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Ionic conductivity in samarium-doped NaCl

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A study of ionic conductivity as a function of temperature has been carried out in NaCl and NaCl doped with 0.5 and 1.0 mol % samarium. The conductivity–temperature plot of NaCl exhibits a well-known three-stage conductivity in the temperature range 100 to 650° C. The knee separating intrinsic and extrinsic regions is at a temperature of about 525° C. The conductivity–temperature plots of samarium-doped NaCl exhibit three-stage extrinsic (II, III and IV) conductivity in the temperature range 100 to 525° C. The intrinsic region I, was not observed in these plots, as the conductivity measurements were taken up to 525° C. From the analysis of these plots activation energies for the migration of cation vacancy, the formation of Schottky pairs, the association of the samarium ion with a cation vacancy and the dilution of samarium ions in the lattice of NaCl are calculated. These values are compared with previously reported ones.

1. Introduction

Ionic conductivity studies provide valuable information on the state of point defects in ionic crystals. Detailed studies of ionic conductivity in NaCl crystals doped with alkaline earth impurities have been carried out by a number of workers [1–4]. Although a large amount of work has been reported on pure and doped NaCl crystals, little work has been reported on NaCl crystals doped with rare-earth impurities such as samarium, europium, terbium, gadolinium, etc. Therefore, in the present investigation, an attempt is made to study conductivity of NaCl crystals doped with samarium. An attempt is also made to calculate E_s, the activation energy for the formation of Schottky pairs in NaCl from microhardness studies.

2. Experimental procedure

Single crystals of NaCl and NaCl doped with 0.5 and 1.0 mol % samarium were grown by the Kyropoulos technique, in our laboratory, in a platinum crucible. The starting materials used for the growth of crystals were BDH AnalaR grade NaCl salts. The rare-earth impurity was added in the form of chloride. The melt was kept at a temperature of 50 to 60° C above its melting point for 6 h to ensure a steady temperature and uniform mixing. The crystals were pulled at a rate of 1 cm h^{-1} and after growth they were annealed at 650° C for 12 h and cooled to room temperature at a rate of 15° C h^{-1}. All the crystals were grown under identical conditions.

The d.c. conductivity of freshly cleaved samples was measured by increasing the temperature at a rate of 60° C h^{-1}. Currents were measured using a Cary 401 vibrating Read Electrometer for resistance higher than $10^8\,\Omega$. Below this range, a Philips d.c. micrometer is

3. Results and discussion

Rare-earth cores such as europium, samarium, gadolinium, etc. can be introduced into the alkali halide lattice as a bivalent or trivalent ion, depending mainly on the temperature at which the additions are made. Przibram [5] reported that rare-earth impurities exist in the trivalent state when an alkali halide crystal is grown from aqueous solutions composed of alkali halides and a rare-earth halide. It occurs in a dry mixture of two salts, pulverized, pressed and presumed to form a pellet. The trivalent form has also occurred in the sintered mixtures just below the melting point. Once the mass was melted and single crystals were grown, only the bivalent form appeared to be present. The reduction of Eu^{3+} to Eu^{2+} occurs if alkali halides which have crystallized with traces of europium are heated to temperatures above 200° C [5]. Further, these results have been confirmed by Gruen *et al.* [6] and Reisfeld and Alasner [7]. As the crystals used in the present studies were grown from the melt by the Kyropoulos technique, it is concluded that samarium exists in the bivalent rather than the trivalent state. Furthermore, Narasimha Reddy *et al.* [8] have confirmed the presence of gadolinium, samarium and terbium in the bivalent state in NaCl crystals grown by the Kyropoulos technique using optical absorption and fluorescence measurements.

The ionic conductivity of alkali halide crystals of NaCl type occurs predominantly through the motion of vacancies. Measurements of mass transport during conduction have further established that, except near employed. The crystal temperature was determined to a precision better than ±0.5° C by means of a calibrated chromel–alumel thermocouple which was placed very close to the sample in the conductivity mount. For good electrical contact, the samples were coated with aquadag paint. The activation energies were calculated to a precision of ±0.02 to ±0.05 eV.

Microhardness measurements were carried out on (1 0 0) faces of undoped NaCl at room temperature using a Vickers hardness tester attached to an NU_2 universal research microscope (Carl–Zeiss, Jena). The

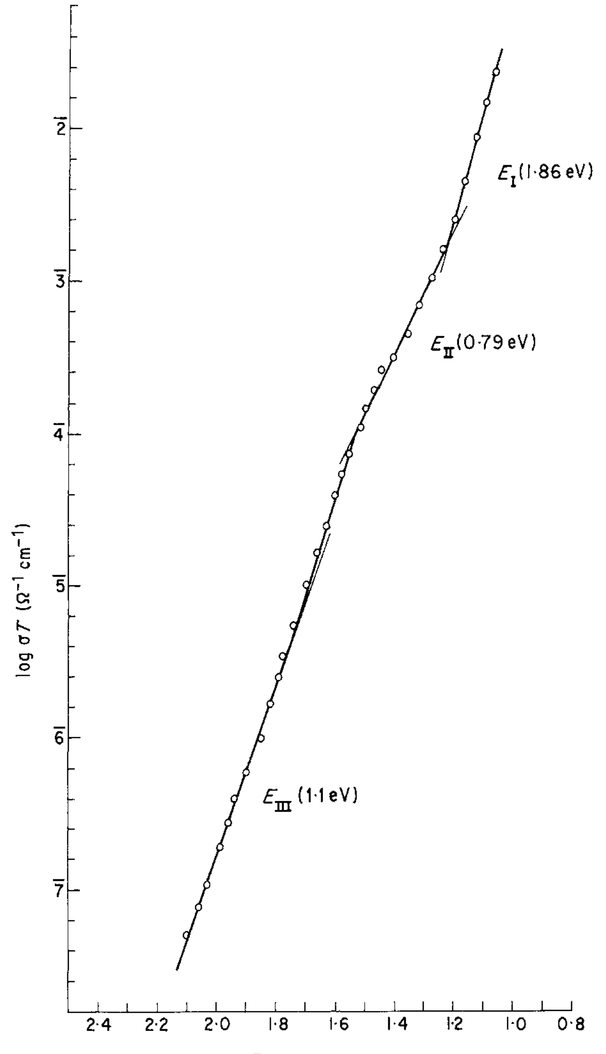

Figure 1 Conductivity–temperature plot of undoped NaCl crystal.

diagonal of Vickers indentor was aligned parallel to the ⟨1 0 0⟩ direction. The indentations were made at a load of 6×10^{-2} N and the indentation time was 10 sec; the microhardness value was obtained from the average of at least ten indentations.

The concentration of background impurities in undoped and doped NaCl crystals (p.p.m.) was estimated by Atomic Absorption Spectrophotometry (Perkin-Elmer Model 2380). The concentration of background impurities was estimated to within ± 1 p.p.m.

the melting point, the current is carried almost entirely by the motion of the cations [9]. The ionic conductivity, σ, is given by the following expression [9]

$$\sigma = ne\mu = \left(\frac{4e^2a^2\nu_0}{kT}\right) n \exp\left(-E_c/kT\right) \quad (1)$$

where n is the concentration of cation vacancies, μ is the mobility of the vacancy, a is the distance between the nearest-neighbour cation and anion (one-half the lattice parameter), E_c is the activation energy for the motion of a cation vacancy, ν_0 is a frequency factor (which contains an effective lattice vibration frequency multiplied by an entropy factor), e and kT have their usual meanings. The expression for the mobility, which results in the right-hand side of Equation 1, is derived from the fact that the mean time, τ_v, between vacancy jumps, is given by

$$\tau_v^{-1} = 12\nu_0 \exp\left(-E_c/kT\right) \quad (2)$$

Here the factor 12 appears because of the 12 nearest-neighbour sites into which the vacancy may go.

Equation 1 suggests that data for conductivity as a function of temperature may be plotted as log σT against $10^3/T$, the conductivity–temperature plot. If the slope of such a plot is set equal to $-E/2.303k$, the quantity E, which represents an effective activation energy, is equal to E_c plus an energy associated with the temperature dependence of n. The conductivity–temperature plot of undoped NaCl crystal is presented in Fig. 1. From this figure, one can notice a well-known three-stage conductivity in the temperature range 100 to 650° C. The notation of Dryfus and Nowick [10] is used here for the different regions of this plot. Region I for intrinsic conductivity where Schottky defects dominate, Region II for free vacancy conduction and Region III for association of divalent impurity with cation vacancies. The knee in the conductivity plot separating intrinsic and extrinsic is at a temperature of about 525° C. The extrinsic range below the knee of the plot also has two straight sections: region II (400 to 525° C) and region III (100 to 350° C). The slopes of these regions give the effective activation energies: $E_{\mathrm{I}} = 1.86$ eV, $E_{\mathrm{II}} = 0.79$ eV and $E_{\mathrm{III}} = 1.1$ eV.

In region I, n is the equilibrium concentration of Schottky defects in the lattice, given by [9]

$$n/N \propto \exp\left(-E_s/2kT\right) \quad (3)$$

where E_s is the energy of formation of a Schottky pair, and N is the concentration of cation lattice sites. Combining equations 3 and 1 gives the effective activation energy, E_{I}, for region I as

$$E_{\mathrm{I}} = E_c + \tfrac{1}{2}E_s \quad (4)$$

The conductivity breaks into region II of Fig. 1, when the number of vacancies introduced by divalent cation impurities (background divalent impurities in undoped NaCl) exceeds the number produced thermally. In this region, the concentration of cation vacancies is constant, equal to the total concentration of divalent metallic impurities. Therefore, the effective activation energy, E_{II}, for this region is simply equal to E_c [11]. Thus, $E_c = 0.79$ eV is obtained. There exists a wide discrepancy in the value of E_c for NaCl quoted by different authors, ranging from 0.659 eV [12] to 0.88 eV [13]. Substituting $E_c = 0.79$ eV and $E_{\mathrm{I}} = 1.86$ eV in Equation 4, a value for $E_s = 2.14$ eV is obtained. This value is in good agreement with the value reported by Dryfus and Nowick [10] and Allnatt and Pantelis [12].

Below 400° C, region II breaks into region III of Fig. 1. Two reasons were given by Lidiard [9] for this discontinuity of region II into region III. The first is

TABLE I Background impurities (p.p.m.) detected in undoped NaCl

Ba	Ca	Mg	Mn	Zn	Rb	Fe	Ni	Pb
8	16	4	2	4	–	10	14	12

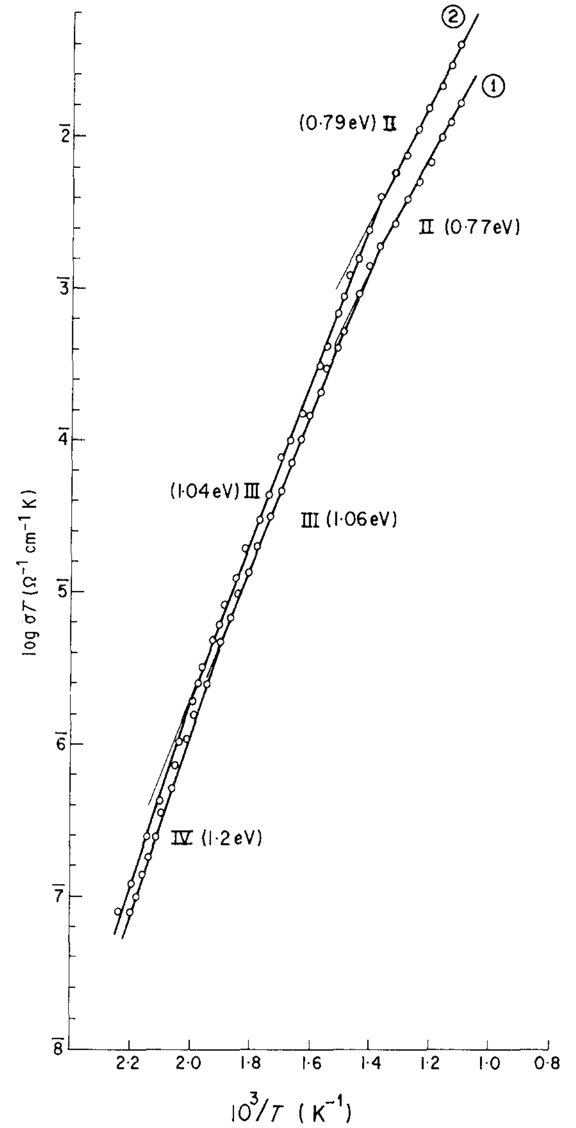

Figure 2 Conductivity–temperature plots of (1) NaCl:Sm (0.5 mol %) and (2) NaCl:Sm (1.0 mol %).

TABLE II Microhardness data of NaCl

Reference	H_v (kg mm^{-2})
Narasimha Reddy *et al.* [16]	21.1
Pratap and Hari Babu [18]	19.6
Kittel [19]	21.3
Present work	20.2

the tendency of the divalent ion and cation vacancy to associate to form a neutral complex. The second is the concentration of divalent ions at temperatures where their concentration in solution begins to exceed the solubility limit. Both of these effects result in a decrease in concentration of cation vacancies and therefore can account for the onset of region III. Because no hysteresis occurred in region III, our results suggest that precipitation is not involved. Therefore, we conclude that region III results from association of divalent ions with cation vacancies. Substitution of the theoretically calculated value $E_A \simeq 0.4$ eV [14, 15] where E_A is the energy for the association of a cation vacancy with background impurity complexes and the present measured value $E_c = 0.79$ eV into $E_{III} = E_c + \frac{1}{2}E_A$, gives $E_{III} = 0.99$ eV. The agreement of this value with the measured value, $E_{III} = 1.1$ eV, indicates the correctness of the notion that region III is controlled by association. When region III is due to the association of divalent ions with cation vacancies, then the effective activation energy is given by

$$E_{III} = E_c + \tfrac{1}{2}E_A \qquad (5)$$

By solving $E_c + \frac{1}{2}E_A = 1.1$ eV, a value for $E_A = 0.62$ eV is obtained.

Our estimation of the concentration of background impurities such as barium, calcium, magnesium, manganese, zinc, rubidium, iron, etc., was found to be 70 p.p.m. in total, in undoped NaCl (Table I). The background impurities may be due to the presence of impurities in the starting material and mainly due to the furnace contamination. The furnace contamination might have become less during the growth of samarium-doped NaCl crystals and we observed a total concentration of background impurities less than 20 p.p m. (This may be because undoped NaCl crystal was grown before attempting to grow samarium-doped crystals, such that all furnace contaminations might have evaporated in the first growth cycle of the undoped crystals.)

Conductivity–temperatures plot of 0.5 and 1.0 mol % samarium-doped NaCl crystals are presented in Fig. 2. These plots indicate that the data can be fitted to three regions (II, III and IV) with different slopes. Each region is labelled with the value of the effective activation energy obtained from the slopes of these plots. The intrinsic region I, was not observed in these plots, as measurements were taken up to a temperature of 525° C. Region II extends from 470 to 525° C while region III extends from 250 to 470° C. In region II, the conductivity increases with increase in samarium impurity concentration (0.5 to 1.0 mol %). This suggests that the carriers in this region are free impurity-induced cation vacancies. The slopes of regions II and III for both concentrations (average values) give the effective activation energies: $E_{II} = 0.78$ eV and $E_{III} = 1.05$ eV. Using these values, a value for $E_A = 0.54$ eV, the activation energy for association of cation vacancy with samarium impurity ion, is obtained.

TABLE III Activation energy for the formation of Schottky defects, E_s, in NaCl calculated and observed

Serial no.	Reference	$R = 0.282$ nm, E_s (eV) observed from conductivity data	E_s (eV) calculated from $H_v = 206.2$ $(E_s/R^3) \times 10^3$
1.	Laredo and Dartyge [3]	2.3	–
2.	Dryfus and Nowick [10]	2.12	–
3.	Allnatt and Pantelis [12]	2.17	–
4.	Brown and Hoodless [20]	2.30	–
5.	Present work	2.14	2.19

TABLE IV Basic parameters for NaCl derived from conductivity experiments

Reference	E_s (eV)	E_c (eV)	E_A (eV)	E_d (eV)
Dryfus and Nowick [10]	2.12	0.79	0.54*	–
		to	0.62 (Cd^{2+})	
		0.82	0.34 (Mg^{2+})	
Nadler and Rossel [1]	2.74	0.72	0.434*	–
			0.501 (Mg^{2+})	
			0.521 (Sr^{2+})	
Allnatt and Pantelis [12]	2.17	0.659	–	–
Laredo and Dartyge [3]	2.30	0.75	0.55 (Sr^{2+})	1.80 (Sr^{2+})
Brown and Hoodless [20]	2.30	0.72	0.53 (Sr^{2+})	1.80 (Sr^{2+})
Bizouard *et al.* [13]	1.97	0.88	–	–
Present work	2.14	0.79	0.62*	
			0.54 (Sm^{2+})	0.68 (Sm^{2+})

*Background impurities.

Region III of conductivity plots of both concentrations terminates another increase in slope to a value corresponding to ~1.12 eV. This will be termed region IV, and it exists due to the precipitation of samarium impurity. These precipitates dissociate during conductivity measurements in the temperature range 100 to 225° C. A similar observation was reported by Narasimha Reddy *et al.* [16] in a study of the variation of microhardness with quenching temperature in samarium-doped NaCl crystals. When NaCl crystals doped with 1.0 mol % samarium were heated to a temperature of ~225° C, the samples were found to be transparent, compared to the unheated ones. This observation confirms that the precipitates present in the crystal dissociate at or below 225° C. The slope of region IV gives an activation energy $E_c + \frac{1}{2}E_d$ where E_d is the activation energy for dilution of precipitated samarium impurity in the NaCl lattice. Substituting $E_c = 0.78\,\text{eV}$ in $E_c + \frac{1}{2}E_d = 1.12\,\text{eV}$, a value of $E_d = 0.68\,\text{eV}$ is obtained for the samarium impurity in NaCl.

Madhu Shukla and Bansigir [17] have established a simple relation between microhardness, H_v and E_s, the energy of formation of Schottky defects in alkali halides. The relation is given by

$$H_v = 206.2\,(E_s/R^3) \times 10^3 \qquad (6)$$

where H_v is expressed in $\text{kg}\,\text{mm}^{-2}$, E_s in eV and R, the interionic distance, in nm.

The measured values of microhardness of NaCl are presented in Table II together with the previously reported values. Substituting $H_v = 20.20\,\text{kg}\,\text{mm}^{-2}$ and $R = 0.282\,\text{nm}$ in Equation 6, a value for $E_s = 2.19\,\text{eV}$ is obtained. The precision in calculation of this value is $\pm 0.03\,\text{eV}$. This calculated value of E_s from the microhardness data is in fair agreement with the experimental value from conductivity data (Table III). The values of conductivity parameters determined in the present study for NaCl are compared with those reported by previous authors and are presented in Table IV.

The data from the present work provide evidence for the validity of the following points.

(a) The activation energy, E_c, for the cation vacancy migration in NaCl is $0.79 \pm 0.05\,\text{eV}$, the energy, E_s, to create a Schottky pair is $2.14 \pm 0.02\,\text{eV}$, while the association energy, E_A, of a divalent samarium ion with a cation vacancy is $0.54 \pm 0.05\,\text{eV}$.

(b) The association between cation vacancies and the samarium impurity ions gives an effective activation energy of $1.05 \pm 0.05\,\text{eV}$. The precipitation of samarium impurities shows an effective activation energy still higher by about $0.15 \pm 0.05\,\text{eV}$.

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