

Electronic Properties of Sodium-C222-sodide

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The electrical conductivity of both polycrystalline and single-crystal $\text{Na}^+\text{C222} \cdot \text{Na}^-$ was measured as a function of temperature from 220 to 280 K and the dielectric constant of polycrystalline samples was studied as a function of frequency from 1 kHz to 10 MHz at several temperatures. The results show both electronic and ionic conductivity for single crystals but the ionic contribution is suppressed in polycrystalline samples. The activation energies for ionic and electronic transport are 1.6 ± 0.2 eV and 1.2 ± 0.1 eV, respectively. After being subjected to a dc potential of >2.0 V for a period of time, single crystals had an open circuit voltage that decayed only slowly with time, showing that the system behaves as an electrochemical cell. When the potential was <2.0 V, the effect was absent. The results are in agreement with ionic conduction by Na^+ superimposed on a background of electronic conduction. © 1987 Academic Press, Inc.

Introduction

The sodide salt, $\text{Na}^+\text{C222} \cdot \text{Na}^-$, is a well-characterized member of a relatively new class of ionic salts, called *alkalides*, in which the positive ions are complexed alkali metal cations and the negative ions are alkali metal anions (1-3). A number of alkalides, in which the cation is complexed by either cryptands such as cryptand[2.2.2], (C222), or by crown ethers, have been prepared and characterized (4, 5).

Electrons are relatively weakly bound by alkali metal anions, so that one might expect alkalides to behave as semiconductors, with a band gap determined by the electron binding energy of the anion. Early

powder conductivity studies of the sodide, $\text{Na}^+\text{C222} \cdot \text{Na}^-$, yielded an apparent band gap of ~ 2.4 eV (3). The optical transmission spectrum of thin films of this compound showed a peak at ~ 1.8 eV that was attributed to a $3s-3p$ bound-bound transition (6). A shoulder at ~ 2.3 eV was also observed that could be a transition to the conduction band. Studies of the conductivities of alkalides have been hampered by two difficulties. First, the synthesis methods usually lead to salts that are heavily doped with trapped electrons. These electrons are in shallow potential wells and dominate the conductivity, leading to apparent band gaps of only 0.6-1.0 eV. Second, alkalides are very reactive toward air and moisture and are also thermally unstable, often decomposing irreversibly at temperatures above -20°C . The first crystalline sodide, $\text{Na}^+\text{C222} \cdot \text{Na}^-$, is more stable than others, can be prepared in pure form

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with a very low concentration of trapped electrons, and millimeter-sized single crystals can be grown. Because of the relative stability and known crystal structure (7, 8) of $\text{Na}^+\text{C}_{222} \cdot \text{Na}^-$ and the ability to prepare large enough single crystals, the present study focused on this "parent compound." We report here conductivity studies of both polycrystalline and single-crystal samples as well as dielectric constant measurements of polycrystalline samples.

Experimental

The sodide, $\text{Na}^+\text{C}_{222} \cdot \text{Na}^-$, was synthesized as previously described (4). It precipitates from solution in the form of small crystallites that were used in the studies on "powdered" samples. Large crystals were grown by redissolving the crystallites in a 1:2 mixture of methylamine and ethylamine and cooling the solution slowly. By cycling the temperature several times before the final slow cooling, crystals of 1- to 2-mm edge lengths could be prepared. The reactivity of alkalis with air and moisture required the use of an inert atmosphere glove box or glove bag when transferring samples.

The cell used for initial powder conductivity measurements is described in detail elsewhere (3, 9). It consists of two stainless steel rods as electrodes and a precision-bore quartz capillary for the sample compartment. The lower electrode is fixed and the upper, spring-loaded electrode exerts an adjustable force on the sample equivalent to pressures up to 50 atm. The cryostat is a triple-walled cylinder that fits on top of a liquid N_2 Dewar in such a way that cold nitrogen first passes through the space between the inner two walls, then over the sample in the center and finally through the space between the outer two walls. Temperature control to within $\pm 0.5^\circ$ was achieved with a Varian 4343 control unit.

Numerous attempts were made to mea-

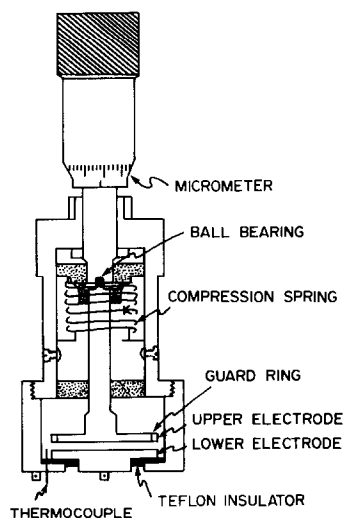


FIG. 1. Two-electrode cell used for single-crystal and powder conductivity studies and for measurement of the complex function at various frequencies.

sure the conductivity of single crystals by a four-probe method (10). While satisfactory contacts could be made by using a suspension of micrometer-sized gold-palladium powder (80:20) in Apiezon stopcock grease, the resistivity of the crystals proved to be too high for four-probe measurements. Therefore, the two-electrode system described below was used in the dc mode.

For permittivity and loss measurements, a variable plate capacitor, as described by Broadhurst and Bur (11) was constructed. The electrodes, of 2.65 cm diameters, were made of silver-plated brass, and the distance between them was controlled to ± 0.03 mm with a micrometer accompanied by a compression spring (Fig. 1). To minimize errors due to surface leakage, a guard-ring geometry (12) was used with the proviso that the thickness of the samples was small compared to the 3-mm of the guard ring. The cell dimensions were reduced to fit the cryostat. An ac voltage was applied to the cell, connected in series with a fixed known resistance (1-700 k Ω) at various fre-

quencies in the range 1–100 kHz. By measuring the voltage drop across the resistance, and the phase difference between the applied voltage and the current with an EG&G Model 5207 Lock-in amplifier, the real and imaginary parts of the complex cell impedance were calculated. The voltage drop across the external resistance was kept at less than 10% of the applied voltage to minimize effects on the phase difference. The complex impedance of the empty cell at the same electrode spacing was also measured. The complex impedance of the cables and any stray capacitance were measured by increasing the electrode spacing to 5 cm.

In the frequency range 0.6 to 10.0 MHz, a Hewlett Packard Vector Impedance Meter Model 4815A was used with a resonance method, and the capacitance was measured to within ± 0.1 pF. From these measurements, the components of the complex dielectric constant (ϵ' , ϵ'') were calculated.

The same cell was used to measure the conductivity of single crystals. For each run, a suitable flat crystal was selected by microscopic examination and loaded, while cold, inside of a nitrogen-filled glove bag, between the parallel plates of the cell. The crystal dimensions varied from sample to sample, but were approximately $1 \times 1 \times 0.5$ mm. The c axis (hexagonal setting (8)) was perpendicular to the electrode surfaces. To prevent fracture of the crystals under pressure, the cell was connected to a Keithley Model 610 BR electrometer, used as a sensitive ohmmeter. The electrode spacing was slowly reduced until a sudden drop in resistance indicated electrical contact. The very high sensitivity of the sodide salt to many chemicals, and its thermal sensitivity, prevented surface coating by evaporation, sputtering, or leaf coating. However, although the crystals fracture under high pressures, they are relatively soft, so that suitable contacts to the flat surfaces are easily made, even without surface coating.

The conductivities of single-crystal samples were measured in two ways: (a) by applying dc voltages in the range of 1–6 V in both the forward and reverse directions; and (b) by using rectangular pulses of alternating polarity and low frequency (0.01–0.10 Hz) with magnitudes of 1–10 V. These pulses were generated with a Wavetek Model 116 V.C.G. Generator. The current was measured in both cases with a Keithley 610 BR Picoammeter. Currents as low as 10^{-12} A could be easily measured in this way. The sample temperature was measured with a copper–constantan thermocouple located inside the sample cell. For a series of different temperatures, the conductivity was calculated from the slopes of I – V plots and the crystal dimensions. For voltages higher than 2 V, a steady decrease in the dc conductivity was observed as a function of time (vide infra). To minimize the time dependence of the conductivity in case (a), the current was permitted to flow through the sample for only a few seconds during each measurement. In case (b) the current through the sample was sequentially measured in both directions.

Open circuit voltages with and without a load resistor were measured with a Keithley Model 617 Programmable Electrometer operating in the voltage mode (input impedance, 10^{16} Ω). These measurements involved (a) a constant applied voltage of 1, 2, 3, or 5 V between the electrodes for time periods of 1–2 hr (charging process); and (b) voltage measurements during discharge with the power supply disconnected. Up to 100 points could be stored, and the sampling rate could be varied from three readings per second to one reading per hour.

The response of the crystals was very different for applied voltages above and below 2 V (see Results). Finally, I – V plots at different temperatures were examined in experiments in which one of the electrodes was covered by sodium metal. Measure-

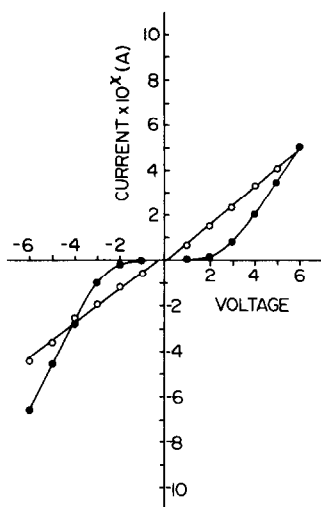


FIG. 2. Current-voltage curves for a single crystal of $\text{Na}^+\text{C222} \cdot \text{Na}^-$ at $+7^\circ\text{C}$ (solid circles, $x = 6$) and at -49°C (open circles, $x = 9$).

ments of the open circuit voltage during discharge and of the total charge passed during charge and discharge cycles were made in this case.

Results and Discussion

Powdered samples of $\text{Na}^+\text{C222} \cdot \text{Na}^-$ generally formed ohmic contacts with the electrodes and current-voltage plots gave straight lines which passed through the origin. The conductivity decreased by a factor of 10^4 as the temperature was decreased by 60° . The behavior is described by

$$\sigma = \sigma_\infty \exp(-E_g/2kT) \quad (1)$$

Notwithstanding some variation of σ values for different powdered samples, the same value of the apparent band-gap energy, $E_g = 2.4 \pm 0.2$ eV, was found for all previous experiments and also in this work. The value of σ_∞ , the extrapolated conductivity at infinite temperature was very high (10^6 – $10^{12} \Omega^{-1} \text{cm}^{-1}$), suggesting intrinsic semiconductivity.

Polarization Behavior

The conductivity behavior of single crystals subjected to dc voltages >2.0 V was strikingly different from that of powders. The single crystals showed distinctly non-linear I-V curves with large polarization. However, at temperatures below approximately -24°C , the I-V curves were nearly linear, and passed through the origin. The same behavior was observed upon both cooling and heating. Representative I-V plots are shown in Fig. 2. Strictly linear I-V plots were found at all temperatures when rectangular pulses of alternate polarity were used to eliminate polarization effects. These results are shown in Fig. 3. Note that one of the lines corresponds to a crushed crystal.

A clue to the nature of the polarization under dc potentials and of the conduction process was obtained by studying the time dependence of the conductivity. With potentials >2 V, the specific conductance decreased significantly with time when the po-

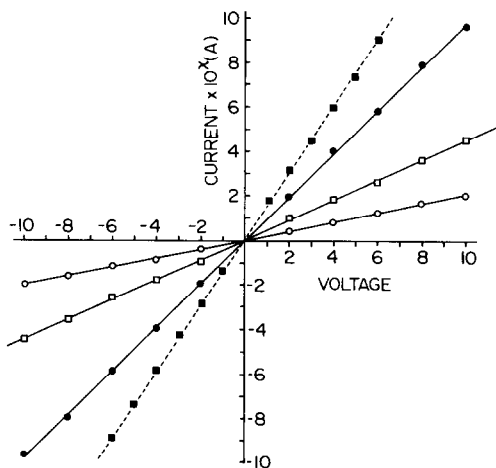


FIG. 3. Current-voltage curves for a single crystal of $\text{Na}^+\text{C222} \cdot \text{Na}^-$ at various temperatures as measured with rectangular voltage pulses of alternating sign. From top to bottom (positive potentials): $t = +0.8^\circ\text{C}$, $x = 12$ (crushed crystal); $t = -4.8^\circ\text{C}$, $x = 8$; $t = +3^\circ\text{C}$, $x = 6$; $t = -24.6^\circ\text{C}$, $x = 10$.

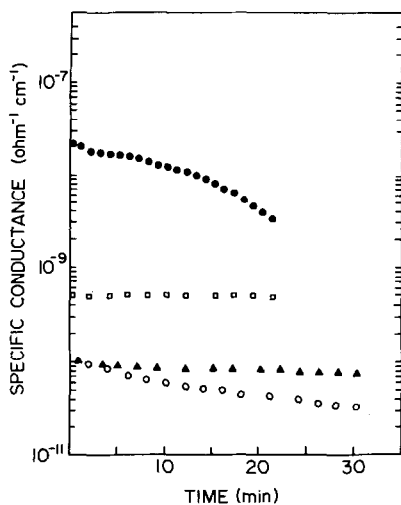


FIG. 4. Time dependence of the specific conductance of a single crystal of $\text{Na}^+\text{C}_{222} \cdot \text{Na}^-$. From top to bottom: 5 V, 20°C; 2 V, 20°C; 3 V, 0°C; 5 V, 0°C. Since the same crystal was used successively, the specific conductances are not the same as for a fresh crystal.

tential was maintained, while lower voltages resulted in no change with time (Fig. 4). When alternating rectangular voltage pulses at the 5-V level were used, there was no time dependence. It is well-known that when a constant voltage is applied to a solid ionic conductor, the current flowing through the crystal is time dependent because of polarization effects near the electrodes, where a depletion layer forms. When this occurs, the initial conductivity is higher than the steady-state value reached after a long time. When the voltage is too low to permit an electrochemical reaction at the electrodes, only electronic conduction processes can contribute. In the case of $\text{Na}^+\text{C}_{222} \cdot \text{Na}^-$, it appears that the potential must be high enough (>2 V) to reduce Na^+ to Na(s) before ionic conduction can occur. At low temperatures, the ionic contribution becomes small compared with the electronic contribution, so that the polarization effects disappear. The use of an

alternating current (rectangular pulses) also eliminates the polarization because of restoration of the concentration when Na(s) , plated out during one half-cycle, is oxidized to Na^+ on the next half-cycle.

To check these assumptions, and to determine the limiting electrochemical reaction, experiments were carried out with metallic sodium covering one of the electrodes. The results, shown in Fig. 5, provide dramatic verification of the polarization mechanism. When the potential of this electrode was positive, marked polarization occurred due to the discharge of Na^+ . Upon reversal of the voltage, however, the polarization disappeared. The apparent finite current at zero voltage is a result of the electrochemical cell behavior to be described later.

It should be pointed out that polarization could also occur at the positive electrode if, for example, Na^- were discharged. To test

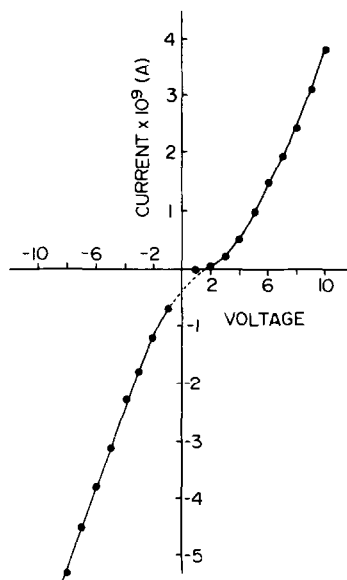
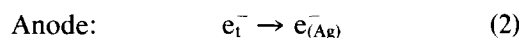
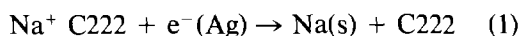


FIG. 5. Current-voltage curves for a single crystal of $\text{Na}^+\text{C}_{222} \cdot \text{Na}^-$ when one electrode was precoated with Na(s) . The sign of the potential given here corresponds to that of the uncoated electrode. The potential was first swept in the positive direction.

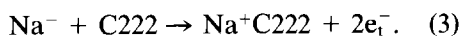
this possibility, the conductivity of a single crystal of $\text{Na}^+\text{C222} \cdot \text{I}^-$ was measured under similar conditions to those used with $\text{Na}^+\text{C222} \cdot \text{Na}^-$. As with $\text{Na}^+\text{C222} \cdot \text{Na}^-$, the iodide salt showed a marked decrease in conductivity with time, decreasing by a factor of six over 5-hr period. Polarization was pronounced and there was no evidence of residual electronic conductivity. The polarization disappeared with alternating rectangular pulses, and a residual current at zero applied voltages suggested voltaic action due to the deposition of sodium.

Although the nature of the electrode reactions cannot be determined with certainty, we postulate the following processes:

Cathode:



in which e_t^- is a trapped electron, as is present in electrides (3). This species could be formed by the reaction



The anodic reaction when sodium is present on the anode would then be the reverse of reaction (1). The sodium was present initially in some experiments but was formed in the electrochemical process at the cathode in all cases. Thus, rectangular pulses show no polarization because of reversible plating and oxidation of sodium on successive cycles.

According to this scheme, the conducting ionic species in both $\text{Na}^+\text{C222} \cdot \text{Na}^-$ and $\text{Na}^+\text{C222} \cdot \text{I}^-$ is the cation, probably migrating from one cryptand molecule to another. In the sodide, there is an additional contribution from electrons, thermally excited from Na^- to the conduction band. The specific conductance studies described below are in accord with this picture.

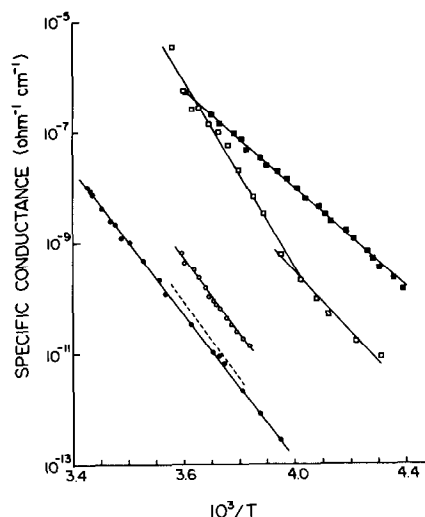


FIG. 6. Specific conductance versus $10^3/T$ for single crystals and powders of $\text{Na}^+\text{C222} \cdot \text{Na}^-$. From top to bottom: single crystal subject to a dc voltage of 5 V; single crystal subject to successive rectangular pulses of ± 5 to ± 10 V of alternating sign; single crystal subject to alternating ± 2 V pulses; crushed crystal subject to a dc voltage of 5 V (dashed line); powdered sample (results are independent of voltage).

Conductivity Studies

Single-crystal and powder conductivities were determined from the slopes of $I-V$ plots at various temperatures and the crystal dimensions, or from the area and thickness of the powdered samples. In the latter case, the effective filling factor was determined by weighing the sample.

The results obtained with a unidirectional voltage of 5 V are not very meaningful because of the polarization and the time dependence. As shown in Fig. 6, the apparent slope of a semilog plot of the specific conductance versus $1/T$ is much lower than is obtained with rectangular pulses. The behavior was also different for heating and subsequent cooling cycles as expected from the effect of polarization and time-dependent depletion.

The results obtained for a constant dc voltage of only 2.0 V are very different, be-

ing some 3–4 orders of magnitude below that obtained with a potential of 5.0 V. This reflects the much lower value of the electronic conductivity. The activation energy of the latter is 1.2 ± 0.1 eV, the same value as is obtained for powdered samples. The conductivity when rectangular pulses of amplitude up to ± 10 V were used shows a changing slope in the semilog plot at low temperatures. This may be due to a contribution from electronic conductivity. The activation energy for the ionic contribution to the conductivity is 1.6 ± 0.2 eV. The iodide salt had an activation energy of 1.5 ± 0.2 eV.

It is interesting to note the differences between the results of single-crystal studies and those obtained with powders. The dashed line in Fig. 6 is the result obtained when a single crystal was crushed under pressure. The conductance behavior in this case is very similar to that obtained with powdered samples. Presumably, the ionic contribution to the conductance is "quenched" in powdered samples. This might result from a resistance to movement of Na^+ across grain boundaries. The order-of-magnitude drop in the *electronic* contribution in going from single crystals to powders is commonly observed with semiconductors and can be attributed to grain-boundary effects.

Electrochemical Behavior

The proposed electrochemical scheme given by Eqs. (1) and (2) suggests that a crystal subject to a dc potential for a period of time should behave as a voltaic cell. The first evidence of such behavior was the extrapolation of the conductivity data to zero potential. Finite currents remained, as shown in Fig. 5. This behavior was always observed upon prolonged electrolysis. To be certain that this was not caused by the participation of the silver electrodes (for example, by the electrochemical formation of Ag^+), the experiments were repeated

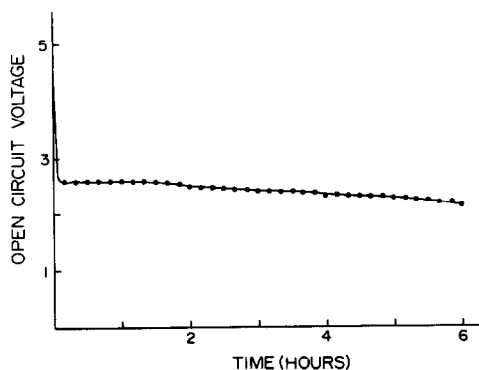


FIG. 7. Open circuit voltage versus time for a single crystal of $\text{Na}^+\text{C}_{222} \cdot \text{Na}^-$ that had been subject to a dc voltage of 5 V for 1 hr.

with squares of platinum foil on the electrodes. The behavior was the same. After subjecting a single crystal to a dc potential of 5 V for 1 or 2 hr, the open-circuit voltage was measured as a function of time. The voltage dropped rapidly to about 2.6 V and gradually decreased over a time period of 10 min to about 2.2 V. When the charging potential was 1.0 V for the same period of time, the open-circuit voltage dropped quickly to zero at essentially the capacitance discharge rate. When one of the electrodes was covered with sodium metal and this electrode was held at -5 V for a period of time, the open-circuit voltage decayed only slightly over a 6-hr period (Fig. 7). When, however, the sodium-covered electrode was made the positive electrode during charging, the open-circuit voltage dropped quickly to zero, presumably because *both* electrodes were now covered with sodium and no *net* change had occurred during the charging cycle. This suggests that the anodic reaction (2) is less favored than the reverse of (1).

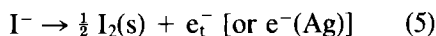
Coulometric studies with a series load resistance of $8.5 \times 10^9 \Omega$ gave a total charge of 1.6×10^{-6} C during charging, while during discharge, the crystal produced $0.6 \times$

10^{-6} C of charge, an efficiency of about 36%. Electronic conductivity, incomplete coverage of the cathode with sodium during the charging cycle, and interruption of the sodium film during discharge would all lead to a low efficiency.

It was possible also to obtain electrochemical cell behavior with single crystals of $\text{Na}^+\text{C222} \cdot \text{I}^-$. Presumably the same anodic reaction could occur during discharge,



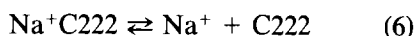
The cathodic reaction must be different, however, since this compound does not contain Na^- . Perhaps the oxidation reaction



can occur.

Visual observation of crystals of $\text{Na}^+\text{C222} \cdot \text{Na}^-$ immediately after prolonged charging tends to support the scheme outlined above. The surface in contact with a negatively charged silver electrode remained bronze-colored but the electrode surface had a deposit on it (presumably sodium). Identification of this film by analysis was not possible because of the small amounts and because of the high concentration of sodium in the crystal, which would give a positive result for sodium in any case. The other surface of the crystal was black, the color of an electride.

All of the observations described above are in agreement with a model of mixed ionic-electronic conductivity, in which Na^+ migrates toward the cathode. Dissociation of the complexed cation according to



might occur, followed by motion of Na^+ through the lattice until it encounters a free complexant molecule. Because of its small radius, Na^+ could easily occupy the normally empty pseudo-tetrahedral holes formed by closest packing of the large com-

plexed cation (Na^- occupies the pseudo-octahedral holes). The observed polarization would then originate from the voltage-dependent discharge of Na^+ at the cathode. Since the silver electrodes are blocking for Na^+ and since no Na^+ is supplied at the anode, one expects the dc current to decay with time as observed, and to be more pronounced at high temperatures because of the higher mobilities for a given voltage. The fact that no observable decrease in conductivity with time occurs with a bias of 2 V or less indicates that, as expected for electronic conductivity, no irreversible processes take place under these conditions. The observed activation energy at high temperatures is then the energy required to move Na^+ from one complexant molecule to the next, while the activation energy at low temperatures, or low potentials, is one-half the band-gap energy of the sodide. The ohmic behavior observed for pressed powders, the lower activation energy, and the much lower conductivity, suggest that movement of Na^+ or Na^- across grain boundaries is inhibited and only the electronic contribution is observed.

Dielectric Constant Measurements

Measurement of the complex impedance of $\text{Na}^+\text{C222} \cdot \text{Na}^-$ as a function of frequency had to be made with powdered samples, since the cable capacitance was too large to give reliable results with small single crystals. Over the frequency range 1–100 kHz at a filling factor of 1.5 the value of ϵ' was 2.4 ± 0.2 (standard deviation) at -31°C , while between 0.6 and 10.0 MHz the value was 2.0 ± 0.2 . A second sample that was compressed to a filling factor of 1.15 gave values of 2.6 ± 0.2 between 1 and 100 kHz at $+9^\circ\text{C}$ and 2.5 ± 0.3 at -15°C , while at $+14^\circ\text{C}$ between 0.6 and 10.0 MHz the value was 2.1 ± 0.2 . In all cases the value of ϵ'' was within experimental error of zero. The data are shown in Figure 8.

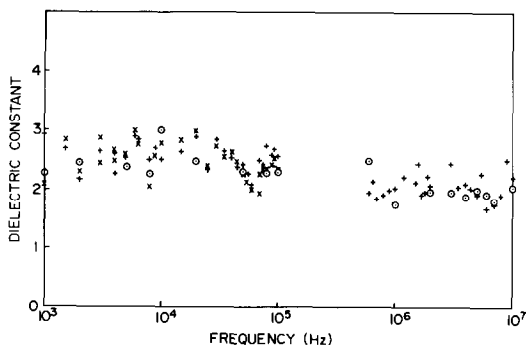


FIG. 8. The dielectric constant (ϵ') versus frequency for powdered samples of $\text{Na}^+\text{C}_{222} \cdot \text{Na}^-$: \circ , filling factor = 1.50, $t = -31^\circ\text{C}$; $+$, filling factor = 1.15, $t = +9^\circ\text{C}$ ($+14^\circ\text{C}$ for frequencies above $6 \times 10^5\text{Hz}$); \times , filling factor = 1.15, $t = -15^\circ\text{C}$.

While there could be a small decrease in the dielectric constant between 10^5 and 10^6 Hz, it was in this frequency range that the measuring method was changed. This, combined with random standard deviations of ± 0.2 to ± 0.3 makes it difficult to conclude that there is any significant change in the dielectric constant with frequency. We therefore tentatively conclude that the dielectric constant is 2.4 ± 0.4 , independent of frequency and temperature.

Acknowledgments

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