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Original Scientific Paper

## Electrical Conductivity of Semiconducting $\text{Na}_2\text{Te}^*$

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A new method for the preparation of the semiconducting compound  $\text{Na}_2\text{Te}$  as well as electrical conductance measurements in the system Na-Te is described. The composition of the samples nearly corresponded to  $\text{Na}_2\text{Te}$ , but with a small excess of tellurium. The conductance of each sample was measured three times. Between consecutive measurements the excess quantity of tellurium was gradually reduced by evaporation of the liquid phase, until the remaining sample had the exact composition  $\text{Na}_2\text{Te}$ . All measurements were carried out between room temperature and 620°C. The experimental curves were fitted mathematically. The most plausible explanation of conductance variation with temperature appears to be the following. The samples exhibit mixed ionic conduction of  $\text{Na}_2\text{Te}_2$  and  $\text{Na}_2\text{Te}_6$ , and intrinsic electronic conduction of  $\text{Na}_2\text{Te}$ . Characteristic activation energies for ionic conduction were calculated. For  $\text{Na}_2\text{Te}$  the energy gap  $E_g = 2.3$  eV.

### INTRODUCTION

Sodium telluride  $\text{Na}_2\text{Te}$  is a compound of the group  $A_2^I B^{VI}$ , whose semiconducting properties have already been predicted. It satisfies Mooser-Pearson's criteria for semiconductivity<sup>1</sup> but has not been examined experimentally. It may be said in advance that because of a large electronegativity difference between the component atoms in the compound, a large ionicity of the chemical bond and therefore a high energy gap together with small mobilities of electrons and holes<sup>2,3</sup> can be expected. Theoretical calculations of Bube<sup>4</sup> give the energy gap  $E_g = 1.7$  eV, while according to Suchet<sup>5</sup>  $E_g = 2.0$  eV.

Experimental examinations of  $\text{Na}_2\text{Te}$  and other compounds of type  $A_2^I B^{VI}$  are very delicate because of their instability in the air and the difficulty of manipulating alkali metals. But experimental data on basic parameters of semiconductors in this group are necessary for the checking and further development of theory.

### EXPERIMENTAL

For the preparation of sodium telluride samples a new method was used in which the reaction between sodium and tellurium takes place in a vacuum. It gives the samples an appropriate form for the measurement of their electrical

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resistance immediately after the preparation, without any additional manipulation in air. Such a method is necessary because in contact with air the samples oxidize and decompose.

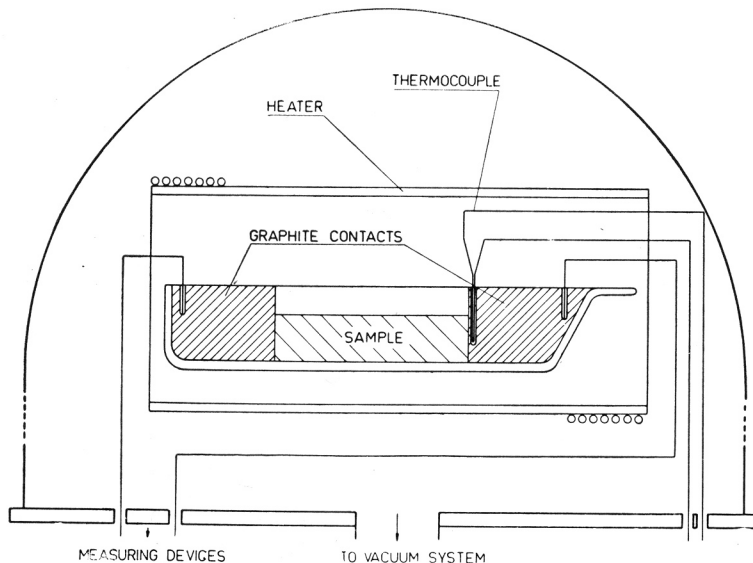


Fig. 1. Device for the preparation of telluride samples

Sodium and tellurium of high purity were placed between graphite contacts in a small  $\text{Al}_2\text{O}_3$  boat, which was surrounded by the heater on a silica tube. A Pt-RtRh thermocouple for temperature measurements was located near the sample on a graphite block. The whole device was placed under the pyrex bell of a high vacuum apparatus (Fig. 1). The cutting of sodium as well as the measurement of its volume was carried out in pure toluene.

The reaction between sodium and tellurium starts when the boat is heated to about  $270^\circ\text{C}$ . It is an exothermic reaction and liberated heat causes a rapid overheating of the sample and evaporation of some sodium. All samples, therefore, contain an excess of tellurium over the stoichiometric ratio for  $\text{Na}_2\text{Te}$ . In order to obtain a smooth surface or uniform cross-section of the sample, the boat was finally heated until a liquid phase appeared.

#### RESULTS

Six samples prepared from sodium and tellurium of different commercial origin were examined. The measurements were carried out in the following way: first, the resistance was measured from room temperature up to  $446^\circ\text{C}$ . At this point the measurement had to be interrupted, because the resistance changed even at constant temperature owing to evaporation of the liquid phase. At  $446^\circ\text{C}$  the sample was heated for 15 minutes. Then the whole measurement was repeated starting from room temperature to  $597^\circ\text{C}$ , where the sample was heated again for 15 minutes. Finally, the resistance was measured a third time from room temperature to  $620^\circ\text{C}$ . The measurements cannot be performed accurately at higher temperatures because of  $\text{Na}_2\text{Te}$ -sublimation. The results of one experiment are shown in Fig. 2, where the reciprocal values of the resistance  $R$  or conductance are plotted vs.  $10^3/T$ . The specific conductivities could not be given instead, because the

cross-section of the sample could not have been determined until all resistance measurements had been completed.

The cross-section was measured and the type of conduction examined with a thermal probe in an atmosphere of pure argon. All samples in the experiment were of dark yellow colour and showed weak p-type conduction at room temperature.

#### DISCUSSION

The equilibrium diagram of the system Na-Te is necessary in the interpretation of the described experimental results. We compiled the pertinent information from two monographs<sup>6,7</sup> using also the data of C. A. Kraus and S. W. Glass<sup>8</sup>. From this diagram and from earlier literature about the preparation of tellurides<sup>6,7</sup>, it follows that the sample after the reaction and cooling to room temperature is a mixture of the compounds  $\text{Na}_2\text{Te}$ ,  $\text{Na}_2\text{Te}_2$  and  $\text{Na}_2\text{Te}_6$ . Since the average composition of the mixture is near to 66.7 atomic % of Na, the relative amount of  $\text{Na}_2\text{Te}_2$  in the sample must be small, and that of  $\text{Na}_2\text{Te}_6$  still smaller. The same composition is observed also at higher temperatures, up to the eutectic point of the  $\text{Na}_2\text{Te}_2$ — $\text{Na}_2\text{Te}_6$  system at 319°C. Between 319°C and the peritectic point of  $\text{Na}_2\text{Te}$ — $\text{Na}_2\text{Te}_2$  system the higher tellurides liquefy. Above 355°C only solid  $\text{Na}_2\text{Te}$  and a liquid phase exist. In the whole interval from room temperature to 620°C, in which the resistance measurements were made, the relative amount of solid  $\text{Na}_2\text{Te}$  is practically constant. Since after the first and the second resistance measurements the samples are heated at constant temperature, the relative quantities of the liquid phase and of the higher tellurides decrease owing to evaporation. After the second measurement and heating, the sample consists practically only of solid  $\text{Na}_2\text{Te}$ .

Thus, knowing the phase-relations in the sample we can try to explain the dependence of conductance on temperature represented in Fig. 2. Generally, one can distinguish two temperature intervals, the first from about 20°C to 319°C, and the second, from 355°C to higher temperatures. In the first interval the experimental data can be fitted by the equation

$$1/R = (1/R)_1 \exp(-E_1/kT) + (1/R)_2 \exp(-E_2/kT)$$

where  $(1/R)_1$  is  $6.68 \times 10^4 \text{ ohm}^{-1}$ ,  $1.60 \times 10^3 \text{ ohm}^{-1}$ ,  $3.06 \times 10^2 \text{ ohm}^{-1}$  and  $(1/R)_2$  is  $2.64 \times 10^{-4} \text{ ohm}^{-1}$ ,  $6.34 \times 10^{-4} \text{ ohm}^{-1}$ ,  $1.21 \times 10^{-4} \text{ ohm}^{-1}$  for the upper, middle and lower curves, respectively. The energies are  $E_1 = 0.93 \text{ eV}$  and  $E_2 = 0.35 \text{ eV}$ . Experimental curves of other samples follow nearly the same law of conductance variation with temperature. Accordingly, within a 5% error the energy  $E_1$  is constant for all samples, but  $E_2$  varies from about 0.3 eV up to 0.5 eV. The ratio of energies  $E_1/E_2$  was always between 2 and 3. We therefore believe that in our samples the ionic conduction of the compounds  $\text{Na}_2\text{Te}_2$  and  $\text{Na}_2\text{Te}_6$  preponderates in this temperature range. Polarisation effect in Na-Te system was observed earlier by Kraus and Glass<sup>8</sup>.

At 319°C a liquid phase appears. Its relative quantity increases rapidly to 355°C because the whole amount of  $\text{Na}_2\text{Te}_2$  and  $\text{Na}_2\text{Te}_6$  melts in that interval. This process is followed by a rapid increase of the electrical conductance due to an increase of ion mobilities in the liquid phase just formed. However,

in the second and third measurements this increase is not so marked because the quantity of the liquid phase diminishes.

Finally, in the interval starting at 355°C the experimental curves can be represented by the equation

$$1/R = (1/R)_i + (1/R)_0 \exp(-E_g/2kT)$$

where  $(1/R)_i$  is  $6.92 \times 10^{-3} \text{ ohm}^{-1}$ ,  $1.15 \times 10^{-4} \text{ ohm}^{-1}$  and  $1.51 \times 10^{-5} \text{ ohm}^{-1}$  for

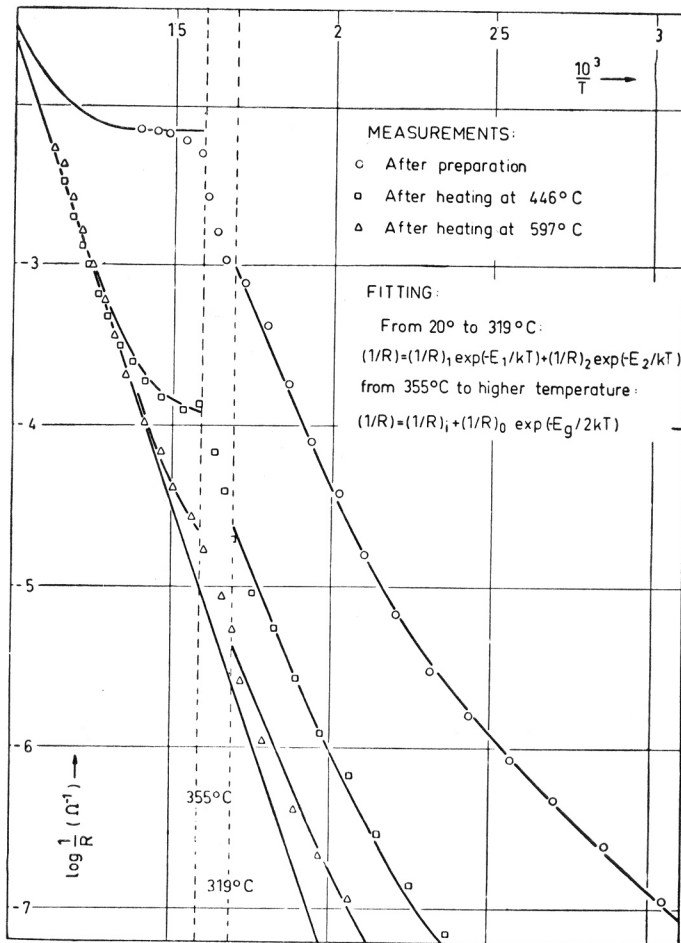


Fig. 2. Results of the experiment and fitting curves

the upper, middle and lower curves, respectively. The energy  $E_g$  and the constant  $(1/R)_0$  are the same for all curves *i.e.*  $E_g = 2.3 \text{ eV}$  and  $(1/R)_0 = 1.34 \times 10^4 \text{ ohm}^{-1}$ . Nearly the same results can be obtained from measurements on any other sample. We explain such a variation of the conductance with temperature by supposing that in the first and in the second measurements both ionic con-

duction of the liquid phase and electronic conduction of solid  $\text{Na}_2\text{Te}$  exist. The ionic part of the conduction is represented in the last equation by the constant  $(1/R)_i$  while the electronic part, as usually, changes exponentially with temperature.

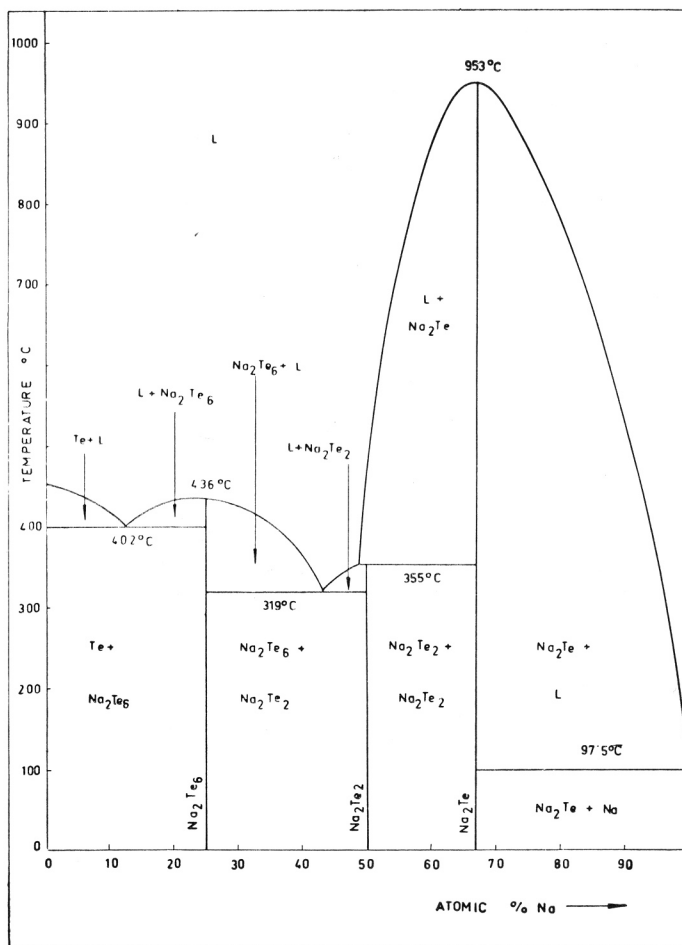


Fig. 3. Equilibrium diagram of Na-Te system

In the course of the third measurement, the yield of ionic conduction in the sample is very small, because the liquid phase during the heating at  $597^\circ\text{C}$  almost disappears. Therefore,  $(1/R)_i$  can be neglected. After the third measurement in which only  $\text{Na}_2\text{Te}$  exists, the dimensions of the sample were measured and the conductivity calculated. Thus, the last equation is now of the form

$$\sigma = \sigma_0 \exp(-E_g/2kT)$$

where  $\sigma_0 = 3.38 \times 10^5 \text{ ohm}^{-1} \text{ cm}^{-1}$  and  $E_g = 2.3 \text{ eV}$ .

All these facts lead to the conclusion that normal sodium telluride,  $\text{Na}_2\text{Te}$ , is a real semiconductor for which the electrical measurements give an energy gap equal to 2.3 eV. Its intrinsic range of conductivity begins at about  $400^\circ\text{C}$ , and the variation of conductivity with temperature can be represented in this range by the above equation. The energy gap calculated from our measurements is only in approximate accordance with the theoretical predictions of Suchet<sup>5</sup> (2.0 eV).

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## IZVOD

Električna vodljivost poluvodiča  $\text{Na}_2\text{Te}$ 

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Opisana je nova metoda dobivanja uzoraka poluvodičkog natrijeva telurida različitoga kemijskog sastava, i višestruko mjerenje ovisnosti njihove električne vodljivosti o temperaturi. Svi uzorci su u prvom mjerenju imali sastav blizak stehiometrijskom sastavu za  $\text{Na}_2\text{Te}$ , ali sa malim viškom telura. U ostalim mjerenjima višak je postepeno reduciran isparavanjem u vakuumu. Posljednje mjerenje vodljivosti vršeno je na čistom čvrstom  $\text{Na}_2\text{Te}$ , od sobne temperature do  $620^\circ\text{C}$ .

Rezultati mjerenja pokazuju da se promjene električne vodljivosti sistema Na-Te mogu tumačiti istovremenim postojanjem ionske vodljivosti spojeva  $\text{Na}_2\text{Te}_2$  i  $\text{Na}_2\text{Te}_t$  i vlastite elektronske vodljivosti poluvodičkog spoja  $\text{Na}_2\text{Te}$ . Iz eksperimentalnih krivulja izračunate su uobičajenim postupcima karakteristične energije aktivacije za ionsku vodljivost i širina zabranjene zone  $E_g$  za  $\text{Na}_2\text{Te}$ . Rezultat  $E_g = 2,3$  eV je u približnom slaganju sa teoretskim proračunima Sucheta.

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