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Kinetics of Isothermal Annealing of Chlorite in γ-Irradiated Lanthanum Chlorate Hexahydrate and Lanthanum Chlorate Monohydrate Crystals

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Kinetics of thermal annealing of chlorite in the γ-radiolysis of lanthanum chlorate hexahydrate crystals and lanthanum chlorate monohydrate crystals has been studied at different temperatures in the range of 85–155°C. The chlorite is found to anneal by the combination of first and second order processes. The former being fast virtually reaches completion within a few hours. This process is then followed by a second order process which is observed to be a slow process. The annealing pattern of chlorite in both the systems is observed to be same. A suitable mechanism of annealing process is proposed.

INTRODUCTION

Although a considerable amount of work has been carried out on the thermal annealing of damage fragments formed in chlorates[1–3], thermal annealing of chemical radiation damage in rare earth chlorates has not been studied in sufficient details. Lanthanum chlorate hexahydrate and lanthanum chlorate monohydrate appear to be suitable systems to study the influence of water of crystallisation on the isothermal annealing pattern of the chlorite fragments. In continuation to our earlier work[4, 5], we report here the annealing of chlorite in γ-irradiated lanthanum chlorate hexahydrate and lanthanum chlorate monohydrate as it is seen that total dehydration is not possible.

EXPERIMENTAL

Lanthanum chlorate hexahydrate was synthesised by addition of lanthanum carbonate to ice-cold chloric acid solution. It was dried in a vacuum desiccator. It was observed that still one water molecule remained in the crystal lattice. Hence the same $La(ClO_3)_3 \cdot H_2O$ was taken for further study.

The dry samples were irradiated with γ-rays from a ^{60}Co source to a total dose of 40 Mrad at a dose rate of 0.46 Mrad/h. The irradiated samples were annealed in a thin-walled glass tube in a thermostat maintained to within ± 0.5°C the desired temperature. The estimations of chlorite and hypochlorite were carried out iodometrically[6]. Chlorite in the sample was estimated iodometrically[7] after destroying the hypochlorite by the addition of KCN. The detailed analytical procedure for the above mentioned species was described earlier[1]

RESULTS AND DISCUSSION

The buff colour induced by γ-irradiation disappeared during the thermal annealing. The irradiated samples were subjected to isothermal annealing for different time intervals. The fraction annealed is defined as $\phi = X/a$, where a is the initial amount of micromoles of the particular species per gram of the sample and X is the amount of species changed by annealing at time t. Comparative results of $La(ClO_3)_3 \cdot 6H_2O$ and $La(ClO_3)_3 \cdot H_2O$ are observed to be interesting. Usual annealing characteristic is observed for all the temperatures for chlorite annealing in $La(ClO_3)_3 \cdot 6H_2O$ and in $La(ClO_3)_3 \cdot H_2O$. After the loss of most of the water of crystallisation which is probably at above 100°C the lattice mobility increases. It brings about rapid initial recovery even on long heating.

The fraction annealed in both the cases increases rapidly in the beginning and slows down later (Figs. 1 and 2). The fraction annealed ϕ in the first 10 h annealing for ClO_2^- in lanthanum chlorate hexahydrate was 0.825 and it is increasing only to 0.90 after 35 h of heating at 155°C. In the case of lanthanum chlorate monohydrate these values are 0.610 and 0.685 respectively. These results indicate

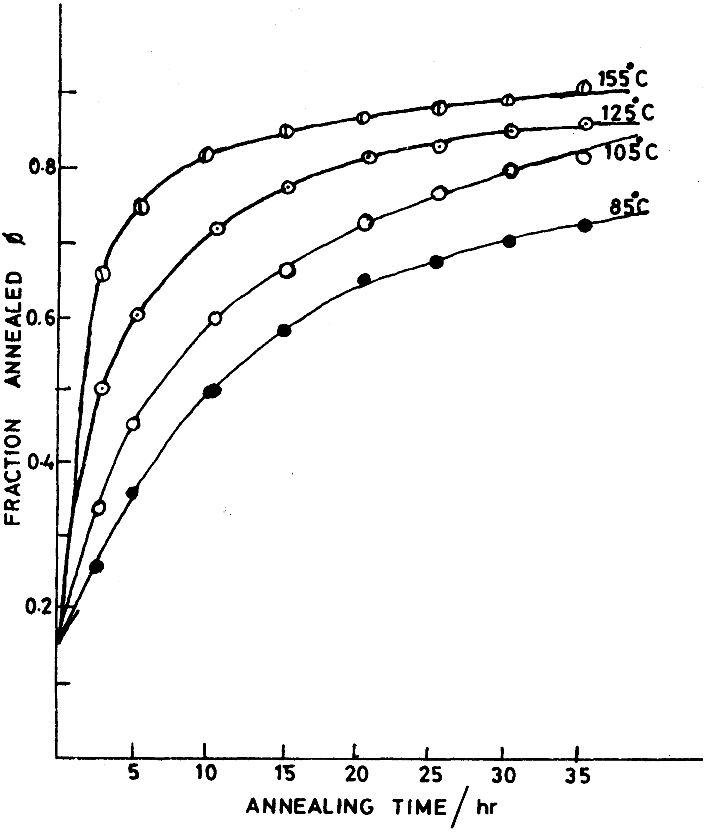

Fig. 1. Fraction annealed with time of annealing in $La(ClO_3)_3 \cdot 6H_2O$ (Chlorite)

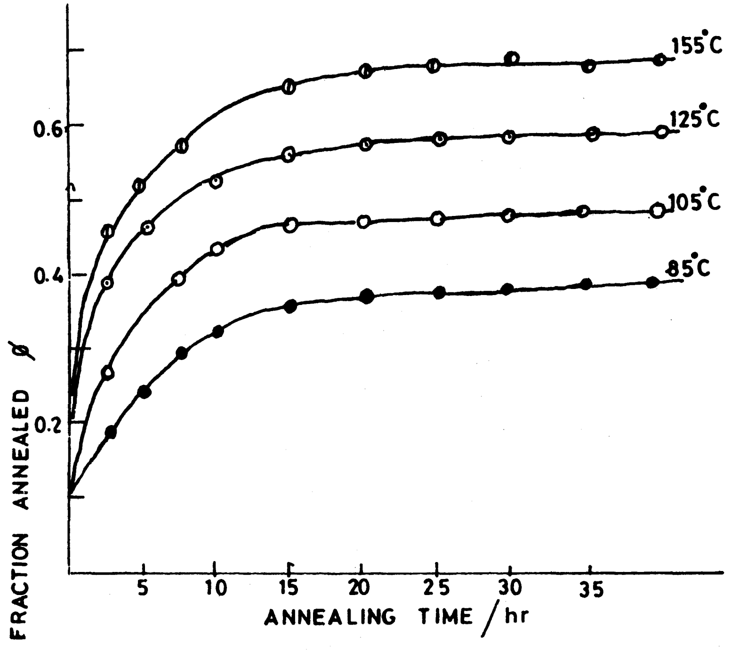

Fig. 2. Fraction Annealed with time of annealing in $La(ClO_3)_3{\cdot}H_2O$ (Chlorite)

that the fraction annealed ϕ values for all the temperatures are always higher in the case of hexahydrate than corresponding values in monohydrate form. The hydrated calcium chlorate is observed to be less susceptible towards radiation decomposition as compared to monohydrate form[2].

After partial dehydration also a separate plateau value is obtained for each temperature. Lattice mobility liberates the damaged oxygen and a portion of this recombines with the chlorine-bearing fragment ClO_2^- to reform chlorate. Since the lattice mobility also leads to the escape of radiolytic oxygen from the crystals, very little annealing occurs further.

The kinetics of isothermal annealing of the damaged ClO_2^- in lanthanum chlorate hexahydrate and lanthanum chlorate monohydrate was explored by conventional method at different temperatures ranging from 85 to 155°C for various time intervals. In the case of inverse of the chlorite concentration as a function of time for both the systems studied linear relation is obtained except for the initial period of annealing. From the Arrhenius plots the energy of activation for the second order process of annealing of chlorite is found to be 11.9 and 24.54 KJ mol^{-1} respectively for hexahydrate and monohydrate forms.

In the initial stage of annealing the difference between the total chlorite and the amount recombined by the second order processes has been determined for different temperatures. This residual ClO_2^- which does not anneal by the second order process is found to obey the first order rate law (Figs. 3 and 4). The rate constants obtained for first and second order processes are following the usual pattern.

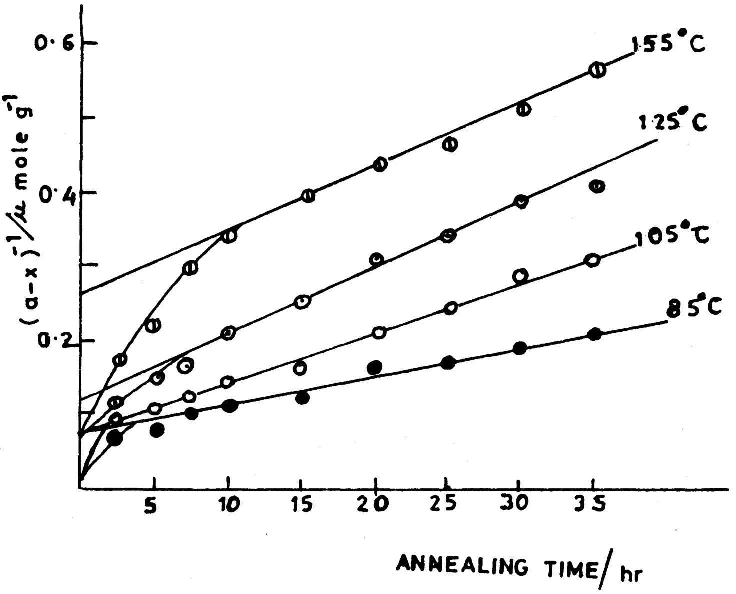

Fig. 3. Second order plot for the annealing of chlorite in $La(ClO_3)_3 \cdot 6H_2O$

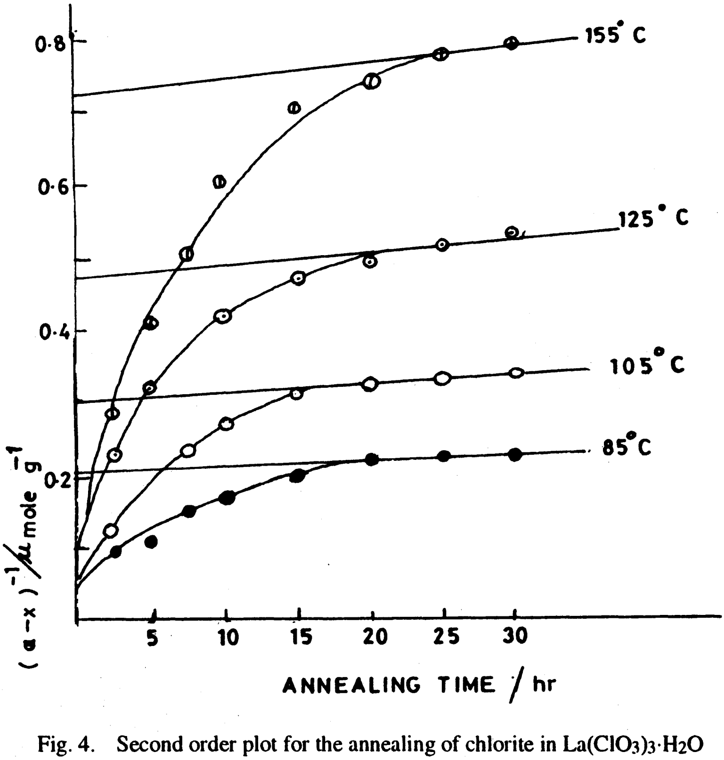

Fig. 4. Second order plot for the annealing of chlorite in $La(ClO_3)_3 \cdot H_2O$

The activation energies obtained from Arrhenius plot for the first order processes are found to be 15.6 and 3.06 KJ mole^{-1} for hexahydrate and monohydrate systems respectively. The overall annealing of chlorite is found to be a combination of first and second order processes. Many workers have reported such a combination of the two rate orders for the annealing of chlorite in various chlorate systems. The identity and the yields of various fragments/ionic species as Cl^-, ClO^-, ClO_2^-, ClO_4^-, O_3^- and radicals as ClO, ClO_2, ClO_3 besides molecular oxygen have been well established. It is reasonable to assume that the chlorine containing oxygen fragments remains in lattice positions and free oxygen gets trapped in the interstitial positions close to the damage site or may diffuse into the crystal matrix. In the annealing process, these latter species are remobilised and react with the charged fragments Cl^-, ClO^- and ClO_2^-.

It is seen that the chlorite is annealed by a combination of first and second order processes as revealed by the kinetic data. The first order process of the annealing of chlorite is a combination of close spaced fragments in the highly damaged region

$$ClO_2^- + O \rightarrow ClO_3^- \qquad (1)$$

while second order process may involve a random reaction

$$ClO_2^- + O_2 \rightarrow ClO_3^- + O \qquad (2)$$

or the second order reaction may be presented by

$$2ClO_2^- + O_2 \rightarrow 2ClO_3^- \qquad (3)$$

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