Volume expansion in heavily gamma irradiated NaCl and LiF single crystals

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Abstract
Linear expansion and stored energy measurements have been performed on NaCl and LiF single
crystals gamma irradiated up to 150 MGy. The thermal recovery steps of the radiation-induced
linear expansion upon heating coincide with the energy release peaks for both materials. This,
together with the amount of volume expansion measured after irradiation, leads to the
conclusion that this expansion is related to the formation of divacancies and divacancy clusters.

1. Introduction

Since about 1950 it has been well established that alkali halide crystals expand upon ionizing irradiation. Different experimental techniques, such as density change measurements, capacitance-type dilatometry and photoelastic techniques as well as measurements of changes in the lattice parameter, were used in the past to study radiation-induced volume expansion in alkali halide crystals mostly irradiated with x-rays at low doses. Many authors found a close relationship between the volume expansion and the formation of F related centres and their corresponding interstitials in alkali halides irradiated at room temperature [1–9] as well as below room temperature [9–12]. However, Lin [2] and Rabin [3] attributed the crystal expansion to radiation-generated divacancies (Schottky defects). Also, from measurements of the changes in the lattice parameter of KCl during irradiation it was concluded that the induced volume expansion must be ascribed to Schottky defects [13, 14].

On the other hand, stored energy measurements on heavily gamma irradiated alkali halides indicate that F-type centres and their corresponding interstitials are only a minor part of the total of radiation-induced defects [15]. Divacancies and divacancy clusters have been demonstrated to be induced by ionizing irradiation in alkali halides, their recombination with alkali halide molecules being responsible for the stored energy release [16]. Radiation-induced divacancies have also been detected by optical techniques in some irradiated alkali halides [17]. The aim of this communication is then to elucidate whether the generated Schottky defects are involved in the volume expansion induced by irradiation in heavily gamma irradiated alkali halide crystals and, for this purpose, measurements of stored energy and linear expansion have been performed on gamma irradiated NaCl and LiF single crystals. In this sense it is noteworthy that recent experiments with swift heavy-ion irradiated LiF have shown that the observed volume expansion is related to an intermediate region around the ion trajectory in which complex defect structures, such as small Li colloids and vacancy and molecular fluorine clusters, are formed, while single defects (such as F centres), formed in the external halo, do not contribute significantly to this swelling [18, 19].

2. Experimental details

Parallelepiped samples several mm in size were cleaved from NaCl and LiF Harshaw single-crystal blocks which were previously gamma irradiated at room temperature using a ^{60}Co gamma source at 12 Gy s^{-1} up to 150 MGy. Thermal expansion measurements were performed with a T. A. Instruments, Q400 model, thermomechanical analyser (TMA) while a T. A. Instruments, Q600 model, differential thermal analyser (DTA) was used for stored energy measurements, both operated at 10 °C min^{-1} with high purity nitrogen in the sample chamber. The devices were calibrated in temperature by melting known amounts of pure metals. Expansion calibration of the TMA was carried out with a standard aluminium sample and heat flow calibration of the DTA was achieved with a standard sapphire sample.
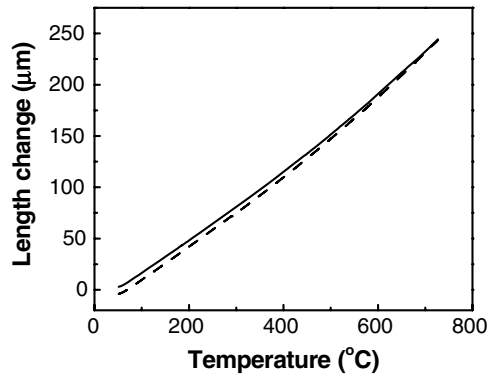
Figure 1. Length change during heating of a NaCl sample gamma irradiated up to 150 MGy: as-irradiated (full curve) and after annealing the sample up to 730 °C (dashed curve).
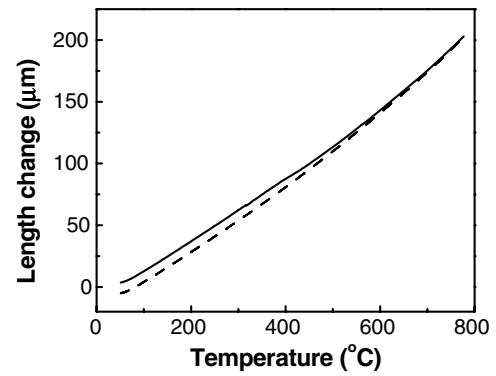

Figure 3. Length change during heating of a LiF sample gamma irradiated up to 150 MGy: as-irradiated (full curve) and after annealing the sample up to 780 °C (dashed curve).
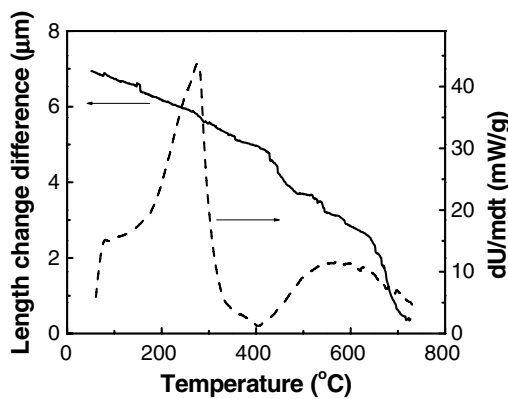

Figure 2. Difference between the two curves of figure 1 (full curve) and stored energy spectrum of an irradiated NaCl sample (dashed curve).
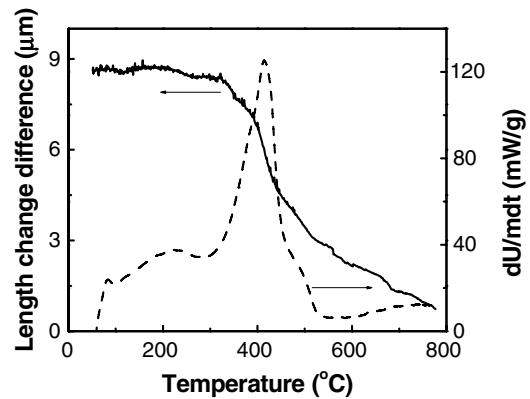

Figure 4. Difference between the two curves of figure 3 (full curve) and the stored energy spectrum of an irradiated LiF sample (dashed curve).

3. Results and discussion

The length increase during heating of an irradiated NaCl sample is shown in figure 1. After heating the irradiated sample up to 730 °C, a second heating run was performed, the results being also depicted in this figure. It can be seen that the sample length at the beginning of this second run is shorter than that of the as-irradiated sample, the thermal expansion curve being always under that of the first run. The difference between the two curves, which represents the contribution of irradiation-induced defect annealing to changes in the sample length, has been plotted in figure 2. Assuming that all defects have been annealed out at 730 °C [15, 16, 20], the value for this difference at room temperature, 6.9 μm, is the linear expansion induced by irradiation. This gives a relative value $\Delta l/l$ of 1×10^{-3}. Upon heating, a continuous decrease in the length change difference between 50 and 730 °C can be seen. The changes in the slope of the annealing curve indicate that different annealing stages occur.

The stored energy spectrum of an irradiated NaCl sample, also plotted in figure 2, shows two main energy release regions between 75 and 410 °C (peaked at 275 °C), and 410 and 740 °C (peaked at 570 °C), respectively. The total amount of stored energy is 54 J g^{-1}, that is, 3.4×10^{20} eV g^{-1}. These results agree with previously reported data [20].

A similar behaviour occurs in LiF samples. Figure 3 shows the thermal expansion results for an irradiated sample. The difference between the thermal expansion curves of the first heating run (up to 780 °C) and the second one is shown in figure 4 together with the stored energy spectrum of an irradiated LiF sample. The value for the linear expansion induced by irradiation is 8.6 μm, giving a relative value $\Delta l/l$ of 1.5×10^{-3}. The length change difference starts to decrease at around 180 °C and shows a very big annealing step between 320 and 780 °C. The stored energy release occurs in two main regions (with peaks at about 220 and 417 °C, respectively) below 550 °C and a final one above this temperature. The total stored energy in LiF is 143 J g^{-1}, or 8.9×10^{20} eV g^{-1}, in good agreement with previous results [20].

The different stored energy peaks for both NaCl and LiF correspond to the thermal annealing of different types of radiation-induced damage [20]. Although in figures 2 and 4 it is difficult for some of the peaks in the stored energy spectrum to find a clear correspondence with an annealing step in the thermal annealing curve for the radiation-induced linear expansion, it can be seen that the whole energy release occurs simultaneously with the complete annealing of the radiation-induced expansion. Moreover, at least the main energy release peaks for both NaCl and LiF clearly coincide

with a step in the expansion annealing curve. Hence it is sensible to conclude that all the expansion annealing is related to the stored energy release and therefore that the same types of defects are involved in the two processes. Taking into account that the expected F centre–interstitial recombination energy is well below 10 eV per recombination [21–23], it was previously shown that an unexpected very high value for the concentration of vacancy centres based upon F-type centres and their corresponding interstitial halogen atoms should have been induced by gamma-ray irradiation in alkali halide crystals if their recombination is to account for an energy release as high as these values (Lidiard pointed out that the total amount of F-type vacancy centres is at most a few times 10^{18} g^{-1} [24]). Since thermally quenched or plastically deformed samples show similar stored energy spectra to the irradiated ones, it was proposed that the energy release results from the recombination of anions and cations with divacancies [15]. Stored energy and ionic conductivity measurements on NaF support this conclusion [25]. Further studies of the lattice defects related to the stored energy release indicate that for irradiated samples they coalesce near the sample surfaces, giving rise to microcavities and some surface roughening or reconstruction, the conclusion that clusters of divacancies could account for the stored energy being again proposed [20]. The above findings are supported by the detection, by means of ionic thermocurrent measurements, of Schottky defects directly induced by either irradiation or quenching or plastic deformation [16]. It is also well known that heavy ionizing radiation leads to the formation of halogen bubbles and metallic colloids [24] and to the generation of perfect interstitial dislocation loops [26]. More recently, the formation of large vacancy voids, which require agglomeration of vacancies in both anion and cation sublattices, has been reported [27–30]. Therefore it can be concluded that the volume expansion induced by irradiation is related to the presence of divacancies, mostly clustered [16], and their complementary anion and cation defects. The contribution of F centre related defects, if any, is not significant, as was earlier proposed for ion irradiated LiF [18, 19].

No anisotropy in volume expansion has been found to occur in gamma irradiated crystalline materials [31]. Then the above stated relative linear expansion ($\Delta l/l$) values indicate that the radiation-induced relative volume expansion $\Delta V/V$ is 3×10^{-3} for NaCl and 4.5×10^{-3} for LiF. Assuming that each divacancy created by the gamma-ray irradiation produces a volume increase equal to its own volume (or that of the ion pair which it has replaced) [2], the total relative volume increase is given by $\Delta V/V = n_0 \times d^3/4$, n_0 being the divacancy concentration and d the lattice constant. From the total stored energy values shown above, values for the energy per ion pair–divacancy recombination of 11.0 eV for NaCl and 8.4 eV for LiF are obtained.

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