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Experimental setup and first results

BERTHEVILLE, Bernard, et al.

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Reference

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IONIC CONDUCTIVITY OF Na$_2$S SINGLE CRYSTALS BETWEEN 295 AND 1350 K EXPERIMENTAL SETUP AND FIRST RESULTS

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Abstract—We study the ionic conductivity versus temperature and frequency of large Na$_2$S single crystals by using a calibrated impedance apparatus. The experimental setup used for the ionic conductivity measurements up to 1350 K and its calibration are described. The apparatus allows to measure complex impedances between 0.1 Ω and 10 GΩ. The high temperature conductivity data were analyzed in terms of the conventional Frenkel defect model. We assume that cation vacancies and cation interstitials are the dominant intrinsic defects. The energy of motion was found to be 0.61 ± 0.05 eV for a cation vacancy. The energy of formation of a Frenkel defect pair is 2.51 ± 0.05 eV. Results are given that show clear evidence of a superionic behaviour close to the melting point, similar to the one found in alkaline earth fluorides and several halides. Furthermore, X-ray diffraction experiments on a high optical quality single crystal were performed. The cell parameter and the population parameter of Na$^+$ were accurately determined (6.5373 Å and 0.988, respectively). © 1997 Elsevier Science Ltd.

Keywords: A. inorganic compounds, B. crystal growth, C. X-ray diffraction, D. dielectric properties, D. electrical conductivity

1. INTRODUCTION

Crystals with the fluorite structure have received a great deal of experimental and theoretical attention due to their simplicity (cubic structure) and their ionic properties. One particularly interesting property is the appearance of a fast ionic conduction region at high temperatures where the conductivity tends to values similar to the ones of good ionic electrolytes. β-PbF$_2$ [1] and SrCl$_2$ [2, 3] are typical superionic compounds with low melting points ($T_m = 1103$ K and 1146 K), well-defined transition temperatures ($T_c = 712$ K and 1001 K) and a high ionic conductivity near $T_c$ ($σ = 1$ Ω$^{-1}$ cm$^{-1}$). The existence of the superionic state is established, but the nature of the transport mechanisms and the possible involvement of defects, are still controversial. Among the AB$_2$ compounds, there exist distinct families crystallizing in the anti-fluorite structure (antimorphous to CaF$_2$). One of them is the alkali sulfide family (Li$_2$S, Na$_2$S, K$_2$S). Probably, the higher reactivity of the alkali sulfides limited the field of electrochemical research to some basic experiments. Fused Na$_2$S or K$_2$S attack most materials including silica, alumina and platinum. They are rather volatile near their melting point and deteriorate very rapidly when exposed to air. Only recently a few experimental investigations and theoretical studies have been published on these materials, mainly on Lithium and Sodium sulfides.

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The anti-fluorite structure can be described as a primitive cubic array of cations with half of the cube centers occupied by the anions. The unoccupied cube centers play an important role as they provide possible effective interstitial sites. X-ray powder diffraction data of anhydrous Na$_2$S were reported by Zintl et al. [4] in 1934 (cell parameter = 6.526 Å). The published isobaric specific heat data [5] exhibit a broad specific heat anomaly at a temperature $T_c$ of 1276 K. Other high temperature experiments known are nuclear magnetic resonance (NMR) investigations [6] and conductivity measurements from Möbius et al. [7] on polycrystalline powder samples, but both were limited to 1100 K, far below $T_c$. The NMR study showed that the fluctuating interactions due to the relative diffusion of Na$^+$ ions and atomic defects contributes importantly to the relaxation. In the intrinsic region, the diffusion of Na$^+$ in Na$_2$S was about two times faster than Li$^+$ in Li$_2$S and the apparent activation energy did not exceed 1.5 eV. The data were in good agreement with the results in Ref. [7]. Lattice dynamical properties at 50 K including elastics constants and mean-square ionic displacements were obtained from phonon-dispersion curves measured by using inelastic neutron scattering on Na$_2$S single crystals by Bührer and Bill [8, 9]. They obtained that the low energy phonon branches are essentially due to Na$^+$ motion, whereas the heavier sulfur ions were mainly involved in the higher optic modes. This inverse behaviour of the ions was already observed in β-AgI [10] and in Li$_2$S. They further established that Na$^+$ ions in Na$_2$S performed very large
Johnson Matthey Ltd. Crystal growth bases on a vertical crystals were additively discolored by exposing them to the presence of small quantities of sulfur polymers (Na₂S₂, Na₂S₃, Na₂S₄ and Na₂S₅) [22]. Some of the single crystals were additively discolored by exposing them to sodium vapour under an Argon pressure of 0.2 atm., between 700°C and 800°C. Samples treated at the lower temperature limit were afterwards colorless, whereas at higher temperature a blue coloration appears. For the conductivity experiments, the as-grown samples had to be brought to shape to fit between the electrodes. With the aid of a string saw, disks were cut parallel to (111) cleavage plans. Then, the surfaces were rigorously polished to better than 1 μm. Typically, the sample thickness varied from about 2 to 3.5 mm with a cross section of approximately 150 mm². All the operations were performed under paraffin oil in order to prevent reactions in the presence of moisture.

3. X-RAY DIFFRACTION EXPERIMENTS

A selected optically controlled crystal with dimensions of 0.09 × 0.14 × 0.17 mm was in a first step attached to a quartz fiber by using commercial polyacrylate glue. Rapid contact between the Na₂S single crystal and the glue allows to fix the crystal even under paraffin. A oil filled glass tube was then slipped over the crystal and fixed to the sample holder. The cell parameter a = 6.5373(1) Å was refined from 25 reflections, measured on a CAD4 automatic diffractometer (cooper radiation, λ = 1.5418 Å) with 65° < Θ < 70°. This value is found to be slightly larger than the one reported in Ref. [4] (6.526 Å). A complete sphere of 548 reflections was measured. Three standard reflections were monitored at one hour interval. The maximum variation of these reflections was 1.6%. No systematic decrease was found during the measuring time (24 h) and the optical control after the measurement revealed no surface damage due to hydration. The absorption was corrected, based on the morphology of the crystal; values of (λn(λmin=0.055/0.079) were calculated. Table 1 summarises the results and further data. A full matrix least squares refinement of five variables was made by using the XTAL refinement package [23] on F² using 27 independent reflections. The refinement converged to a final residual value of R_w = 0.023.

Table 1. Crystallographic data for Na₂S

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Cubic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>Fm3m (No. 225)</td>
</tr>
<tr>
<td>Unit cell dimension a (Å)</td>
<td>6.5373 (1)</td>
</tr>
<tr>
<td>Cell volume (Å³)</td>
<td>279.380 (13)</td>
</tr>
<tr>
<td>X-ray density (g cm⁻³)</td>
<td>1.885</td>
</tr>
<tr>
<td>Formula units</td>
<td>4</td>
</tr>
<tr>
<td>Reflections measured (observed I &gt; 3σ)</td>
<td>548 (548)</td>
</tr>
<tr>
<td>R(ω,I)</td>
<td>0.072</td>
</tr>
<tr>
<td>Radiation source (wavelength in Å)</td>
<td>CuKα(1.5418)</td>
</tr>
<tr>
<td>S</td>
<td>1.87</td>
</tr>
<tr>
<td>(∆ρ)min max (e Å⁻³)</td>
<td>-0.35/ + 0.17</td>
</tr>
<tr>
<td>Extinction parameter</td>
<td>0.62(3)</td>
</tr>
</tbody>
</table>
Ionic conductivity of Na$_2$S single crystals

Table 2. Atomic positions, displacement parameters ($\AA^2 \times 100$) and population parameters

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>$U \times 100$</th>
<th>Population</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>1.78 (3)</td>
<td>0.988 (3)</td>
</tr>
<tr>
<td>S</td>
<td>0.00</td>
<td>0.50</td>
<td>0.50</td>
<td>1.24 (4)</td>
<td>1.000</td>
</tr>
</tbody>
</table>

As a result only minor deviations of the anti-fluorite structure were found (see Table 2):

1. The refinement of the population of Na$^+$ was made. The value of 0.988(3) indicates an almost stoichiometric crystal (within 4σ) with only few defects on the Na site. Those defects almost certainly contribute to the intrinsic ionic conductivity found at high temperatures.

2. The dynamic atomic displacement factor of Na$^+$ is larger (0.0178 $\AA^2$ (3)) than the one calculated for S$^{2-}$ (0.0124 $\AA^2$ (4)) in agreement with the higher mobility of the sodium ions in the sublattice.

If the sulfur sublattice is underpopulated there will be static displacements of the Na$^+$ ions from their cubic lattice sites. This effect would not contribute towards an increase in ionic conduction.

4. IONIC CONDUCTIVITY EXPERIMENTS

4.1. Experimentals

Our impedance spectroscopy setup measures directly the real and imaginary components of the voltage applied to the sample and compares it to the voltage appearing on a reference resistance in series, with the aid of a double phase-sensitive detector. The real and imaginary components yield the impedance and/or admittance. The calibration of the system allows us to measure complex impedance values between 0.1 $\Omega$ and 10 GΩ. We use a SR 530 lock-in amplifier to detect and measure the small ac signals. This amplifier is particularly apt because of the narrow band-pass characteristics and the very high gain at the band center ($Q = 10^6$), well beyond the capabilities of passive electronic filters. A typical band width is 0.0025 Hz, with a frequency range extending from 0.5 to 100 KHz. Voltages from 500 mV down to 100 nV full scale can be measured. The lock-in amplifier is equipped with automatic phase-locked loops for frequency study. The measurements yield the amplitude of the signal and the phase between the signal and the reference. With the aid of models (see appendix a) we calculate the real part of the imaginary part of the impedance. The reference impedances used were high precision pure resistors having nominal values between 1 $\Omega$ and 10 MΩ (decade values) with a guaranteed accuracy of 0.1%. A computer is used to pilot the different parts of the setup via RS232 interfaces. The temperature of the furnace and of the sample in the measurement cell are controlled to a precision of 0.25° by two Omega CN 76000 temperature controllers. The computer program accepts as input data the initial and final temperatures, the temperature step. Then, a delay time before starting a measurement can be selected and, the frequency range and the number of frequency points. Successive cycles are easily programmed. The measurement cell (see Fig. 1) was designed for high temperature measurements (up to 1350 K). The sample is squeezed between two vitrous carbon disk electrodes of 15 mm diameter. These electrodes gave reproducible results under thermal cycling and were found to present no reactivity with sulfides, even at the highest temperatures. Other electrode materials such as silver paint were found unsuitable due to their temperature limitations. Nevertheless, we verified that those two electrode geometries gave the same bulk conductivity values from the low temperature impedance spectra. Two Nickel rods conduct the current to the electrodes and a chromel–alumel thermocouple is placed near the sample. Nickel screens are mounted at several heights of the cell. We use ultra pure sintered boron nitride spacers as insulators ($R = 10^8 \Omega$ cm at 1000°C) between the rods and the screens. The temperature profile of the cell was measured and a temperature gradient of less than 1° mm$^{-1}$ was observed near the sample. All the conductivity runs were made under Argon and reproducible
results were obtained after two or three thermal cycles. A frequency dependence of the conductivity was noted at low temperatures \((T < 600 \text{ K})\) as well as at high temperatures \((T > 1000 \text{ K})\), whereas at intermediate temperatures no frequency dependence was found.

4.2. Calibration procedure of the impedance apparatus

We calibrated and evaluated the performance of our impedance spectroscopy set-up by using different series-parallele combinations of frequency-independent resistors and capacitors. Previous measurements, especially on high impedance circuits \((R > 1 \text{ M}\Omega)\) with a capacitance of less than 10 pF showed that it was important to take into account all stray capacitances and the input impedances of the lock-in amplifier. One way to estimate those effects is to perform experiments on simple R–C circuits assembled with precision resistors and capacitances of known value. The results are then compared with the equation obtained from the model devices. Best agreement was obtained with the formula derived from the circuit shown in Fig. 2, where \(Z_L\)

![Fig. 2. Schematics of the sample and load circuits used for the measurement of complex impedance.](image)

represents the input impedance of the SR 530 lock-in, \(Z_i\) the input impedance of the signal amplifier, \(Z\) the unknown impedance and \(R_f\) the standard reference resistors (1 Ω to 10 MΩ). The resistive part, \(R_L\), of \(Z_L\) was fixed to 100 MΩ as specified in the SR 530 technical specifications whereas the total capacitive part, \(C_L\), was deduced from the results of our calibration experiments, and estimated to 203 pF, including the stray capacitance of our connecting BNC cables and the one of an electronic switch box. \(Z_i\) was found to be equal to 600 Ω. The complete formulae used to calculate the complex impedance are given in Appendix A. Results of representative calibration experiments are reported in Figs 3–6. In order to compare them, it was more convenient to separate the real from the imaginary part and to represent each one as a function of frequency. Indeed the simple logarithmic \(Z\) diagram (‘Cole–Cole’ diagram) could hide important information about the frequency dependence. The parallel R–C circuits having a real part of the impedance of less than 1 GΩ give very satisfactory performance of the system (see Fig. 3), even in the situation where two parallele R–C circuits are in series.

![Fig. 3. Simple series–parallel combination of resistance and capacitor \((R1 = 110 \text{ M}\Omega\) and \(C1 = 15 \text{ pF}\). The points represent the experimental measurements and the solid lines show the theoretical curves.](image)

![Fig. 4. Two parallel R–C circuits in series \((R1 = 110 \text{ M}\Omega, R2 = 22 \text{ M}\Omega, C1 = 15 \text{ pF}\) and \(C2 = 1.8 \text{ pF}\).](image)

![Fig. 5. As in Fig. 4 but \(R1 = R2 = 110 \text{ M}\Omega, C1 = 15 \text{ pF}\) and \(C2 = 150 \text{ pF}\).](image)
Fig. 6. Single Parallel R-C circuit ($R_1 = 12.235 \text{ G}\Omega$ and $C_1 = 1 \text{ pF}$).

(see Figs 4 and 5). The frequency dependent position of the maximum of the imaginary part is well reproduced and at low frequencies the value of the real part is in very close agreement with the resistor value. When the resistive part is very high ($12.235 \text{ G}\Omega$) and the capacitive part very small ($< 1 \text{ pF}$), the limit of the setup begins to be reached (see Fig. 6). Nevertheless, it is possible to obtain results of satisfactory precision ($\pm 5\%$) for the real part of high impedances. Furthermore, under normal experimental conditions, it is necessary to shunt the unknown impedance in the equivalent circuit with a capacitance representing the cell capacitance: $C_p$. This one was determined experimentally and found to be equal to 1.75 pF. When small $R$ values are measured ($R < 10 \text{ G}\Omega$), it is necessary to include in addition to $C_p$ also the series resistance of the cell. We found that at highest temperatures ($T > 1100 \text{ K}$), the complex impedance of the cell is given by:

$$Z_{\text{cell}} = Z'_{\text{cell}} + iZ''_{\text{cell}}$$

where the real part and imaginary part take the form:

$$Z'_{\text{cell}}(f) = 0.25 + 0.30 \exp[0.7\log_{10}(f/10^5)]\Omega$$

$$Z''_{\text{cell}}(f) = -0.79\exp[0.85\log_{10}(f/10^5)]\Omega$$

The corrections contain further a frequency dependent part to take into account the skin-effect of the alternating current. They are essential for an accurate determination of high conductivities and can greatly modify the results, especially at high temperatures where conductivity less than $1 \text{ G}\Omega^{-1} \text{ cm}^{-1}$ is observed.

4.3. Data analysis

Anion Frenkel defects are the dominant intrinsic defects in the alkaline earth fluorides as their formation energies are low (from 1.8 eV to 2.8 eV) compared to the ones of Schottky defects (5–6 eV) [24–26]. Since the anti-fluorite structure is antimorphous to the fluorite structure it seems reasonable to consider cation Frenkel defects as the predominant thermally-induced point defects. Previous studies on Li$_2$O [27, 28], Li$_2$S [29] and Na$_2$S [8, 9] showed that the cation is the more mobile species and confirmed this hypothesis. Therefore, the intrinsic ionic conductivity can be attributed to Na$^+$ vacancy and Na$^+$ interstitial motion. The known thermodynamic parameters of defect formation of pure fluorite compounds indicate that vacancies are the more mobile defects at low temperatures whereas at higher temperatures the mobility of interstitials becomes preponderant. The possible mechanisms for vacancy diffusion consist of the direct motion of the neighbour cation into a cationic vacancy along the (100) direction or along the (110) direction as shown in Fig. 7. As the temperature increases, cationic interstitial diffusion may appear with two possible mechanisms: the direct interstitial mechanism involving (110) jumps or the non-collinear interstitial one (see Fig. 7). This latter mechanism is the more probable as it requires a much smaller energy to produce ionic motions. Complications come from the superposition of the different diffusion mechanisms (by vacancies and simultaneously by interstitials) and can prevent a simple conductivity analysis: indeed, the intrinsic conductivity region does not yield a simple straight line plot in an Arrhenius diagram ($\log_{10}\sigma$ versus $1000/T$). If we further consider the interactions among the defects as correlation and displacement effects, the number of parameters involved becomes high with the concomitant uncertainties of the analysis. The method most often used with fluoride and chloride compounds for high accuracy has been the least-square fitting method [30–32], including Debye–Hückel activity coefficients in the mass action equations for defect concentrations, and Onsager–Pitts mobility corrections. This method gives very satisfactory results if the analysis
is performed simultaneously on highly pure crystals and on doped crystals of precisely known impurity concentration, as the influence of these ones is primordial in controlling the defect population.

The analysis of conductivity data in an Arrhenius diagram could be made as follow: at low temperature (region I), the conductivity arises from defects created by the presence of unknown impurities. Associated with this region is an Arrhenius migration enthalpy, $\Delta h_v$, due to Na\textsuperscript{+} vacancy motions (the more mobile species). At higher temperatures, the regions of intrinsic conductivity are observed in which the conductivity is due only to thermally induced defects (the number of impurity induced defects becomes negligible). The Arrhenius energy then includes both, the energy of creation and of motion. In region II, the Na\textsuperscript{+} vacancies are the main thermally induced defects which contribute to the intrinsic conductivity. The slope of the Arrhenius plot is given by $-\Delta h_v - h_F/2$. Fitting the Arrhenius relation to this part yields the cation Frenkel defect formation enthalpy $h_F$. In region III, the intrinsic conductivity is dominated by the motion of thermally induced Na\textsuperscript{+} interstitials. The associated Arrhenius enthalpy is $-\Delta h_i - h_F/2$ and leads to the determination of $\Delta h_i$ (interstitial migration enthalpy). Then, the total set of conductivity data could be fitted to an equation of the form:

$$\sigma T = A_f \exp \left( -\frac{\Delta h_v}{kT} \right) + A_i \exp \left( -\frac{\Delta h_i}{kT} \right) \exp \left( -\frac{h_F}{2kT} \right)$$

The exponential prefactors $A_f$, $A_i$ and $A_{ii}$ include the vacancy migration entropy, $\Delta S_v$, the Frenkel defect formation entropy, $S_f$, and the interstitial migration entropy, $\Delta S_i$, respectively. At low temperatures $\Delta S_v$ can be evaluated if the conductivity measurements include experiments on doped crystals of precisely known concentration, by using the equation:

$$A_f = \frac{c(Ze)^2v^2}{k} \exp \left( \frac{\Delta S_v}{k} \right)$$

where $c$ is the vacancy concentration determined by that of the impurity, $(Ze)$ is the effective charge of the vacancies, $\lambda$ is the jump distance and $v$ is the standard lattice vibration frequency.

The accuracy of the fit could be known by considering the deviation between experimental and calculated values in a plot of the form $[(\sigma T)_{\text{exp}} - (\sigma T)_{\text{calc}}]/(\sigma T)_{\text{exp}}$ against $1000/T$ (K). The experimental errors comprise those due to the resistance measurements, the temperature measurements and the determination of the geometrical factor of the sample. The error introduced by our impedance spectroscopy apparatus ranges from 0.1% for a measured resistance of less than 100 M$\Omega$ (the standard reference resistors accuracy) to 5% for a measured resistance higher than 1 G$\Omega$ (see Section 4.2). The temperature is well-defined and controlled to $\pm$ 0.25 K by the two temperature controllers. During the frequency conductivity measurements, temperature variations of less than 1 K were always found. The experimental error on the geometrical factor could be important and can lead to a large error in the determination of absolute conductivity values. It was minimised by using samples of lateral dimensions much larger than the thickness and by ensuring an intimate contact between the electrodes and the material. Note that this error remains constant for a series of measurements on one sample and does not affect the evaluation of enthalpy values. It appears rather difficult to determine the cumulative errors on the parameters in this type of analysis, but enthalpy values should be reasonably accurate, to at least $\pm$ 0.05 eV.

4.4. Results and discussion

Since a strong frequency dependence of the conductivity was noted at low temperatures, we use the impedance representation to evaluate the bulk conductivity of Na$_2$S near room temperature. This phenomenon is well-known and is attributed to the imperfect nature of the crystal-electrodes contact [33, 34]. Fig. 8 shows typical impedance spectra recorded at low temperatures, between 310 and 388 K. The spectra show two parts: a high frequency region due to the electrical properties of the bulk, and a low frequency region being function of the nature of the electrode and of the contact. The former region, which is rather independent of the electrodes, can be approximated by a semi-circle in the impedance diagram for evaluation of the conductivity $\sigma$.
of the crystal using the well-known relation:

\[ \sigma = \frac{e}{s \cdot \mathcal{R}} \]

where the ratio \(e/s\) is the geometrical factor of the sample \(e\), thickness; \(s\), area.

As the temperature increases, the bulk semi-circle moves to higher values of frequency and joins the upper frequency limit of our impedance apparatus. We present in Fig. 9 the low temperature Arrhenius plot obtained by using bulk conductivity values as described. The graph exhibits one principal linear region with an apparent Arrhenius activation energy of 0.59 eV, whereas at lower temperatures (\(1000/T > 2.9\)) a small curvature indicates the appearance of one supplementary extrinsic conductivity region, known as the association region. There, electrically neutral pairs are formed by the association of impurities with oppositely charged defects on neighbouring sites. We further compare the conductivity data measured at fixed frequency with those evaluated from bulk semi-circles between 298 K and 500 K. The conductivity as a function of the angular frequency, \(\sigma(\omega)\), is given by:

\[ \sigma(\omega) = \frac{e}{s \cdot \mathcal{R}} \left[ \frac{Z'(\omega)}{Z'(\omega)^2 + Z''(\omega)^2} \right] \]

where \(Z'(\omega)\) and \(Z''(\omega)\) are the real and imaginary parts of the complex impedance of the crystal with \(\omega\) equal to \(2\pi f\). Fig. 10 presents the results obtained at \(f = 10^5\) Hz and those calculated from the complex impedance plots. The values of \(\sigma(\omega)\) show good agreement above 450 K (see curves 1 and 2). At this temperature the effect of the imperfect electrode contact tends to disappear and the resistance of the sample remains frequency independent.

A typical conductivity versus temperature run (up to 1350 K) of a second single crystal of Na\(_2\)S is also presented in Fig. 10 (see curve 3). The comparison between the two crystals allows us to separate the intrinsic region from extrinsic ones. The different conduction regions are marked with the corresponding roman numeral used in the data analysis (see Section 4.3). The intrinsic region clearly shows a behaviour analogous to classical superionic fluorides as CaF\(_2\), BaF\(_2\), or SrF\(_2\): at temperatures a few hundred degrees below the melting temperature, \(T_m\), the conductivity plot exhibits a rapid rise in the ionic conductivity before the occurrence of a high conductivity region where the values become comparable so that in the molten salt. This last region has a low apparent Arrhenius energy (\(< 0.5 \text{ eV}\)). This breakdown is attributed to the transition towards a fast-ion conduction region (region IV) and has already been reported for a number of fluorite structured compounds. The precise determination of the transition temperature, \(T_c\), from conductivity experiments is rather difficult as a continuous slow change in curvature is observed during the transition. The value of 1276 K reported in Ref. [4] for a broad specific heat anomaly seems to agree quite well with our results. In order to determine the thermodynamic defect parameters, we fitted our conductivity data between \(1000/T = 1.4\) (715 K) and \(1000/T = 0.9\) (1110 K). All data points...
above the fast-ion transition temperature were excluded from the analysis. Fig. 11 presents the result of the fit. The curves representing the cation-vacancy and cation-interstitial contributions to the total conductivity are also reported (see curves 1, 2 and 3). Table 3 gives the parameters obtained, and the accuracy of the computer fit, expressed in percentage, is indicated in Fig. 12. The quality of the fit (average accuracy of 1.8%) appears to be satisfactory considering the data analysis used. The Na⁺ vacancy migration enthalpy, Δhₐ, found (0.63 eV) is very close to the value of 0.59 eV deduced from impedance plots and is not very far from values obtained in previous NMR investigations of Na⁺ diffusion (Eₐ = 0.7 eV) [6] and conductivity measurements by Möbius et al. (Eₐ = 0.75 eV) [7]. The cation Frenkel defect formation enthalpy, hₕ, is found to be 2.51 eV. It is difficult at this moment to compare this value with results from series of other anti-fluorite type compounds because there is lack of published data. The only experimental value reported concerns the isostructural compound Li₂O with hₕ = 2.53 eV by Chadwick et al. [27]. These authors compare their experimental value with the one obtained from calculations based on shell model potentials. They find 2.12 eV for the cation-Frenkel enthalpy and 5.15 eV for the Schottky disorder enthalpy. Note that Na₂S and Li₂O have almost identical ratios of the cationic radius over the anionic one (Rₐ/ι = 1.07/1.84 = 0.554 Å and Rₐ/ι = 0.76/1.40 = 0.543 Å) [35].

The apparent activation Arrhenius energy in the region occurring just below Tₑ (region III) amounts to 3.16 eV, leading to a possible interstitial migration enthalpy value, Δhᵢ, of 1.89 eV. This value is appreciably higher than the one reported for non-collinear interstitial motion in alkaline earth fluorides (0.7 eV < Δhᵢ < 1 eV) [24, 36] and rules out the idea that the rapid rise in ionic conductivity occurring before Tₑ could be due only to a change from intrinsic conduction by vacancies to intrinsic conduction by interstitials. Note that we also made the approximation to neglect coulombic interaction between point defects in our approach. Conductivity studies on KI crystal [37], using a Debye–Hückel treatment of coulomb interaction, showed that σ can be higher by as high as 25% at high temperatures. Furthermore, paths of enhanced diffusivity may also exist, linked to possible mechanical deformations of the crystal for instance due to dislocations, and can lead to an even more marked curvature adjacent to the intrinsic region. Therefore, supplementary experimental diffusion studies around the transition temperature, Tₑ, are needed.

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Table 3. Exponential prefactors and defect enthalpies derived from the computer analysis of the conductivity measurements

<table>
<thead>
<tr>
<th>Crystal</th>
<th>A₁ (cm⁻¹ K⁻¹)</th>
<th>Aᵢ (cm⁻¹ K⁻¹)</th>
<th>Aᵢ (cm⁻¹ K⁻¹)</th>
<th>hₕ (eV)</th>
<th>Δhₐ (eV)</th>
<th>Δhᵢ (eV)</th>
<th>Number of data points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂S #2</td>
<td>1.08 × 10³</td>
<td>7.39 × 10¹⁰</td>
<td>4.28 × 10¹⁶</td>
<td>2.512</td>
<td>0.633</td>
<td>1.879</td>
<td>74</td>
</tr>
</tbody>
</table>

Fig. 11. Conductivity analysis of crystal #2. The solid lines represent the calculated curves from the parameters given in Table 3: (1) extrinsic vacancy contribution; (2) intrinsic vacancy contribution; (3) intrinsic interstitial contribution. The Tₑ arrow represents the transition temperature of Ref. [4].

Fig. 12. Difference between experimental and calculated conductivity data, expressed in percentage, as obtained from the conductivity analysis of crystal #2.
APPENDIX A.

All of the symbols are complex quantities (the equivalent circuit used for formula is represented in Fig. 2).

\[ C_p: \text{cell capacitance (} C_p = 1.75 \mu \text{F} \text{).} \]

\[ Z_L: \text{input impedance of the SR 530 lock-in (} R_L = 100 \Omega, C_L = 203 \mu \text{F} \text{).} \]

\[ Z_i: \text{input impedance of the signal amplifier (} Z_i = R_i = 600 \Omega. \]

\[ Z = Z(\sigma): \text{unknown impedance of the crystal.} \]

\[ U = U(\sigma): \text{measured voltage of the reference channel.} \]

\[ V = V(\sigma): \text{measured voltage of the test channel.} \]

\[ X = X(\sigma): \text{source voltage.} \]

The resolution of eqn (3) with respect to \( \alpha \) allows us to calculate the real and imaginary parts of the unknown impedance \( Z' \), by using \( Z' = \alpha - R_f \).

\[ V(ZL)(Z' + R_f) + ZL(R_i + Z') + R_f(R_i + Z') \]

\[ ZL = \frac{R_L}{1 + i\omega R_C C_L} \]

In the test channel:

\[ X = \frac{V(ZL)(Z' + R_f) + ZL(R_i + Z') + R_f(R_i + Z')}{ZL} \]

\[ \frac{X - U}{R_i + Z'} = \frac{U}{R_f} + \frac{U}{Z_L} \]

\[ X = \frac{V(ZL)(Z' + R_f) + ZL(R_i + Z') + R_f(R_i + Z')}{ZL} \]

From (eqn (1)) and (eqn (2)) with \( \alpha = Z' + R_f \):

\[ -U(R_f + Z_f)\alpha^2 + [\alpha V R_f (Z_L + R_f) - U(R_f Z_L - (R_f + R_i)(R_f + Z_f))] = 0 \]

\[ (R_f + R_i)(R_f + Z_f)] \alpha - VR_f R_f Z_L = 0 \]

The resolution of eqn (3) with respect to \( \alpha \) allows us to calculate the real and imaginary parts of the unknown impedance \( Z' \), by using \( Z' = \alpha - R_f \).

REFERENCES


