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Disappearance of voids in lithium fluoride single crystals

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The disappearance of radiation-induced voids in LiF single crystals is investigated. The activation energy of the process is determined by studying the temperature dependence of the rate of disappearance of individual needle-shaped voids. The value obtained is in good agreement with the figures reported for F^- ion diffusion. On the basis of kinetic studies it is shown that radiation-induced voids contain gas under low pressure.

1. Introduction

If a vacancy supersaturation is created in a crystal, nucleation and growth of vacancy condensates will begin. The formation of voids in the crystal is connected with an increase in the energy of the system and therefore at high temperatures the voids tend to disappear. Their size decreases via vacancy emission, i.e. atoms are transported from sources towards the surface of the voids by vacancy migration. The process is diffusion-controlled and the local vacancy equilibrium is maintained at all boundary surfaces. The rate of disappearance of a spherical void of radius r is given by the expression [1]:

$$\frac{\mathrm{d}r}{\mathrm{d}t} = \frac{D}{\epsilon r}\left\{\exp\left[\left(\frac{2\gamma}{r} - p\right)\frac{\Omega}{kT}\right] - 1\right\} \quad (1)$$

where D is the effective diffusion coefficient, Ω the atomic volume, ϵ a correlation factor, p the pressure of the internal gas and γ the surface energy.

In the case of ionic crystals where two types of vacancies coexist, the effective diffusion coefficient D will depend on the diffusion coefficients of the two types, i.e.

$$D = \frac{2D_+D_-}{D_+ + D_-}. \quad (2)$$

The present paper deals with voids created as a consequence of coagulation of radiation-induced vacancies in LiF. Lithium fluoride seemed particularly appropriate for such studies since the very large capture cross-section of Li^6 with respect to thermal neutrons brings about a high vacancy supersaturation upon irradiation with moderate doses.

Irradiation-induced voids in LiF were originally observed by Senio [2], Smallman and Willis [3] and by Gilman and Johnston [4]. The voids are crystallographic forms. Indeed, only cubic forms are present in the growth forms. Their sizes reach several microns (Fig. 1).

Studies on the healing of voids in LiF have also been performed by Geguzin *et al.* [5]. These authors consider that the transport of matter takes place only at the corners (owing to the perfection of the faces which build up the pore) and that this transport process rather than the transfer of matter along the faces determines the healing kinetics. Under these assumptions the pores should retain their shape during the process. In the case of needle-shaped pores (of dimensions l_x, l_y, l_z) a shortening is predicted which follows the law

$$l_z = l_{z_0} - \frac{D\Omega\gamma}{kTl_xl_y}t. \quad (3)$$

Needle-shaped pores in LiF were experimentally investigated by Geguzin *et al.* [5]. The pores were formed after an irradiation up to 10^{17} neutrons cm^{-2} and their disappearance was studied in the temperature interval 600–760° C for comparatively short times. From the rate of shortening of different pores at each temperature, an average diffusion coefficient was determined and from its temperature dependence an activation energy of

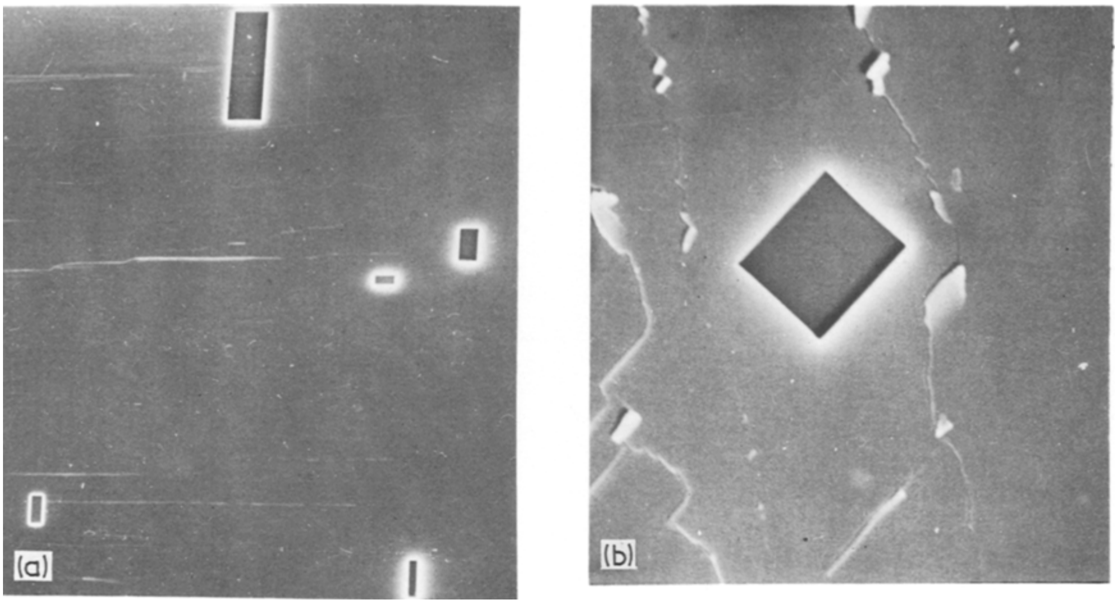

Figure 1 SEM micrographs of cross-section of a growing needle shaped pore,: (a) 2500 X ; (b) 8300 X.

diffusion 45 ± 3 kcal mol^{-1} (1.95 ± 0.13 eV) was obtained.

By studying the kinetics of disappearance of needle-shaped voids in LiF at wider experimental conditions (two different doses, longer annealing times, higher temperatures) the present work aims at elucidating the processes which lead to the healing of radiation-induced pores in ionic crystals.

2. Experimental

The crystals were irradiated in the Sofia Research nuclear reactor up to doses 10^{16}–10^{17} neutrons cm^{-2}. Samples with sizes of the order of millimetres, cleaved from large LiF single crystals along the {1 0 0} faces, were used. The investigations were carried out in the temperature interval 700–836° C (the melting point of LiF is 845° C). The pores were observed and measured in transmitted light and by a scanning electron microscope.

3. Results

3.1. Needle-shaped pores in crystals irradiated up to doses of 10^{16} neutrons cm^{-2}

The disappearance of the pore brings about the predicted linear change in its length (Fig. 2) with an apparently constant cross-section (Fig. 3). The different rate of shortening of the two illustrated pores is due to their different cross-sections. From Expression 3 it can be seen that in order to determine the diffusion coefficient it is necessary to know all three dimensions of the pore. Unfortunately, we have no means of determining the depth and, in the case of very thin pores, a diffraction contour appears which hinders the accu-

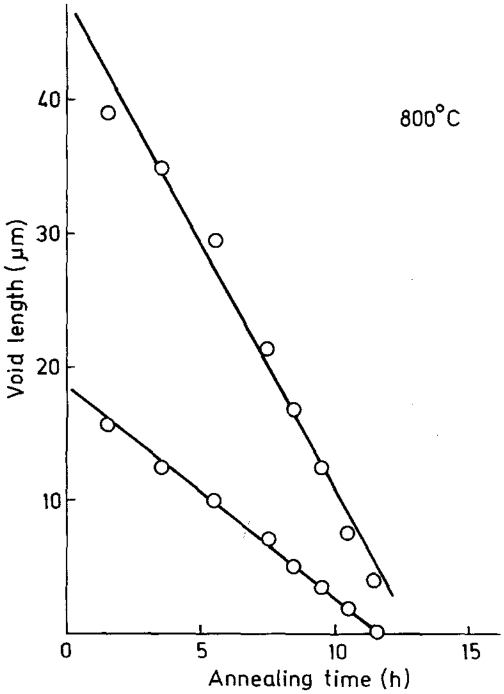

Figure 2 Length of the needle-shaped voids as a function of annealing time at 800° C.

Figure 3 Optical micrograph of a disappearing needle-shaped void at 800° C: (a) 0 h; (b) 8 h.

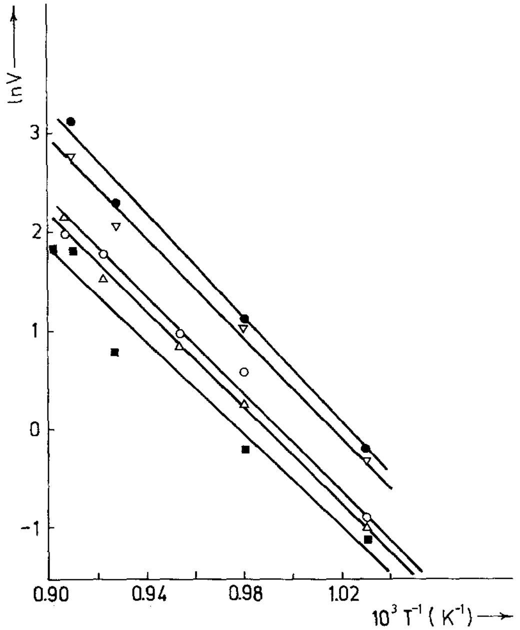

Figure 4 Dependence of ln V on $1/T$ for needle-shaped voids in crystals irradiated with doses of up to 10^{16} neutrons cm^{-2}.

rate measurement of their widths. In order to obviate the effect of these inaccuracies the behaviour of the individual voids was studied at five different temperatures in the range 700–836° C and the dependence $\ln V = f(1/T)$ was plotted for each individual pore where V is the the velocity of disappearance. The activation energy of the process of disappearance of the pores was determined from the slope of the straight line (Fig. 4). In plotting the logarithmic dependence, the quantities l_x and l_y, which cannot be determined accurately, do not affect the slope of the straight line and consequently the activation energy is not affected either. In this way the determination of the activation energy of 25 pores in two crystals yielded the average activation energy of the process of disappearance of the pores. Its value is 2.13 ± 0.15 eV which is in good agreement with the figures reported in the literature for the activation energy of the F^- diffusion (2.2 eV according to Eisenstadt by nuclear magnetic relaxation [6] and 2.09 ± 0.08 eV by Narayan Rao and Ruoff [7] from high temperature creep of LiF) and slightly higher than Geguzin's results [5].

3.2. Needle-shaped pores in crystals irradiated with doses of up to 2×10^{17} neutrons cm^{-2}

At these doses the shape of the $l(t)$ dependence is no longer linear, as observed in the crystals irradiated with smaller doses and in Geguzin's paper [5]. At a given pore size, which is larger at higher temperature, its rate of disappearance begins to decrease (Fig. 5).

In the papers of Kubo [8] and Gilman and Johnston [4] the question about the content of the radiation-induced voids has not been unambiguously answered. The experiments of these authors show that the cavities are either filled with gas or are actual voids. However, it is hard to make a choice between these two possibilities. The observed decrease of the disappearance rate in the small size range upon increase in the irradiation dose finds its logical explanation if one assumes that the voids are filled with gas. Probably this is F_2 and not He directly produced by the nuclear reaction. It is indeed known (Felix [9]) that noble gases rapidly leave the crystals at elevated temperatures. The kinetic studies performed do not make it possible to identify the gas.

In order to explain these phenomena we shall use Expression 1. The gas pressure in the void can be connected with its size and the number of gas atoms in the void, n. Then the formula can be written in the following way

$$\frac{\mathrm{d}r}{\mathrm{d}t} = \frac{D}{\epsilon r}\left\{\exp\left[\left(\frac{2\gamma}{r} - \frac{3kTn}{4\pi r^3}\right)\frac{\Omega}{kT}\right] - 1\right\}. \quad (5)$$

When the void is not spherical r has the meaning of an "effective radius" connected with the volume in the following way

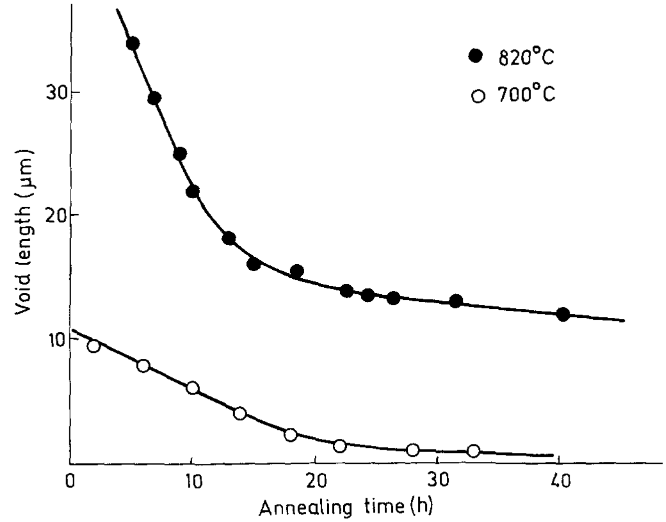

Figure 5 Annealing curves of needle-shaped voids in LiF crystals irradiated with doses of up to 10^{17} neutrons cm^{-2}.

$$r = \sqrt[3]{\left(\frac{3V}{4\pi}\right)}. \qquad (6)$$

Obviously the gas pressure will begin to affect substantially the rate of disappearance of the void when the two components of the exponential term become comparable. At a given n (depending on the irradiation dose) this takes place at larger void sizes when the temperature is raised (Fig. 5). At a fixed temperature, the sizes at which the pressure begins to exert an effect are larger at larger irradiation doses. Such a compensation should begin also at small irradiation doses, but this would take place at sizes invisible under the optical microscope.

A rough estimate of the pressure which should begin to exert a noticeable effect yields, under our experimental conditions, a value of a few tenths of an atmosphere which is in good agreement with the existing hypotheses [4, 8] concerning the content of the pores.

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