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PREPARATION AND IONIC CONDUCTIVITY OF OH^--FREE SODIUM FLUORIDE CRYSTALS DOPED WITH CALCIUM*†

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ABSTRACT

A series of OH^--free NaF single crystals has been prepared and the influence of substitutional calcium ions on the ionic conductivity has been studied. The activation energy for migration of a cation vacancy in NaF:Ca is 1.36 ± 0.1 eV. An isothermal plot of ionic conductivity vs. divalent impurity concentration has been used to analyze several nominally pure NaF samples for divalent impurity levels.

Introduction

Ionic conductivity measurements have been very useful in the detection of divalent impurities in alkali halides. Lehfeldt in 1933 reported the ionic conductivity as a function of temperature for several nominally pure alkali halides (1). Although others have since investigated the ionic conductivity of many of these compounds intentionally doped with divalent impurities (Table I), there does not appear to have been any such study involving sodium fluoride doped with divalent ions.

Sodium fluoride is a material of considerable interest in solid state research, being one of the few solids which is naturally isotopically pure. It is therefore very useful for the investigation of many lattice dynamical properties. These properties are, however, extremely sensitive to the chemical purity of

the sodium fluoride crystal used, and especially to the presence of divalent and molecular impurities.

TABLE I

Some Previously Studied Systems

Reference	Host	Dopant
2	LiF(Cl,Br,I)	Mg
3	NaCl	Cd
4	NaBr	Ba
5	KCl	Ca,Sr,Ba
6	KCl	Sr
7	KBr	Ca
8	KI	Cd
9	CsCl	Sr
10	CsCl	Ba

For low concentrations of impurity, an isothermal plot of ionic conductivity vs. impurity concentration is linear (11). If the temperature is not too low (12,13), and assuming substitutional solution, association effects are minimal and each divalent impurity ion present in the crystal lattice generates one positive ion vacancy in order to preserve electrical neutrality. The energy of activation for migration of these cation vacancies can be determined from the slope of the log conductivity vs. reciprocal temperature plot. In the presence of molecular impurities such as OH^-, however, the ionic conductivity for a particular divalent impurity concentration and temperature is reduced from the ionic conductivity observed for an OH^--free crystal (14,15). This phenomenon appears to result from the formation of complex ions between the molecular and divalent impurities (14).

The present investigation was undertaken to determine the effect of divalent impurity ions on the ionic conductivity of sodium fluoride. Because of the sensitivity of the ionic conductivity to molecular impurities, especially OH^-, it was first nec-

essary to develop a technique for the preparation of OH^--free sodium fluoride crystals. The quality of the crystals produced was monitored subsequently through infrared absorption spectroscopy and chemical analysis.

Experimental

A. Salt Handling and Crystal Growth

"Suprapur" NaF from Merck (Darmstadt, Germany) was used as the crystal host material, and Baker-Adamson Reagent Grade CaF_2 as the dopant. Pure and calcium-doped single crystals of NaF were prepared by the Kyropoulos-Czochralski technique (16-18). A schematic diagram of the apparatus and argon purification system (to be described below) is shown in Figure 1. The seed pulling rod and furnace chamber are stainless steel, water-cooled. The seed crystal is welded with a propane torch to a platinum wire held on the end of the rod.

FIG. 1

Crystal growing furnace and argon purification system. The numbered components of the apparatus are: (1) seed pulling rod, (2) seed, (3) the melt, (4) graphite heating element, (5) graphite shield for heating element, (6) wall of furnace, (7) power stud, (8) support for crucible, (9) cold trap, (10) liquid nitrogen, (11) activated charcoal, (12) acetone-dry ice mixture at -80°C, (13) heater at 375°C, (14) 87.5% Zr - 12.5% Ti getter alloy, (15) argon supply.

Extensive work was carried out to determine a suitable method for eliminating OH^--contamination of the NaF prior to crystal growth. Treatment of molten NaF with Matheson anhydrous hydrogen fluoride succeeded in eliminating OH^-, but introduced trace amounts of Cl^- contamination. Attempts to purify the hydrogen fluoride by fractional distillation were not successful.

The best method for removing OH^- was finally found to be an extended bakeout of the salt. The NaF powder was initially spread on glass plates in a vacuum oven at about .05 torr. The temperature was raised 6°C per day for a period of two weeks. After the salt was then allowed to cool back to room temperature, argon was admitted to return the oven to atmosphere pressure.

The NaF was next transferred to an 80 cm^3 capacity platinum crucible, the appropriate weight of CaF_2 added and the crucible mounted in the furnace. The furnace and empty crucible had previously been cleaned thoroughly and baked under vacuum at approximately 5×10^{-5} torr for four hours at 1200°C. Once the salt had been loaded, the furnace was pumped on at room temperature for six to ten hours before another bakeout procedure was initiated. The temperature was then raised to 500°C over a period of several days. After one day at any given intermediate temperature the pressure typically stabilized at 2×10^{-6} torr. Only 50 grams of NaF was used for each crystal, in order to increase the effectiveness of this bakeout by having the platinum crucible only half filled.

The crystals were grown under a slight positive pressure of Matheson Ultrahigh purity argon gas, which was purified further by passage through a zirconium-titanium getter alloy held at 375°C (Figure 1). The argon then passed through a stainless steel chamber filled with activated charcoal held at -80°C with a dry ice-acetone bath. This charcoal trap was vacuum-baked at 800°C for four hours prior to each use. As a final precaution, the argon was passed through a liquid nitrogen cold trap before being admitted to the furnace to an overpressure of about 5 psi. The

furnace was sealed, the temperature increased to melt the salt, and the growing procedure carried out.

Using this technique, pure and calcium-doped NaF boules approximately 2 cm square and 5 cm long were obtained. The crystals were pulled from the melt at a speed of about 2 cm per hour. After growth was completed, the furnace temperature was lowered gradually for a period of ten hours, with the boule hanging freely above the remainder of the NaF in the crucible.

A more elaborate method was also used to prepare a pure NaF crystal. The standard methods of zone-refining, so successful in the preparation of certain alkali halides especially low in multivalent ion impurities (19-22), are not applicable to alkali fluorides because F^- attacks quartz apparatus. Peech et. al. (23) have shown, furthermore, that exposure of a salt to air during transfer from the zone-refining apparatus to the crystal growing furnace can result in serious surface contamination of the salt. Mindful of these considerations, G. Schmidt of this laboratory has used a variation of the Kyropoulos-Czochralski method to, in effect, zone-refine NaF by repeated seed-pulling from the melt under the same protective argon atmosphere described above. A six-times grown NaF crystal was thus prepared by repeated seed-pulling followed by remelting and rejection of some of the unpulled melt each time. The net result was a highly pure NaF crystal zone-refined and grown without changing the protective atmosphere.

B. Ionic Conductivity Measurements

The ionic conductivity of pure and Ca^{2+}-doped NaF samples was measured as a function of temperature from 420°C to 220°C using the apparatus described by Barsis (24). Single crystals of NaF were cleaved into samples approximately 1 mm square and 5 mm in length. The ends were coated with Dag dispersion No. 154 colloidal graphite in alcohol, thinned with acetone. The high purity graphite electrodes and other graphite parts of the conductivity apparatus were purified by heating at 1000°C in chlorine prior to use in measurements. Measurements were taken in a vacuum at

5×10^{-4} torr. A 45 volt potential was applied across the crystal mounted between the graphite electrodes. The current flowing through the crystal was determined with a Cary Vibrating Reed Electrometer Model 31, which measured the voltage drop across a known resistor in series with the crystal and voltage source.

C. Infrared Absorption and Chemical Analysis

Each NaF crystal was checked routinely for the presence of molecular impurities using a Perkin Elmer Model 521 Spectrophotometer. Scans were taken over the infrared region from 2.5 to 20 microns.

Portions of the NaF crystals as close as possible to the samples used for ionic conductivity measurements were analyzed for calcium content by the Cornell Analytical Chemistry Facility. The most successful method for calcium determination proved to be emission spectroscopy. A Jarrell-Ash emission spectrograph with a DC arc and 30 mm slit width was used. The NaF samples were powdered and mixed with lutetium as an internal standard. The calcium concentration was determined from the intensity ratio of the 3009 cm^{-1} line for calcium and the 2911 cm^{-1} line for the lutetium standard. This method is considered accurate to about 15%, with limits of detection approaching 2 ppm.

Results and Discussion

The ionic conductivity as a function of temperature was measured for the series of OH^--free calcium-doped NaF crystals. From the slope of the ionic conductivity vs. reciprocal temperature plots for the various NaF:Ca samples, the activation energy for migration of a cation vacancy was calculated to be 1.36 ± 0.1 eV.

Figure 2, an isotherm at 667°K of the ionic conductivity vs. calcium concentration, demonstrates the linear relationship between these parameters. From the best fit straight line it is found that

$$\sigma = 3.0 \times 10^{-26} \, N(ohm^{-1}cm^{-1})cm^3$$

for T = 667°K, where N = number of Ca^{2+} ions/cm^3. Using ΔE_{ex} = 1.36 eV as the activation energy in the extrinsic region along with the above equation, it is found that the ionic conductivity in the extrinsic region for NaF:Ca obeys

$$\sigma = 3.0 \times 10^{-16}\ e^{-(\frac{1.36\ eV}{kT})} N\ (ohm^{-1}cm^{-1})cm^3.$$

FIG. 2

Ionic conductivity vs. concentration of calcium ions in OH^--free NaF for T = 667°K (solid circles). The open circles represent nominally pure NaF samples as follows: A) Lehfeldt crystal (1); B) Singly-grown crystal, this investigation; C) Six-times grown crystal, this investigation.

No OH^- was detected in the infrared spectra of any of these samples within the observable limits of absorption constant, $K < 0.01\ cm^{-1}$. Although these samples will subsequently be referred to as "OH^--free," specific heat measurements by Harrison et. al. (25) have shown that the OH^- concentration is about 0.1 ppm for NaF crystals from this laboratory showing no OH^- infrared absorption.

Related work in this laboratory (26) has shown that the presence of appreciable OH^- lowers the conductivity of NaF:Ca considerably. This agrees with the findings of Stoebe (14) for LiF

containing OH^-. For example, a crystal of NaF containing 50 ppm Ca^{2+} and considerable OH^- (absorption constant K = 0.31 cm^{-1} at 2.80 μ) had an ionic conductivity of 2 x 10^{-9} ohm^{-1} cm^{-1} at 667°K. This is more than ten times lower than the conductivity of the correspondingly Ca^{2+}-doped but OH^--free NaF sample in Figure 2. Thus, ionic conductivity studies with alkali halides doped with divalent cations require exclusion of OH^-.

Figure 2 can now be employed to estimate the divalent impurity concentration for nominally pure NaF crystals. When their ionic conductivity at 667°K is plotted on the isotherm extrapolated to 0 ppm divalent impurity concentration, the abscissa of the plot gives their divalent impurity concentration. Thus, point A in Figure 2 corresponds to the sample of Lehfeldt (1), which evidently contains about 125 ppm divalent impurity, assuming the sample to be OH^--free. Point B represents a singly-grown OH^--free NaF sample, from the present investigation, which appears to contain about 7 ppm divalent impurity. Finally, point C corresponds to the six-times grown NaF sample, which is the purest of all with about 2 ppm divalent impurity. Implicit in this use of the isotherm in Figure 2 is the assumption that all divalent impurities affect the ionic conductivity in the same way. This assumption is certainly valid for all the alkaline earth ions, as noted by Kelting and Witt (5) in the case of KCl doped with Ca^{2+}, Sr^{2+}, and Ba^{2+}, and it is these ions which would most likely be present as impurities in NaF.

The purity of the six-times grown NaF is comparable to or better than that of most other "high-purity" alkali halide crystals, which generally contain on the order of 10 ppm divalent impurities. Only in the case of KCl which was zone-refined and subsequently grown under the same protective atmosphere have impurity levels considerably below 1 ppm been obtained (23).

In summary, the influence of divalent impurity ions on the ionic conductivity of NaF was determined. It has been shown that

measurement of ionic conductivity can also be a useful means of analyzing NaF crystals for divalent impurity concentration. It is essential to exclude OH^- from the crystals, however, and an extended bakeout of the salt prior to crystal growth has been found to be the best method for removing OH^-. Furthermore, a multiple growth technique has been found successful in reducing the divalent impurity level in NaF crystals. The NaF crystals six-times grown from pre-baked salt are probably the purest NaF crystals yet produced with respect to molecular and divalent impurities.

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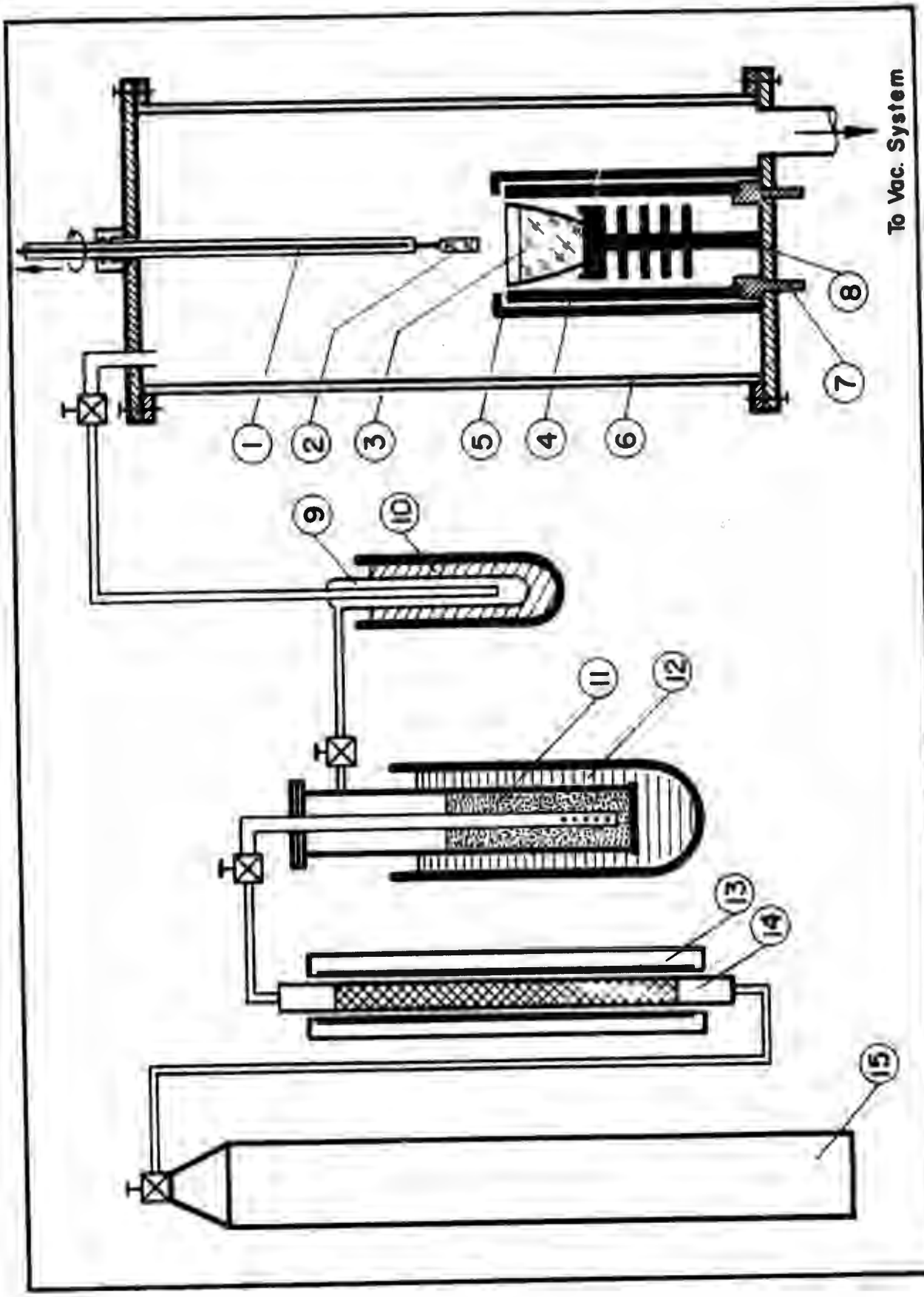

Figure 1

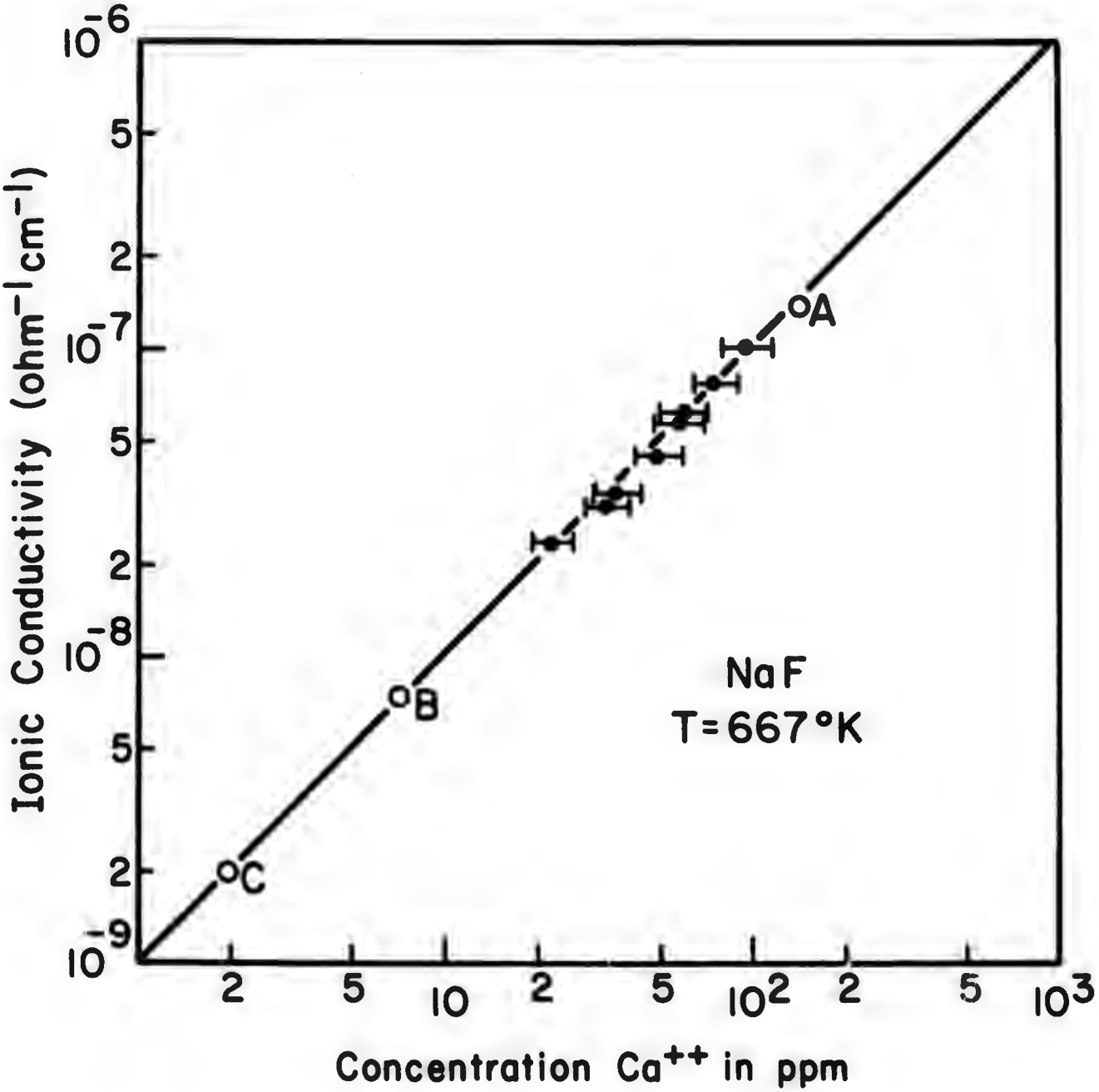
Ionic Conductivity (ohm^{-1}cm^{-1})
10^{-6}
5
2
10^{-7}
5
2
10^{-8}
5
2
10^{-9}
A
B
C
NaF
T=667°K
2
5
10
2
5
10^2
2
5
10^3
Concentration Ca^{++} in ppm

Figure 2