

Phase Transitions in MHBO₄ Type Crystals

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Dielectric dispersion for RbHSO₄, RbDSO₄, NH₄HSO₄, NH₄HSeO₄ crystals at frequencies up to 10¹¹ Hz was measured. X-ray investigation of NH₄HSeO₄ crystal at temperatures above and below *T_c* was made. It was found that dispersion for all compounds at frequencies lower than 10⁹ Hz is of the relaxation type. At higher frequencies the signs of the oscillation type dispersion were observed. Dielectric spectrum of the NH₄HSeO₄ crystal appeared to be especially complicated. The dispersion peculiarities are discussed on the basis of the structural data.

§1. Introduction

At present several ferroelectric crystals of MHBO₄ type: RbHSO₄, NH₄HSO₄, RbHSeO₄, NH₄HSeO₄ and their deuterated analogs are known. In comparison with MHSO₄ crystals which have been exhaustively investigated¹⁻⁵⁾ the study of MHSeO₄ crystals has begun only in recent years.⁶⁻⁹⁾ The data obtained show that the ferroelectrics of MHSeO₄ type in some aspects differ from MHSO₄ ones. We have carried out the dielectric and X-ray structural investigations of MHBO₄ type crystals. Some experiments have been made with the deuterated compounds to clarify the role of *H*-bond in the formation of spontaneous polarization *P_s*. Additional information was obtained from the results of $\epsilon(T)$ and *P_s(T)* measurements under hydrostatic pressure.

§2. Results of Structural Investigations

The structure of hydrogen sulphates has been investigated earlier.¹⁻³⁾ The monoclinic structure of the crystals above *T_c* was found to be pseudoorthorhombic one. The presence of two nonequivalent structural SO₄ groups playing different roles at phase transitions was shown by X-ray and other microscopic methods.¹⁰⁾ In the ferroelectric phase one of the nonequivalent structural SO₄ groups is tilted about its initial position. The center of symmetry connecting two sublattices of such groups disappears.¹⁻³⁾ The statistical theory on the phase transitions in MHSO₄ has been elaborated.¹¹⁾ This theory satisfactorily describes temperature behaviour

of thermal and dielectric properties of the MHSeO₄ crystals.^{12,13)}

The structure of NH₄HSeO₄ above *T_c* has been obtained earlier.⁹⁾ X-ray analysis of ferroelectric phase at 223 K was made (Fig. 1). The parameters of unit cells in both phases are shown in Table I, where the parameters of

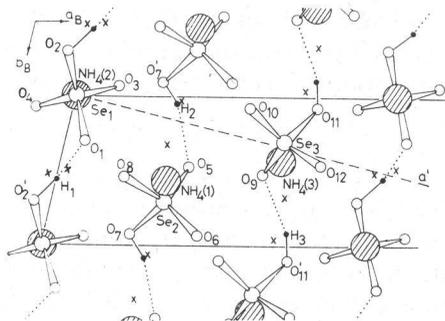


Fig. 1. *ab*-projection of the NH₄HSeO₄ structure in the ferroelectric phase (*T* = 223 K). Pseudoorthorhombic axis-*a'* is shown by dashed line. Hydrogen positions in paraelectric phase are marked (*x*).

Table I. Structure parameters of NH₄HSeO₄.

| Structure parameters | Paraelectric phase <i>T</i> = 293 K | Ferroelectric phase <i>T</i> = 223 K |
|----------------------|--|---|
| Space group | B2 (12) | B1 |
| <i>Z</i> | 6 (6) | 6 |
| <i>a</i> | 19.75 (19.27) Å | 19.593 Å |
| <i>b</i> | 4.61 Å | 4.598 Å |
| <i>c</i> | 7.55 Å | 7.507 Å |
| α | 90° | 90° 1' |
| β | 90° | 89° 2' |
| γ | 102° 31' (89° 54') | 102° 8' |

pseudorthorhombic cell are given in brackets.

Similar to other MHBO₄ crystals the basis of NH₄HSeO₄ structure form the separated SeO₄-tetrahedra bound through the set of hydrogen bond into chains along b-axis. Two SeO₄-groups are nonequivalent in their symmetries: SeO₄(I) lies on the double axis and SeO₄(II) is in its general position. The comparison between NH₄HSeO₄ and NH₄HSO₄ structures shows that both of them are characterized by the pseudoperiod along the a'-axis (Fig. 1). The positions of the mass centers of tetrahedral groups are the same. However the tilts of SeO₄ groups below T_c have not been observed unlike SO₄-groups in sulphates. The main changes in NH₄HSeO₄ structure at phase transition consist in the ordering of "acid" protons along the hydrogen bonds. The structure of RbHSeO₄ has also been investigated.¹⁴ One can conclude that the RbHSeO₄ and NH₄HSeO₄ are isomorphic crystals.

§3. Dielectric Dispersion

RbHSO₄: Dielectric dispersion $\varepsilon^*(\omega)$ appears at the frequency about 10⁸ Hz.¹⁵ $\varepsilon(\omega, T)$ dependences for the frequencies up to $f = \omega/2\pi = 5$ GHz are expressed by the Debye equation

$$(\varepsilon_0 - \varepsilon_\infty)/[\varepsilon^*(T, \omega) - \varepsilon_\infty] = 1 + i\omega/\omega_D(T) \quad (1)$$

where $\varepsilon_0 - \varepsilon_\infty = C/(T - T_c)$; $\omega_D(T) = A(T - T_c)$, the Curie-Weiss (CW) constant is determined to be $C = 120$ K in nonpolar phase, the CW temperature $T_c = 263.7$ K and $\varepsilon_\infty = 5.7$. In the temperature region of $T = T - T_c \approx 0.3$ K $\varepsilon^*(T)$ behaviour can not be expressed by eq. (1). At frequencies above 5 GHz the oscillation dispersion mechanism with attenuation has been revealed. The dielectric contribution of this mechanism was found to be rather small ($\Delta\varepsilon \approx 2$ far above from T_c). Both polarization mechanisms were strongly correlated. It was manifested in the distribution character of the dispersion near T_c. The $\varepsilon'(T)$ and $\varepsilon''(T)$ dependences at high frequencies (Fig. 2) and $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ dependences showed that the characteristic dispersion frequency f_0 is independent of temperature, whereas the attenuation decreases when approaching T_c.

RbDSO₄ and NH₄HSO₄¹⁸ crystals have two types of dielectric dispersion (Table II). NH₄HSeO₄: The measurements in NH₄HSeO₄

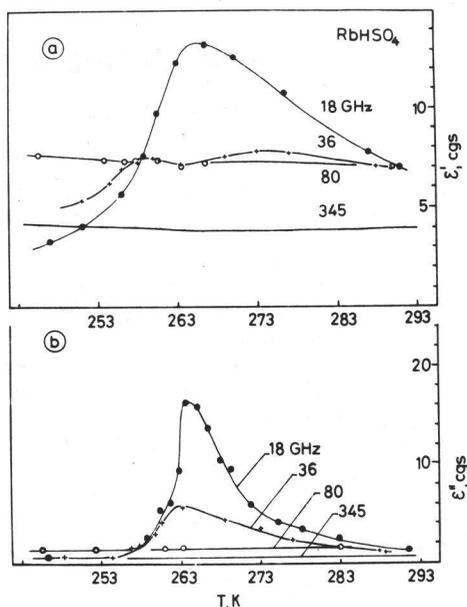


Fig. 2. Dielectric constant ε'_c , (a) and dielectric loss ε''_c , (b) of RbHSO₄ measured at high frequencies as a function of temperature.

Table II.

| Crystal | A, GHz/K | f_0 , GHz | $\Delta\varepsilon$, CGS | $\Delta(\delta\nu_2)$, cm ⁻¹ |
|----------------------------------|--------------------|-------------|---------------------------|--|
| NH ₄ HSO ₄ | 0.9 ¹⁸⁾ | 130 | 4 | 4 |
| RbHSO ₄ | 1.1 | 180 | 3 | 6 |
| RbDSO ₄ | 1.2 | 240 | 3 | 8 |

were difficult to carry out due to the presence of great nonanomaly contribution to ε' and its nonlinearity. $\varepsilon^*(\omega, T)$ dependences were investigated up to $f = 80$ GHz. The dielectric permeability decreased substantially at $f = 10^7$ Hz, however its dependence on the value of ac-field (E) remains.⁷⁾ The value of nonanomaly contribution to ε'_b increases and the dielectric anomaly at T_c was not observed when $E_{\sim} \geq 1$ v/cm. The dispersion frequency of this contribution was found to be about 6 GHz. The character of the dispersion differs from the relaxation one probably because of the strong nonlinearity. Above $f = 80$ GHz the dipole contribution practically disappeared. At frequencies about 30 GHz the third dispersion mechanism was observed when the main dipole contribution decreased with temperature lowering. This mechanism displayed itself only at small E_{\sim} and near $T = 230$ K.

§4. Discussion

The dynamic theory of phase transitions in $MHSO_4$ has been suggested recently.^{17,18)} The theory gives good description of $RbHSO_4$ dielectric spectrum at low frequencies. Besides low-frequency mode the dynamic model results in the second high-frequency relaxation mode in $\varepsilon^*(\omega)$ spectra. However the parameters of high frequency dispersion experimentally observed for $MHSO_4$ do not support the existence of the high-frequency mode.

The model with two phenomenological variables of relaxation (P) and oscillation (η) types is the most suitable for the description of experimental $\varepsilon^*(\omega, T)$ spectra. The equations of motion can be written as

$$\tau \dot{P} = -\frac{\partial F}{\partial P}; \quad \frac{1}{\omega_0^2} \ddot{\eta} + \frac{1}{\gamma} \dot{\eta} = -\frac{\partial F}{\partial \eta} \quad (2)$$

Using the P and η interaction in the form of $\xi P\eta$ and the procedure, described in ref. 19, it was obtained:

$$\varepsilon^* - \varepsilon_0 = \frac{\Delta \varepsilon}{\Delta + i\omega\tau - \xi^2 \left[1 - \left(\frac{\omega}{\omega_0} \right)^2 + i \frac{\omega}{\omega_0} \gamma \right]^{-1}} \quad (3)$$

This equation describes qualitatively the experimental spectra and their temperature dependences. η is responsible for ferroelastic properties of the crystals.²⁰⁾

The dipole movement corresponding to a high-frequency dispersion is revealed in Raman spectrum. The changes of the linewidth correlating with the internal vibration ν_2 of SO_4 ions were found in $MHSO_4$ crystals below T_c .²¹⁾ The detailed measurements of linewidth $\delta\nu_2$ in the region of phase transitions in $MHSO_4$ have been made at our Institute. The results are given in Table II. It is seen that $\Delta(\delta\nu_2)$ and f_0 obtained from the dielectric measurements are approximately equal.

To clarify the role of H -bonds in phase transition of NH_4HSeO_4 the dielectric measurements with powder of NH_4DSeO_4 ($\sim 70\%$ D) were made. It was determined that $T_{c1} \approx 298$ K, and it is about 50 K higher than T_c for NH_4HSeO_4 . The hydrostatic pressure decreases T_{c1} in NH_4HSeO_4 , and $dT_{c1}/dP \approx -2$ K/kbar.

Three types of dielectric dispersion may be

explained qualitatively on the basis of structural data. It can be supposed that low-frequency part of ε_b corresponds to the polar vibration of the sublattices $SeO_4(II)$. Its high-frequency part corresponds to the antipolar vibration of the sublattices. Unusually large ε_b -value is probably determined by the high mobility of SeO_4 -groups and protons along H -bonds in the structure of NH_4HSeO_4 .

Thus the minor distinctions in crystal structures of hydrogen sulphates and selenates of $MHBO_4$ -type lead to substantially different mechanisms of P_s -appearance and dielectric dispersion.

The authors are grateful to Dr. V. Shabanov and A. Vtjurin who provided us with data on Raman spectrum for $MHSO_4$ prior to publication.

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