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Ionic conductivity and stored energy in gamma-irradiated NaF

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Abstract. Gamma irradiation reduces the ionic conductivity of NaF single crystals due to the decrease of the extrinsic cation-vacancy concentration. Irradiation also makes the binding energy of the impurity–cation-vacancy dipole higher than that for unirradiated samples. The thermal recovery of these effects takes place between 270 and 600 °C, which is the range in which the main stored-energy release peak occurs. The energy released below 600 °C, when the irradiated sample is heated, is 1.9×10^{20} eV g⁻¹. It is proposed that these processes are related to radiation-induced divacancies, that behave as traps for the impurity–cation-vacancy dipoles.

It is well known that the ionic conductivity of alkali halides is mainly due to the motion of cation vacancies, at least between 20 and 600 °C [1]. Below about 150 °C (the so-called region IV), the extrinsic cation vacancies compensating aliovalent impurities are bound to these, forming impurity–vacancy dipoles. Above this temperature (region III), these begin to dissociate, the released cation vacancies enhancing the ionic conductivity. At around 250 °C all dipoles are already broken and the extrinsic cation vacancies are the majority carriers between 250 and 400 °C (region II). Above 500 °C (region I or the intrinsic region) the thermally generated cation vacancies dominate. Each of these regions has a different activation energy, leading thus to a straight line with a different slope when $\log \sigma T$ (σ being the conductivity and T the absolute temperature) is plotted against $1/T$ [2, 3]. So, the slope in region II gives the cation-vacancy migration energy (E_m) while the activation energy in region III is equal to E_m plus half the dipole binding energy (E_b). It has been shown that ionizing irradiation induces a decrease in the ionic conductivity of these materials [4–10] between room temperature and 600 °C. The generation of some type of damage, which inhibits the impurity–cation-vacancy dipole dissociation, has been found to be responsible for this effect in KCl and NaCl [7, 10]. On the other hand, stored-energy and ionic thermocurrent measurements have led to the conclusion that divacancy clusters and dislocations are created by ionizing irradiation [11–13]; these defects are closely related to the radiation-induced effects on the ionic conductivity of these alkali halides. The above-explained results were obtained for samples from different batches. To get a clearer understanding of these processes it is useful to make parallel-conductivity and stored-energy measurements on gamma-irradiated samples from the same batch. This has been done in

this work. Moreover NaF has been chosen, representing a change of the halide ion with respect to KCl and NaCl, in order to construct a more complete set of data on alkali halides and to check that the observed effects are general for this kind of material. The results obtained support our previous conclusions.

Samples measuring $15 \times 15 \text{ mm}^2$ and about 1.5 mm thick, for the ionic conductivity measurements, and of size $4 \times 1.5 \times 1.5 \text{ mm}^3$, for the stored-energy measurements, were cut from a nominally pure Harshaw single-crystal block. They were annealed in vacuum for four hours at $700 \text{ }^\circ\text{C}$ and then cooled down to room temperature at $10 \text{ }^\circ\text{C min}^{-1}$. It was checked that consecutive ionic conductivity measurements between 20 and $620 \text{ }^\circ\text{C}$ of some of the samples annealed in this way give the same values at each temperature, therefore indicating that, with this annealing procedure, the initial states of the samples are always the same. The samples for use in the ionic conductivity measurements were irradiated using a ^{60}Co gamma source at 0.15 Gy s^{-1} up to $3 \times 10^6 \text{ Gy}$, while those for use in the stored-energy measurements were irradiated at 13.5 Gy s^{-1} up to $5.6 \times 10^7 \text{ Gy}$. The reason for exposing these latter samples to a much higher dose than the others is that the stored-energy technique is much less sensitive than the ionic conductivity method in detecting radiation-induced effects. It has however been observed for KCl and NaCl that the processes that affect the ionic conductivity are present for any irradiation dose, at least in the range from tens of Gy to tens of MGy [7, 10].

The ionic conductivity measurements were performed with a Keithley 610 C electrometer in a standard circuit. The experimental set-up has been described elsewhere [14]. The samples were polarized with a dry battery and the voltage (12 V) was selected to provide an Ohmic regime. A Setaram M-5 differential thermal analyser was used for the stored-energy measurements. The device had been calibrated as regards both temperature and energy by melting known amounts of pure metals and alkali halides. A heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ was employed in both types of measurement.

The ionic conductivity of an unirradiated sample and that of a gamma-irradiated one are shown in figure 1. It can be clearly seen that gamma irradiation induces a decrease in the ionic conductivity over the whole temperature range between 20 and $620 \text{ }^\circ\text{C}$. A second heating run for an irradiated sample leads to the same conductivity curve as that for an unirradiated one. The thermal recovery of this radiation-induced effect has been studied by performing, for a previously irradiated sample, conductivity measurements in consecutive heating runs, each time up to a temperature higher than that reached in the previous run (that is, using a pulsed thermal annealing method). Some of these results are also plotted in figure 1. As the temperature reached in these partial annealings becomes higher, the ionic conductivity approaches that of an unirradiated sample. From the $\log \sigma T$ against $1/T$ plots, the temperature evolution of the cation-vacancy concentration has been obtained for each heating run. To do this, the vacancy mobility was calculated from the expression

$$\mu = (4ea^2\nu/kT) \exp(-E_m/kT) \quad (1)$$

where all symbols have their usual meaning [1], with $\nu = 7 \times 10^{12} \text{ s}^{-1}$ [15] and $E_m = 0.86 \text{ eV}$ [16]. In this way, for each $\log \sigma T$ versus $1/T$ curve, one has a curve for the free-cation-vacancy concentration against the temperature. As for other alkali halides [7, 10], the vacancy concentration at any temperature for an irradiated sample is lower than that for an unirradiated one, and it increases as the pulsed thermal annealing proceeds. From these curves, the thermal recovery behaviour can be well studied by plotting the vacancy concentration at a given temperature against the annealing temperature, this being that reached in the previous heating run. The results are shown in figure 2, in which it can be seen that a wide recovery step for the cation-vacancy concentration occurs between 270

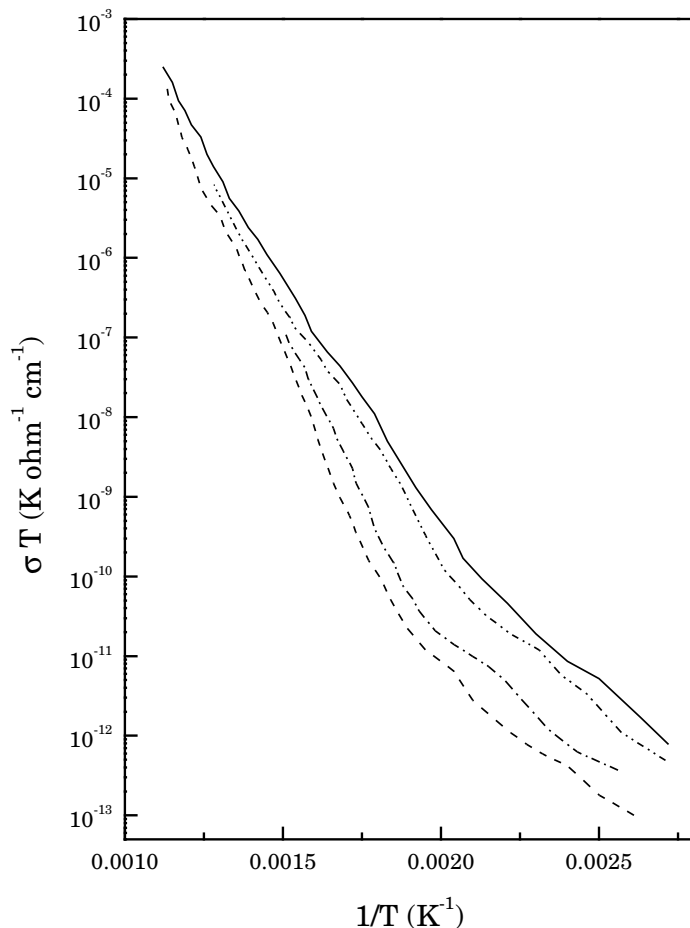


Figure 1. The ionic conductivity of an unirradiated NaF sample (—), of a sample gamma irradiated up to 3×10^6 Gy (---), and of a sample irradiated and annealed up to 330 (— · —) and 450 °C (— · · —) prior to the measurement.

and 600 °C. Some thermal annealing of the radiation-induced effects might also take place below 270 °C.

As stated before, the dipole binding energy (E_b) can be calculated from the slope for region III of the $\log \sigma T$ against $1/T$ curves. The E_b -values obtained during the pulsed thermal annealing experiment also appear in figure 2. The value for an unirradiated sample is 0.78 eV, while that for a gamma-irradiated one is 1.94 eV. The thermal recovery of the dipole binding energy also occurs over a wide step which coincides in temperature with that for the cation-vacancy concentration.

The stored-energy spectrum of a 5.6×10^7 Gy gamma-irradiated sample (figure 3) shows a main peak at about 450 °C and another one at about 790 °C. The release of the energy stored in the sample during irradiation starts at about 50 °C; a shoulder at around 300 °C may also be observed. The temperature range in which the 450 °C main peak and this shoulder appear is the same as that in which the recovery steps for both the cation-vacancy concentration and the dipole binding energy take place. The total energy released between room temperature and 900 °C is 41 J g⁻¹—that is, 2.6×10^{20} eV g⁻¹—of which

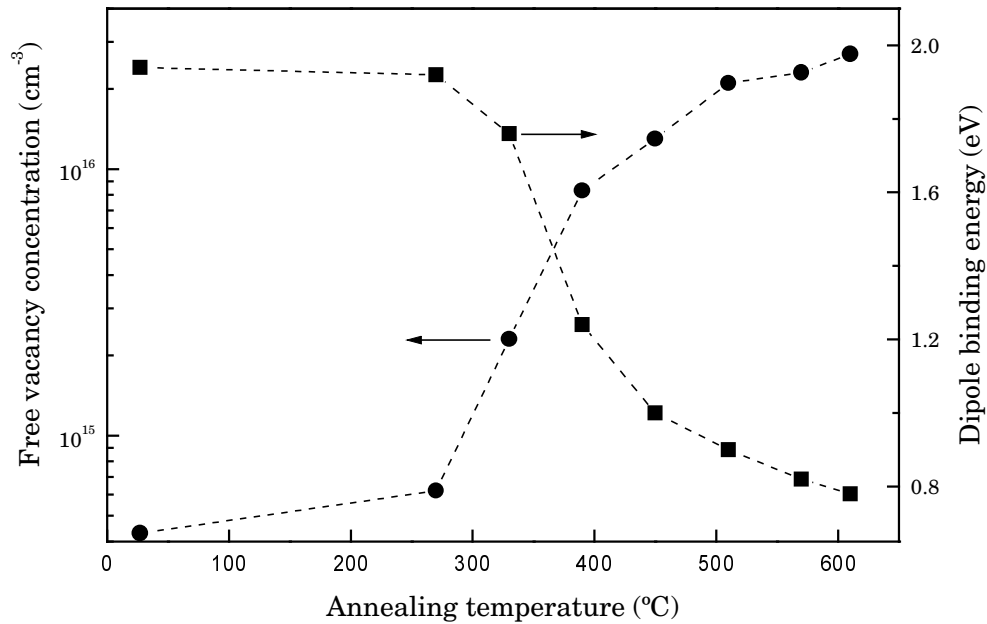


Figure 2. The thermal recovery of the free-cation-vacancy concentration measured at 290 °C (●) and of the dipole binding energy (■) of a gamma-irradiated NaF sample.

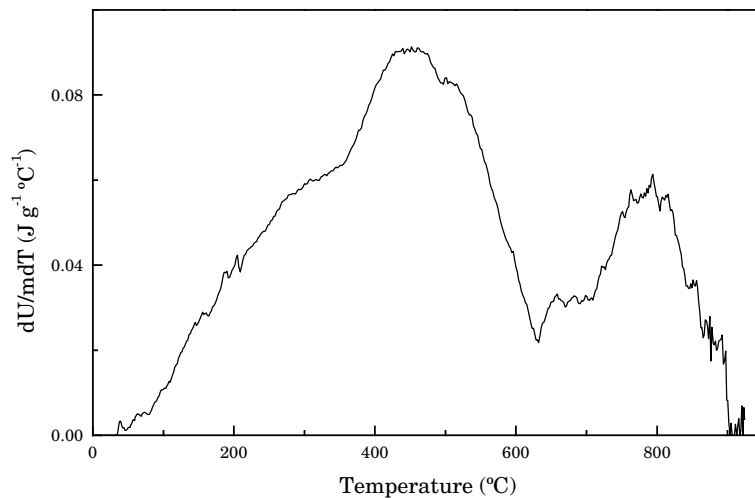


Figure 3. The stored-energy spectrum of a NaF sample gamma irradiated up to 5.6×10^7 Gy.

about 30.5 J g^{-1} ($1.9 \times 10^{20} \text{ eV g}^{-1}$) are released below 620 °C.

As has been shown in this work, the radiation-induced ionic conductivity decrease is due to the decrease of the concentration of extrinsic cation vacancies, which are the majority carriers. Since these vacancies compensate aliovalent impurities, forming impurity–vacancy dipoles at low temperature, it is straightforward to conclude that some radiation damage stabilizes these dipoles, therefore inhibiting their dissociation. This is supported by the observed radiation-induced increase of the dipole binding energy. The occurrence of a

unique thermal recovery step in the cation-vacancy concentration as well as in the dipole binding energy indicates that gamma irradiation induces one type of dipole trap and that these traps anneal out between 270 and 600 °C.

It is known that radiation-induced F-type centres in NaF disappear below 350 °C [17]. On the other hand, from the coincidence in temperature of that recovery step and the main energy-release process, it seems sensible to assume that both reflect the thermal annihilation of the same type of defect. Since the estimated F-centre–interstitial-halogen-atom recombination energy is less than 10 eV per recombination, one would have an unexpectedly high concentration of F-type centres, even for the heavy irradiation dose employed for stored-energy measurements, if this type of recombination were responsible for the energy release (1.9×10^{20} eV g⁻¹ below 620 °C). It was also found that, for the same irradiation dose, the total amount of stored energy per unit mass between 20 and 400 °C in alkali halides increases when the cation size decreases [18]. This has also been checked in stored-energy measurements up to temperatures near the melting point with our experimental set-up, and indicates that the cation sublattice plays an essential role in these processes. Therefore the possibility of defects based upon F centres and their corresponding interstitial halogen atoms being responsible for both the radiation effects on the ionic conductivity and the stored energy can be excluded.

The high temperature at which the radiation-induced damage related to the ionic conductivity anneals out suggests that some divacancy clusters may be involved. Experimental evidence for the presence of these defects in other gamma-irradiated alkali halides has been obtained from stored-energy and ionic thermocurrent measurements [11–13], which indicate that Schottky defects (divacancies) are formed by irradiation in the bulk and near the surfaces. Divacancies have also been optically detected in a number of alkali halides [19]. It can then be concluded that gamma irradiation generates in NaF either free or clustered divacancies, which behave as traps for the impurity–cation-vacancy dipoles. Their thermally activated recombination with alkali halide molecules accounts for the stored-energy release and leaves these dipoles free, thus allowing dipole dissociation which in turn makes the ionic conductivity increase.

Two thermal recovery steps for the cation-vacancy concentration occur in gamma-irradiated KCl and NaCl between about 250 and 600 °C [7, 10]. The first one takes place at temperatures below those at which the unique step in NaF appears. Also, as in LiF, two main energy-release processes are observed in their stored-energy spectra [11, 12], the first one being related to bulk divacancy clusters and the second one to near-surface damage [12]. This latter could also be the case for the 790 °C peak in NaF. No recovery step for the extrinsic cation-vacancy concentration and for the dipole binding energy has been observed at this temperature, probably because of the much lower irradiation dose employed for ionic conductivity measurements.

References

- [1] Fuller R C 1972 *Point Defects in Solids* vol 1, ed J H Crawford and L Slifkin (New York: Plenum)
- [2] Lidiard A B 1957 *Handbuch der Physik* vol 20, ed S Flügge (Berlin: Springer)
- [3] Dreyfus R W and Nowick A S 1962 *Phys. Rev.* **126** 1367
- [4] Ingham H S and Smoluchowski R 1960 *Phys. Rev.* **117** 1207
- [5] Christy R W and Harte W E 1958 *Phys. Rev.* **109** 710
- [6] Christy R W and Fukushima E 1960 *Phys. Rev.* **118** 1222
- [7] Vignolo J and Alvarez Rivas J L 1980 *J. Phys. C: Solid State Phys.* **13** 5291
- [8] Mariani F and Vignolo J 1982 *Phys. Status Solidi b* **112** K85
- [9] Mariani D F and Vignolo J 1987 *J. Mater. Sci. Lett.* **6** 993

- [10] Mariani D F, González F and Jiménez de Castro M 1988 *Physica B* **245** 219
- [11] Jiménez de Castro M and Alvarez Rivas J L 1985 *J. Phys. C: Solid State Phys.* **18** L1079
- [12] Jiménez de Castro M and Alvarez Rivas J L 1990 *J. Phys.: Condens. Matter* **2** 1015
- [13] Mariani D F, Jiménez de Castro M and Alvarez Rivas J L 1994 *J. Phys.: Condens. Matter* **6** 945
- [14] Mariani D F and Vignolo J 1982 *J. Phys. E: Sci. Instrum.* **15** 990
- [15] Omar M A 1975 *Elementary Solid State Physics: Principles and Applications* (New York: Addison-Wesley)
- [16] Diller K M 1975 *Harwell Laboratory Report AERE TP 693*
- [17] Mariani D F and Alvarez Rivas J L 1978 *J. Phys. C: Solid State Phys.* **11** 3499
- [18] Delgado L and Alvarez Rivas J L 1980 *J. Phys. C: Solid State Phys.* **13** 1185
- [19] Lushchik A, Lushchik Ch, Lushchik N, Frorip A and Nikiforova O 1991 *Phys. Status Solidi b* **168** 413