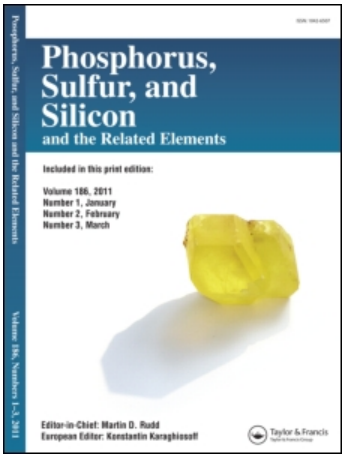

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ON THE MECHANISMS OF REACTIONS OF ME(II)-PHOSPHATES IN THE SOLID STATE

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Abstract By study of topotactic reactions conclusions on their mechanisms on an atomic scale were derived.

INTRODUCTION

Aim of this paper is to give contributions to the knowledge of mechanisms on an atomic scale of solid state reactions. One way to obtain information in this respect is to investigate topotactic reactions by diffraction methods. We use the term "topotactic" for crystallographically oriented reactions in which structural units large enough to transfer their original orientation are taken over nearly undisturbed from the educt into the product structure.

Subject of our investigations were solid state reactions in the systems PbO-P_2O_5-H_2O and CaO-P_2O_5-H_2O which proceed crystallographically oriented (Figure 1). The reactions were investigated by X-ray diffraction, thermogravimetry and paper chromatography. Conclusions on their mechanisms were deduced by comparison of the crystal structures of educt and product.

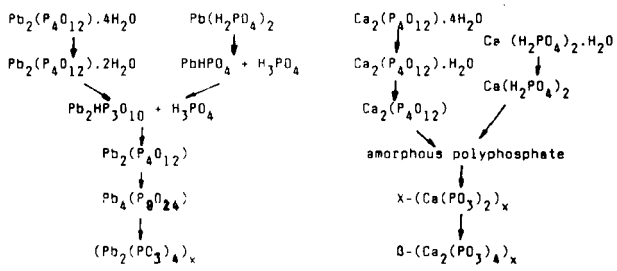


FIGURE 1. Survey of investigated reactions.

ORIENTATION TRANSFER IN TOPOTACTIC REACTIONS

In Figure 2 the orientations are shown in which from $Pb_2(P_4O_{12}).4\ H_2O$ at first the 2-Hydrate and than $Pb_2HP_3O_{10}$, a chain phosphate, are formed (Figure 1)[1]. One can see that two of the crystallographic axes remain strictly in one and the same plane and the cross sections of the unit cells with this plane are nearly constant in area. This leads to the idea that the structural units which are responsible for the oriented course of the reactions are parallel to this plane.

Inspection of the three crystal structures shows layers of PbO_x polyhedra parallel to this plane and moreover that during the reactions every second of these layers remains unchanged in its atomic arrangement (Figure 2). All the structural alterations occur in the layers between them. Therefore the first ones should be the structural units which transfer the orientation into the product crystallites.

An interesting case of orientation transfer has been observed in the reactions starting with $Ca_2(P_4O_{12}).4\ H_2O$ (Figure 1)[3]. There is an intermediate amorphous phase which does not interrupt the orientation transfer. That this phase is truly X-ray amorphous was checked by overexposed X-ray photographs. Nevertheless it should contain structural units

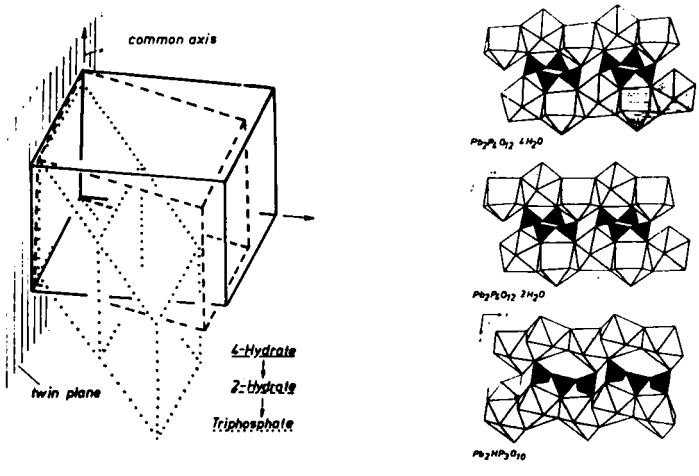


FIGURE 2. Orientation of the unit cells in the first steps of dehydration of $Pb_2(P_4O_{12}).4\ H_2O$ and undisturbed layers in the resp. structures

which are at least poorly oriented and therefore able to induce the oriented continuation of the reaction.

CHANGE IN CHEMICAL FUNCTION OF ATOMS DURING REACTION

In the reaction $Pb_2(P_4O_{12}).4\ H_2O \longrightarrow Pb_2(P_4O_{12}).2\ H_2O$ only dehydration takes place and no change in anion constitution (Figure 1). In order to obtain information on the mechanisms acting there we compare the crystal structures in their relative orientation (Figure 3). We do this by 3-dimensional superposition of the two structures. With the hypothesis that the large atoms tend to preserve their positions we come to the conclusion that half of the water lost is original water of crystallization while the other half is formed from oxygen originally bound to P in the anion (Figure 3). Mass spectrometry of the water lost during dehydration of $Pb_2(P_4{}^{16}O_{12}).4\ H_2{}^{18}O$ confirmed this conclusion.

THE ROLE OF GLIDE PROCESSES

By short heating at 100 °C or storing in moist air $Pb(H_2PO_4)_2$ becomes an oriented intergrowth of $PbHPO_4$ with H_3PO_4.[2] Its amorphous part, H_3PO_4, can easily be extracted.

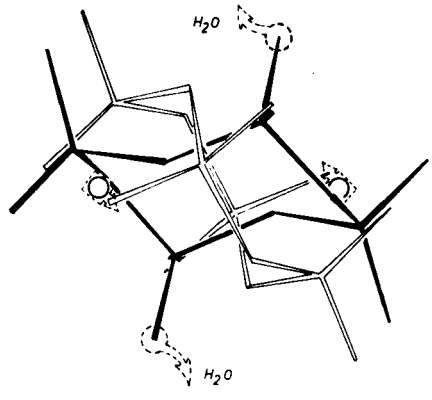
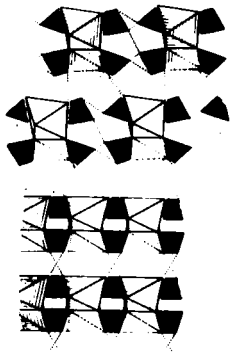


FIGURE 3. Considered range in the superposition of the 4-Hydrate (full lines, O = water) and 2-Hydrate (open lines) structures. Broken lines enclose atoms changing their chemical functions.



$Pb(H_2(As,P)O_4)_2$

As : P = 59 : 41

$PbH(As,P)O_4$ + $H_3(As,P)O_4$

83 : 17 (82 : 18) 36 : 64 (35 : 65)

FIGURE 4. Structures of $Pb(H_2PO_4)_2$ (top) and $PbHPO_4$ and example for observed and expected (in parantheses) As/P ratios in the reaction product of a mixed crystal. Layers and slip vector: Horizontal, H-bridges: dotted

Comparing the structures of $Pb(H_2PO_4)_2$ and $PbHPO_4$ (FIGURE 4) we have the following assumption of the reaction mechanisms: Layers shared with one another by hydrogen bonds slip along their plane relative to the neighboured layers. In connection with this process from every pair of $(H_2PO_4)^-$ ions along the slip vector one at a time is segregated.

If this topotactic model is true consequences derived from it should be fulfilled. So we can ask for a rule of selection of the anions to be segregated. With mixed crystals $Pb(H_2(As,P)O_4)_2$ we found no difference between the occupation factors of the two crystallographically independent anion positions but large differences between As/P in the two product phases (Figure 4). With the rule "phosphate is exsolved in priority to arsenate" observed and expected As/P ratios are in accordance. An epitactic reaction with favoured incorporation of As in the product crystals is excluded because the As/P distribution in these crystals is homogenous. Therefore our topotactic model is supported.

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