dark as well as illuminated properties of gallium arsenide (GaAs) photoelectrodes improve considerably, resulting in solar conversion efficiencies between 12% and 14%.

The photoanodes were (100) GaAs, Te doped with $N_d = 4.5 \times 10^{16}$ cm^{-3}. Surface modification was carried out by matte-etching the polished sample in 1:1 30% H_2O_2:H_2SO_4 and then dipping in 0.01 M hydrated RuCl$_3$ in 0.1 N HNO$_3$ for one minute. Ohmic contacts were made by evaporating In–Au (90:10 wt ratio) alloy on the back of the sample, followed by annealing at 450°C in Ar–H$_2$ (10:1 volume ratio) for three min. Samples were mounted on a Teflon holder with silicone rubber. After inserting the photoanode, the electrolyte (1 M KOH, 0.1 M Na$_2$Te/Na$_2$Te$_x$) was purged with argon gas for 30 min through a silica gel filter fitted at the bottom of the Perspex electrochemical cell before each experiment.

I–V studies showed a reduction in dark current density J_o from 0.82 μA cm^{-2} to 0.054 μA cm^{-2} and a decrease in ideality factor n from 3.2 to 1.8 due to Ru surface modification. C–V studies showed corresponding increase in flat-band potential V_{fb} from -1.42 V/Pt to -1.50 V/Pt.

The spectral response was studied using a Jarrell–Ash monochromator whose output was calibrated using a silicon photodiode. The response curves shown (Figure 1) before and after Ru modification indicated an increase of photocurrent response between $\lambda = (400–930)$ nm and reduction of sub-band gap response (inset of Figure 1) as reported earlier[3,4] for InP and CdTe. The effect of Ru-surface modification is thus to reduce surface recombination velocity thereby improving the effective minority carrier-diffusion length (L_p), and hence J_{sc}. L_p can be determined as the x-intercept or the inverse of the slope of a plot of $(\eta_q)^{-1}$ vs $[\alpha(\lambda)]^{-1}$, where η_q = quantum efficiency of electron-hole generation and $\alpha(\lambda)$ is the absorption coefficient. From Figure 2 it was thus found that L_p increased from 0.54 μm to 0.66 μm owing to Ru surface modification. A further contribution to the increase of J_{sc} is the increase of effective surface area on matte-etching. It is to be noted that both matte-etching and Ru treatment are essential for the reported improvement.

It has been shown by Jastrzebski et al.[5] that in the presence of surface recombination the effective minority carrier-diffusion length L_{eff} is reduced from the bulk value L_0 by

$$L_{eff}^2 = L_0^2 \left(1 - \frac{s}{s+1} \right) \exp\left(-\frac{Z}{L_0} \right),$$

where s is the reduced surface recombination velocity SL_0/D (D is the diffusion coefficient and S the surface recombination velocity). Thus increase of L_{eff} results from decrease of surface recombination velocity. For n-GaAs Nelson et al.[6] has shown that for unmodified surfaces $S = 5 \times 10^5$ cm sec^{-1}. Assuming $L_0 = 1.0$ μm ($\mu_p = 385$ cm^{2}V^{-1} sec^{-1}, $\tau_p = 10^{-9}$ sec) and excitation at the
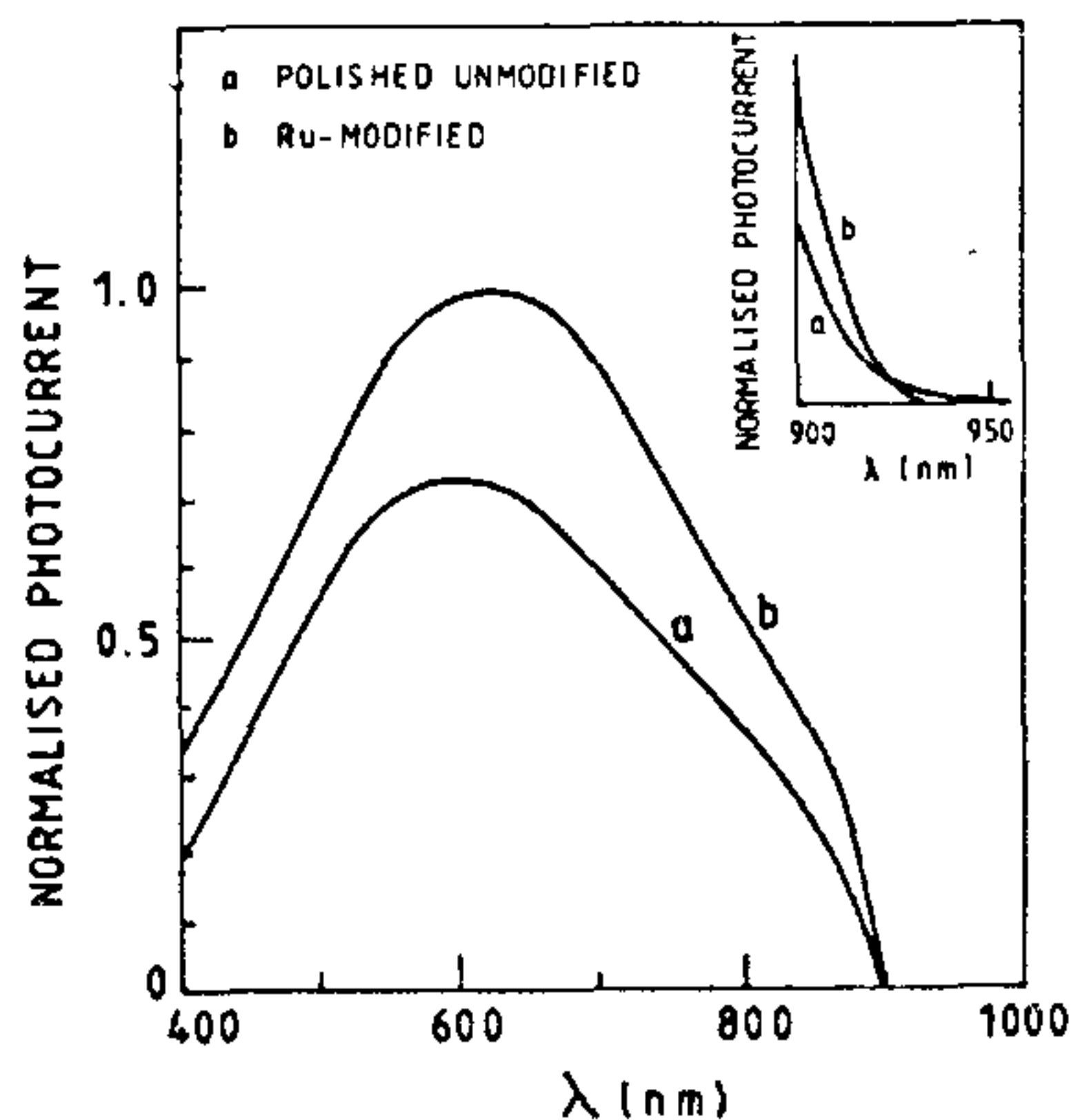

Figure 1. Spectral response of n-GaAs photoanode in 1 M KOH–0.1 M Na$_2$Te/Na$_2$Te$_x$–C redox-electrolyte system, showing increased photoresponse after Ru modification. Inset shows a reduction in sub-bandgap (900–950) nm response at a magnified scale.