Stabilization of the monoclinic phase of KH$_2$PO$_4$ under restricted geometry conditions

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From the analysis of X-ray diffraction patterns the crystal structure of KH$_2$PO$_4$ embedded from an aqueous solution into the pore space of porous glass with an average pore diameter of 7 ± 1 nm was determined. It has been established that at room temperature KH$_2$PO$_4$ nanoparticles crystalizes in a monoclinic structure, which is metastable in bulk KH$_2$PO$_4$ under normal conditions. The characteristic size of potassium dihydrogen phosphate nanoparticles was determined to be $(27 \pm 3$ nm$)$ in the pores of this matrix.

Keywords: potassium dihydrogen phosphate, crystal structure, diffraction, nanocomposite materials, nanoporous glass.

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It was established experimentally that restricted geometry conditions (i.e., size effects) induce in certain cases not only a significant change in macroscopic physical properties of nanostructured materials, but also a modification of their structure. Specifically, the emergence of previously unknown crystalline phases [1–5] or stabilization of structures, which were metastable under normal conditions [6–9], were observed; notably, the fabrication history of samples played a significant part in this context [2,5,8]. Potassium dihydrogen phosphate KH$_2$PO$_4$ (KDP) is a model ferroelectric with an order−disorder phase transition [10,11]. The phase transition in a bulk material from the paraelectric tetragonal phase (space group $I\bar{4}2d$) to the ferroelectric orthorhombic one (space group $Fdd2$) occurs under normal conditions at $T_C = 122$ K and is associated with ordering of hydrogen atoms. Structural transitions in KDP have been examined thoroughly (even under high pressures). However, the influence of restricted geometry on the crystal structure of this material has remained essentially uninvestigated. The sole exception is study [9], where the stricture of high-deuterated KDP (DKDP) embedded in a porous borosilicate glass with an average pore diameter of 7 nm (PG7) was examined by neutron diffraction. The aim of the present study is to determine whether the case of DKDP is unique and attributable to a high degree of sample deuteration or the observed features are intrinsic to potassium dihydrogen phosphate itself under restricted geometry conditions. The same porous borosilicate glass PG7 was used as a matrix for fabrication of a nanocomposite material (NCM) containing common KDP. Pores in such glasses form a 3D interconnected dendritic network of through channels [12]. The overall porosity of PG7 used was $\sim 25\%$ of the sample volume. The average pore diameter $(7 \pm 1$ nm$)$ was determined using mercury porosimetry. The pore space was filled with the ferroelectric material by crystallization from a saturated aqueous solution; i.e., thin (0.5 mm) PG7 plates were introduced into a hot KDP solution (to increase the degree of pore filling) and kept there until the solution dried out completely at temperatures of 343 and 403 K. The surface of samples was then cleaned thoroughly to remove residual bulk material. The degree of pore filling was determined gravimetrically to be $41.5 \pm 0.5\%$ in the case of filling at 343 K and $39.5 \pm 0.5\%$ at 403 K; i.e., it was virtually independent of the solution temperature. Measurements were carried out with a DRON-8N X-ray diffractometer for both samples at the CuK_α wavelength and room temperature. Two cycles with a time interval of four months were performed. Measurements for empty glass PG7 were also performed in order to define more accurately the shape of background scattering off a blank matrix. The resolution function of the diffractometer was determined from measurements with a LaB$_6$ reference. The diffraction patterns for samples fabricated at filling temperatures of 343 K (Fig. 1) and 403 K have essentially the same overall shape, and no changes in these patterns were found four months later. Pronounced KDP diffraction peaks are seen clearly against the intense background of scattering off the PG7 matrix itself (black curve) in Fig. 1.

Owing to the size effect, diffraction reflections are broadened considerably relative to those expected from the bulk material. At the next stage, diffraction patterns for KDP in tetragonal and orthorhombic phases were modeled and compared to those obtained for the PG7+KDP NCM after subtraction of the porous glass background, smoothing, and normalization. The results are presented in Fig. 2. It follows from the comparison of data in Fig. 2 that the crystal structure of KDP embedded in PG7 at room temperature corresponds neither to the expected paraelectric tetragonal
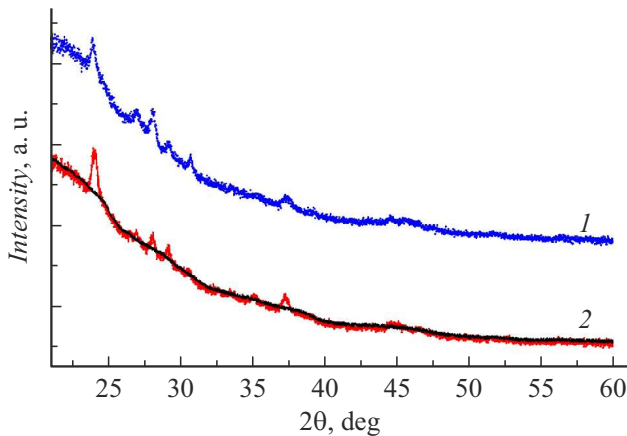
Figure 1. Diffraction patterns for empty porous glass PG7 (black curve) and PG7+KDP NCMs fabricated at filling temperatures $T = 343\,\text{K}$ (circles *1*) and 403 K (circles *2*). For ease of comparison, the patterns are shifted vertically.
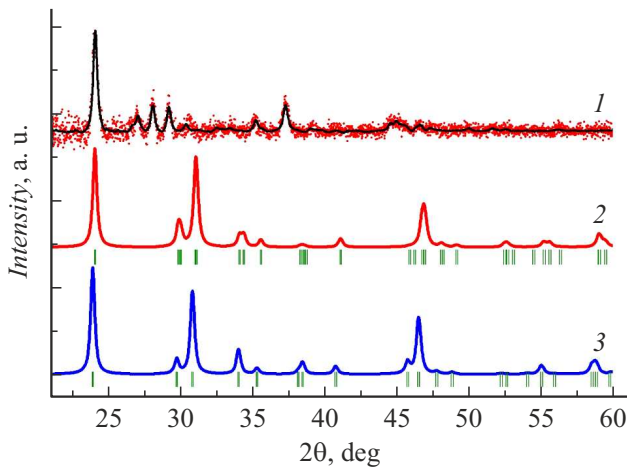

Figure 2. *1* — Experimental data for the PG7+KDP NCM (circles) and the corresponding model diffraction pattern (monoclinic structure) after background subtraction. *2, 3* — Model diffraction patterns for KDP in orthorhombic (curve *2*) and tetragonal (curve *3*) phases. For ease of comparison, the patterns are shifted vertically. Vertical dashes denote the positions of Bragg reflections for orthorhombic and tetragonal phases.

phase nor to the ferroelectric orthorhombic one. Since the statistics is insufficient for a full-profile analysis of the NCM structure, further processing was performed within the so-called „matching mode" approach implemented in the standard FullProf package [13] with the use of literature data for other known crystal phases of potassium dihydrogen phosphate. Specifically, the transition from the tetragonal phase to the monoclinic one ($P2_1$ or $P2_1/m$) was observed in the process of heating [14] at $\sim 460{-}468\,\text{K}$. The authors of [15], using a lengthy procedure that took several months, were able to synthesize a monoclinic phase of bulk KDP with space group $P2/c$, stable under normal conditions.

The monoclinic crystal phase with space group $P2_1/c$ was obtained in [16] after an approximately week-long synthesis from a mixture of $1.25\,\text{g}$ K_2CO_3 and $5\,\text{ml}$ H_3PO_4 (2M) kept in an autoclave under pressure at a temperature of 453 K. Notably, this phase remained stable after cooling to room temperature. The authors emphasized that exposure at a temperature of 453 K is mandatory; failure to implement such temperature conditions results in crystallization into the tetragonal phase. Monoclinic phase $P2_1$ of potassium dihydrogen phosphate has also been demonstrated long ago [17] for DKDP at a deuteration level on the order of 98% under the conditions of crystallization from an aqueous solution. It should be noted that this phase is unstable under normal conditions and transforms fairly rapidly into the tetragonal phase in air at room temperature. At the same time, stabilization of this phase (even after long-term exposure under normal conditions) for DKDP in cooling from room temperature down to 90 K has been proven experimentally for the PG7+DKDP NCM in [9].

All these types of structures were taken into account in our attempts at characterizing the diffraction pattern obtained for the PG7+KDP NCM. An adequate fit to experimental data was found for structures with space groups $P2_1/m$, $P2_1/c$, and $P2_1$. It is known that the fabrication history of samples may have a significant effect on the crystal structure of samples of nanocomposite materials [2,5,8]. On the one hand, since our samples were fabricated at a fairly high temperature, a phase with structure $P2_1/c$ or a high-temperature phase of the $P2_1/m$ type were to be expected in the PG7+KDP NCM. On the other hand, we did not notice any significant difference between the samples fabricated at 343 and 403 K, and a reduction of the formation temperature of structural phases from 453 K [16] (for $P2_1/c$) or 468 K (for $P2_1/m$) [14] to 343 K is fairly profound and unlikely even for nanocomposite materials. In addition, special conditions, which were not implemented in the present case, were
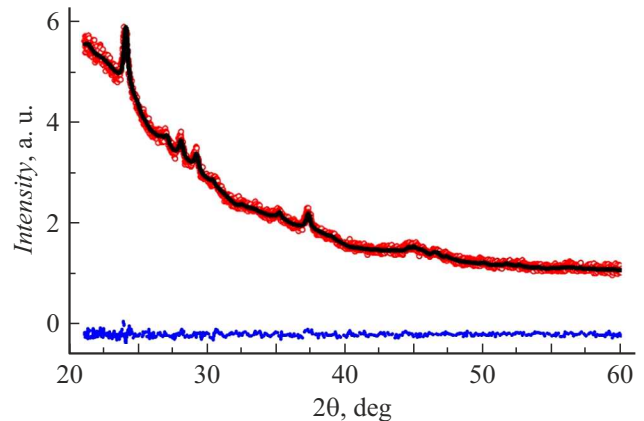

Figure 3. Experimental data (circles), results of fitting within space group $P2_1$ (black curve), and residual between the fit and the data (curve at the bottom) for the PG7+KDP NCM.

Lattice cell parameters of known monoclinic KDP/DKDP structures (with space group $P2_1$)

a, Å	b, Å	c, Å	β, °	Sample	Reference
7.464(3)	14.656(6)	7.068(4)	92.66(3)	DKDP embedded in 7 nm porous glass	[9]
7.45(1)	14.71(2)	7.14(1)	92.31(1)	Single crystal of high-deuterated DKDP	[18]
7.37(1)	14.73(1)	7.17(1)	92	High-deuterated DKDP crystallized from an aqueous solution	[17]
7.44(8)	14.518(1)	7.602(5)	103.107(7)	Single crystal of KDP grown by slow evaporation of an aqueous solution containing KH$_2$PO$_4$ and K$_4$P$_2$O$_7$ in a molar ratio of 1:1	[19]
7.335(2)	14.551(4)	7.009(2)	92.98(2)		This study

required for the formation of phases with structures of the $P2_1/c$ and $P2_1/m$ type. Therefore, we chose the phase with structure $P2_1$; the results of fitting are presented in Fig. 3. The characteristic size of the coherent scattering region (size of KDP nanoparticles) was estimated to be 27 ± 3 nm based on an analysis of the broadening of diffraction reflections taking into account convolution with instrumental resolution. This size was used to model the spectra for tetragonal and orthorhombic phases shown in Fig. 2. The following lattice parameters were determined for phase $P2_1$: $a = 7.335(2)$ Å, $b = 14.551(4)$ Å, $c = 7.009(2)$ Å, and $\beta = 92.98(2)°$. Literature data on lattice parameters of KDP/DKDP in monoclinic phase $P2_1$ are presented in the table for comparison.

Thus, it is fair to say that after filling PG7 with a saturated aqueous solution of KDP and drying, the latter in the PG7 + KDP NCM crystallizes in the monoclinic phase (the most probable structure is $P2_1$), which remains stable for a long period of time (at least four months) under normal conditions, in channels of the porous glass matrix.

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Conflict of interest

The authors declare that they have no conflict of interest.

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