DESTRUCTION OF KDP SINGLE CRYSTALS AT TETRAGONAL-TO-MONOCLINIC MODIFICATION PHASE TRANSITION

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ABSTRACT

The effect of the annealing of KH_2PO_4 single crystals at 180-210°C on their structural quality and phase composition was studied by the X-ray and metallographic methods. The phase transition $/\bar{4}2m/ \rightarrow /P2_1/ \rightarrow /\bar{4}2m/$ which occurs at heating and a following cooling of samples is shown to be accompanied by a structural transition - single crystal textured polycrystal. This transition results in the loss of transparency and sharp drop of the strength due to the formation of a branched system of cracks. An essential difference in the degree of structural perfection and phase composition in the surface-adjacent damaged layer (DL) and in the bulk of the crystal is observed, including the anisotropy of the I and II kind of the angular distribution of crystalline fragments. It is shown that the transition temperature strongly depends on the distortions of the surface-adjacent layer in which the process of the fragmentation nucleation begins. The lowering of the temperature of the initial compound decomposition with the formation of a new phase - anhydrous salt KPO_3 also takes place in this layer. The concentrational profile of this phase correlates with those of the DL distortions and is localized in the region 7-10 µm in thickness.

KEYWORDS

X-ray analysis, damaged layer, phase transformations, destruction, cracks, single crystal, textured polycrystal.

KDP single crystals are known to undergo a phase transition from the tetragonal modification $/\bar{4}2m/$, stable at room temperature, to the monoclinic one $/P2_1/$ at the temperature increase. The values of the transition temperature T_t according to different authors differ by 20-30°C, which is quite essential. The attention of specialists to the behaviour of these crystals at elevated temperatures is conditioned both by purely scientific interest and the necessity of solving practical problems - choice of optimal parameters for isothermal annealing and operational conditions of products. At present the annealing of the KDP single crystals is widely applied for the improvement of quality, optical homogeneity, mechanical and laser strength (Azarov et al.,1983). However the data on the effect of annealing on structure and phase transformations in the bulk and in the damaged layer (DL) are practically absent. DL due to a high concentration of point defects, cracks, dislocations, presence of a polycrystalline component, being the result of the mechanical treatment, is distinquished by an elevated reaction ability as compared to the bulk, i.e. is activated. The present paper is dedicated to the study of the destruction processes taking place in the bulk and on the activated surface of KDP crystals at the isothermal annealing.

KH_2PO_4 single crystals were grown by the recirculation of aqueous solutions on the prism-like seeds at a rate of 0.5 mm/day along [001]. The samples, 50x50x30 mm^3, were cut with a continuously wetted filament. A further mechanical treatment included polishing with abrasive powders of electrocorundum M40, M28, M14, M10 and finishing with diamond powders ACM 5/3, ACM 0.5/0 under a specific pressure of 10kPa. The samples were oriented along the planes (100), (010) and (001) with a precision of ± 0.05°.

The annealing of the samples, preliminarily placed into a special container, was performed in the gradient free zone of the furnace in air at normal pressure and temperature range of 180-210°C. According to different authors it is just this temperature range in which the point of phase transition exists; the latter - from a stable at room temperature tetragonal modification of KH_2PO_4 /42m/ to a high temperature monoclinic one /$P2_1$/. In (Volkova et al.,1988) a conclusion is made that the temperature of this transition strongly depends on the concentration of point and linear defects as well as on the impurity composition, in particular, on the iron concentration. The regime of heating and cooling the samples was selected experimentally in the annealing process and did not exceed 5°C/hr. The isothermic exposure was 24 hours.

The degree of the structural quality and phase composition were studied using the X-ray diffraction analysis. For the phase analysis light power graphite monochromators (002) were used, those giving the anguler divergence of the primary beam 0.1°. The registration was performed in CuK_α and CuK_β radiation according to the scheme θ-2θ. For the layer-by-layer analysis of the surface-adjacent layer the beam was directed onto the sample at glancing angles α, taking the given discrete values. The interference lines were registered by rotating the detector with a narrow imput window. This allows to obtain the dependences of intensity, physical broadening, crystal lattice period on the angle α, to recover the profiles of the polycrystalline and plastically deformed areas of the damaged layer or phases' distribution over the depth (Rom and Tkachenko, 1988). To determine the structure perfection degree registered were the rocking curves (ω-method) in the mode of two-crystal spectrometer. In this case the resolution was increased by the application of perfect germanium crystals as monochromators; the angular divergence of the primary beam was 0.005°. For precise measurements the registration scheme(n,n,-m) giving the resolution ≤ 0.0003° was used, with this two crystals formed a little diverging beam with the minimal spectral dispersion. The registration was performed in the CuK_{α_1} radiation. The damaged layer of the finished single crystals was studied by the registration of ω-curves in the asymmetric Bragg's case. The rotation of the sample around the diffraction vector allows to vary α-angles in the given range from some tenth parts to tens of degrees with a required step. The further mathematical processing gives the possibility to recover the profiles of the parameters that characterize the degree of the DL structure quality.

The analysis of the results of the study of KH_2PO_4 samples after the isothermal annealing at 180-210°C give evidence to the fact that all of them preserve their initial geometric form, however at the elevation of the annealing temperature grows the probability of the transparency loss and appearance of "marble" inclusions in separate parts of the samples which are raudomly distributed in the bulk. This fact was mentioned in the paper by Chan Khai Guin (1975), where the loss of transparency was observed at heating KH_2PO_4 crystals. In contrast to the existing opinion the author assumed turning the sample white to be caused by the formation of multiple small cracks and not to be connected with chemical decomposition.

The microscopic analysis of the surface of "marble" inclusions revealed a rather branched system of cracks. Such volumes of crystals easily broke down into small fragments almost without efforts. A prolonged exposure of the annealed crystals to air only makes destruction easier, probably due to a moisture penetration into the crystal. The found by us structure of a "stone-like" break gives evidence to the presence of the intergrain damage, typical for not a single crystal but for a small-grain polycrystal.

The rocking curves from the transparent parts of the annealed crystals show no changes in their structure as compared to the initial state. On the other hand the clouded "marble" regions give essentially broadened rocking curves (Fig.1), for which characteristic is the availability of numerous sharp maxima at the intensity distribution over a wide angular region. This testifies to the structural transition of the single crystal into a textured polycrystal. In the irradiated volume there are both large particles with a disorientation 0.1-1° and significantly smaller ones. The large fragments preserve the orientation close to the initial one and the small ones are probably arranged chaotically, i.e. represent a quasiisotropic polycrystal which is confirmed by the presence of the interference lines (hko) and (hkl) at the registration in the geometry θ-2θ of the crystal faces (100) and (001). The formation of the textured polycrystal (Fig.2) is caused by the stresses arising during the rearrangement of the tetragonal lattice into the monoclinic one at heating the sample and at the reverse transition in the process of its cooling. The transition bears a fragmentary character owing to big discrepancy between the lat-

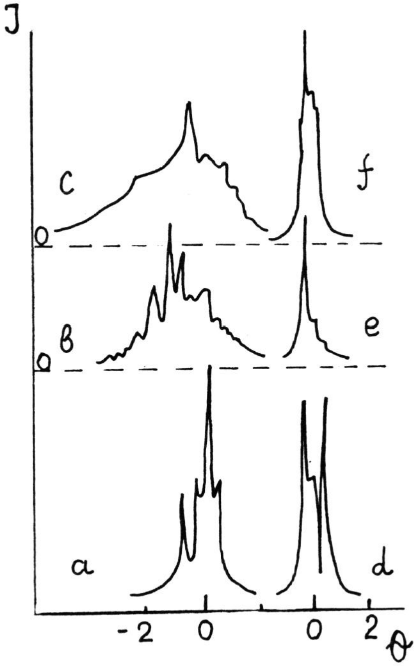

Fig.1. Rocking curves of annealed KH_2PO_4 :a,b:(020) reflection, rocking around [001] and [100] axes, respectively; c,d:(200) reflection, rocking around [001] and [010] axes, respectively; e,f: (008) reflection, rocking around [010] and [100], respectively. $CuK_{\alpha 1}$ radiation.

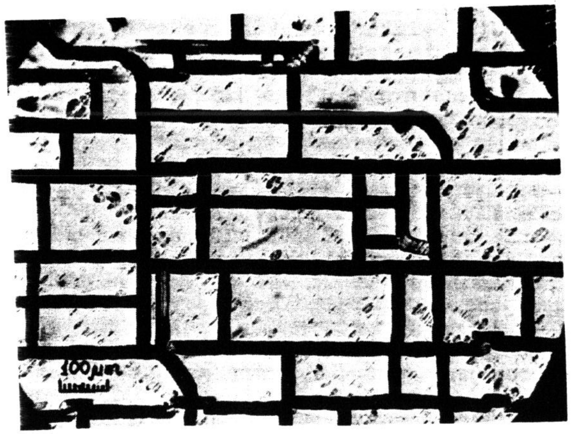

Fig.2. Micrograph of (001) face surface obtained after isothermal annealing and etching (44-fold magnification).

tices of one and the other phases. According to Tomas (1974) the directions of the monoclinic phase axes c_m, a_m and b_m form with the corresponding axes of the tetragonal phase a_q, b_q and c_q the angles $\varphi_1 = (\vec{a}_q, \vec{c}_m) \sim 14°$, $\varphi_2 = (\vec{b}_q, \vec{a}_m) \sim 5°$ and $\varphi_3 = (\vec{c}_q, \vec{b}_m) \sim 14°$. At cooling there occurs the reverse transition $P2_1 \rightarrow 4\bar{2}m$, which in its turn may lead to an additional fragmentation of the sample's volume. When analyzing the surface-adjacent layer it was found that the rocking curves (Fig.1) characterizing the angular distribution of fragments differ in the anisotropy of the I and II kind. This may be explained by a specific character of the lattice reorientation at the phase transition. In the bulk of the material the anisotropy of the I kind is preserved and, as it is shown in Fig.3c, the reflection (008) is characterized by some smeared maxima separated by angles of the order of 1° while the reflections (200) and (020) are smeared in a wide angle range (Fig. 3a,b) and have no well distinquished maxima. This may give evidence to the fragments' anisotropy, i.e. they may represent plate-like formations with a larger plane close to (001). The comparison of the Fig.1 and Fig.3 allows to state that after the annealing the surface-adjacent polycrystalline layer possesses a higher degree of structural quality than the volume of KDP which is conditioned probably by the recrystallization processes initiated by the activated surface.

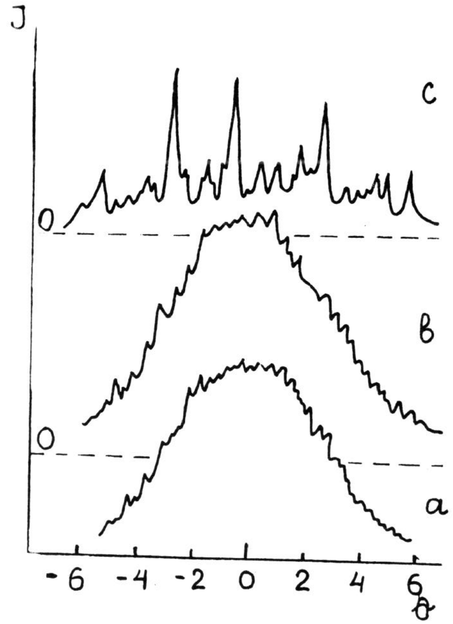

Fig.3. Rocking curves of annealed KH_2PO_4 crystals obtained after removing 3 mm thin surface-adjacent layer: a,b,c: (020), (200) and (008) reflections, respectively. $CuK_{\alpha 1}$ radiation.

The phase analysis of the DL for the mechanically treated after the annealing revealed the existence of the compound KPO_3. This phase was observed irrespective of the fact whether the investigated volume had remained the transparent single crystal or it had transformed into the crack-containing polycrystal. We determined the concentration profile of the phase KPO_3 over the depth of the DL after the annealing of the crystal. The character of the profiles was found to be exponential, this corresponding to the distortion distribution in the DL.

It should be noted that the formation of KPO_3 takes place at 180–210°C, whereas, as seen from the state diagram presented by Tomas (1974), the decomposition of KH_2PO_4 is initiated starting from 250°C. In this connection it seems reasonable to assume that the thin DL formed in the process of mechanical treatment may be considered as a dispersed material with a large area of activated surface, and the decomposition temperature for this layer is essentially lower than the one of the crystal volume.

CONCLUSIONS

1. The gradient-free isothermal annealing of KH_2PO_4 crystals carried out at temperatures 180–210°C leads to the structural transition single crystal - polycrystal with a sharp texture component. This transition is accompanied by the losses in the crystal's transparency and strength and is caused by the stresses arising in the process of the phase transition $\bar{4}2m \rightarrow P2_1 \rightarrow \bar{4}2m$ in the said temeparture range.

2. The annealing initiates both the nucleation of a new phase and recrystallization phenomena taking place on the surface activated by mechanical treatment. Therefore the surface-adjacent layer and the volume of the annealed crystals have different degrees of structural perfection.

3. The presence of the compound KPO_3 in the DL testifies to the decrease of the decomposition temperature for KH_2PO_4 in dispersed DL in comparison with that characteristic of the massive single crystal.

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