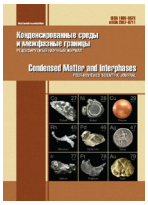

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Effect of pore size on phase transitions in rubidium tetrachlorozincate nanoparticles in porous glass matrices

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Abstract

It is well known that below a certain temperature (T_i), local displacements of individual atoms from their original positions occur in ferroelectric crystals with incommensurate phases. They form a spatial wave with a length of λ, which is incommensurate with the lattice period *a*, i.e. the λ/*a* ratio is irrational. The wavelength increases as the temperature decreases. Near the phase transition temperature T_C it reaches a length comparable to the size of the ferroelectric domains, as in the model rubidium tetrachlorozincate crystal (Rb_2ZnCl_4).

In ultrafine Rb_2ZnCl_4 crystals, the increase in λ is hindered by the size of the crystallite. Therefore, the physical properties of nanocrystalline rubidium tetrachlorozincate are expected to be considerably different from those of the bulk sample.

One of the methods for producing nanosized ferroelectric materials is a method based on embedding the material from a solution into porous matrices with nanometre-sized through-pores. We applied this method to study the effect of the size of ultrafine rubidium tetrachlorozincate crystallites on its dielectric properties and the phases occurring in the nanocrystallites.

For the experiment, we used samples of polycrystalline Rb_2ZnCl_4 and composites obtained by incorporation of Rb_2ZnCl_4 salt from aqueous solution into porous silicon oxide matrices with an average through-pore diameter of 46 and 5 nm (RS-46 and RS-5, respectively). The temperature dependencies of their dielectric permittivity were studied within the range of 100 to 350 K. We determined the temperatures of transition to the incommensurate (T_i) and ferroelectric (T_C) phases, as well as the mobility deceleration temperatures of ferroelectric domain boundaries in rubidium tetrachlorozincate nanocrystallites in the RS-46 composite. In Rb_2ZnCl_4 particles in the RS-5 composite, only the transition to the incommensurate phase occurs. In contrast to the bulk material, it shows features of the first-order phase transition.

Keywords: Incommensurate phase, Composite, Porous glass, Ferroelectric phase transition, Dielectric permittivity

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1. Introduction

Crystals with incommensurate phases are crystal structures where, at a certain temperature, local displacements of individual atoms from their initial positions occur. They form a spatial wave with a length of λ, that is incommensurate with the lattice period *a*, i.e. the ratio of λ/*a* is irrational. More generally, any material can be considered incommensurate, if there are two or more features of the translational symmetry which are mutually incompatible [1, 2].

Crystals with incommensurate phases attract interest, because the incommensurate modulation breaks the translational symmetry, so that the crystal is not in the true crystalline state. The spatial modulation waveform, originally described as sinusoidal, evolves with temperature. Its period increases as it gets farther from the incommensurate phase transition temperature (T_i), and the wave transforms into a soliton structure.

Rubidium tetrachlorozincate (Rb_2ZnCl_4) is a model ferroelectric material with an incommensurate phase [1–3].

The transition from the regular paraelectric to the incommensurate phase in the material is achieved at a temperature $T_i \approx 303$ K, called the Lifshitz temperature. The transition from the incommensurate to the commensurate ferroelectric phase occurs at $T_C \approx 192$ K [1, 3].

Below T_i, the wavelength λ in rubidium tetrachlorozincate increases with decreasing temperature, reaching the size comparable to the size of the ferroelectric domains near T_C [3].

However, the size of the crystallite in ultrafine crystals prevents an unlimited increase in the wavelength λ. Naturally, we can expect that this fact can significantly affect the phase states occurring in the material and considerably change its physical properties.

It should be noted that the properties of regular nanosized ferroelectrics have been intensively studied over a long time [4–10], whereas the physical processes in nanosized ferroelectrics with incommensurate phases have hardly been investigated so far.

Among various methods for obtaining nanocrystalline materials, the method of incorporation of the substance into porous matrices with nanometre-sized through-pores from the liquid state is probably the simplest [11].

We used this method to study the effect of the size of ultrafine rubidium tetrachlorozincate crystallites on its dielectric properties and the phases occurring in it.

2. Experimental

For the experiments, we used nanocrystalline Rb_2ZnCl_4 contained in the composites obtained by embedding rubidium tetrachlorozincate salt from aqueous solution into porous silicon dioxide plates with overall dimensions of 10×10×0.5 and 8.5×4.5×0.65 mm and average diameters of through-pores of ~ 46 and 5 nm, respectively. (The composites were abbreviated as RS-46 and RS-5).

The technology for the production of porous glass with a fine mesh of through-pores is described in detail in [12]. The porous glass used in our study initially had a relative volume of unfilled pores of 55% for RS-46 and 36% for RS-5.

Rubidium tetrachlorozincate salt was embedded into heat-treated porous glass plates from a saturated aqueous solution of Rb_2ZnCl_4 salt at temperatures of 90–98 °C, the process took about 3.5 hours. Following the procedure, the samples were dried in a thermostat with a gradual increase in temperature to 350 °C to remove residual moisture. The drying time was about 10 hours.

Using the weighing method, we found that the relative volume of embedded material in the porous matrix with an average pore diameter of about 46 nm was ≈ 19 %, and in the matrix with an average pore diameter of about 5 nm it was ≈ 15 %. In both cases, the proportion of Rb_2ZnCl_4 in relation to the total volume of the sample was about 8 %.

X-ray phase analysis of the synthesised composites was carried out using a Bruker D2 PHASER X-ray diffractometer (Cu-*K*α-radiation). The diffraction pattern obtained for the RS-5 composite is shown in Fig. 1. It can be seen that the angular dependence of the X-ray scattering intensity can be represented as a blurred maximum characteristic of glass located near the angle 2θ ≈ 24° and distinct peaks of intensity corresponding to the crystal lattice of bulk rubidium tetrachlorozincate.

The average particle size (d) of Rb_2ZnCl_4 in the composites was determined by X-ray diffraction analysis using the specialised TOPAS 4.2 software [13]. The estimates resulted in $d \approx 51$ for RS-46 and 18 nm for RS-5.

In addition to the composite materials, we also used a bulk (polycrystalline) rubidium tetrachlorozincate sample in the experiment for comparative analysis. It was obtained by compacting from the Rb_2ZnCl_4 salt.

The structural phase transitions were determined by analysing dielectric response measurements in the temperature range of 100–350 K.

Prior to the measurements, conductive paste was applied to the large surfaces of the samples to form the plane capacitor electrodes after drying. The samples were installed in a measuring cell fitted into a cryostat containing a platinum resistance thermometer, which allowed us to monitor the sample temperature with an error not exceeding ± 0.2 K. The dielectric permittivity (ε) was measured using an E7-20 LCR meter at a frequency of 10 kHz during sample cooling/heating at a rate of 1 to 2 K/min.

Each measurement cycle was preceded by heating the sample together with the measuring cell in a vacuum at about 380 K to remove moisture adsorbed from the air.

3. Results and discussion

The results of the experiment are shown in Fig.2 as temperature dependence ε diagrams. In the case of polycrystalline rubidium tetrachlorozincate (Fig. 2a), the curves ε(T) show two maxima. The dielectric permittivity maximum near the temperature $T_i \approx 307$ K is due to the transition from the regular paraelectric phase to the incommensurate phase. Its position on the ε(T) dependence diagrams when heating and cooling the sample remains almost unchanged, which is a characteristic feature of the second-order structural phase transition.

The second ε maximum occurs when the sample is cooled at $T_{Cc} \approx 187$ K, and when it is heated at $T_{Ch} \approx 196$ K. This ε maximum corresponds to the ferroelectric phase transition. Depending on the measurement mode (heating/cooling), its shift shows that the ferroelectric phase transition in the Rb_2ZnCl_4 bulk sample is

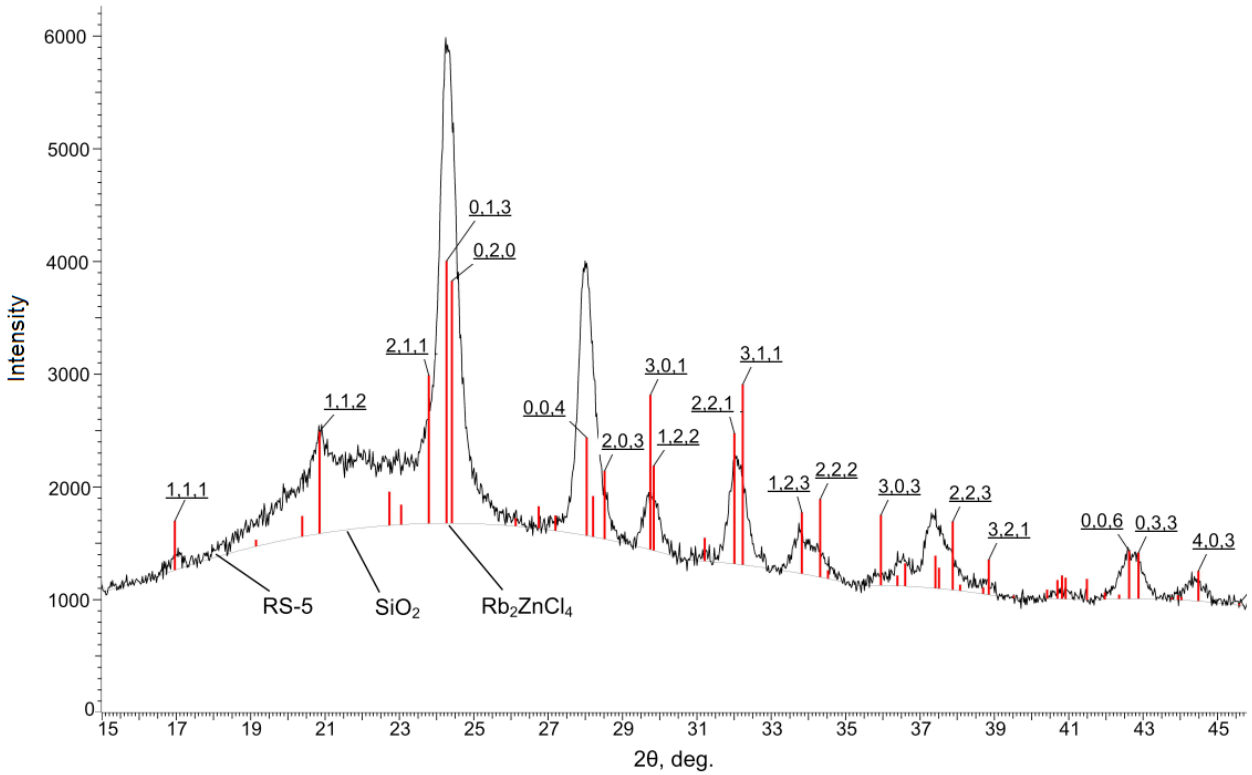

Fig. 1. The X-ray diffraction pattern of the RS-5 composite

a first-order phase transition, which is consistent with the known literature data [1, 2].

Some of the dielectric properties of the RS-46 composite were discussed in study [14]. The ε(*T*) dependences show specific features around 160, 245, and 307 K (Fig. 2b). As in the polycrystalline sample, the maximum of ε, observed around 307 K, is due to the transition from the incommensurate to the paraelectric phase in the embedded Rb_2ZnCl_4 particles. Near this maximum, there is a blurred heat capacity peak C_p (Fig. 2, insert). It should be noted that the corresponding temperature (≈ 285 K) is slightly lower than T_i. Further research is required to clarify this issue.

The step-like anomaly of ε at about 240 K, registered when cooling the sample, corresponds to the maximum heat capacity observed near 232 K, as illustrated in the inset to Fig. 2. This C_p maximum has a specific shape characteristic of monocrystalline Rb_2ZnCl_4 in the temperature range corresponding to the ferroelectric phase transition [15].

In the temperature dependency of the dielectric permittivity measured when heating the sample, there were no dielectric response features indicative of a ferroelectric phase transition.

Moreover, we observed a blurred maximum of ε at $T^* \approx 160$ K (shifted towards 158 K on the cooling curve). It is almost symmetrical, the temperature hysteresis forming only its right slope. Remarkably, there were no specific features in the $C_p(T)$ dependence around T^*.

This fact suggests that the above maximum of ε is due to a phase transition at the boundaries of the ferroelectric domains and the consequent reduction in their mobility. The phenomenon has been reported for monocrystalline rubidium tetrachlorozincate [15–17]. In the case of crystals with a lot of lattice defects, a blurred maximum of the dielectric response was observed around T^*, the temperature at which the mobility of domain boundaries ceases [15].

Notably, the temperature dependences of dielectric permittivity obtained upon heating and cooling of the studied material do not coincide, forming a temperature hysteresis of ε over a wide temperature range. The range lies above the temperature T^*, where the mobility of

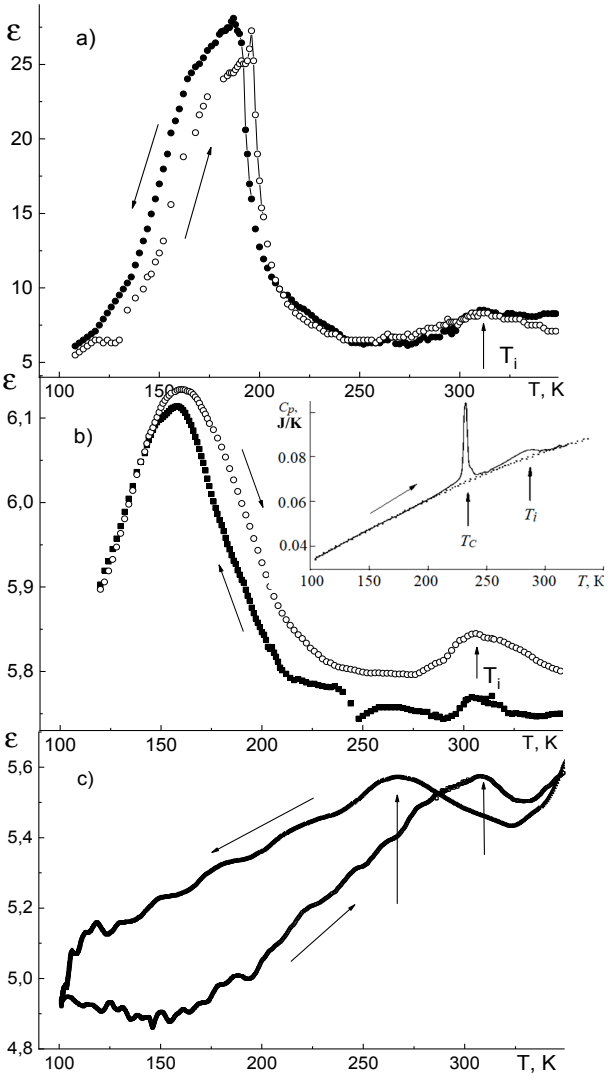

Fig. 2. Temperature dependences of dielectric permittivity for the crystalline Rb_2ZnCl_4 sample (a), and RS-46 (b) and RS-5 (c) composites obtained by heating and cooling. The insert shows the temperature dependence of the specific heat capacity of the RS-46 composite [11]

domain boundaries ceases. However, at $T < T^*$, the temperature hysteresis of e was not observed.

In the case of the monocrystalline sample, a similar dielectric response behaviour was reported [15–17]. However, unlike the above composite material, the temperature hysteresis of ε in Rb_2ZnCl_4 monocrystal is limited to T^* from below and to the Lifshitz temperature T_i from above. According to the authors who studied this phenomenon in Rb_2ZnCl_4 [15–17], the anomalously wide temperature hysteresis of dielectric permittivity is due to the fixation of the domain boundaries and solitons on lattice defects.

Due to the strong interaction with the defects, the polar domains can be "drawn" into the nonpolar phase from the ferroelectric phase during the heating of the sample [18]. This is probably the reason why the ε(*T*) dependence when heating the RS-46 composite, goes above the ε temperature dependence obtained during its cooling.

Let us now consider the dielectric properties of the RS-5 composite (Fig. 2c). Near the value of T_i, there is a small peak of dielectric permittivity. On the cooling curve, its position corresponds to ≈ 268 K, and on the heating curve it is ≈ 307 K. The observed temperature hysteresis of T_i confirms that, in rubidium tetrachlorozincate crystallites embedded in porous silicon dioxide with an average pore diameter of about 5 nm, the transition from the regular paraelectric phase to the incommensurate phase exhibits the features of the first-order phase transition. The hysteresis of T_i is due to the fixation of the incommensurate wave of atomic displacements by the lattice defects, including the defects on the particle surface. Subsequently, the wave detaches from the stops upon "overheating" or "overcooling" of the sample compared to the phase equilibrium temperature.

No features of a dielectric response indicating a ferroelectric phase transition or a transition in the domain structure were observed in the ε(*T*) dependences under the experimental conditions. Therefore, we can conclude that the ferroelectric phase does not occur in Rb_2ZnCl_4 particles in the RS-5 composite.

Moreover, the temperature hysteresis of ε for the RS-5 composite covers the entire temperature range used in the experiment, indicating the presence of metastable states in the material and their relaxation over a wide temperature range. Apparently, the existence of such a wide temperature hysteresis of ε is a common feature of ferroelectrics with incommensurate phases incorporated into porous matrices [19].

In contrast to the RS-46 composite, the ε(*T*) dependence for heating goes below the ε, temperature dependence for cooling of the sample. This indirectly indicates that the ferroelectric phase domains, which usually make a significant contribution to the dielectric response, were not formed in the case of the RS-5 composite.

4. Conclusions

Based on the results of the research, we made the following conclusions.

1. The Lifshitz temperature $T_i \approx 307$ K in Rb_2ZnCl_4 rubidium tetrachlorozincate crystallites localised in silicon dioxide pores with an average diameter of 46 and 5 nm changed little as compared to the temperature T_i in the bulk sample. At the same time, the phase transition exhibited the features of the first-order phase transition, which were most pronounced in the case of Rb_2ZnCl_4 particles in the RS-5 composite. For this material, the temperature of the transition from the incommensurate to the paraelectric phase remained approximately the same as that of the bulk sample. However, when the temperature change was reversed, the value of T_i decreased to ≈ 268 K. Thus, the interaction of rubidium tetrachlorozincate particles with the matrix stabilised the nonpolar commensurate phase. This interaction seems to be predominantly chemical, as the transition to the incommensurate phase was not accompanied by either polarisation or a noticeable deformation of the Rb_2ZnCl_4 lattice.

2. Under the experimental conditions, we observed no transition from the incommensurate to the commensurate ferroelectric phase in Rb_2ZnCl_4 nanocrystallites in the RS-5 composite.

3. In rubidium tetrachlorozincate particles in a porous silicon dioxide matrix with an average pore size of ≈ 46 nm, the transition to a ferroelectric phase was registered. According to the combined data of dielectric and calorimetric measurements, the temperature of the transition was around 240 K. This is approximately 50 K higher than in the monocrystalline material.

4. The dielectric permittivity maximum observed around 160 K for the RS-46 composite corresponds to the dielectric anomaly occurring due to rearrangement in the domain structure of monocrystalline Rb_2ZnCl_4 with a high defect concentration [15]. Thus, we can state that, at low temperatures, ferroelectric domains are formed in rubidium tetrachlorozincate crystallites embedded into silicon dioxide with through-pores averaging 46 nm in diameter. The domain

mobility decelerates significantly at ≈ 160 K, as in bulk Rb_2ZnCl_4 monocrystal.

Author contributions

Korotkov L. N. – concept of the research. Stekleneva L. S. – carrying out the experiment. Bryanskaya A. A. – preparing samples for the experiment. Pankova M.A. – preparing the manuscript. Popov S. V. – attestation of samples, processing of experimental data, and making figures.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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