[21]V. A. Propstl and H. C. Wolf, Z. Naturforsch. 18a, 822 (1963).

[22]A. Schmillen and J. Kohlmannsperger, Z. Naturforsch. 18a, 627 (1963).

[23]V. L. Zima and A. N. Faidysh, Opt. i Spektroskopiya 20, 1022 (1966) [Opt. Spectry. (USSR) 20, 566 (1966)].

[24]V. L. Zima, A. D. Kravchencko, and A. N. Faidysh, Opt. i Spektroskopiya 20, 441 (1966) [Opt. Spectry. (USSR) 20, 240 (1966)].

[25]A. Hammer and H. C. Wolf, Mol. Crystals 4, 191 (1968).

[26]T. B. El Kareh and H. C. Wolf, Mol. Crystals 4, 195 (1968).

[27]K. W. Benz and H. C. Wolf, Z. Naturforsch. 19a, 181 (1964).

[28]S. Mansour and A. Weinreb, Chem. Phys. Letters 2, 653 (1968).

[29]J. D. Dow, Phys. Rev. 174, 962 (1968).

[30]R. G. DeLosh and W. J. C. Grant, Phys. Rev. B 1, 1754 (1970).

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Effects of X Irradiation on the Ionic Conductivity of Doped SrF_2 Crystals

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The ionic conductivity of SrF_2 doped with various concentrations of Nd^{3+} and Tb^{3+}, as well as of nominally pure SrF_2 crystals, was measured in the extrinsic region. The conductivity was found to increase with the concentration of the dopant, and was attributed mainly to F^- interstitials. The conductivity of the Tb-doped crystals was considerably higher than that of the Nd-doped samples. The difference is attributed to the difference in association between these rare-earth ions and the F^- interstitials. The effect of x irradiation at 80 °K on the extrinsic ionic conductivity was investigated. The x irradiation caused a decrease in the conductivity of the pure and the slightly doped samples, but did not notably influence the conductivity of the heavily doped specimens. The activation energies were not affected by the x irradiation. After annealing to about 600 °K, the original conductivity of all the x-rayed samples was restored. It is assumed that, as a result of the x irradiation at low temperature, F^- interstitial ions transformed to F° atoms. During the heating of the samples, these atoms recombined with electrons trapped at the sites of rare-earth ions and reformed F^- interstitials.

I. INTRODUCTION

The electrical ionic conductivity and its temperature dependence provide a convenient tool for the study of defects in ionic crystals.

It is known that alkaline-earth fluorides, doped with trivalent cations, contain F^- interstitial ions. These interstitials compensate for the excess charge of the trivalent ions, which occupy sites of divalent cations in the lattice.[1,2] The ionic conductivity of the doped crystals in the extrinsic region is due mainly to the motion of these interstitials. Croatto and Bruno[3] measured the ionic conductivity of $SrF_2:LaF_3$, and found an activation energy of 1.06 eV for the F^- interstitials's motion. Barsis and Taylor[4] found an activation energy of 1.0 ± 0.03 eV for the ionic conductivity of pure SrF_2 in the extrinsic region, but they could not determine whether the charge carriers were F^- interstitials or vacancies. The contribution of the cation sublattice to the conductivity was found to be negligible.[5,6]

In the present work the ionic conductivity of SrF_2 single crystals, doped with rare-earth ions of various concentrations, was measured in the extrinsic region and compared with the conductivity of nominally pure SrF_2 crystals. The influence of x irradiation at liquid-nitrogen temperature on the ionic conductivity at higher temperatures was also investigated. The effects of the x irradiation on the conductivity of the various samples enabled us to draw some conclusions concerning the types of defects created by the irradiation.

II. EXPERIMENTAL TECHNIQUE

For our experiments nominally pure SrF_2 crystals and crystals doped with Nd^{3+} (in concentrations of 0.05 and 0.2 at.%) and Tb^{3+} (0.03, 0.1, and 0.3 at.%) were used. These crystals were grown by the crystal-growing laboratory at the Hebrew University of Jerusalem (hereafter referred to as J). Nominally pure SrF_2 crystals were also obtained from Harshaw Company (referred to as H). The specimens were of 1-cm^2 cross section, and about 2 mm thick. The crystals were kept in a vacuum cryostat and were clamped between nickel electrodes.

The electrical circuit consisted of a 300-V dc battery and a Keithley 410 micromicroammeter. The x irradiations were carried out with a tungsten x-ray tube, operated at 50 kV and 15 mA. The temperature was measured by a copper-constantant thermocouple. After irradiation of 30 min at 80 °K (which was found to be more effective than irradiation at room temperature) various thermally-stimulated-current (TSC) peaks appeared during the warm up of the samples from 80 to 400 °K.[7] After annealing to about 400 °K, the sample was recooled to 300 °K, and then the ionic conductivity was measured. These measurements of the ionic conductivity were carried out at various temperatures between 350 and 550 °K, prior to the x irradiation, and after it. Before each measurement the sample was kept at a certain constant temperature until a steady current was reached.

III. RESULTS

The ionic conductivity σ of the pure and the variously doped crystals was measured in the region between 350 and 550 °K. In this region the conductivity of the doped unirradiated crystals was found to increase with the concentration of the dopant, and the conductivity of the "pure" specimens was considerably lower than that of the doped ones. Under equal conditions the conductivity of the Tb-doped crystals was considerably greater than that of the Nd-doped crystals. The conductivity of the pure-H specimens was found to be lower than that of the pure-J specimens. In Fig. 1 and Table I, results of these measurements are given. Figure 1 shows plots of σT vs $1/T$ on a semilogarithmic scale, for the various unirradiated crystals. From a best fit of the expression

$$\sigma T = A e^{-E/kT} \tag{1}$$

to the experimental data, the values of E and A were computed. These computed values and their standard deviations are summarized in Table I. The activation energies E for the conductivity of the nominally pure samples were found to be 1.01 eV for the J, and 1.24 eV for the H samples, while an activation energy of about 2.1 eV would be expected for the intrinsic conductivity of a pure crystal.[4] This indicates that both the H and J samples contained certain amounts of impurities. The relatively higher activation energy of the H samples, as well as their obviously lower conductivity, indicate that the impurity concentration in the pure-H crystals is smaller than that of the pure-J crystals. This fact has also been supported by recent TSC measurements[7] which indicated that the impurities are trivalent ions.

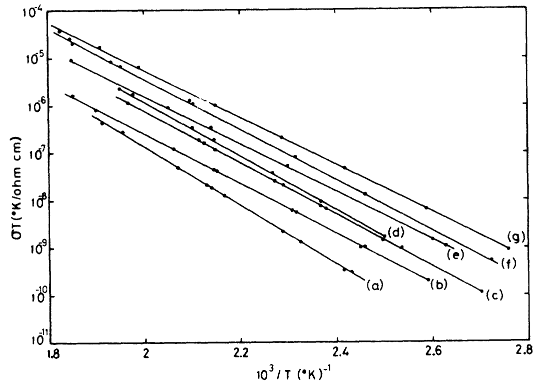

FIG. 1. σT vs $10^3/T$ (on a semilogarithmic scale) for pure SrF_2 crystals and for doped crystals. (a) Pure-H samples; (b) pure-J samples; (c) doped with 0.05-at.% Nd; (d) doped with 0.2-at.% Nd; (e) doped with 0.03-at.% Tb; (f) doped with 0.1-at.% Tb; (g) doped with 0.3-at.% Tb.

In the present work the ionic conductivity was measured at relatively low temperatures, where the influence of intrinsic defects is known to be very small, and where the measured conductivity is due mainly to extrinsic defects. Etzel and Maurer[8] have given an expression for the dependence of the ionic conductivity σ on the concentration of the impurity c, assuming that the number of the intrinsic thermal charge carriers is negligible compared to the number of the free (unassociated) carriers introduced by the doping process. They formulated this dependence by

$$c = L\sigma^2 + F\sigma , \tag{2}$$

where L and F are temperature-dependent parameters $L/F^2 = K_2(T)$, and $K_2(T)$ is the equilibrium constant of the quasichemical reaction

$$\text{unassociated impurity ion} + \text{unassociated charge carrier} \rightleftarrows \text{impurity charge-carrier complex} .$$

We evaluated $K_2(T)$ from our experimental data. For this purpose L and F were computed by a least-squares fit of our data to expression (2). These computed values of $K_2(T)$ at various temperatures are given in Table II for the SrF_2: Tb^{3+} crystals. For the Nd^{3+}-doped samples, values of $K_2(T)$ could be computed only at higher temperatures. At 550 °K, $K_2(T)$ was found to be 27145, compared to 7250 in the Tb-doped crystals at the same temperature.

In Fig. 2, the ratio of the conductivities σ of the SrF_2: Tb, to the conductivity σ_0 of the pure-H sample is given at various temperatures as a function of the concentration. The dots represent the experimental data, and the solid line gives the computed function using values of L and F computed by the best-fit method.

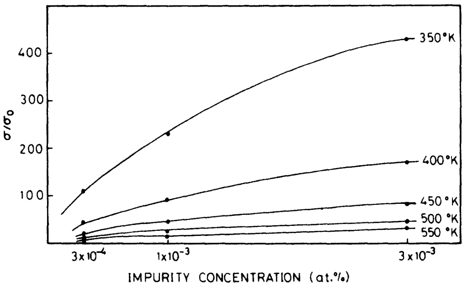

FIG. 2. σ/σ_0 vs concentration for Tb-doped SrF_2 crystals. σ, the conductivity of the doped samples; σ_0, the conductivity of the pure H samples.

X irradiation at 80 °K caused a notable decrease in the conductivity of the pure crystals. A decrease was also detected in the slightly doped samples, while the conductivity of the heavily doped specimens remained almost unchanged. In all cases, the activation energy E was unaffected by the irradiation.

In Fig. 3, the conductivities of several samples before and after x irradiation are compared. In Table III, the ratio of the conductivities at 450 °K, before x irradiation, σ, and after it, σ_x, are given for various impurity concentrations. The annealing for about an hour at 600 °K, of the x-rayed pure and Tb-doped crystals, restored their original conductivity. The 0.05-at.% Nd-doped samples already regained their original conductivity after annealing to about 500 °K.

IV. DISCUSSION

The experimental results show that the ionic conductivity increases with the concentration of the rare-earth (RE) ions. These results are in accordance with previous measurements of alkaline-earth fluorides doped with other trivalent ions,[3] and support the assumption that F^- interstitials are the dominant carriers in these doped crystals.

Brown *et al.*[9] investigated, by ESR methods, the symmetries of various RE ions in a SrF_2 host lattice and found that the F^- interstitials, which are responsible for the charge compensation of the RE ion, tend to be closer to the lighter RE ions than to the heavier ones. They also calculated the association energy between the RE^{3+} ion and the F^- interstitial as a function of the ionic radius of the RE^{3+}, and showed that the decrease in the association is due to the decrease of the ionic radius with increasing atomic number. Weber and Bierig[2] reached similar results by ESR and luminescence methods in CaF_2: RE crystals.

TABLE I. The activation energies E and the proportional factors A as evaluated by a best fit of the experimental results to the expression $\sigma = (A/T)e^{(-E/kT)}\ \Omega^{-1}\,cm^{-1}$, where ΔE and ΔA are the standard deviations.

	A (°K/Ω cm)	$\Delta A/A$	E (eV)	ΔE (eV)
SrF_2 pure H	4.05×10^5	0.337	1.237	0.011
SrF_2 pure J	3.95×10^3	0.186	1.015	0.006
SrF_2 + 0.03-at.% Tb	2.41×10^4	0.288	1.009	0.009
SrF_2 + 0.1-at.% Tb	1.88×10^5	0.126	1.061	0.005
SrF_2 + 0.3-at.% Tb	1.06×10^5	0.273	1.013	0.009
SrF_2 + 0.05-at.% Nd	5.80×10^4	0.089	1.080	0.003
SrF_2 + 0.2-at.% Nd	9.80×10^5	0.548	1.178	0.018

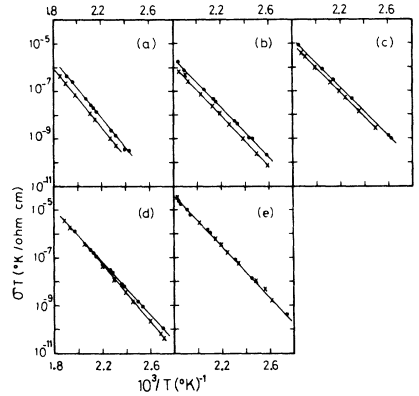

FIG. 3. σT vs $10^3/T$ for various pure and doped SrF_2 crystals. ●, before x irradiation; ×, after x irradiation. (a) Pure-H sample; (b) pure-J sample; (c) doped with 0.03-at.% Tb; (d) doped with 0.05-at% Nd; (e) doped with 0.1-at.% Tb. The 0.2-at.% Nd-doped and the 0.3-at.% Tb-doped samples showed the same behavior as the 0.1-at.% Tb-doped samples [Fig. 3(e)].

Our results show that at 550 °K the equilibrium constant K_2 of Nd-doped crystals is considerably greater than that of the Tb doped crystal. This indicates that the association between the Nd ion and the F^- interstitial is stronger than the association between the Tb ion and the F^- interstitial. This is also in accordance with the results of Brown, taking into account that Nd is the fourth and Tb the ninth member of the Lanthanide series. The relatively strong association between the Nd^{3+} and the F^-_{int} results in a smaller number of free F^- interstitials in the Nd^{3+}-doped samples. At low temperatures, expression (2) therefore could not be applied for the computation of K_2. The use of (2) for SrF_2 : Nd at low temperatures would, in fact, result in negative values of K_2.

The measurements of ionic conductivity as a function of temperature, as given in Fig. 1, show that the conductivity of the Nd-doped crystals is

TABLE II. The equilibrium constant K_2 of SrF_2 : Nd at various temperatures.

T (°K)	350	400	450	500	550
K_2	8745	8253	7805	7495	7250

TABLE III. The ratio of the ionic conductivities of some pure and variously doped SrF_2 samples at 450 °K, before (σ) and after x irradiation (σ_x).

Sample	Pure H	Pure J	+0.03-at.% Tb	+0.05-at.% Nd	+0.1-at.% Tb	+0.2-at.% Nd	+0.3-at.% Tb
σ_x/σ	0.37	0.38	0.62	0.82	1	1	1

lower than that of the Tb-doped crystals. This behavior is also in accordance with the differences in their association energies.

Irradiation of $MeF_2:RE^{3+}$ (Me = Ca, Ba, Sr) with ionizing radiation at liquid-nitrogen temperature results in the reduction of the trivalent RE ions to a divalent state and in the creation of V_K centers.[10,11] These V_K centers are stable up to about 160 °K only. Beaumont *et al.*[10] investigated EPR and absorption spectra of $SrF_2:Tm^{3+}$ and found that at 300 °K about half of the original V_K centers have recombined with electrons trapped at RE^{2+} sites, while the rest have converted into nonparamagnetic hole centers. Tzalmona and Pershan[11] found in variously doped SrF_2 crystals that at 300 °K all the paramagnetic hole centers were annealed. Merz and Pershan[12] investigated thermoluminescence (TL) in CaF_2 crystals doped with RE ions and suggested that the TL peak at 330 °K is due to the diffusions of F^0 interstitial atoms to the sites of RE^{2+} ions, and to the radiative recombination of the F^0 hole with an electron of the RE^{2+}.

Our experimental results showed that the x irradiation reduced the ionic conductivity of the slightly doped and the "pure" samples, but did not influence the activation energy for the motion of the carriers. This indicates that the x irradiation causes a decrease in the number of the F^- interstitials rather than a decrease in their mobility. By the irradiation of the crystals at 80 °K, V_K centers are created, and it is assumed that during the heating of the crystals to 300 °K, part of the holes released by the unstable V_K centers are captured by F^- interstitial ions, forming F^0 interstitial atoms. This process is responsible for the observed decrease of the ionic conductivity which is due mainly to the F^- interstitials.

Above room temperature, F^0 interstitials diffuse to RE^{2+} sites and recombine there with electrons, restituting RE^{3+} ions and F^- interstitials.[12] We suppose that this recombination is responsible for the recovery of the ionic conductivity to its original value. Our results showed indeed that the heavily doped x-rayed samples regained their original conductivity after heating to about 400 °K. This is probably due to the relatively small distances, between the impurity ions in these heavily doped samples. In the slightly doped samples, however, the F^0 atoms have to diffuse greater distances in order to recombine with the RE^{2+} ions, and these samples therefore reach their original conductivity only at higher temperatures (500 °K for the SrF_2 + 0.05-at.% Nd, and above 600 °K for the SrF_2 + 0.03-at.% Tb and the "pure" samples). This explains also the fact that the ratio of the ionic conductivities before (σ) and after (σ_x) x irradiation increases at a given temperature with the concentration of the impurity, as shown in Table III for 450 °K.

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[1] E. Zintl and A. Udgard, Z. Anorg. Allgem. Chem. 240, 150 (1939).

[2] M. J. Weber and R. W. Bierig, Phys. Rev. 134, A1492 (1964).

[3] U. Croatto and M. Bruno, Gazz. Chim. Ital. 78, 95 (1948).

[4] E. Barsis and A. Taylor, J. Chem. Phys. 45, 1154 (1966).

[5] R. W. Ure, J. Chem. Phys. 26, 1363 (1957).

[6] M. E. Baker and A. Taylor, Am. Ceram. Soc. Bull. 47, 363 (1968).

[7] N. Kristianpoller and Y. Kirsh (unpublished).

[8] W. Etzel and R. J. Maurer, J. Chem. Phys. 18, 1003 (1950).

[9] M. R. Brown *et al.*, J. Chem. Phys. 50, 891 (1969).

[10] J. H. Beaumont *et al.*, Proc. Roy. Soc. (London) A315, 69 (1970).

[11] A. Tzalmona and P. S. Pershan, Phys. Rev. 182, 906 (1969).

[12] J. L. Merz and P. S. Pershan, Phys. Rev. 162, 217 (1967).