

## X-Ray, Dielectric, and Thermophysical Studies of Rubidium Tetrachlorozincate inside Porous Glasses

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**Abstract**—Results are presented from studying the X-ray diffraction, heat capacities, dielectric permittivities, and coefficients of the volumetric thermal expansion of composite materials obtained by embedding of  $\text{Rb}_2\text{ZnCl}_4$  salt into the porous matrices of borosilicate glass with average pore diameters of 46 and 320 nm in the temperature range of 120–350 K. The temperatures of transitions to the incommensurate and ferroelectric phases are determined, along with the freezing temperature of the mobility of domain boundaries in  $\text{Rb}_2\text{ZnCl}_4$  particles. A substantial increase in their Curie temperature is observed.

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Studying phenomena associated with size effects in different materials, especially in systems of ultrafine particles of different topology and dimension is currently of interest in solid state physics and physical materials.

The effect constrained geometry has on electro-physical properties [1–5], structure [6, 7], and phase transitions [1–7] in the particles of model ferroelectrics (e.g., TGS,  $\text{KH}_2\text{PO}_4$ , and  $\text{NH}_4\text{HSO}_4$ ) has been thoroughly studied. At the same time, the physical properties of ultrafine ferroelectrics with incommensurate phases have not been studied, except for sodium nitrate [6, 7]. However, the existence of the incommensurate phase in introduced  $\text{NaNO}_2$  particles has yet to be confirmed, due likely to the very narrow temperature range of its existence ( $\sim 1$  K).

There are similar materials with an incommensurate phase that occupies a wider range of temperatures. An example of this is rubidium tetrachlorozincate ( $\text{Rb}_2\text{ZnCl}_4$ ), a ferroelastic. In the bulk crystal, the transition from a paraelectric to an incommensurate phase occurs at a temperature of  $T_i = 303$  K, and the transition from the incommensurate to the ferroelectric phase occurs at a temperature of  $T_C = 195$  K [8]. The area of the existence of the incommensurate phase in this material is around 108 K. This material is therefore a better object for studying the effect con-

strained geometry has on phase transitions at  $T_i$  and  $T_C$  temperatures.

The aim of this work was to perform a comprehensive investigation of the effect constrained geometry has on the physical properties of rubidium tetrachlorozincate and the processes of cooperation that occur inside it.

Our experiments were conducted on a polycrystalline sample of rubidium tetrachlorozincate and composites obtained by embedding  $\text{Rb}_2\text{ZnCl}_4$  salt in glassy matrices: plates with dimensions of  $10 \times 10 \times 0.5$  mm and average through-pore diameters of  $\sim 46$  and 320 nm. The abbreviations RS-46 and RS-320 are used below to denote the composite, respectively.

The material was embedded into preliminarily annealed matrices from a saturated aqueous solution of  $\text{Rb}_2\text{ZnCl}_4$  over 3.5 h at temperatures of  $\sim 100^\circ\text{C}$ . The samples were then removed from the solution and dried thoroughly over 10 h at a temperature of  $330^\circ\text{C}$ . The density of unfilled matrices of both types was  $\sim 1.2$  g/cm<sup>3</sup>, the relative pore volume was around 55%, the volume part of  $\text{Rb}_2\text{ZnCl}_4$  in pores was  $\approx 10\%$ , and its part relative to the full volume of a sample was  $\approx 6\%$ .

X-Ray diffraction analysis was performed using a D2 PHASER diffractometer with a characteristic  $\lambda_{\text{Cu}}$  radiation wavelength of 1.5418 Å. Our results show the embedded material crystallized in the pores of the matrices as crystallite with a structure corresponding

to the bulk  $\text{Rb}_2\text{ZnCl}_4$ . The sizes of the particles embedded in the pores were estimated using TOPAS 4.2 software [9]; diameters  $d$  were around 70 and 51 nm for samples RS-46 and RS-320, respectively.

The diffraction spectra for the RS-46 sample were studied in detail in the temperature range of 143–320 K with  $\text{CuK}\alpha$  radiation, using a D8 ADVANCE diffractometer (Bruker) equipped with an Anton Paar camera and a VANTEC linear detector. The measurements were made in the angle range  $2\theta = 10^\circ\text{--}90^\circ$  with a step of  $0.016^\circ$ ; the runtime was 1 s per step.

To perform our dielectric studies, silver electrodes were applied onto the surfaces of samples. The samples were put into a cryostat in which the temperature was changed from 100 to 350 K and controlled with a platinum resistance thermometer with an error of less than  $\pm 0.2$  K. The dielectric constant was measured using an E7-12 impedance meter at a frequency of 10 kHz while cooling and heating a sample at a rate of 1–2 K/min. The samples were annealed at  $\approx 400$  K before each measurement to remove moisture adsorbed from the air.

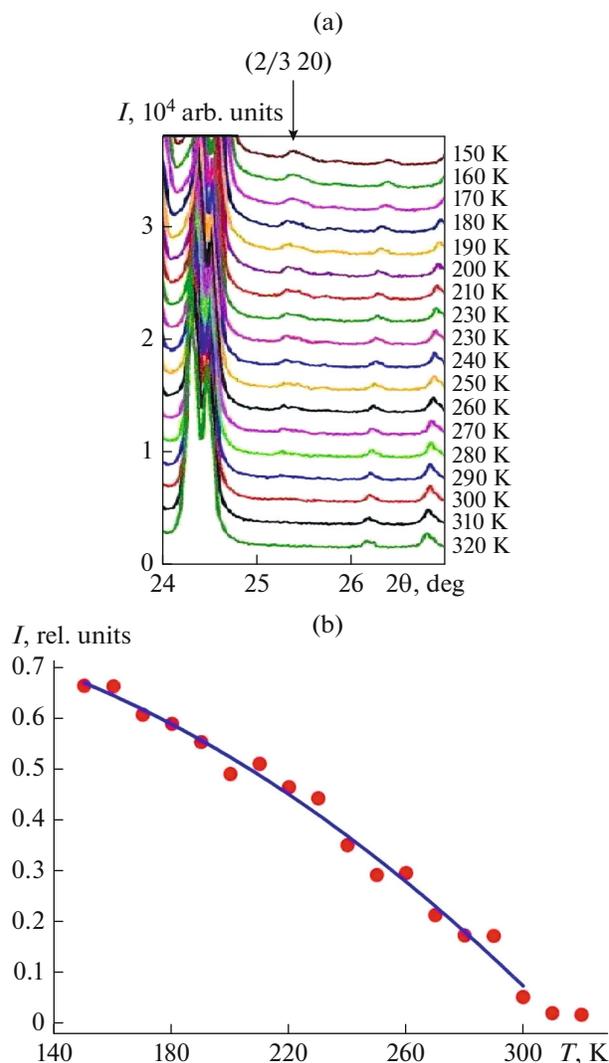
Heat capacity  $C_p(T)$  was measured in a wide range of temperatures using the automated adiabatic calorimeter described in [10]. The measurements were made in a vacuum of  $10^{-6}$  mm Hg in discrete and continuous heating modes. The error of measurement was less than  $\pm 1.0\%$ .

Thermal expansion was studied using a DIL-402C dilatometer; the measurements were made in the temperature range of 100–370 K in the dynamic mode in a helium atmosphere with a 3 K/min rate of temperature change.

Our measurements of the linear expansion coefficient of glassy matrices revealed no unusual behavior, and its value was  $\alpha \leq 5 \times 10^{-6} \text{ K}^{-1}$ .

Analysis of X-ray spectra obtained in the temperature range of 140–320 K for the RS-46 composite showed that a superstructure peak (2/3 2 0) corresponding to the  $T_i$  temperature of bulk  $\text{Rb}_2\text{ZnCl}_4$  appeared below 310 K (Fig. 1a). The intensity of this peak grew as the sample was cooled (Fig. 1b). No other superstructure lines were observed during the experiment, in contrast to the results presented in [8], where monocrystalline samples of  $\text{Rb}_2\text{ZnCl}_4$  were studied. This could be due to the fairly small amount of ferroelectric component in the composite.

The structure of  $\text{Rb}_2\text{ZnCl}_4$  crystallites under conditions of constrained geometry was determined at temperatures of 320, 205, and 143 K (Table 1). Good agreement was observed in comparing the parameters of a unit cell at room temperature and the data for the monocrystalline sample in [8]. Cell volume  $V$  of the crystallites corresponding to formula number  $Z$  fell slightly upon cooling (Table 1) and almost coincides with the data in [8] at all temperatures.



**Fig. 1.** Fragment of the XRD pattern for RS-46 composite and different temperatures: (a) superstructural peak (2/3 2 0) indicated by the arrow, and (b) dependence of the intensity of superstructural peak (2/3 2 0).

The  $V/Z$  ratio obtained at different temperatures allows us to estimate volume expansion coefficient  $\beta$  of  $\text{Rb}_2\text{ZnCl}_4$  particles in the RS-46 composite. Volume expansion coefficient  $\beta$  was calculated using the data given in Table 1. Its value was  $\approx 153 \times 10^{-6} \text{ K}^{-1}$ , which is close to the one determined for the rubidium tetrachlorozincate single crystal in [11] (Fig. 2).

With the RS-46 and RS-320 composites, the temperature dependences of  $\beta$  were much lower than that of bulk  $\text{Rb}_2\text{ZnCl}_4$  (Fig. 2). This was because they mostly consist of alkaline borosilicate glass with a very small  $\beta$  coefficient ( $\beta \leq 15 \times 10^{-6} \text{ K}^{-1}$ ) in the temperature range of 100–310 K [12].

In light of this, we may conclude that the particles embedded in porous matrices experience tensile strain upon cooling.

**Table 1.** Parameters of the crystal structure of the  $\text{Rb}_2\text{ZnCl}_4$  in matrix of porous glass with an average pore diameter of 46 nm

Temperature $T$ , K		320	205	143
Space group		$Pnma$	$Pnma: -1ss$	$Pn2_1a$
Cell parameters	$a$ , Å	9.2759 (3)	27.681 (2)	27.603 (3)
	$b$ , Å	7.2926 (2)	7.2557 (5)	7.2328 (8)
	$c$ , Å	12.7523 (4)	12.6613 (7)	12.616 (1)
Cell volume $V$ , Å <sup>3</sup>		862.64 (5)	2543.0 (3)	2518.7 (5)
Formula number $Z$		4	12	12
$V/Z$ , Å <sup>3</sup>		215.66	211.92	209.92

No features were observed on the  $\beta(T)$  dependences for RS-46 and RS-320 composites in the areas of  $T_i$  and  $T_C$ . They were also barely noticeable for  $\text{Rb}_2\text{ZnCl}_4$  single crystal in [11] (Fig. 2).

The temperature dependences of the dielectric constant obtained for our materials are given in Fig. 3a. The  $\epsilon(T)$  dependence obtained for bulk  $\text{Rb}_2\text{ZnCl}_4$  has at least two maxima. The first one appears near  $T_i \approx 307$  K and corresponds to the transition from the paraelectric to the incommensurate phase. The second well-resolved asymmetrical peak at  $T_C \approx 192$  K corresponds to the transition between the ferroelectric and the incommensurate phases. In the range of temperatures below  $T_C$ , the dielectric constant remains relatively high, forming a so-called plateau region due to the high mobility of domain boundaries [13].

In monocrystalline  $\text{Rb}_2\text{ZnCl}_4$  samples, freezing temperature  $T^*$  of anomalous high domain mobility is 154 K. It is accompanied by a weak anomaly in the

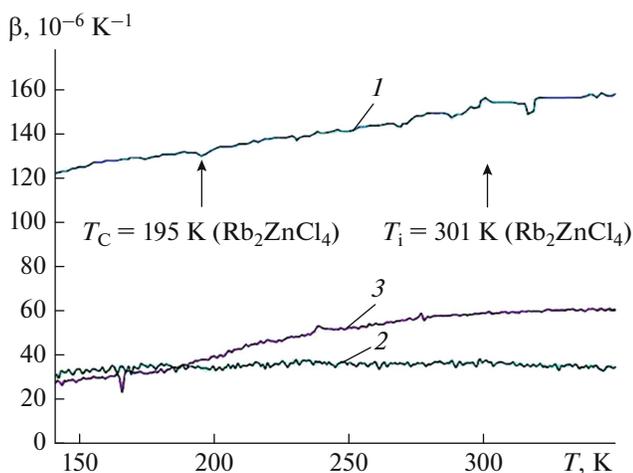
heat capacity [13, 14] and the maximum of the tangent of dielectric loss [13, 15].

The  $\epsilon(T)$  curves for RS-46 and RS-320 composites (Fig. 3a) are almost identical. This is apparently due to the difference between the part of the embedded substance and the average size of  $\text{Rb}_2\text{ZnCl}_4$  particles in pores being negligible, despite the considerable difference between the average diameters of the matrices' pores. Three anomalies are observed on  $\epsilon(T)$  dependences near 160, 245, and 307 K. The maximum of  $\epsilon$  at around 307 K is close to the temperature below which the superstructural reflex appears (2/3 2 0). This allows us to associate the maximum with the transition between the incommensurate and paraelectric phases.

To identify other features of the dielectric response, the heat capacity of the RS-46 composite was measured in addition to performing the X-ray diffraction experiment (Fig. 3b). Two maxima are clearly seen on the  $C_p(T)$  curve obtained upon heating. The broad peak localized at  $\sim 285$  K is likely associated with the transition from the incommensurate to the paraelectric phase. The reasons for the mismatch between its position and the  $\epsilon$  maximum near  $T_i \approx 307$  K require additional research that is beyond the scope of this work.

The clear peak of  $C_p$  near 232 K has the same form as the anomaly of the heat capacity for monocrystalline rubidium tetrachlorozincate near  $T_C$  [14], indicating this peak of the heat capacity was due to the ferroelectric phase transition. A steplike anomaly is observed on the  $\epsilon(T)$  dependences obtained while cooling the RS-46 and RS-320 samples near the  $C_p$  peak at a temperature of  $\approx 245$  K. No clear anomalies of the dielectric response indicating the ferroelectric phase transition were found on the  $\epsilon(T)$  dependences obtained upon heating.

Let us consider the broad maximum of dielectric constant at  $T^* = 160$  K. Unlike the anomalies of  $\epsilon$  near  $T_i$  and  $T_C$ , the maximum at  $T^*$  is not accompanied by any feature on the  $C_p(T)$  curve. This indicates this maximum is not connected with the structural phase



**Fig. 2.** Temperature dependences of the volumetric thermal expansion coefficients for our (1)  $\text{Rb}_2\text{ZnCl}_4$  single crystal [11] and (2) RS-320 and (3) RS-46 composites.

transition and was apparently caused by restructuring in the domain structure. Such a maximum of  $\epsilon$  near 160 K was found earlier for a  $\text{Rb}_2\text{ZnCl}_4$  single crystal with a high concentration of defects [14].

A temperature hysteresis of the dielectric constant appeared upon a cyclic change in temperature above  $T_0 \approx 151$  K (Fig. 3a). No hysteresis was observed at temperatures below  $T_0$ . A similar hysteresis limited from below and above by  $T_0$  and  $T_i$ , respectively, was observed for monocrystalline  $\text{Rb}_2\text{ZnCl}_4$ . It is believed this hysteresis was mostly due to the fixing of solitons and domain boundaries with lattice defects [13–15].

In contrast to the monocrystalline  $\text{Rb}_2\text{ZnCl}_4$ , the  $\epsilon$  hysteresis seems to be much higher than  $T_i$  for composites RS-46 and RS-320. We may assume that in addition to the abovementioned mechanisms, there is an additional contribution to the irreversibility of the  $\epsilon(T)$  dependence in the composites that is associated with the relaxation of elastic stresses arising in the embedded particles due to the difference between the  $\alpha$  temperature coefficients of the composites' components.

Based on the results from our measurements, we may conclude that the temperature of the transition to the incommensurate phase ( $T_i$ ) in the  $\text{Rb}_2\text{ZnCl}_4$  embedded into porous matrices with pore sizes of 46 and 320 nm changes slightly, compared with the monocrystalline sample.

Analysis of our experimental results shows that the mobile domain structure forms in the ferroelectric phase of  $\text{Rb}_2\text{ZnCl}_4$  nanoparticles and freezes at  $T_0 \approx 151$  K, as in the bulk material.

Along with this, the temperature of ferroelectric phase transition under conditions of constrained geometry rises at  $\Delta T_C \approx 50$  K. Since elastic tensile stresses  $\sigma$  appear in  $\text{Rb}_2\text{ZnCl}_4$  particles upon cooling, we may assume these particles are responsible for the rise in  $T_C$ . Let us estimate the maximum elastic stress in a particle:  $\sigma \approx \beta c \Delta T \approx 3.5 \times 10^7$  Pa, where  $\beta$  is volume expansion coefficient for  $\text{Rb}_2\text{ZnCl}_4$  single crystal;  $c$  is the average value of the elastic modulus, obtained using the data given in [16]; and  $\Delta T \approx 100$  K is the difference between the temperature of embedding and  $T_C$ . Since  $dT_C/dP = -50$  K/GPa for  $\text{Rb}_2\text{ZnCl}_4$  [17], the resulting  $\Delta T_C$  value is  $\approx 1.5$  K, which is much lower than the observed shift of the Curie temperature.

We may assume that the ferroelectric phase transition in an individual  $\text{Rb}_2\text{ZnCl}_4$  nanoparticle occurs when wavelength  $\lambda$  of the spatial displacements of atoms, which grows as  $T_i$  shifts toward lower temperatures, becomes comparable to particle size  $d$ . Experimental temperature dependence  $\delta$  of the disparity parameter was used to estimate the length of  $\lambda$  [8];  $\delta \approx 0.026$  at  $T = 250$  K. We can calculate  $\lambda$  by considering translations  $C \approx 1$  nm:  $\lambda = C/\delta \approx 38.5$  nm. We find that the real particle sizes ( $d \approx 70$  and 51 nm for RS-46 and

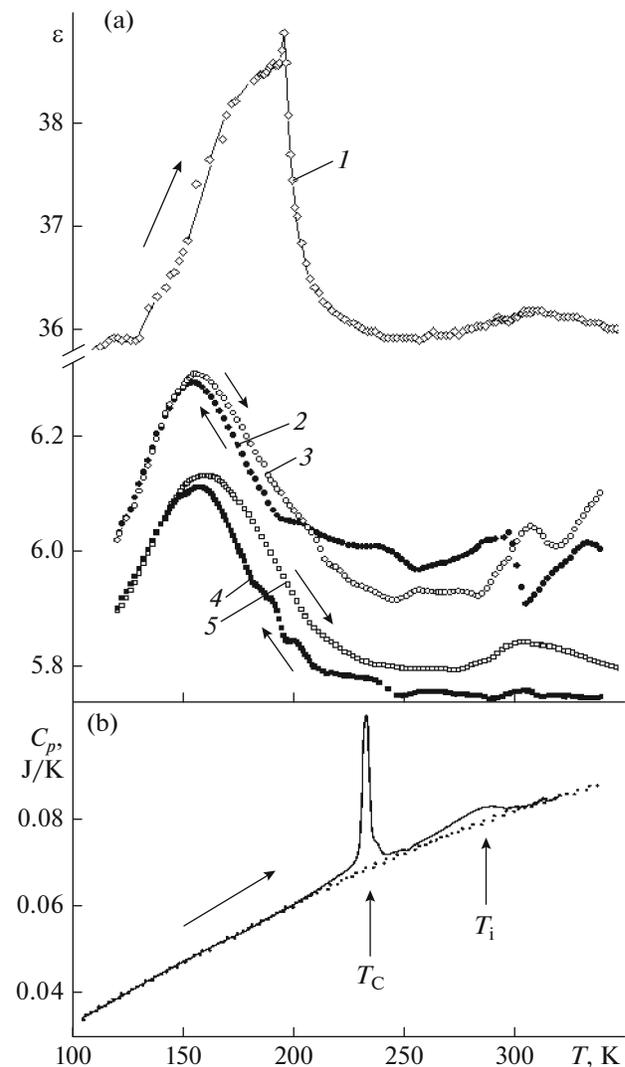


Fig. 3. (a) Temperature dependences of the dielectric constants for (1) our  $\text{Rb}_2\text{ZnCl}_4$  crystal sample and (2, 3) RS-320 and (4, 5) RS-46 composites obtained upon (1, 3, 5) heating and (2, 4) cooling; (b) temperature dependence of the heat capacity of our RS-46 composite.

RS-320, respectively) are comparable to  $\lambda$  near the temperature of the ferroelectric phase transition in the  $\text{Rb}_2\text{ZnCl}_4$  particles embedded in the porous matrices.

This assumption, however, requires additional experimental tests.

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