

## Pre-heat Treatment Study of Recoil $^{128}\text{I}$ in Lithium and Copper Iodates

S. P. MISHRA,\* ARCHITA PATNAIK AND D. P. WAGLEY

Nuclear and Radiation Chemistry Laboratory, Department of Chemistry, Banaras Hindu University, Varanasi – 221005, India

Received 22nd February, 1983

The effect of pre-heat treatment on the ( $n, \gamma$ ) reaction of  $\text{LiIO}_3$  and  $\text{Cu}(\text{IO}_3)_2$  targets is an increase in the initial retention in  $\text{Cu}(\text{IO}_3)_2$  and decrease in  $\text{LiIO}_3$ . This has been ascribed to the competitive participation of oxidizing and reducing inherent crystal defects. Annealing kinetic studies reveal two apparent first-order processes for both the pre-heated and untreated iodates. An exciton mechanism is proposed to explain the higher plateau values and annealing kinetics in pre-heated  $\text{Cu}(\text{IO}_3)_2$  and  $\text{LiIO}_3$ .

The formation of precursors in an irradiated matrix has not yet been established by methods in which the crystals are dissolved for analysis, since on dissolution these species may be changed considerably. However, the nature of these precursors may be investigated by adopting indirect means such as pre-neutron irradiation heat treatment and post-irradiation perturbation, *e.g.* thermal annealing. When samples whose thermal annealing has been interrupted in a plateau region are crushed or irradiated with a low  $\gamma$ -dose and subsequently annealed at the same temperature, further rapid annealing occurs, thereby providing direct evidence for the effect of dislocations or radiation-produced defects on annealing.<sup>1</sup> The role of inherent crystal defects has been elucidated by Jones and Warren.<sup>2,3</sup>

The deliberate introduction of defects of different kinds into the crystals before neutron activation may affect the transient reactions of the precursor(s)-forming events after the recoil and thus may influence both the initial yields and pseudo-plateau values. Various attempts have been made in the past to find the effect of pre-heat treatment on recoil stabilization in different halogenates.<sup>4</sup> Bearing in mind that the defects produced by a concomitant  $\gamma$ -dose may mask<sup>5</sup> the role played by inherent crystal defects, the present studies were carried out with a low concomitant  $\gamma$ -dose (*ca.*  $172 \text{ rad h}^{-1}$ ) associated with the neutron source. The effect of pre-irradiation thermal treatment on the retention of  $^{128}\text{I}$  and subsequent thermal annealing in  $\text{LiIO}_3$  and  $\text{Cu}(\text{IO}_3)_2$  has been investigated. Such studies should provide information about the role of precursors which are stable in lattices and hence the mechanism of recoil reactions.

### EXPERIMENTAL

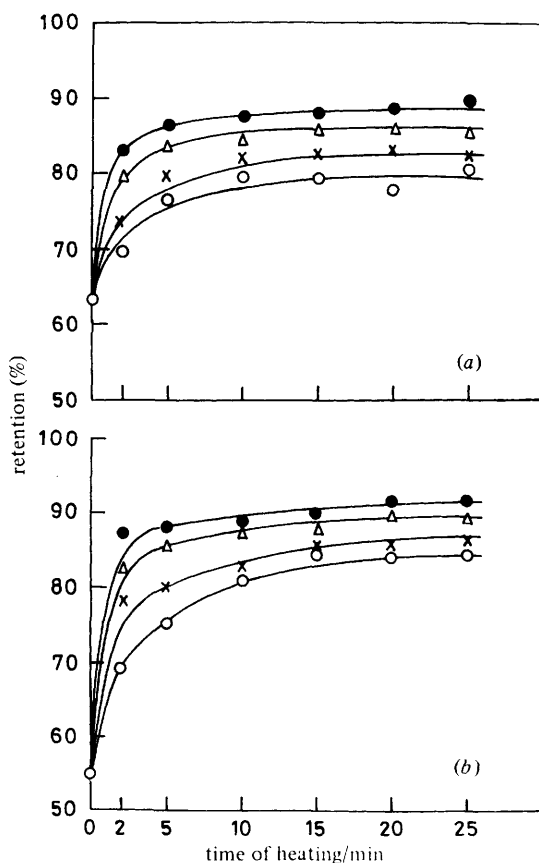
300 mg of reagent-grade  $\text{LiIO}_3$  and  $\text{Cu}(\text{IO}_3)_2$  (anhydrous) (Ventron) targets contained in very thin boron-free sealed glass ampoules were irradiated at ambient temperatures for 3 h by paraffin-thermalized neutrons from a 300 mCi Ra-Be neutron source with an integrated flux of  $3.2 \times 10^6 \text{ neutron cm}^{-2} \text{ s}^{-1}$ . Irradiation at  $-196^\circ\text{C}$  was carried out dipping the neutron source and sample into a Dewar flask containing liquid nitrogen, which was periodically replenished. The whole assembly was surrounded by a paraffin block.

Pre-heat treatments and thermal annealing were performed in an electronically controlled oven maintained to within  $\pm 1^\circ\text{C}$ . Bulk amounts of target materials were pre-heated [ $\text{LiIO}_3$  at  $200^\circ\text{C}$  and  $\text{Cu}(\text{IO}_3)_2$  at  $175^\circ\text{C}$ ] for 1 h and thereafter transferred to a desiccator to cool them slowly. For post-recoil thermal annealing the irradiated  $\text{LiIO}_3$  and  $\text{Cu}(\text{IO}_3)_2$  targets were heated for various lengths of time in an oven maintained at the desired temperature.

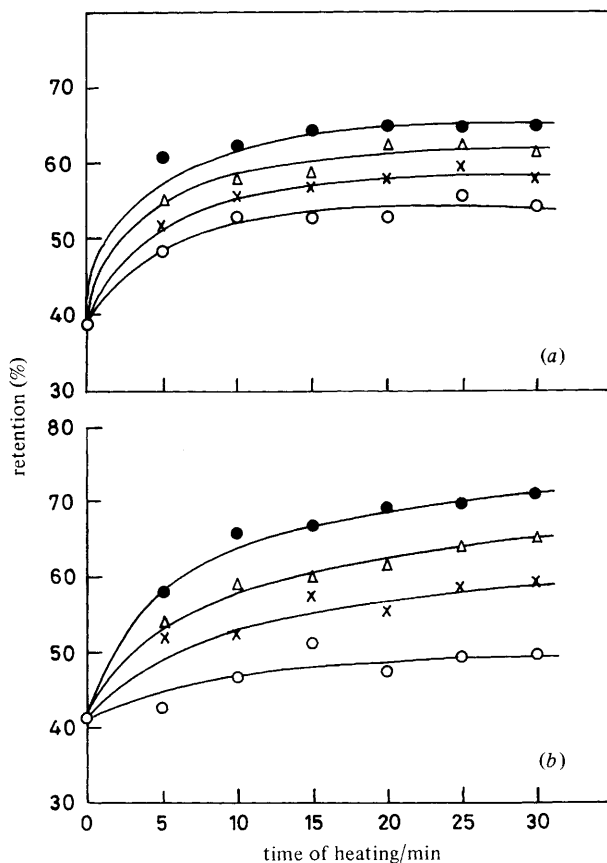
The irradiated materials were dissolved in  $10\text{ cm}^3$  of ammoniacal solution. Chemical analysis was made by the fractional precipitation procedure<sup>6</sup> and the radioactivities of the different fractions as their silver salts were counted with the help of an end-window Geiger-Müller counter under conditions of constant geometry. Retention values were computed after the usual necessary corrections.

## RESULTS

The retention values of  $^{128}\text{I}$  reported are an average of at least three independent experiments with an accuracy of  $\pm 2\%$ . The initial retentions,  $R_0$ , of  $^{128}\text{I}$  in untreated  $\text{LiIO}_3$  and  $\text{Cu}(\text{IO}_3)_2$  are found to be 63.28 and 38.5%, respectively, while for pre-heated targets the respective values are 54.7 and 41.5%. Our value for the initial retention of  $\text{LiIO}_3$  is nearly in agreement with the values of 67 and 61% reported by Cleary *et al.*<sup>7</sup> and Ambe and Saito,<sup>8</sup> respectively.



**Fig. 1.** Annealing isotherms for  $\text{LiIO}_3$  irradiated at room temperature ( $31^\circ\text{C}$ ) by thermal neutrons: (a) untreated, (b) pre-treated (pre-heated at  $200^\circ\text{C}$  for 1 h).  $\circ$ , 125;  $\times$ , 150;  $\triangle$ , 175 and  $\bullet$ ,  $200^\circ\text{C}$ .



**Fig. 2.** Annealing isotherms for  $\text{Cu}(\text{IO}_3)_2$  irradiated at room temperature ( $31^\circ\text{C}$ ) by thermal neutrons: (a) untreated, (b) pre-treated (pre-heated at  $175^\circ\text{C}$  for 1 h).  $\circ$ ,  $70^\circ$ ;  $\times$ ,  $100^\circ$ ;  $\triangle$ ,  $125^\circ$  and  $\bullet$ ,  $150^\circ\text{C}$ .

An inspection of the thermal annealing isotherms (fig. 1 and 2) reveals the usual trend, *i.e.* a fast initial rise followed by temperature-dependent pseudo-plateau regions. At any annealing temperature the plateau values,  $R_\infty$ , for both the pre-heated  $\text{Cu}(\text{IO}_3)_2$  and  $\text{LiIO}_3$  were higher in comparison with the untreated samples. Pre-heating causes a decrease in initial retention for  $\text{LiIO}_3$  whereas the reverse is the case for  $\text{Cu}(\text{IO}_3)_2$ . Pre-heat treatment shifted the time required for saturation from *ca.* 5 to *ca.* 2 min in the case of  $\text{LiIO}_3$  whereas no such trend was observed for  $\text{Cu}(\text{IO}_3)_2$ . The annealing rate constants for both the pre-heated and untreated lithium and copper iodates (tables 1 and 2) were computed from the slope of plots of  $\log(R_\infty - R_t)$  against time of heating,  $R_t$  being the retention at a particular time of the annealing isotherm. The plot revealed the presence of a combination of two apparent first-order processes, one being much faster than the other. The rate constant at a particular temperature is greater for both the untreated samples (*cf.* tables 1 and 2) than the corresponding pre-treated ones. Activation energies were computed from the classical Arrhenius plot (*cf.* tables 1 and 2). The lower activation-energy values obtained for both the pre-heated targets in comparison with the untreated ones indicate the increased propensity for annealing reactions in the pre-heated iodates. We have also refined the value of the

PRE-HEAT TREATMENT STUDY OF RECOIL<sup>128</sup>I IN IODATES**Table 1.** Isothermal annealing data<sup>a</sup> for LiIO<sub>3</sub> irradiated by thermal neutrons at 31 °C [ $R_0 = 63.28 \pm 2\%$  ( $54.70 \pm 2\%$ )]

$T/^\circ\text{C}$	$R_\infty$	slow component		
		$R_\infty - R_0$	$t_{1/2}/\text{min}$	$k/10^{-2} \text{ min}^{-1}$
200	88.5 (91.0)	25.22 (36.30)	2.0570 (3.4555)	$33.69 \pm 0.82$ ( $20.05 \pm 0.83$ )
175	87.0 (89.0)	23.72 (34.30)	2.8795 (3.3284)	$24.07 \pm 0.37$ ( $20.82 \pm 0.58$ )
150	82.5 (87.0)	19.22 (32.30)	3.1134 (4.4239)	$22.26 \pm 0.63$ ( $15.66 \pm 0.28$ )
125	79.5 (84.0)	16.22 (29.30)	3.7010 (4.2066)	$18.72 \pm 0.14$ ( $16.47 \pm 0.27$ )
activation energy <sup>b</sup>				
Arrhenius kinetics			Fletcher–Brown model	
/kcal mol <sup>-1</sup>		/eV	/kcal mol <sup>-1</sup>	/eV
$2.7209 \pm 0.2071$ ( $1.3018 \pm 0.2378$ )		$0.1180 \pm 8.984 \times 10^{-3}$ ( $0.0564 \pm 0.0103$ )	16.36 (14.80)	0.70 (0.64)

<sup>a</sup> Values in parenthesis are for the pre-heated sample. <sup>b</sup> 1 kcal  $\equiv$  4.1840 kJ.

**Table 2.** Isothermal annealing data<sup>a</sup> for Cu(IO<sub>3</sub>)<sub>2</sub> irradiated by thermal neutrons at 31 °C. [ $R_0 = 38.50 \pm 2\%$  ( $41.50 \pm 2\%$ )]

$T/^\circ\text{C}$	$R_\infty$	slow component		
		$R_\infty - R_0$	$t_{1/2}/\text{min}$	$k/10^{-2} \text{ min}^{-1}$
150	65.0 (71.0)	26.5 (29.5)	3.8253 (6.2428)	$18.12 \pm 0.33$ ( $11.10 \pm 0.62$ )
125	61.0 (65.0)	22.5 (23.5)	4.0238 (6.7673)	$17.22 \pm 0.13$ ( $10.24 \pm 0.15$ )
100	58.0 (59.0)	19.5 (17.5)	4.4428 (6.5432)	$15.60 \pm 0.16$ ( $10.59 \pm 0.14$ )
70	54.0 (49.5)	15.5 (8.0)	4.9519 (7.3428)	$13.99 \pm 0.20$ ( $9.44 \pm 0.66$ )
activation energy <sup>b</sup>				
Arrhenius kinetics			Fletcher–Brown model	
/kcal mol <sup>-1</sup>		/eV	/kcal mol <sup>-1</sup>	/eV
$0.9548 \pm 0.0186$ ( $0.5043 \pm 0.0659$ )		$0.0414 \pm 8.069 \times 10^{-4}$ ( $0.0218 \pm 2.859 \times 10^{-3}$ )	10.12 (7.60)	0.43 (0.32)

<sup>a</sup> Values in parenthesis are for the pre-heated sample; <sup>b</sup> 1 kcal  $\equiv$  4.1840 kJ.

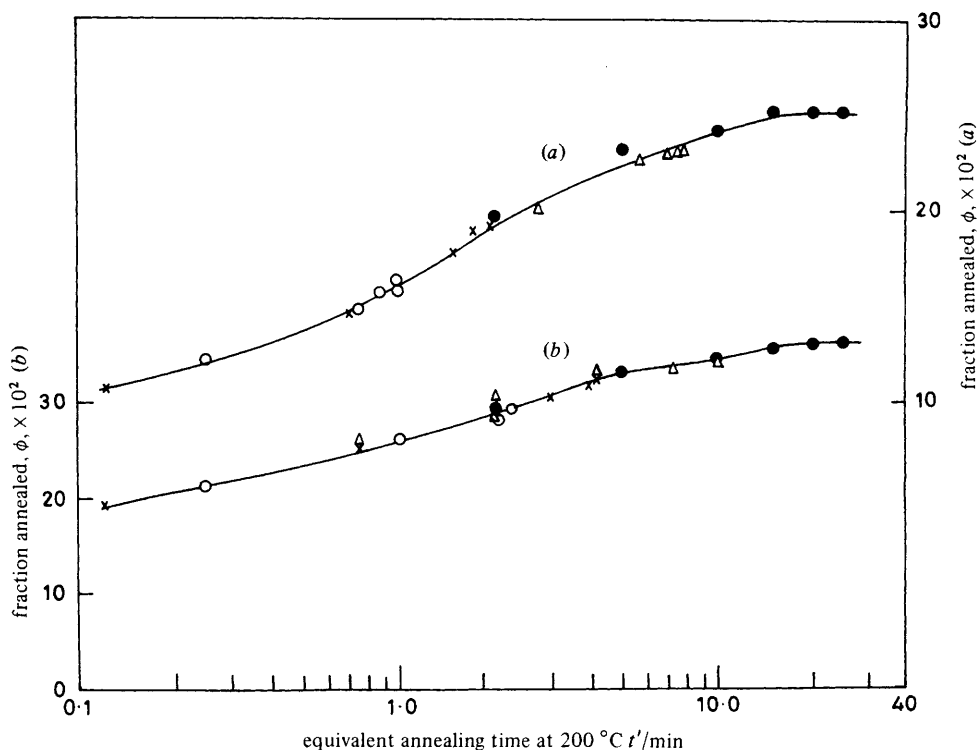


Fig. 3. Fletcher-Brown composite annealing curves for various recoil fragments in ( $n, \gamma$ )-irradiated  $\text{LiIO}_3$ : (a) untreated, (b) pre-treated (pre-heated at  $200^\circ\text{C}$  for 1 h).  $\circ$ ,  $70^\circ$ ;  $\times$ ,  $100^\circ$ ;  $\Delta$ ,  $125^\circ$  and  $\bullet$ ,  $150^\circ\text{C}$ .

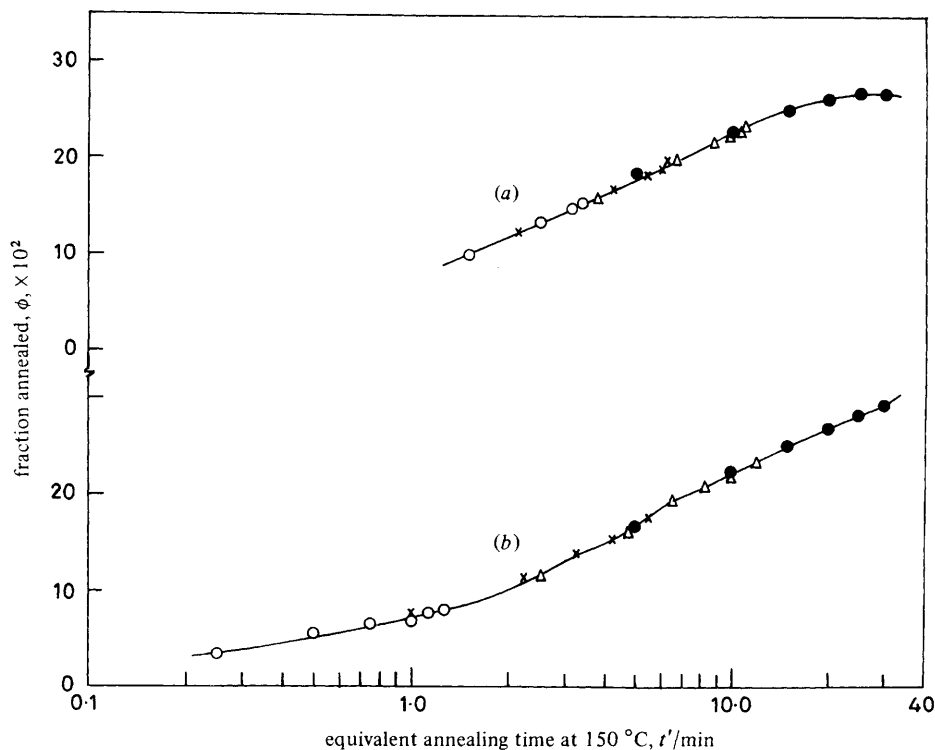
annealing rate constant and energy of activation by a least-squares technique by which the probable associated errors involved in these parameters were also calculated (*cf.* tables 1 and 2). These trends have been confirmed by fitting our annealing data to the Fletcher-Brown<sup>9</sup> model. The composite annealing curves are shown in fig. 3 and 4. Activation energies were obtained from the slope of a linear plot of  $\log t'/t$  (where  $t'$  is the equivalent annealing time) against  $1/T$  (*cf.* tables 1 and 2).

## DISCUSSION

The low initial retention values observed in the present work for  $\text{Cu}(\text{IO}_3)_2$  ( $28.46 \pm 2\%$ ) and  $\text{LiIO}_3$  ( $39.5 \pm 2\%$ ) activated at  $-196^\circ\text{C}$  compared with ambient-temperature irradiation values show that intrinsic thermal annealing is occurring even at lower temperatures. Since radiation annealing is thermally activated, the effect of the  ${}^6\text{Li}(n, \alpha)\text{T}$  reaction is blocked at  $-196^\circ\text{C}$ . Moreover, since retention values at  $-196^\circ\text{C}$  are too high to be accounted for by the failure of bond rupture during the initial act of recoil, the reaction should be diffusion-controlled second-order intrinsic annealing as suggested by Andersen:<sup>10</sup>



Fast intrinsic annealing might be the reason for the inability of previous workers to obtain evidence for  $\text{IO}_2^-$  ion formation in irradiated iodates.

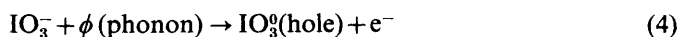


**Fig. 4.** Fletcher-Brown composite annealing curves for various recoil fragments in  $(n, \gamma)$ -irradiated  $\text{Cu}(\text{IO}_3)_2$ : (a) untreated, (b) pre-treated (pre-heated at  $175^\circ\text{C}$  for 1 h).  $\circ$ ,  $125^\circ\text{C}$ ;  $\times$ ,  $150^\circ\text{C}$ ;  $\triangle$ ,  $175^\circ\text{C}$  and  $\bullet$ ,  $200^\circ\text{C}$ .

The initial retention data in the present work may be explained by considering the roles played by inherent crystal defects in direct and competitive oxidation and reduction. Pre-heat treatment increases the initial retention of  $\text{Cu}(\text{IO}_3)_2$  from  $38.5 \pm 2$  to  $41.5 \pm 2\%$  due to the removal of reducing defects which would otherwise stabilize recoil iodine in the reduced form as in the untreated case. Arnikaar *et al.*<sup>1</sup> have also found an increase in the retention of  $^{128}\text{I}$  on pre-heating  $\text{HIO}_3$ . However, the decrease in the initial retention for  $\text{LiIO}_3$  from  $63.28 \pm 2$  to  $54.7 \pm 2\%$  on pre-heat treatment may be ascribed to the fact that the reducing defects are situated at deep trapping levels and are unable to stabilize the recoil atom in its reduced form. On pre-heat treatment they are either promoted to less deep trapping levels to stabilize recoil iodine in its reduced state or are promoted to the conduction band and are annihilated with the positive holes which would otherwise stabilize, as in the untreated case, the recoil atom in a higher-valent form. Thus both possibilities permit a decrease in the initial retention of  $\text{LiIO}_3$  on pre-heat treatment.

Andersen<sup>12</sup> has proved by thermoluminescence and electrical-conductivity measurements that recoil annealing is an electronic phenomenon which originates through the release of charge carriers. In an irradiated crystal the number of defects is normally far greater than the number of recoil atoms. If thermal annealing were due to diffusion of ionic species in the rate-determining step its activation energy would be in the range 1–2 eV.<sup>13</sup> In fact the activation energies in all the present investigations are less than this range, and we agree with the defect mechanism proposed by Lin and

Wiles<sup>14</sup> involving exciton capture at the recoil site in the rate-determining step. The following mechanism is proposed:



The production and annihilation of holes and electrons [reaction (4)] would be an important step in thermal annealing. A sequence of reactions (6), (6), (7), (6), (6), (7) *etc.* would give rise to retention in the parent form.

Our data on thermal annealing may be further explained on the basis of the exciton mechanism. Since the defects produced by internal-conversion phenomena (as the recoil atom dissipates its electronic and translational excitation energy) and self-radiolysis in both  $\text{LiIO}_3$  and  $\text{CuIO}_3$  samples and by  ${}^6\text{Li}(n, \alpha)\text{T}$  in  $\text{LiIO}_3$ <sup>15</sup> are common to both pre-heated and untreated targets we can assume that, by virtue of annealing-out inherent crystal defects in pre-heat treatments, the lattice of a pre-heated sample is more ordered than in the untreated case. Thus the probability that excitons reach recoil iodine sites in order to deposit their energy and thus allow annealing to occur in pre-heated samples is greater than in the more disordered untreated iodates. In untreated samples, owing to the relatively large number of inherent crystal defects some of the excitons produced are stopped or captured and are thus not able to reach the recoil sites. We have obtained (as expected from the exciton mechanism) higher pseudo-plateau values and lower values of the activation energy for both pre-heated iodates than for the untreated ones. However, we face a difficulty in explaining the lower value of the annealing rate constant for both pre-heated targets than for the corresponding untreated ones. The apparent discrepancies may be due to the dangers of formally applying Arrhenius kinetics to describe processes in solid systems where the compensation effect may apply.<sup>16</sup> Such an effect reveals that the pre-exponential factor in the Arrhenius equation varies exponentially with the energy of activation. Furthermore, a process cannot be described as being strictly unimolecular or first order when the amount of material reacting is a function of the temperature at which the experiment is conducted.

Fletcher and Brown<sup>9</sup> showed that annealing should depend upon a factor  $t/\tau$  where  $\tau$  is the average jump time and  $t$  is the time of isothermal annealing, provided that the vacancy moves through the crystal by jumping to an adjacent side. As  $\tau$  entirely governs the temperature dependence of annealing, the isothermal annealing data at different temperatures can be combined to obtain (*cf.* fig. 3 and 4) a single curve of equivalent annealing at a single reference temperature by multiplying the time scale of each isothermal curve by an appropriate factor. The resultant composite annealing curves may be fitted by unimolecular, bimolecular or error-function expressions or any combination of these. The gradations in activation energy for the untreated and pre-heated targets are found to be similar from both the Fletcher–Brown model and Arrhenius kinetics, which indicates the success of the present analysis.

Thus it can safely be concluded that the annealing propensity for recoil stabilisation

is enhanced on pre-heating  $\text{Cu}(\text{IO}_3)_2$  and  $\text{LiIO}_3$  in accordance with the exciton mechanism, bearing in mind that plateau values are greater for the pre-heated iodates than for those that are untreated.

We thank the Head of the Department of Chemistry, Banaras Hindu University for providing the necessary facilities, the C.S.I.R. for the award of a junior research fellowship to Archita Patnaik and the Ministry of Education, New Delhi for a general cultural scholarship to D. P. Wagley. We also thank Drs R. N. Singh and R. A. Singh for useful discussions.

- <sup>1</sup> T. Andersen and A. G. Maddock, *Nature (London)*, 1962, **194**, 371.
- <sup>2</sup> C. H. W. Jones and J. L. Warren, *J. Inorg. Nucl. Chem.*, 1968, **30**, 2289.
- <sup>3</sup> C. H. W. Jones and J. L. Warren, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2119.
- <sup>4</sup> C. W. Owens, in *Chemical Effects of Nuclear Transformations in Inorganic Systems*, ed. G. Harbottle and A. G. Maddock (North Holland, Amsterdam, 1979), p. 145.
- <sup>5</sup> I. G. Campbell, *Radiochim. Acta*, 1968, **9**, 7.
- <sup>6</sup> G. E. Boyd and Q. V. Larson, *J. Am. Chem. Soc.*, 1969, **91**, 4639.
- <sup>7</sup> R. E. Cleary, W. H. Hamill and R. R. Williams, *J. Am. Chem. Soc.*, 1952, **74**, 4675.
- <sup>8</sup> F. Ambe and N. Saito, *Radiochim. Acta*, 1970, **13**, 105.
- <sup>9</sup> R. C. Fletcher and W. L. Brown., *Phys. Rev.*, 1953, **92**, 585.
- <sup>10</sup> T. Andersen, *Experimental Investigations of Chemical Effects Associated with Nuclear Transformations in some Inorganic Solids* (Institute of Chemistry, University of Aarhus, Denmark, 1968), chap. 4, p. 65.
- <sup>11</sup> H. J. Arnkar, V. G. Dedgaonkar and K. K. Shrestha, *J. Univ. Poona, Sci. Technol.*, 1970, **38**, 177.
- <sup>12</sup> T. Andersen and K. Olesen, *Trans. Faraday Soc.*, 1965, **61**, 781.
- <sup>13</sup> G. Harbottle and N. Sutin, in *Advances in Inorganic Chemistry and Radio Chemistry*, ed. H. J. Emeleus and A. G. Sharpe (Academic Press, New York, 1958), vol. 1, p. 279.
- <sup>14</sup> Y. C. Lin and D. R. Wiles, *Radiochim. Acta*, 1979, **13**, 43.
- <sup>15</sup> G. E. Boyd and T. G. Ward, *J. Phys. Chem.*, 1964, **68**, 3809.
- <sup>16</sup> V. Talroze, *Proc. Chem. Effect of Nuclear Transformations* (I.A.E.A., Vienna, 1961), vol. 1, p. 464.

(PAPER 3/284)