DIELECTRIC PROPERTIES OF SODIUM TRIHYDROGEN SELENITE*

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The results of permittivity and dielectric loss tangent measurements of a sodium trihydrogen selenite crystal in a weak electric field at acoustic frequency in the temperature range from $-50°C$ to $-185°C$ have been presented. The occurrence of temperature hysteresis in both phase transitions and the influence of the measured intensity field on electric parameters in phase β have been stated. The measured results indicate that both phase transitions are of the first type.

1. Introduction

Crystalline sodium trihydrogen selenite $NaH_3(SeO_3)_2$ (STHS) is a very rare individual crystal which is electrically uniaxial in one phase and multiaxial in the other phase. The ferroelectric properties of crystalline $NaH_3(SeO_3)_2$ have been determined for the first time by Pepinsky [1] in 1959. The temperature of phase change from the paraelectric phase α to the ferroelectric phase β is $-79°C$. Phase γ in the crystal has been deduced by Makita [2] from investigations of specific heat anomaly. Blinc [3, 4] and Gavrilova [5] stated that deuter has a great influence on Curie temperature position in the crystal. On the basis of structural studies [6–8], it is evident that in phase α from the melting point up to $-79°C$ the crystal crystallizes in the monoclinic system and it belongs to point group $2/m$. In phase β from $-79°C$ up to about $-162°C$ it belongs to the triclinic system of point group 1. In phase γ occurring in the temperature below $-173°C$ [8] the crystal belongs to the monoclinic system of the point group m. The system of crystallographic axes (a, b, c) accepted by Miki [8] is presented on Fig. 1. At room temperature in the

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monoclinic system the angle $\beta = 91°10'$. The axis $b(y)$ is a twofold axis of phase α. Other crystallographic systems in the literature are collected in Shuvalov's work [9]. The investigations of the domain structure exhibited [10, 11] that in the crystal of phase β two kinds of domains appear — domains of type y and of type m, while the angle between the polarization vectors in domains is 80° [11]. From the investigations of phase transition in the crystal $NaH_3(SeO_3)_2$ admixed ions Cr by the EPR method it results that phase change $\alpha \leftrightarrow \beta$ in the temperature $-79.5°$ is the change of the first type [12]. Miki [13] stated the occurrence of temperature hysteresis of the expansion linear coefficient in both phase transitions.

The first measurements of crystal permittivity to the axis direction a_1 (see Fig. 1) in the temperature range up to $-100°C$ in the measuring field less than 20 V/cm have been

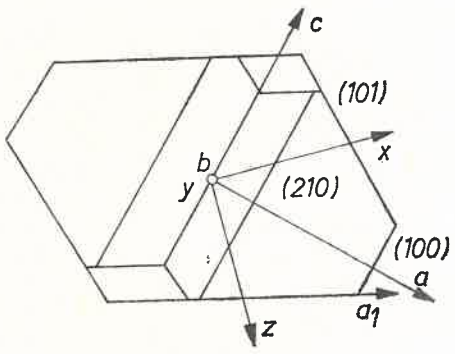

Fig. 1. System of crystallographic axes (a, b, c) and indicatrix axes (x, y, z) in the crystal

carried out by Blinc [4]. The acute peak of permittivity has been observed at phase transition as well as the fulfilling of the Curie-Weiss law by the component a_1 at which the Curie–Weiss temperature was $-81°C$ and temperature hysteresis was absent. From the dielectric measurements carried by Nino [14] for the direction [120] it is clear that for phase transition $\alpha \leftrightarrow \beta$ the temperature hysteresis is equal to 3.2°C from the permittivity measurements and 1.6°C from the measurements of spontaneous polarization; thus for phase transition $\beta \leftrightarrow \gamma$ the hysteresis is adequately 20.1°C and 14.7°C.

Shuvalov [10] investigated the permittivity measurements in the whole referenced temperature range for three orthogonal directions (x, y, z) (Fig. 1) in alternating electric field of intensity 10 V/cm and frequency 800 Hz. No occurrence of temperature hysteresis at phase transition $\alpha \leftrightarrow \beta$ has been observed, but at phase change $\beta \leftrightarrow \gamma$ the hysteresis was 10.5°C. The coordinate system has been selected in such a way that axes (x, y, z) overlap with the main indicatrix axes at room temperature. For crystallo-physic axes x and y the two directions of the bisector optic axis of acute and obtuse angles have been accepted; and the axis z has been oriented perpendicular to the optic axes plane. The axis y overlaps the twofold axis of phase β of the monoclinic system. The same coordinate system (x, y, z) has been accepted in this work.

In this work the results of measurements of permittivity and dielectric loss tangent for all three directions in the temperature range covering all three phases of the crystal have been given.

2. Experimental part

From a stoichiometrical amount of SeO_2 and NaOH dissolved in water after evaporation the polycrystals $NaH_3(SeO_3)_2$ were obtained. From polycrystals so obtained the saturated solution was prepared in which the crystal was grown by evaporation at a stable temperature 28°C. Thin plates of about 1 mm in thickness were cut out from the crystal in such a way that the normal to the surface had the directions consistent with the main indicatrix axes (x, y, z) (Fig. 1). On polished surfaces the silver electrodes were vaccum evaporated. The measurements of permittivity ε and dielectric loss tangent tan δ of the sample located in cryostat were carried out, while the temperature was lowered from room temperature down to about -185°C, and next while the temperature was increased (Fig. 2, 3, 4). Temperature was measured with the use of a copper-constantan thermocouple. Temperature read-out error was 0.03°C, but absolute error due to calibration of the thermocouple is evaluated as 0.5°C. In order to reduce the measuring error of the sample connected with the finite thermal conductivity of the crystal, inspection measurements have been carried out during which the end of the thermocouple was inserted in the opening inside the sample. The measurements during cooling and heating were performed under continuous temperature change, the rate of which being about 0.1°C/min. in the vicinity of phase transition and about 0.7°C/min. far from phase transition. Measurements ε and tan δ were taken with the aid of automatic capacitance bridge MERATRONIK E315a in an electric field of intensity 6–8 V/cm and frequency 1 kHz. The measurement results are presented in Fig. 2, 3, 4, 6. In order to investigate the influence of magnitude of measuring intensity on the values of permittivity the additional measurements were carried out in the system built-up from audio-frequency generator, capacity bridge with loss compensation and selective nanovoltmeter. The frequency of the generator was 10 kHz. The measurements were made under static conditions with the sample at stable temperature (Fig. 5).

3. The measurement results

The temperature course of relative permittivity and tan δ for the y component in the electric field of intensity 8 V/cm and frequency 1 kHz have been presented in Fig. 2. Permittivity changes linearly with temperature in paraelectric phase from -50 up to -78.8°C where a rapid increase of permittivity from the value of 180 to 3600 is observed. Permittivity diminishes monotonically with the temperature decrease down to -178°C where the abrupt drop in permittivity down to the value 12 is observed. For temperatures below -180°C the permittivity is stable — it does not depend on temperature. During the temperature increase permittivity remains stable up to -165°C, where the abrupt rise of permittivity takes place. Temperature hysteresis is 13°C at $\beta \leftrightarrow \gamma$ phase transition and

0.8–1°C at $\beta \leftrightarrow \alpha$ phase transition. The numerical values of permittivity for the temperature rise are lower than for the temperature decrease in phase β but they do not depend on the direction of temperature changes in phase α and γ.

In the temperature range from phase change $\alpha \rightarrow \beta$ up to -90°C additional measurements of permittivity have been taken in a field of intensity 0.8 V/cm and they have been marked on the diagram by a broken line. In a "weak" electric field permittivity is evidently

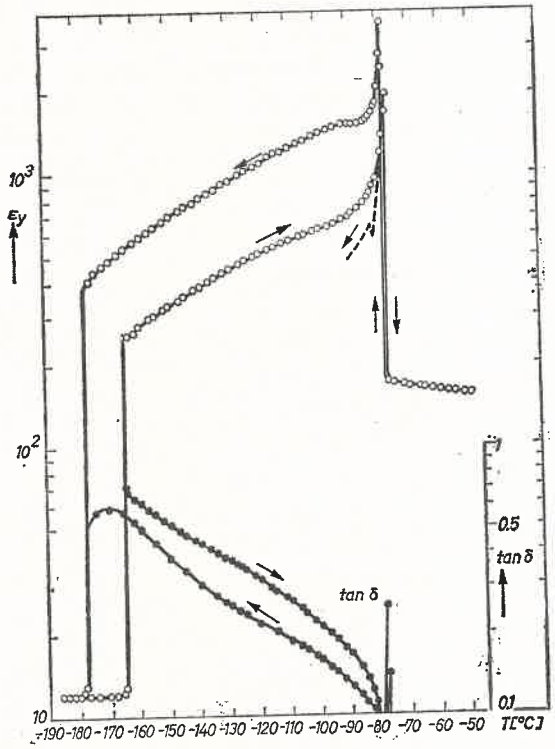

Fig. 2. Temperature dependence of permittivity and dielectric loss tangent in the direction of the y axis

smaller than in a "strong" field. In phase α and γ $\tan \delta < 10^{-3}$. Near the phase change $\alpha \leftrightarrow \beta$ an acute loss peak appears. The minimum loss tangent value 0.08 in phase β takes place at temperature -80°C, whereas the maximum value 0.6–0.7 appears near the phase transition $\beta \leftrightarrow \gamma$. The value of $\tan \delta$ similarly to that of ε increases together with the rise of intensity in the measuring field.

Temperature run of the x component of permittivity and $\tan \delta$ is presented in Fig. 3. The measurement has been taken in the field 6 V/cm during the diminishing and increasing of the temperature. Abrupt changes of permittivity occur at 78.8°C with hysteresis 0.8°C, whereas at the phase change $\beta \leftrightarrow \gamma$ at the temperature -178°C they are with hysteresis 16°C. In phase γ permittivity is 20 and temperature changes are very small of the order of 1%. Temperature run $\tan \delta$ is the same as for the y component. Changes refer only to numerical values in phase β, the minimum being 0.043 and the maximum -0.85.

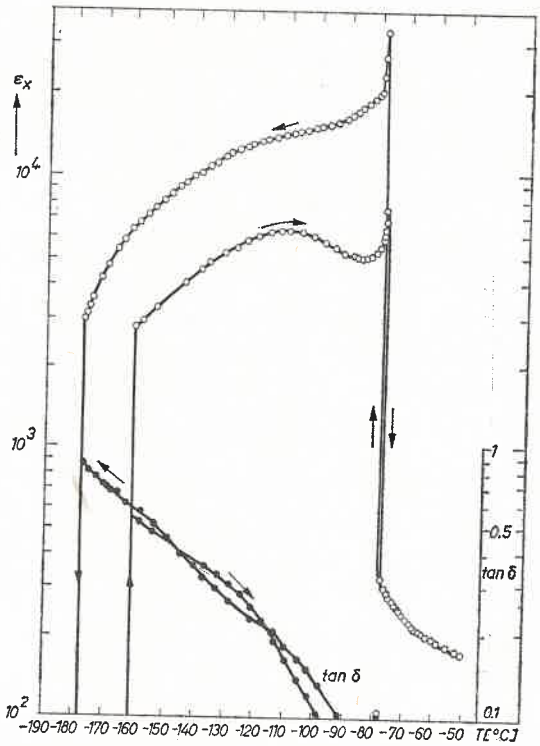

Fig. 3. Temperature dependence of permittivity and dielectric loss tangent in the direction of the x axis

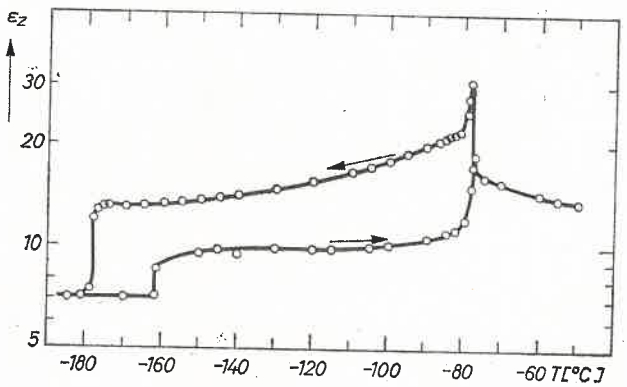

Fig. 4. Temperature dependence of permittivity in the direction of the z axis

z-component of permittivity as a function of temperature is presented in Fig. 4. The measurements were made in a field of intensity 6 V/cm. Temperature hysteresis for both phase changes occurs alike as for the x component. Permittivity values depend on the directions of temperature change in phase β, while in phase α and γ they do not depend on it. Permittivity in phase γ is temperature independent.

Loss tangent did not exceed the value 10^{-3} except for the temperature near the phase transitions. Because of a small permittivity value and a small value of intensity of electric field applied, the measuring error of the component ε_z was high (about 20%).

By repeating several times the measurements for ε_x, ε_y components at various rates of cooling and various times of stay in the phase γ, it has been stated that the $\beta \rightarrow \gamma$ phase transition occurs at different temperature within the $-175 \div -178$°C range, while the

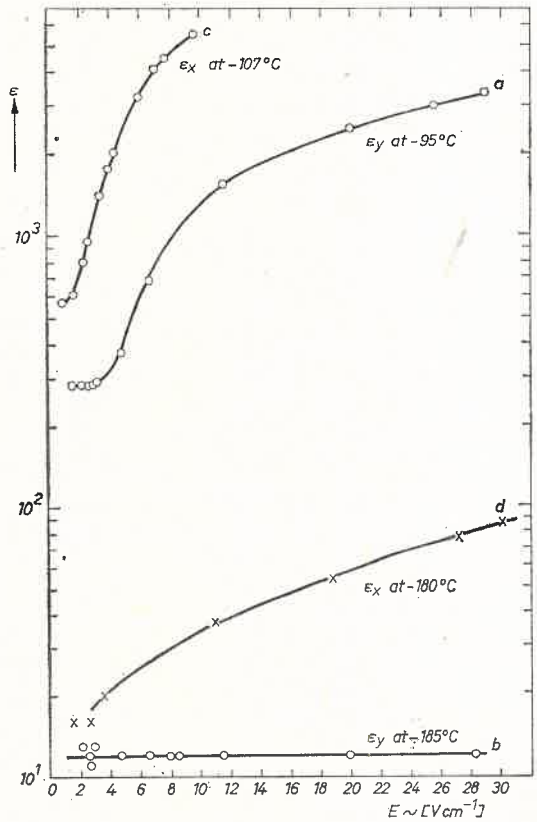

Fig. 5. Temperature dependence of permittivity on measuring electric field strength at frequency 10 kHz with the definite crystal temperature

$\gamma \rightarrow \beta$ phase transition occurs within the $-161 \div -165$°C temperature range. The obtained data are yet not sufficient to define the influence of the experimental conditions on the phase transition temperature.

Measured values of permittivity depend strongly on the values of intensity of the measuring field. Measurement results are presented in Fig. 5. The measurements have been carried out in a field of 10 kHz frequency at a definite temperature 20 minutes after the moment of the adjustment of temperature. Fluctuations of temperature during the measurements did not exceed 1°C. On the basis of these measurements the following can be stated:

(a) in phase β both ε_y (Fig. 5*a*) and ε_x (Fig. 5*c*) quickly increase together with the rise of intensity of the field used for measurement,

(b) in the field smaller than 3 V/cm ε_y do not depend on the value of the field,

(c) in phase β tan δ quickly increases together with the rise of intensity of the electric field (it is not shown on the figure),

(d) in phase γ component ε_x (Fig. 5*d*) depends on the value of intensity of the electric field, and the component ε_x (Fig. 5*b*) does not depend on it,

(e) in phase α the components ε_x, ε_y, ε_z in the range of measured field do not depend on the value of the field.

For small values of ε and small intensities of fields the sensitivity of measuring systems is small and that is why a great scatter in the measured results are observed. It may be mentioned that the values of applied fields — up to 30 V/cm — are significantly smaller than

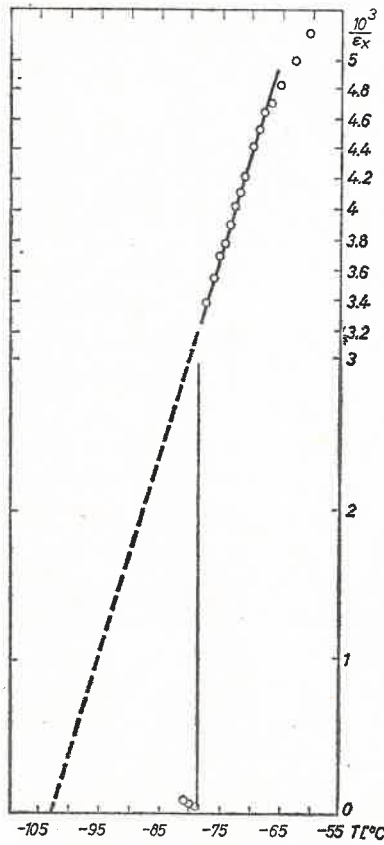

Fig. 6. Temperature dependence of the reciprocal permittivity measured in the direction of the x asis

coercive field which is for the measurement conditions: for the curve a $E_{cy} = 1.5$ kV/cm, for the curve c $E_{cx} = 1.4$ kV/cm, for the curve d $E_{cx} = 30$ kV/cm [10].

In Fig. 6 the dependence of the reciprocal of permittivity for the x component in the temperature function has been shown. In the temperature range $-67°C \div -77°C$ the

Curie–Weiss law is followed. The constant Curie $C = 7.6\ 10^{-3}$°C has been determined from the diagram and Curie–Weiss temperature $T_0 = -103$°C is about 24°C below the temperature of phase transition $\alpha \leftrightarrow \beta$.

4. *Conclusions*

The results of measurements presented in Fig. 2, 3, 4 allow for the statement of existence of temperature permittivity hysteresis both for phase transition $\beta \leftrightarrow \gamma$ and $\alpha \leftrightarrow \beta$. Magnitude of hysteresis is included in the temperature ranges $10 \div 16$°C and $0.8 \div 1$°C respectively. In the ferroelectric phase β permittivity diminishes in time. Consequently the numerical values depend on the rate of temperature changes. Evident changes of the curve may take place near the phase transition $\alpha \leftrightarrow \beta$ where secondary temperature derivatives are great.

Evident differences which occur in permittivities presented on Fig. 2, 3, 4 and Fig. 5 under the same measuring conditions (equivalent components, temperatures and intensities of field) are caused mainly by the fact that the first of them were made under dynamic conditions and the second (Fig. 5) under static ones. On the basis of abrupt change of permittivity in phase changes and a great difference between phase transition temperature and Curie–Weiss temperature it may be concluded that phase changes $\alpha \leftrightarrow \beta$, $\beta \leftrightarrow \gamma$ are of the first type. In phase γ the independence of permittivity on electric field strength (Fig. 5*b*) proves that there exists a lack of ferroelectric state in the y axis direction and simultaneously it proves the occurrence of the ferroelectric state in the x axis direction (Fig. 5*d*). Loss tangent occurring in phase β is caused by the movement of domain walls. The electric conduction contribution is of no importance because $\tan \delta < 10^{-3}$ in paraelectric phase near phase transition.

On the other hand it can be stated for sure that considerable departure in the temperature course of permittivity from the typical behaviours of ferroelectric crystal with phase transition of the first type. Following differences can be counted:

(1) The reverse direction of permittivity changes at phase transition $\alpha \rightarrow \beta$.

(2) Great differences between temperature hysteresis at phase change $\alpha \leftrightarrow \beta$ (1°C) and Curie–Weiss temperature shift in relation to Curie temperature ($T_c - T_0 = 24$°C) for the component ε_x.

(3) Different temperature courses of components $\varepsilon_x, \varepsilon_y, \varepsilon_z$ in paraelectric phase.

It is suggested that the ferroelectric phase change might have been described by triggered ferroelectric phase transition as postulated by Holakovsky [15].

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