

The mechanism of the defect centers influence on the paraelectric-to-incommensurate phase transition in rubidium-potassium zinc chloride crystals

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The $(x-T)$ phase diagram of mixed $(\text{Rb}_{1-x}\text{K}_x)_2\text{ZnCl}_4$ crystals has been studied. The effect of impurity defects on the paraelectric-to-incommensurate phase transition has been shown to be due to straining compression of the Rb_2ZnCl_4 structure cell at K^+ ions substitution for Rb^+ .

Исследована $(x-T)$ фазовая диаграмма смешанных кристаллов $(\text{Rb}_{1-x}\text{K}_x)_2\text{ZnCl}_4$. Показано, что влияние примесных дефектов на переход из параэлектрической фазы в несоизмерную обусловлено деформационным сжатием структурной ячейки Rb_2ZnCl_4 при замещении Rb^+ ионами K^+ .

The modern progress in the field of ferroelectricity is connected, in particular, with study of the crystals with incommensurately modulated structure [1]. Due to structural features, the compounds of A_2BX_4 family are among the most intensively studied incommensurate crystals [2, 3]. A key role of structural defects near incommensurate phase transitions was demonstrated in a number of experiments. It is obvious that analysis of the problem, both on microscopic, and on phenomenological level, demands a substantiated model of the defective center in each specific case [4]. Among various ways to control the quality of the object being investigated (doping, variation of the crystal growth conditions and post-growth processing, creation of radiation defects), introducing of impurities has some advantages. The suitable choice of the doping ion and substituted one allows to know surely the position and state of the impurity defect in the lattice. That is why the solid solutions of rubidium Rb_2ZnCl_4 (RZC) and potassium K_2ZnCl_4 (KZC) zinc

chlorides are popular objects for studying of the defect influence on the incommensurate system properties [5].

RZC and KZC crystals are structurally isomorphous and undergo the same sequence of phase transitions [2, 6]. The cooling below T_i (Table) results in the transition from paraelectric phase (PP) (space symmetry group D_{2h}^{16}) to the incommensurate one (IP) with a wave vector of structural modulation oriented along pseudo-hexagonal axis $q_i = (1/3 - \delta(T))a^*$ ($\delta(T)$ being the incommensurability parameter). At a further cooling below T_C , the transition to commensurate ferroelectric phase (FP) (C_{2v}^7 symmetry group) occurs at the polar direction along c axis. In this work, the mechanism of the impurity defect influence on the phase transition from PP to IP in $(\text{Rb}_{1-x}\text{K}_x)_2\text{ZnCl}_4$ ($\text{R}_{1-x}\text{K}_x\text{ZC}$) system is considered basing on numerical estimations.

The $\text{R}_{1-x}\text{K}_x\text{ZC}$ crystals ($x = 0.01; 0.02; 0.04; 0.1$), activated with Mn^{2+} paramagnetic centers were grown by Czochralsky technique. The concentration x of K^+ impu-

Table. The crystal parameters used for numerical estimations [6, 9–12].

Crystal	T_i , K	T_C , K	Cation radius, Å	Unit cell parameters in PP, Å	Baric factor dT_i/dp , K/GPa
RZC	303	192	$r_{\text{Rb}^+} = 1.48$	$a = 9.26$ $b = 12.73$ $c = 7.28$	+32
KZC	553	403	$r_{\text{K}^+} = 1.33$	$a = 9.038$ $b = 12.68$ $c = 7.32$	+110

urity is indicated in accordance with KCl contents in the initial blend used. The dielectric permittivity and EPR spectra of Mn^{2+} were investigated before in the temperature range including the temperatures T_i and T_C of PP-IP-FP phase transitions [7]. The PP-IP transition was detected by appearance of the "forbidden" hyperfine doublets $\Delta m_I = \pm 1$ in $M_S = +1/2 \leftrightarrow -1/2$ fine group of EPR spectrum. The IP-FP transition was registered basing on dielectric permittivity and EPR spectra measurements. The phase diagram obtained is shown in Fig.

Specific features of the IP-FP phase transition in $\text{R}_{1-x}\text{K}_x\text{ZC}$ system are due to interaction of the impurity defects with structural modulation and were discussed in [7]. Let us consider the concentration dependence of the PP-IP transition point T_i . Increasing T_i with x growth (see Fig.) is described by linear dependence $T_i[\text{K}] = 304.9(0.2) + 95(5) \cdot x$ with a slope approximately two and a half times less than that of the straight line connecting the outermost points $T_i(x=0) = 303 \text{ K}$ and $T_i(x=1) = 553 \text{ K}$ in the $(x-T)$ phase diagram (see Table). It is to note that dielectric measurements in [5] have revealed linear increase of T_i for the whole interval $x=0$ to 1. The concentration shift of the transition point $\Delta T_i/\Delta x = (95 \pm 5) \text{ K}$ must evidence that in the investigated $\text{R}_{1-x}\text{K}_x\text{ZC}$ crystals, the real concentration of K^+ ions is two and a half times lower than in the initial blend.

The data given in [8–11] and gathered in the Table, allow to reveal the property of K^+ impurity related to increasing T_i in the series of solid solutions. The difference between the RZC and KZC unit cells consists in substituting of K^+ cation with a smaller radius for Rb^+ one. The influence of low K^+ impurity concentration on PP-IP transition can be assumed to be equivalent to compression of RZC unit cell as a result of a pressure applied to the crystal. This assumption is confirmed qualitatively by the positive sign of baric factors for temperature T_i in

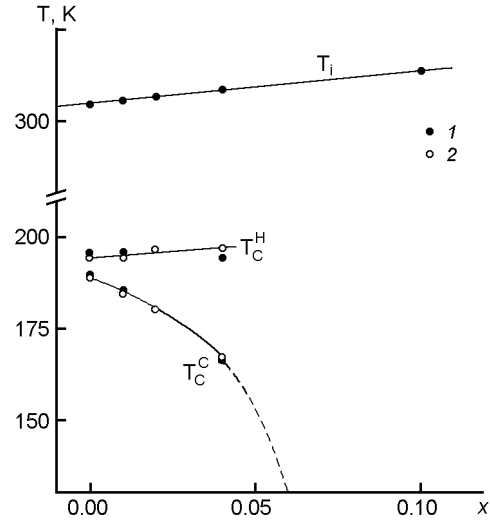


Fig. 1. $(x-T)$ phase diagram of $\text{R}_{1-x}\text{K}_x\text{ZC}$ crystals (1, EPR data of Mn^{2+} centers, 2, results of the dielectric permittivity measurements) [7]. T_C^C , T_C^H are IP-FP transition points at cooling and heating run, respectively.

RZC and KZC under hydrostatic pressure (see Table).

Quantitative estimations may be obtained by relating the transition point shift under hydrostatic pressure with the concentration dependence of T_i vs x

$$\frac{\partial T_i}{\partial p} = \left\{ \left(\frac{1}{V} \frac{\partial V}{\partial p} \right) \left(V \frac{\partial x}{\partial V} \right) \right\} \cdot \frac{\partial T_i}{\partial x}, \quad (1)$$

where V is the unit cell volume. In agreement with the data presented in the Table and results from [5], the concentration shift of phase transition point can be estimated as

$$\frac{\partial T_i}{\partial x} = T_i(x=1) - T_i(x=0) = 250 \text{ K}. \quad (2)$$

The volume compressibility can be found from RZC elastic properties studied in [12]

$$\frac{1}{V} \frac{\partial V}{\partial p} = -(S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{13} + S_{23})) = -0.071 \text{ GPa}^{-1}. \quad (3)$$

Assuming that unit cells parameters vary linearly with x , the concentration dependence of $V(x)$ can be described as

$$\frac{1}{V} \frac{\partial V}{\partial x} = \frac{1}{a} \frac{\partial a}{\partial x} + \frac{1}{b} \frac{\partial b}{\partial x} + \frac{1}{c} \frac{\partial c}{\partial x} \approx -2.24 \cdot 10^{-2}. \quad (4)$$

Substituting (2, 3) and inverse to (4) value into (1), we get

$$\frac{\partial T_i}{\partial p} \approx 792 \text{ K/GPa},$$

that exceeds more than by one order the experimental value of baric factor for RZC (see Table).

The above estimation shows that K^+ impurity influence on RZC unit cell cannot be reduced to hydrostatic compression. Such conclusion is supported by the fact that decrease of KZC unit cell volume in comparison with RZC one occurs mainly due to straining along the a axis. Relative change of the lattice parameter a ($-2.4 \cdot 10^{-2}$) exceeds approximately 6 times change of b ($-0.39 \cdot 10^{-2}$) and 4.5 times change of c ($0.55 \cdot 10^{-2}$) (Table).

A similar comparison of T_i shift under uniaxial pressure is presented below. As it has been shown in [13], the shift of T_i in RZC under uniaxial pressure applied along a axis is described by a factor

$$\frac{\partial T_i}{\partial \sigma_a} \approx 80 \text{ K/GPa}. \quad (5)$$

To estimate the concentration change of the unit cell volume (4) more accurately, it is necessary to take into account thermal expansion of the lattice. As V is a function of several variables (T , x , p), the dependence of the unit cell volume on x should be determined at other parameters being the same. Therefore, the parameters of KZC unit cells given in the Table for $T = 570 \text{ K}$ [9] are extrapolated to $T = 300 \text{ K}$, at which the parameters of RZC lattice are presented. Accounting for regular parts of the thermal

expansion factors for KZC ($\alpha_a = 45 \cdot 10^{-6} \text{ K}^{-1}$, $\alpha_b = 56 \cdot 10^{-6} \text{ K}^{-1}$, $\alpha_c = 44 \cdot 10^{-6} \text{ K}^{-1}$ [14]), we obtain $\frac{1}{V} \frac{\partial V}{\partial x} \approx -6.1 \cdot 10^{-2}$ for concentration decrease of the unit cell volume instead (4). Taking into account (2, 5), we find the value

$$\frac{\partial T_i}{\partial \sigma_a} = \left\{ \left(\frac{1}{V} \frac{\partial V}{\partial \sigma_a} \right) \left(V \frac{\partial x}{\partial V} \right) \right\} \cdot \frac{\partial T_i}{\partial x} \approx 61 \text{ K/GPa}, \quad (6)$$

which is close enough to the experimental data (5).

Thus, the numerical estimations show that increase of T_i with growing x in $R_{1-x}K_x\text{ZC}$ solid solutions is caused by straining compression of RZC unit cell at Rb^+ replacement with K^+ ion. This straining occurs predominantly along structural modulation axis a and is equivalent to the uniaxial pressure effect.

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**Механізм впливу дефектних центрів на перехід
із параелектричної до неспівмірної фази у кристалах
рубідій - калієвих тетрахлорцинкатів**

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Досліджено ($x-T$) фазову діаграму змішаних кристалів $(\text{Rb}_{1-x}\text{K}_x)\text{ZnCl}_4$. Показано, що вплив домішкових дефектів на перехід з параелектричної фази у неспівмірну обумовлений деформаційним стисненням структурної комірки Rb_2ZnCl_4 (RZC) при заміщенні Rb^+ на іони K^+ .