CCA-181 548.0:537:549.732.22

Electrical Conductivity of Borax*

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Received May 27, 1960

The crystal structure of sodium tetraborate decahydrate (borax) solved in 1956 by Morimoto[1] lead to the actual formula of this compound as $B_4O_5(OH)_4 \cdot Na_2\,8\,H_2O$. The anionic part of the structure is composed of $B_4O_5(OH)_4$-polyions linked by hydrogen bonds, while the cationic set of the chains is formed by sodium ions surrounded octahedrally with water molecules. These two types of chains are connected through hydrogen bonds running throughout the crystal parallel to its z-axis.

It seemed that it might be interesting to study the electrical conductivity of borax because of this continuous hydrogen bond network. We wish to report on a few preliminary experiments along this line.

We used two different samples of powdered material. One was an original powder of *Merck* borax (Fig. 1/a), while the other was prepared by crushing and grinding large crystals of *Analar* borax in a mortar (Fig. 1/b,c).

The resistivity was measured in the press described by Kamenar, Ban, and Dadić.[2] We made a minor alteration by replacing the heating coil with a jacket supplied with water from a temperature controlled bath ($\pm 0.05^0$C). Owing to the limited scope of the *Siemens* AC bridge some of the measurements had to be done with a *Pye* DC Wheatstone bridge.

The results are shown in Fig. 1 in a log specific resistivity vs. $\frac{1}{T}$ plot. (The straight lines were drawn by visual matching.)

At present we should like only to note a few interesting points deferring the detailed analysis od these results to another occasion.

It should be borne in mind that during these measurements borax was subject to unidirectional pressure. The pellets became homogeneous and glassy. Their X-ray diagrams revealed preferential orientation and some of the lines became diffuse, although the general pattern of an original powder diagram of borax seems to be preserved. There are also characteristic discontinuities between 20 and 30°C (Fig. 1) depending on the applied pressure, which we hope to study in more detail. However, the energy of activation for the straight line portion of the plots in Fig. 1 could be evaluated to better than $\pm 10\%$. It changes with pressure to some extent, but is about 1 eV in all cases and for both samples.

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* Partially reported at the I Yugoslav Congress for Pure and Applied Chemistry, Zagreb, June 1960.

The established range of conductivities (10^{-6} to 10^{-9} Ω^{-1} cm^{-1}), the E_a values, and particularly the positive temperature gradient of conductivity strongly suggest that borax could be placed among semiconductors.

According to Menzel,[3] borax can be partially dehydrated below 50°C without changing its crystal structure into that of sodium tetraborate pentahydrate. Products of such dehydration retaining only one mole water of crystallization still show the general features of a borax X-ray diagram. Loss of 8 moles H_2O results in an almost amorphous X-ray diagram. We dehydrated our *Analar* sample of borax in a vacuum of about 0.1 mm Hg over P_2O_5 at room temperature.

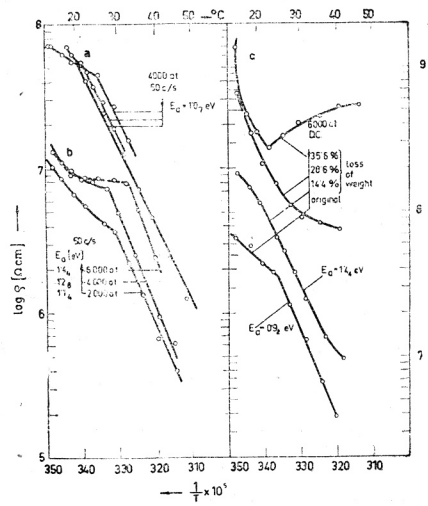

Fig. 1. The dependence of electrical resistivity of borax on temperature: a) reproducibility of results at constant pressure, b) effect of pressure and c) effect of dehydration.

As can be seen from Fig. 1/c dehydration has not only lowered the absolute values of the conductivities, but has also influenced the actual mechanism of conduction as indicated my quite a different log ϱ vs. $1/T$ dependence. It seems to be necessary to remove more than 3 moles of water in order to change this plot from a straight line into a curve.

We are engaged now in experiments on deuterated borax and in measurements on single crystals with a working hypothesis of protonic conduction.

REFERENCES

1. N. Morimoto, *Miner. J.* **2** (1956) 1.
2. B. Kamenar, Z. Ban, and M. Dadić, *Croat. Chem. Acta* **31** (1959) 159.
3. H. Menzel, *Z. anorg. allg. Chem.* **224** (1935) 1.

IZVOD

Električna vodljivost boraksa

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Mjerenjem električne vodljivosti boraksa u zavisnosti od temperature utvrđeno je da se specifična vodljivost kreće od 10^{-6} do 10^{-9} Ω^{-1} cm^{-1}, da ima pozitivni tem-

peraturni gradijent, te da je energija aktivacije oko 1 eV. To sve ukazuje, da bi se boraks mogao klasificirati među poluvodiče. Dehidratacijom se ova svojstva bitno promjene. Nastavlja se s pokusima, kojima je svrha ispitati mogućnost postojanja protonske vodljivosti u sistemu vodikovih mostova boraksa.

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Primljeno 27. svibnja 1960.