

Effect of restricted geometry on structural phase transitions in KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ crystals

VLADISLAV TARNAVICH^{1*}, LEONID KOROTKOV¹, OLJA KARAEVA¹,
ALEXANDER NABEREZHNOV², EWA RYSIAKIEWICZ-PASEK³

¹Voronezh State Technical University, 394026, Voronezh, Russia

²Ioffe Physical Technical Institute, 194021, St Petersburg, Russia

³Institute of Physics, Wrocław University of Technology, 50-370 Wrocław, Poland

*Corresponding author: tarnavich@mail.ru

The dielectric response of crystalline $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{KH}_2\text{PO}_4\text{-SiO}_2$ and $\text{NH}_4\text{H}_2\text{PO}_4\text{-SiO}_2$ composites prepared by embedding salts into porous glasses with the average pore diameter of 320 nm has been studied at the temperature range of 85–300 K. An increase of the structure phase transition temperatures in embedded salts has been observed, which is supposedly due to tensile deformations of embedded crystalline particles. The antiferroelectric phase transition in confined ADP particles becomes diffuse in the temperature region around 10 K.

Keywords: ferroelectrics, antiferroelectrics, composite material, porous glass, phase transition, dielectric permittivity.

1. Introduction

The porous structures filled with various substances are suitable material for optical devices [1]. The use of optically active ferroelectric fillers allows us to create optical devices operated by electrical voltage. However, it is known that the physical properties of ferroelectric materials in confinement are essentially different from the properties of the bulk. For example, the temperature of ferroelectric phase transition T_C in NaNO_2 embedded into porous glasses decreases [2] upon reduction of average pore diameters. On the contrary, for potassium dihydrogen phosphate (KH_2PO_4 – KDP) T_C increases [3] with a decrease of pore diameters. These experimental facts could be explained by both the size effect and interaction between the intrinsic surface of pores and the material embedded.

It was suggested [3] that the observed increase of T_C for embedded KDP particles with a decrease of pore diameters (and sizes of particles) is caused by tensile deformations, which appear owing to different temperature coefficients of

linear expansion of embedded material and matrix. Cooling the sample leads to the appearance of elastic stresses in embedded nanoparticles, and it is possible to interpret this process as an influence of “negative” hydrostatic pressure P . Due to the strong dependence $T_C(P)$ [4] it could be a reason of growth of T_C for KDP nanoparticles.

To check this assumption [3] it is expedient to study the effect of “restricted geometry” on phase transition (PT) temperature for other crystals of KDP family.

For comparative studies we have used the potassium dihydrogen phosphate and ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$ – ADP) embedded into the identical porous glasses. This selection has been determined by the following reasons:

1. Both compositions are crystallized in a tetragonal phase.
2. The values of dT_C/dP for these substances differ essentially ($dT_C/dP \approx -4.5$ K/kbar for KDP and $dT_C/dP \approx -3.4$ K/kbar for ADP [4]).
3. Not only dT_C/dP but the linear expansion coefficients for ADP ($\alpha_1 \approx 34.0\text{--}39.3 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_3 \approx 1.9\text{--}5.3 \times 10^{-6} \text{ K}^{-1}$ within temperature range 203–407 K) are smaller than for KDP ($\alpha_1 \approx 20\text{--}26.6 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_3 \approx 34.3\text{--}44.6 \times 10^{-6} \text{ K}^{-1}$ for KDP within temperature range $T \approx 123\text{--}363$ K) [5]. This lightens the interpretation of experimental results.
4. Both materials are used as active elements of optical convertors.
5. The effect of restricted geometry on antiferroelectric phase transition in KDP-family crystals has not been studied up-to-now.

2. Experiment

The experiments were performed with the samples of composites KDP– SiO_2 and ADP– SiO_2 and polycrystalline ADP. The composites were prepared by embedding at 363–368 K during 4–5 hours a KDP (ADP) saturated water solution into previously annealed porous glass with average pore diameter of 320 nm. The volume fraction of the salts embedded into the porous glass was about 12–17%. The samples were in the form of rectangular plates $\cong 10 \times 5 \times 1 \text{ mm}^3$. Every time before measurements the samples were annealed at ~ 373 K during 4 hours for removing remnant water. Then the samples were clamped between two aluminum electrodes and placed in a cryostat, where the temperature varied from 85 to 300 K and was measured with an error not more than ± 0.2 K. The measurements of dielectric permittivity ε were carried out in the cooling and heating regimes (1–2 K/min) in nitrogen atmosphere, using LCR-meter at the frequency of 1 kHz.

3. Results and discussion

The temperature dependence of dielectric permittivity for KDP– SiO_2 composite sample is presented in Fig.1. The well defined maximum of $\varepsilon(T)$ dependence near 125 K indicates the ferroelectric phase transition. One can see that the transition temperature for embedded material is ≈ 125 K, *i.e.*, 3 K higher than for KDP single

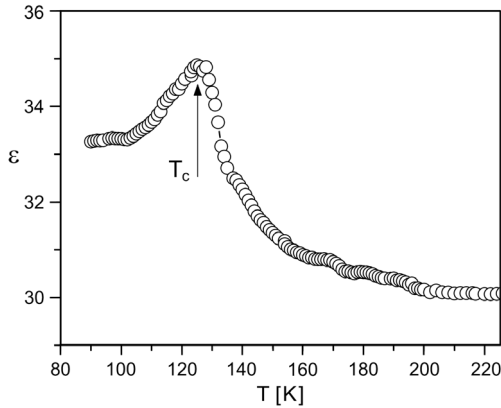


Fig. 1. Dielectric permittivity vs. temperature for KDP–SiO₂ composite obtained at heating regime.

crystal ($T_C \approx 122$ K [4]). The increase of T_C in confined KDP in comparison with the bulk material is in a good agreement with data obtained in reference [3].

It should be noted that the shape of the $\epsilon(T)$ maximum for composite material has qualitative similarity to the shape of $\epsilon_{33}(T)$ dependence observed for KDP single crystal [4] and for polycrystalline KDP [6] in the vicinity of T_C .

Below T_C the so-called *plateau* region is observed. Usually, the *plateau* region in $\epsilon(T)$ dependence is explained by high domain structure mobility which is a characteristic feature of KDP type ferroelectrics [4]. Thus, one can assume the existence of high domain structure mobility in embedded KDP particles within a broad temperature region below the Curie temperature.

The analysis of $\epsilon(T)$ dependences for polycrystalline ADP sample and composite ADP–SiO₂ (Figs. 2 and 3, respectively) has shown their qualitative similarity.

One can see the step-like $\epsilon(T)$ dependence and a wide temperature hysteresis of dielectric permittivity for polycrystalline ADP in the vicinity phase transition temperature. Such behavior of ϵ unambiguously shows that the crystal under study

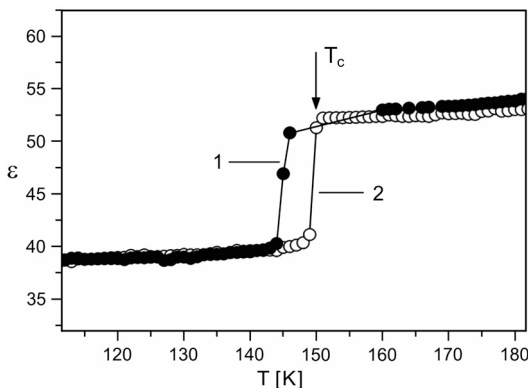


Fig. 2. Dielectric permittivity vs. temperature for polycrystalline ADP (1 – cooling, and 2 – heating).

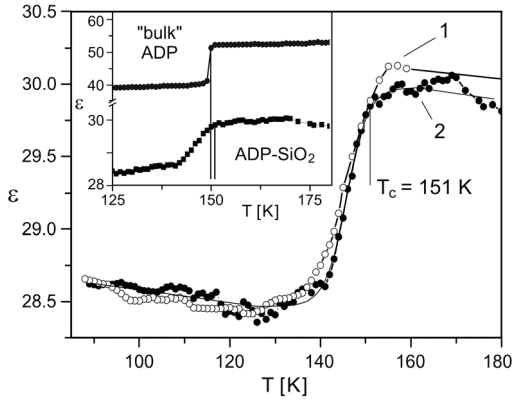


Fig. 3. Dielectric permittivity vs. temperature for ADP–SiO₂ composite (1 – cooling, and 2 – heating); insert: $\varepsilon(T)$ dependences for polycrystalline and ADP–SiO₂ composite, obtained during heating.

undergoes the first order phase transition near $T_C \approx 150$ K that is in agreement with reference data [4, 5].

A similar $\varepsilon(T)$ dependence is observed for ADP–SiO₂ composite. However, the temperature hysteresis of dielectric permittivity for composite material is essentially smaller and the anomaly of $\varepsilon(T)$ near T_C broadens evidently. So, PT in confined ADP becomes diffuse, and we have observed the “rounding” of phase transition as is typical of nanostructured materials. It is possible to suggest that with a decrease of sizes of ADP particles the crossover of PT from the first to the second order will take place. We are going to check this supposition in the future using the porous glasses with smaller average pore diameters.

The broadening of ε anomaly in the phase transition region makes determination of the precise point of T_C complicated. Taking into account the fact that the appearance of a nonzero order parameter leads to a decrease of dielectric permittivity in antiferroelectric crystals [4], we find the $T_C \approx 151$ K to be the temperature at which the dependence $\varepsilon(T)$ decreases rapidly.

4. Conclusions

Having analyzed the experimental results we can conclude what follows:

- An increase of the structure phase transition temperatures in KDP and ADP salts embedded into the porous glass matrices ($d \sim 320$ nm) in comparison with the bulk materials has been found. More pronounced effect of “restricted geometry” on transition temperature is observed for KDP particles. This speaks in favor of the assumption [3] that an increase of phase temperature in embedded crystals of KDP family is caused by tensile deformations effect.

- The antiferroelectric PT in confined ADP particles becomes diffuse in the temperature region of about 10 K.

– The presence of the so-called *plateau* region in $\varepsilon(T)$ dependence below T_C observed for KDP–SiO₂ composite speaks in favor of the existence of a high mobile domain structure in embedded KDP salt below T_C .

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References

- [1] KUMZEROV YU., VAKHRUSHEV S., *Nanostructures within porous materials*, [In] *Encyclopedia of Nanoscience and Nanotechnology*, [Ed.] H.S. Nalwa, American Scientific Publishers, Vol. 10, 2003, pp. 1–39.
- [2] NABEREZHNOV A., FOKIN A., KUMZEROV YU., SOTNIKOV A., VAKHRUSHEV S., DORNER B., *Structure and properties of confined sodium nitrite*, *The European Physical Journal E: Soft Matter* **12**(Supplement 1), 2003, pp. 21–24.
- [3] COLLA E.V., FOKIN A.V., KUMZEROV YU.A., *Ferroelectric properties of nanosize KDP particles*, *Solid State Communications* **103**(2), 1997, pp. 127–130.
- [4] LINES M.E., GLASS A.M., *Principles and Applications of Ferroelectrics and Related Materials*, Clarendon, Oxford, 1977.
- [5] SHASKOLSKAJA M.P., *Acoustic Crystals*, M. Nauka, 1982, pp. 402–425 (in Russian).
- [6] ZOLOTUKHIN I.V., SPITSINA S.V., YANCHENKO L.I., KOROTKOV L.N., *Preparation, structure and dielectric properties of fractale aggregates of KH₂PO₄*, *Fizika Tverdogo Tela* **41**(11), 1999, pp. 2059–2061 (in Russian).

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