A MODEL OF REACTION FRONT PROPAGATION IN CRYSTALS

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A spatio-temporal model of anisotropic propagation of the dehydration front in $Na_3P_3O_9 \cdot 6H_2O$ single-crystals is discussed. It is based on the assumption that dehydration proceeds as a periodic displacement of the reaction front from one reacting elementary block to another, and that experimentally fixed dehydration patterns are composed of a multitude of elementary patterns having the same shape. The model can be applied to other crystals.

On the basis of a kinetic investigation of the dehydration front propagation on the surface and into the volume of sodium cyclotriphosphate hexahydrate $(Na_3P_3O_9 \cdot 6H_2O)$ single-crystals in various directions, depending on the temperature and the relative air humidity, an experimental model of this process has been proposed [1–3]. It has been shown that in vacuum and air at low relative humidity (r) the process takes place according to a scheme of uniform surface localization. The resulting planar reactant-product interface penetrates into the crystal, and the unreacted tranparent nucleus acquires the form of a parallelepiped which, depending on temperature, contracts homothetically or nonhomothetically. At about 30°, homothetic contraction prevails. At 10°, the contraction becomes nonhomothetic and the contracting nucleus gradually elongates along the b axis. If dehydration is carried out in humid air at $r \leqslant 25$–30% ($t = 20$–50°), then the (100), (010) and (001) crystal faces react in the sequence of decrease of their activity, according to a scheme of spot surface localization: first the (100), then the (001) and finally the (010) face. The shape of the well-defined dehydration patterns varies from one face to another. However, the linear rate of dehydration front propagation on faces in one and the same direction remains constant.

The coincidence of the kinetic parameters of the three stages of the overall process (mass loss, destruction of initial crystal lattice and crystallization of a new phase) obtained by independent experimental methods (gravimetry, microscopy and X-ray techniques) allows identification of the visually observed interface with the reaction zone and analysis of the connection between the $Na_3P_3O_9 \cdot 6H_2O$ crystal structure and the dehydration patterns which appear in a wet atmosphere [4].

Analysis of the $Na_3P_3O_9 \cdot 6H_2O$ crystal structure shows that water molecule layers divided by anionic cycle layers exit on the (010) and (001) faces. These layers coincide with the planes of crystal cracking which exit on the same faces. If we draw straight lines along the water molecule layers and join them through one or two unit cells, we obtain simple configurations which on the level of the elementary cell reflect the shape of the experimentally observed dehydration patterns. Thus, the observed dehydration pattern can be regarded as a set of elementary patterns having the same shape. If the penetration of the reaction zone into the volume of the crystal is taken into account, the elementary patterns can be considered as projections of an elementary reacting block to the corresponding crystal face.

In our case the block shape is determined by the spatial arrangement of layers of anionic cycles. Consequently, the dehydration process on the unit cell level can be regarded as a periodic displacement of the reaction front from one reacting elementary block to another. This suggestion has allowed us to explain some pecularities, of the anisotropic decomposition of $Na_3P_3O_9 \cdot 6H_2O$ crystals.

Let us consider the reaction front propagation on the (010) face, where the shape of the elementary dehydration pattern is close to a rectangle (Fig. 1). Let the reaction start with block A and propagate at a rate of two blocks per time unit in direction a, perpendicular to the layers of the anionic cycles, and at a rate of four blocks per time unit in direction c, parallel to both the layers of the anionic cycles and those of the water molecules. Now, if we consider the obtained boundaries at $\tau = 1$, it is seen that the shape of the pattern is similar to a rhombus, the diagonals of which coincide with the directions of largest rates of front propagation, i.e. directions a and c (Fig. 1, dashed line). As far as the real shape of the dehydration patterns on (010) is close to rectangular (double line), it is logical to assume that the adjacent blocks are activated and react rapidly (the cross-hatched ones). Indeed, when the activated blocks react, the water molecules inside them have the possibility to move out from the crystal lattice in two directions: perpendicularly to
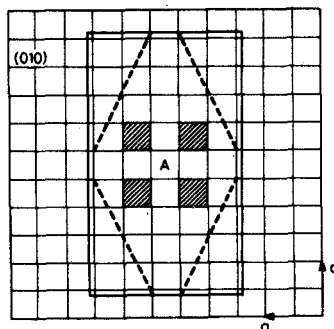

Fig. 1 Scheme of dehydration front propagation on (010) face of the $Na_3P_3O_9 \cdot 6H_2O$ crystal

the crystal face and perpendicularly to the reaction interface. As concerns molecules of water in non-activated blocks, they can move out only in the direction perpendicular to the crystal face. When the four cross-hatched blocks react, eight new blocks will be activated and at $\tau = 1$ we obtain a rectangular dehydration pattern with the double lined boundary. The above consideration can be used while explaining the considerable differences in rates of front propagation on the surface and into the volume of the $Na_3P_3O_9 \cdot 6H_2O$ crystal in identical directions.

If we consider the reaction front propagation into the volume of the crystal, we can see that the water molecules can leave the crystal lattice only in the direction perpendicular to the reaction interface. Surface blocks in contact with the gaseous phase are less stable and react more rapidly as compared with volume ones. Moreover, the water molecules of the surface blocks are in identical conditions with respect to the advance of the reaction zone in various directions on the surface, and there are no reasons to expect serious differences in the values of the effective activation energy for directions a, b and c. This conclusion agrees with the experimental data.

As concerns the water molecules in the volume blocks and their removal from the crystal lattice, the structure differences in various directions play a more important role. Indeed, the activation energy in vacuum for direction b is higher than that for directions a and c, in spite of the fact that the water molecule layers exit on both the (010) and (001) faces. Consideration of the $Na_3P_3O_9 \cdot 6H_2O$ crystal structure shows that molecules of water leaving the volume blocks in direction b have to overcome layers of anionic cycles, while evolution in other directions is favoured by the interlayer character of the process.

When some water molecules leave an elementary reacting block, crystallochemical stages take place, resulting in collapse of the block. So far as the molar volume of the reaction product is somewhat less than that of the initial hydrate, water removal from neighbouring blocks is not limited by the reaction product layer and the reaction proceeds in the kinetic region.

The model considered can be applied to other objects. It will be useful in investigations of the peculiarities of anisotropic reaction front propagation in crystals, depending on the structure of the crystal lattice and on the reactivities of the crystal faces.

References

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Zusammenfassung — Ein Zeit- und Raummodell der anisotropischen Fortschreitung der Dehydratationsgrenzfläche in $Na_3P_3O_9 \cdot 6H_2O$ Einkristallen wird diskutiert. Das Modell ist auf einer Annahme begründet, dass die Wasserabspaltung als eine periodische Propagation der Reaktionsgrenzfläche von einem reagierendem Elementarblock zu anderem verläuft und dass die experimentell fixierte Entwässerungsfiguren aus einer Menge von Elementarfiguren von identischer Form zusammengestellt sind. Das Modell kann auf andere Kristallen verbreitet werden.

Резюме — Рассмотрена пространственно-временная модель анизотропного продвижения фронта дегидратации в монокристаллах $Na_3P_3O_9 \cdot 6H_2O$. Модель основана на предположении, что дегидратация происходит путем периодического перемещения реакционного фронта от одного элементарного реагирующего блока к другому, и что экспериментально фиксируемые фигуры дегидратации составлены из множества элементарных фигур одинаковой формы. Модель может быть распространена на другие кристаллы.