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Ultrasonic investigation of antiferrodistortive phase transitions in betaine compounds

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Introduction

Phase transition phenomenon is one of the most fascinating problems in solid state physics. Among the all types of phase transitions antiferodistortive (AFD) or ferroelastic transitions are most simple from the structural point of view (sometimes there is no change of the point group of symmetry) but still the basic mechanisms of such transitions are not fully understood. The understanding of AFD phase transitions is one of the fundamental problems in the condensed mater physics. To obtain valuable physical information about ferroelasticity and soft elastic modes the ultrasonic method is very important. Usually the dielectric anomalies at the AFD phase transitions are extremely small, therefore the dielectric spectroscopy is not an appropriate method for such investigation. Ultrasonic method directly probes elastic degrees of freedom and enables to obtain important information about the microscopic mechanism of such phase transitions. Typical examples of systems exhibiting antiferodistorsive ordering are betaine family [1] compounds: deuterated betaine phosphate (DBP), deuterated betaine phosphite (DBPI) and their solid solutions DBP_xDBPI_{1-x} , which undergo the ferroelastic phase transitions in the temperature interval 356-366 K. These crystals also have ferroelectric (FE) and antiferroelectric phase transitions [2-5]. The monoclinic crystal structure exhibits the chains of betaine molecules and PO_3 , PO_4 groups directed along the *b* axis [5], therefore DBPI and DBP crystals are highly anisotropic. Below melting point DBPI exhibits a second order phase transition to an AFD phase at T_0=355 K. Phase transition to the FE phase is at T_c = 310 K. The ultrasonic investigation of FE transition in DBPI is presented in [6]. The NMR investigations of DBPI revealed an order-disorder character of the high temperature phase transition [7]. In order to describe the AFD phase transition phenomenologicaly the order parameter was interpreted in terms of the tilt of the betaine molecules out of the mirror plane. In DBPI the temperature dependence of the order parameter was investigated in AFD phase by means of NMR and specific heat measurements [8]. The critical exponent of the order parameter was determined to be β =0.25, which corresponds to the value expected for the tricritical behaviour. The crystals of DBP belong to the same symmetry group as DBPI and the AFD transition occurs at a higher temperature T_0=365 K [2]. The structural similarity of DBP and DBPI allows to obtain the mixed compounds DBP_x $DBPI_{1-x}$ in the whole range of composition. The ultrasonic investigations [9, 10] of pure DBPI and betaine phosphate (BP) revealed the ultrasonic attenuation and velocity anomalies at FE and AFD phase transitions. The interesting feature has been observed in orientation dependencies of the critical ultrasonic behaviour. For longitudinal ultrasonic modes propagating along *a* and *c* axes in DBPI the critical slowing down in ultrasonic velocity and attenuation maximum has been observed at PT. In contrary, the velocity critical slowing down for longitudinal *b* mode was absent at AFD transition. It was proposed that such behaviour is closely related to the crystal structure and determined by long range elastic forces, which are very anisotropic. Therefore the purpose of this investigation was to obtain information about orientation dependencies of ultrasonic velocity and attenuation at the AFD phase transition in solid solutions of DBP_xDBPI_{1-x}. Ultrasonic experiments also allow to obtain important information about the critical dynamics near PT.

The paper is organised as follows: at first we present the description of the structure of BP and BPI (deuteration do not change the structure of these crystals). The details of ultrasonic investigations and sample preparation are presented in the next section. Finally we will present the results of measurements of ultrasonic velocity and attenuation coefficient along all *a, b* and *c* crystallographic directions in the AFD phase transition region for the solid solutions DBP_x $DBPI_{1-x}$.

Description of the structure of BP and BPI

Betaine phosphate ($(CH_3)_3NCH_2COOH_3PO_4$) and betaine phosphite ($(CH_3)_3NCH_2COOH_3PO_3$) are molecular crystals consisting of the amino acid betaine, as the organic, and phosphoric and phosphorous acids, respectively, as the inorganic component. In both compounds the inorganic components (PO_4 or PO_3 groups) are linked by hydrogen bonds to form quasi- one-dimensional chains [1-3] (Fig. 1). Betaine phosphate shows the PT from a paraelectric high temperature phase (space group $P2_1/m$; $Z = 2$) at 365 K into an AFD phase (space group $P2_1/c$; $Z = 4$) [2]. In the high temperature phase the PO_4 groups and betaine molecules are disordered. They both order in the AFD phase, but the hydrogen atoms of the phosphate group linking PO_4 groups remain disordered. The high temperature phase of betaine phosphate has to be described as a lattice with a disordered structure, perpendicular to the mirror plane.

The assumption that the betaine and the phosphate components would lie exactly in the mirror plane produces unacceptable distance of about 2.2 Å from O4 to its equivalent (related by the inversion centre at (½, 0, ½)) and from O6 to it equivalent (centre of inversion at (½, ½, ½)).

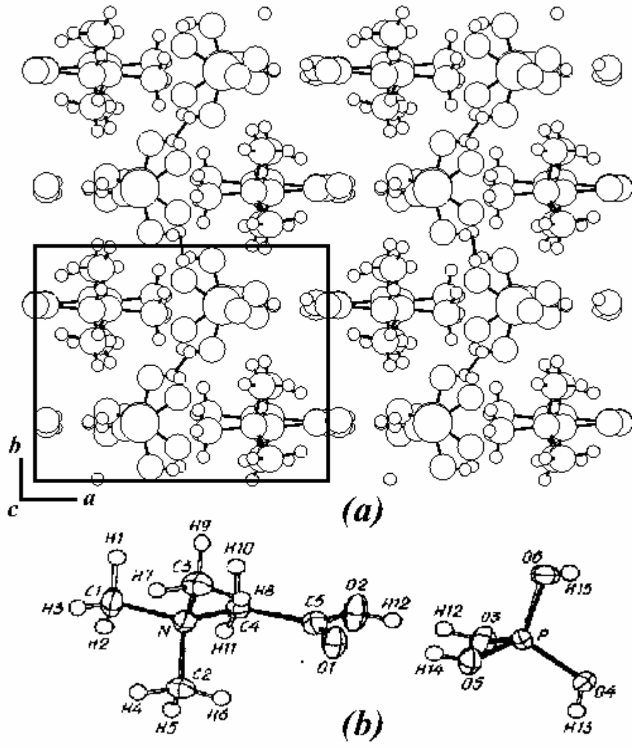

Fig. 1. **The projection of the BP structure in (*ab*) plane at 299 K (a). ORTEP-plot of the betaine phosphate molecule at 150 K (b) [3]**

Thus the PO_4 - tetrahedron must be tilted out of mirror plane by approximately 20 degrees to preserve a distance of about 2.52 Å. This also means that this tilt has to be a collective motion along the *b*-axis, and that the disorder exists only perpendicular to the *a*-*c* plane. A disorder of the betaine molecules is coupled to the disorder of the PO_4 tetrahedra. The phase transition into the AFD phase is characterised by an ordering of the betaine and phosphate molecules producing *c*-glide. The structure may be described as a rope ladder, where the rungs (betaine molecules) are slightly inclined to one side in the one chain and to the other side in the other chain (Fig. 1).

The PO_4 tetrahedron is symmetrically surrounded by hydrogen atoms. H14 is entirely bound to O5, resulting in a longer P - O bond. The best description of arrangement of the H13 and H15 is a disorder of a multiplicity 0.5 in positions related by the centre of inversion (assignment according to [2]) (Fig. 2).

The structure of BPI was determined using x-ray and elastic neutron scattering experiments [2]. It was found that BPI at room temperature is monoclinic (space group $P2_1/c$). BPI crystal also shows two phase transitions: at 355 K and 216 K [1]. The x-ray investigation confirmed the structural affinity to BP. But in contrast to BP, in BPI the hydrogen atom H12 forms hydrogen bonds from the oxygen O2 in the organic part to O3 located in the inorganic component (Fig. 2). The oxygen atom O5 which in BP is attached to the P atom, in BPI is replaced by H14. The betaine groups are almost perpendicular to the chains along the *b* axis and lying in the *ab* plane. In both compounds, BPI and BP, the hydrogen atoms H13 and H15 forms a quasi-one-dimensional chains along the *b* axis.

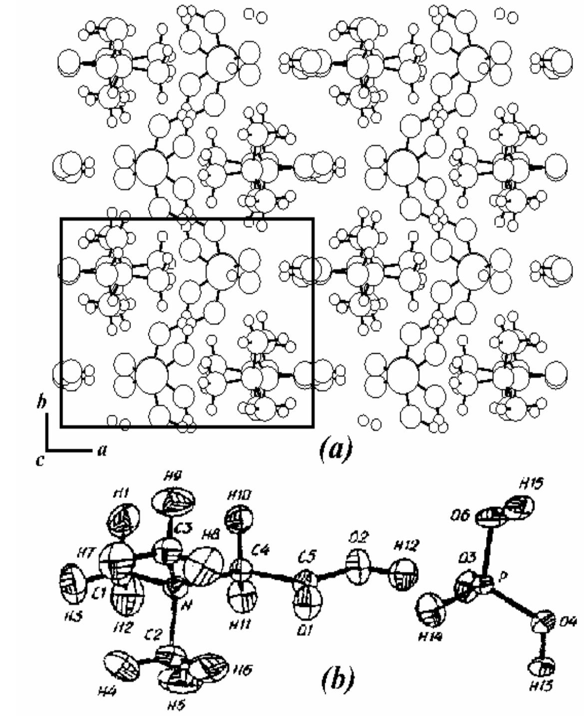

Fig.2. **The projection of the BPI structure in the (*ab*) plane at 295 K (a). ORTEP-plot of the betaine phosphite molecule at 295 K (b) [4]**

Therefore the ordering of the betaine and PO_4 or PO_3 molecules causes the higher temperature phase transition. The main crystallographic element , which can influence the elastic properties of these crystals is the twofold screw axis (2_1) in the direction of the crystallographic *b* - axis which is identical with the direction the one - dimensional chains.

Experimental details

The single crystals of DBPI and solid solutions were grown by controlled evaporation method from betaine and phosphoric acid solutions in heavy water. The ultrasonic measurements were carried out at the 10 MHz frequency. The relative ultrasonic velocity and attenuation coefficient variation have been measured by the phase shift and the amplitude of the received echo signal using computer controlled pulse-echo ultrasonic system [11, 12]. Two overtone polished lithium niobate transducers were used for excitation and detection of the longitudinal ultrasonic wave. The fussed quarts buffer was necessary for better time resolution when working with small samples. Silicon oil was used as the material for making acoustic bonds. The measurement and regulation of temperature was performed by computer controlled devices using cooper-constantane thermocouple as a sensor. The temperature was stabilised with accuracy of 0.02 K. Six samples with different DBP content x = 0, 0.15, 0.3, 0.4, 0.5 and 1 were selected for ultrasonic measurements. The longitudinal ultrasonic propagated along *a*, *b* and *c*-axes, therefore the faces normal to them were carefully polished. Usually the samples had the form of rectangles with dimensions of 0.3×0.2×0.4 cm^3. The ultrasonic data were collected mainly in cooling run.

Results and discussion

The typical *v=f(T)* dependencies for longitudinal waves are shown in Fig.1 along various X, Y and Z directions (these directions correspond to the crystallographic *a, b* and *c* axes) in pure DBPI crystal. The small velocity anomalies near FE phase transition at T_c = 312 K were observed earlier and described in [6].The other large velocity anomaly is clearly seen at the AFD transition at T_o =356.5 K. As one could see the critical ultrasonic behaviour for X and Z longitudinal modes is completely different from that of Y mode. For X and Z modes the ultrasonic velocity exhibits the downward steps; in contrary for the pure longitudinal wave propagating along the Y direction there is only the change of curvature at PT.

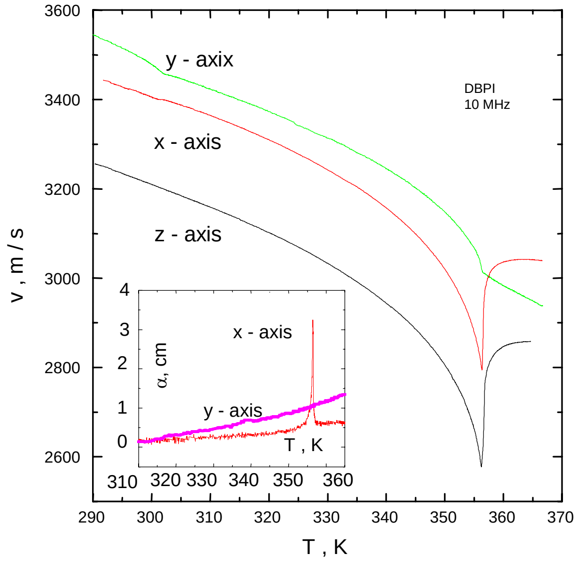

Fig. 3. **Temperature dependence of the longitudinal ultrasonic velocity along X , Y and Z axes in DBPI single crystal. The inset shows the temperature dependence of ultrasonic attenuation**

The ultrasonic velocity minima for X and Z modes correspond to the attenuation peaks. The form and magnitude of the attenuation peak is very similar for both of these modes, therefore we show in Fig.1 (inset) $\alpha = f(T)$ only for X - mode. When longitudinal wave propagates along Y axis in DBPI the attenuation maximum is absent at AFD PT temperature T_o. The total attenuation is higher in all investigated temperature range for this particular mode. It is clear that the critical ultrasonic anomalies are suppressed when ultrasonic wave propagates along Y axis in pure DBPI at AFD phase transition. It is necessary to point out that this transition occurs without the change of point group of symmetry and therefore it is elastic in nature. From this crystallographic point of view we can compare our finding to the elastic behaviour in crystals of chloranile [13], where PT also undergoes without the change of point group. But in this crystal the longitudinal ultrasound anomalies were found along all three crystallographic directions, what is different from DBPI. Theoretically such elastic anisotropy was mentioned in [14], where the influence of long range elastic forces on anisotropic character of fluctuations have been discussed. Very probably that the anisotropy of critical ultrasonic slowing down in DBPI is determined by influence of long range elastic fields which arise along the particular twofold screw axis *b*. The additional contribution in ultrasonic velocity for Y-mode in AFD phase can be described including fourth order terms in free energy expansion as it was done for ferroelectric crystals [15]. In this case the temperature dependence of ultrasonic velocity is proportional to order parameter square $<p_0>^2$.

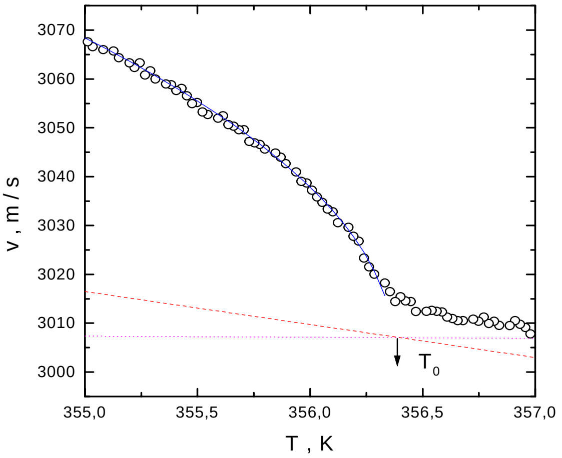

Fig. 4. **Temperature dependence of the longitudinal ultrasonic velocity along Y - axis. Solid line represents the best fit using Eq. 2; dashed and dotted lines are the linear approximation of the velocity background.**

In order to obtain the critical exponent of order parameter, p_0^2 might be described by the equation :

$$p_0^{\ 2} = A(T - T_0)^{2\alpha} \qquad (T<T_0). \tag{1}$$

Here α is the critical exponent. After usual least square fitting procedure of experimental temperature dependence of ultrasonic velocity along Y axis in AFD phase with equation:

$$v = v_0 + aT + B(T - T_0)^{2\alpha}\ , \tag{2}$$

we obtained α = 0.25. The result is shown in Fig.2 by solid line. The values of the other parameters are as follows: v_0 = 3360 m/s, a = -1 m/sK , B =55 m/s×K$^{1/2}$. A good agreement exists in the AFD phase and it indicates the tricritical behaviour. But the temperature dependence of linear background velocity $v = v_0 + aT$ (shown in Fig.4 by dotted line in AFD phase) differs from that of background velocity (dashed line) in the high temperature disordered phase. This could be related to the contribution of proton conductivity along Y - axis to elastic constants of

DBPI. The activation energy of proton conductivity can change at the AFD transition and this will change the slope of background velocity.

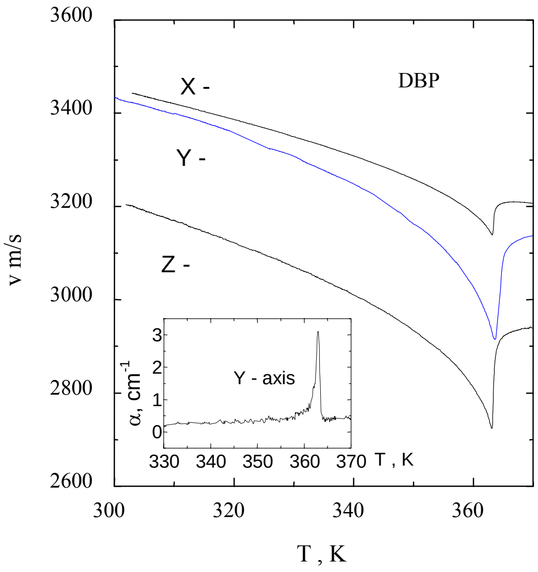

Fig. 5. **Temperature dependence of longitudinal ultrasonic velocity along X , Y and Z axes in DBP single crystal. The inset shows the temperature dependence of ultrasonic attenuation along Y - axis**

The orientation dependence of ultrasonic anomalies at AFD transition for DBP crystals (Fig.4) strongly differs from that of BBPI. In this case we observed critical slowing down of velocity and attenuation maxima along all three X, Y and Z - directions. It shows that elastic anisotropy near PT substantially changes in DBP even if the symmetry remains the same. The temperature dependencies of ultrasonic attenuation and velocity can be explained by the same method as they were already described for DBPI single crystals [10].

Furthermore the ultrasonic velocity and attenuation orientation dependencies of mixed DBP_xDBPI_{1-x} crystals were investigated. Temperature measurements were also made along X, Y and Z - crystallographic directions. The summary of obtained results is presented in Fig. 6 - 9. In Fig. 6 the temperature dependencies of ultrasonic velocity are shown for Z - mode. The most interesting finding is that the PT temperature, which is related to the velocity anomaly, at first increases almost linearly with phosphate concentration x , then reaches a maximum near the concentration x =0.35, and then decreases down to $T_{o\,DBP}$ = 365 K. Velocity anomalies are sharp enough for pure DBP and DBPI but in the middle of composition range they clearly become more wide. This is determined by the increase of the order parameter relaxation time (prefactor τ_0 also has a maximum in the same region of concentration x [10]). This phenomenon is seen more explicitly in $\alpha = f(T)$ dependencies, which are shown in Fig. 7. The width of attenuation peaks is directly proportional to τ_0. As one could see from Fig. 7 relaxation time increases more than by one order with increasing x from zero to 0.4.

Increase of τ_0 also reduces step of velocity at T_0. Therefore, we can assume that the change of static elastic constant for Z-mode is almost independent on phosphate concentration x. In contrary for X - mode the velocity step clearly depends on x (Fig. 8). As one can see from this figure for X - mode the velocity step at T_o at DBP concentrations till 0.4 decreases rapidly from the value $\Delta v/v$ = 7.5 % in pure DBPI and then almost saturates at the value $\Delta v/v$ = 3 % for pure DBP. The increase of relaxation time also reflects in the width of velocity anomalies.

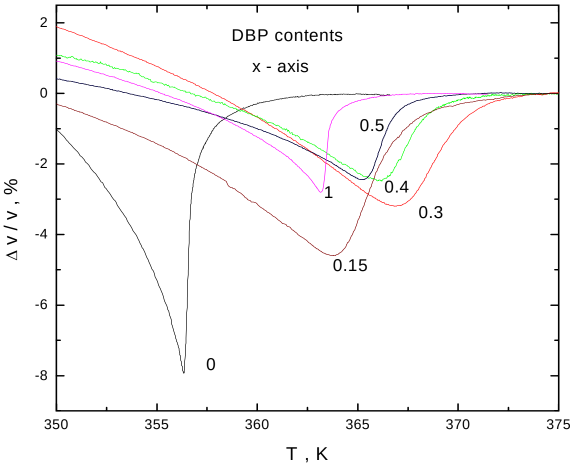

Fig. 6. **The temperature dependencies of longitudinal ultrasound relative velocity for Z - mode in mixed crystals with different DBP content**

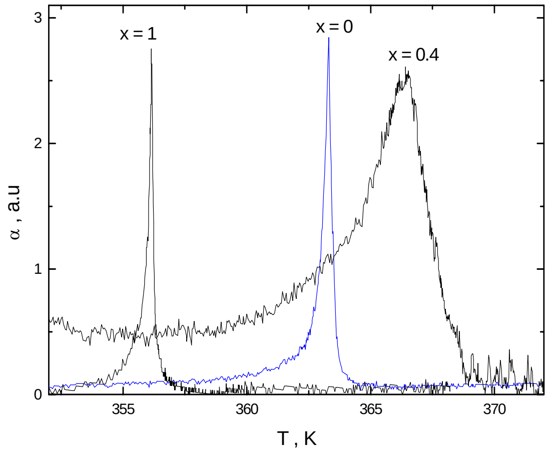

Fig. 7. **The temperature dependencies of longitudinal ultrasound attenuation for Z - mode in mixed crystals with different DBP content.**

For longitudinal ultrasound along Y - axis the relative step at phase transition in velocity is completely absent for phosphate concentrations x < 0.15 then increases rapidly with increasing DBP concentration and reaches the maximum value Δv/v = 7.5 % in pure DBP (Fig. 9). As it was showed above, the additional part of ultrasonic velocity along Y - axis for DBP concentrations x < 0.15 in AFD phase follows the temperature variation of the square of order parameter, which is determined by the degree of order of betaine molecules. In this range of DBP concentration there is no critical dip of ultrasonic velocity, which clearly appears in the temperature dependence of the compound $DBP_{0.3}DBPI_{0.7}$. Therefore we can point out that in the composition range 0.15<x<0.3 long range elastic field shows considerable transformation.

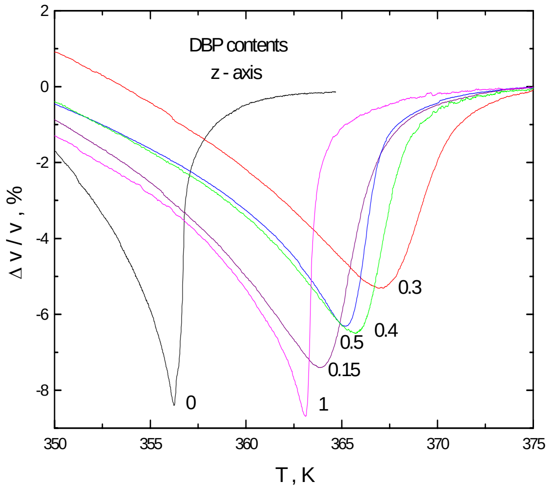

Fig. 8. **The temperature dependencies of longitudinal ultrasound relative velocity for X - mode in mixed crystals with different DBP content.**

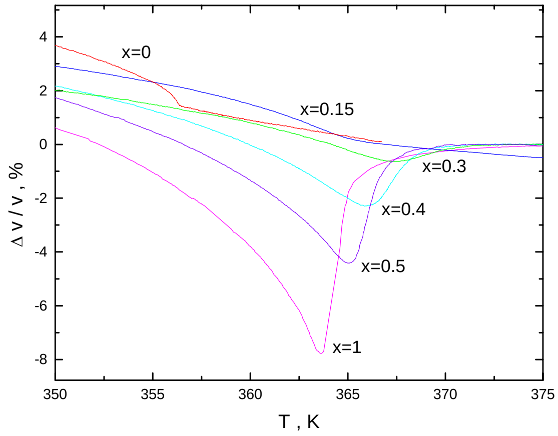

Fig.9. **The temperature dependencies of longitudinal relative ultrasound velocity for Y - mode in mixed crystals with different DBP content**

The differences in ultrasonic anomalies at AFD PT for various solid solutions possibly can be determined by change in the coupling anisotropy of betaine molecule with PO_{4-} and PO_{3-} tetrahedra (i.e. the substitution of one oxygen by proton in tertraedron leads to the reduction of hydrogen bonds from two in DBPI to one in DBP). Structurally it means that the step of a string along screw *b* axis is different for DBPI. We believe that rather subtle structural changes are responsible for such unusual elastic behaviour, but can not at this moment point it out clearly. It is necessary to note that in the same composition range 0.15<x<0.3 AFD PT transition temperature has a maximum. Further X-ray investigations are needed to obtain more precise information about structural changes in these solid solutions (0.15<x<0.3).

Conclusions

The temperature dependencies of ultrasonic velocity and attenuation in DBPI single crystals near the antiferrodistortive phase transition are measured for X, Y and Z directions. For longitudinal ultrasonic modes propagating along X and Z axes the critical slowing down in ultrasonic velocity and attenuation maxima have been observed at PT. In contrary we have not found the critical elastic anomalies for longitudinal Y mode. We attribute such behaviour to the influence of long range elastic forces. In DBP crystals the elastic anomalies appeared at phase transition for all X, Y and Z modes. In mixed crystals of DBP_xDBPI_{1-x} the orientation dependencies of elastic anomalies varied from those of DBPI to those of DBP. In the composition range 0.15<x<0.3 the increase of the phase transition temperature, the maximum of order parameter relaxation time and suppression of the critical elastic anomaly along the crystallographic axis *b* have been established.

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Antiferodistorsinių fazinų virsmų betainų junginiuose ultragarsinis tyrimas

Reziumė

Straipsnyje pateikiami ultragarso bangų greičio ir slopinimo temperatūrinių matavimų rezultatai betainų šeimos DBP/DBPI kristaluose antiferodistorsinio fazinio virsmo aplinkoje. Nustatyta, kad, bangai sklindant išilgai *b* ašies anomalusis slopinimas ir greičio minimumas išnyksta. Toks ultragarso elgesys siejamas su elastinių jėgų toliveikos pasireiškimu. Eksperimentiškai ištirta, kaip ultragarso greičio ir slopinimo anomalijos keičiasi nuo DBP_xDBPI_{1-x} junginio sudėties. Parodyta, kad sudėčiai esant intervale 0,15<x<0,3, žymiai išauga tvarkos parametro relaksacijos laikas ir keičiasi fazines diagramos pobūdis: t.y. fazinio virsmo temperatūra yra maksimali. Ultragarso sklidimo orientacinės priklausomybės siejamos su šių betainų šeimos kristalų sudėtinga erdvine struktūra.

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