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Letter to the Editor

# INVESTIGATION OF $NaH_3(SeO_3)_2$ BY ULTRASONIC AND ELASTIC RESONATOR METHODS[1]

## ИССЛЕДОВАНИЕ ОБРАЗЦОВ $NaH_3(SeO_3)_2$ ПРИ ПОМОЩИ УЛТРАЗВУКА И МЕТОДА УПРУГОГО РЕЗОНАТОРА

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$NaH_3(SeO_3)_2$ crystals have been investigated in the vicinity of the $\alpha - \beta$ phase transition at 195 K using ultrasonic and piezoelectric resonator methods. The dielectric and the elastic anomalies have been found to take place at different temperatures. Hence the occurrence of an intermediate phase within a temperature range of 0.8 K is suggested. This is supported by thermal investigations (DTA).

A first report about ferroelectricity in sodium-trihydrogenselenite (STHS) was given by Pepinsky and Vedam [1]. One crystals were grown from water solution by the method of cooling [2]. STHS is monoclinic in the paraelectric $\alpha$-phase (pointgroup 2/m). At a temperature $T_{\alpha\beta} = 195$ K the crystal passes into the ferroelectric triclinic $\beta$-phase (pointgroup 1). STHS undergoes a second phase transition of first order into another ferroelectric phase. This phase is monoclinic (pointgoup m). Many results concerning the $\alpha$ — $\beta$ phase transition have been reported up to now [3—7]. The nature of this phase transition is not yet completely clear. It has been impossible to describe this transition even by a model of pseudoproper ferroelastic- ferroelectric phase transitions. It has been also impossible to describe the elastic, dielectric, thermal, electromechanical properties as a whole complex. Besides it is difficult to compare these properties when obtained from different measurements. The piezoelectric resonator method [8] enables us to measure the elastic compliance, the dielectric permittivity and the piezoefficient simultaneously, that means, at the same time and with the same sample arrangement. In order to measure by the piezoelectric resonator method the samples had to be rectangular bars with dimensions of $0.5 \times 1.5 \times 10$ mm$^3$. In the largest areas silver electrodes were evaporated. These bars were holdered by flattened tin wires cemented into the vibration node of the bars. This is shown in Fig. 1a.

In order to get reproducible results and to induce piezoelectricity above $T_{\alpha\beta}$ we had to apply a dc-field of more than 5 kV/cm. We applied 7 kV/cm in the $z$-direction. In this way we observed the steplike behaviour of the temperature dependence of the elastic compliance $s_{11}$. The temperature dependence of $\varepsilon_{33}$ shows a peak at $T_\varepsilon$. This is shown in Fig. 2. The interesting fact is that the anomaly of $\varepsilon_{33}$ occurs nearly 0.2 K below that of $s_{11}$. From earlier measurements [9] we had to take into account that a dc-field shifts the transition point $T_{\alpha\beta}$. But it was interesting to learn the value of the temperature difference at the zero field. For STHS it is very difficult to get results with the piezoelectric resonator method without a dc field.

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Another method to investigate elastic properties are ultrasonic methods. But it was difficult to measure the elastic stiffness and the dielectric permittivity simultaneously with a high accuracy in the same sample, because the sample was a cube with lengths of 7 mm. The resulting capacitance of the sample was very small. But it was not necessary to get the accurate value of the dielectric permittivity but to get the accurate temperature of the anomaly of $\varepsilon_{33}$. The results of these measurements are plotted in Fig. 3. It is to be seen that the anomaly of $c_{22}$, which is a sharp step, takes place at a temperature which is 0.8 K higher than the temperature of the dielectric anomaly of $\varepsilon_{33}$. This shows that these methods are able to give results complementing one another.

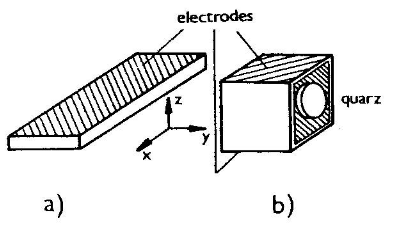

Fig. 1. a) Piezoelectric resonator; b) ultrasonic sample.

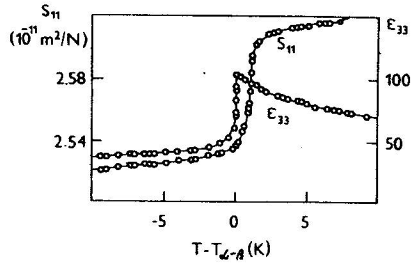

Fig. 2. Temperature dependence of the elastic compliance $s_{11}$ and of the dielectric constant $\varepsilon_{33}$.

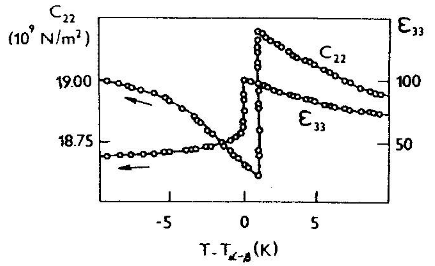

Fig. 3. Temperature dependence of the elastic stiffness $c_{22}$ and of the dielectric constant $\varepsilon_{33}$.

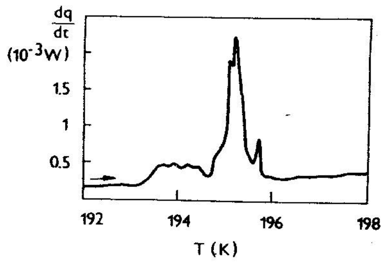

Fig. 4. Temperature dependence of the heat capacity $dq/dt$.

Every method has its advantages. The elastic resonator method allows the simultaneous measurement of the elastic, dielectric and electromechanical properties, whereas the ultrasonic methods allow measurements at zero field and in samples which are not piezoelectric. It is often necessary to apply an electric dc-field to a piezoelectric resonator. Another difference between the two methods is the different frequency range in which they are working. In order to compare the results obtained by the elastic resonator method and the ultrasonic method we measured the heat capacity of the sample by DTA-measurements. This illustrated in Fig. 4. The two peaks which are shown in this figure can be related to the anomalies of $s_{11}$ and $\varepsilon_{33}$. From these results the existence of an intermediate phase between the $\alpha$ and the $\beta$-phase is suggested. Since we could not find any piezoelectricity the symmetry of this phase which exists in a temperature range of 0.7—0.8 K should be 1.

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