On Aluminum Phosphates of Composition $\mathrm{Al_2O_3\cdot 3P_2O_5}$ and on the Interaction of $\mathrm{Al_4(P_4O_{12})_3}$ with Molten Potassium Chloride

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Abstract

Full Text

Chemistry

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On Aluminum Phosphates of Composition $Al_2O_3 \cdot 3P_2O_5$ and on the Interaction of $Al_4(P_4O_{12})_3$ with Molten Potassium Chloride

(Presented by Academician I. V. Tananaev, September 9, 1963)

Until recently, only one modification of the compound of composition $Al_2O_3 \cdot 3P_2O_5$ was known, belonging to the cubic system, in which, as was established by X-ray structural analysis (^{1}), the PO_4 tetrahedra form isolated four-membered rings. In attempting to reproduce the synthesis of this compound by the described method (^{2,3}), by heating a solution of alumina hydrate in phosphoric acid, we found that in the reaction products, along with isotropic crystals, anisotropic crystals are also present, sometimes in rather considerable quantities. This fact is confirmed by d' Yvoire (^{4}), who synthesized by various methods four new modifications of this compound, which he designated by the indices (B), (C), (D), (E). By means of chromatography this author showed that, upon their decomposition, polyphosphoric acids are obtained. Some of these modifications he found as by-products in the synthesis of the cubic mineral—the modification (A).

Fig. 1. X-ray diffraction patterns of aluminum phosphates:
a $-Al_2O_3 \cdot 3P_2O_5$ (C); *b* $-Al_2O_3 \cdot 3P_2O_5$ (G)

Two types of structural formulas may correspond to the stoichiometric ratio $Al_2O_3 \cdot 3P_2O_5$: (a) with radicals $(P_{nO_{3n}})^{-n}$, consisting of PO_4 tetrahedra linked into isolated rings, where $n = 3 \div 4$; (b) with PO_4 tetrahedra linked into infinite chains $(PO_3^-)_n$. Modification (A) belongs to the first type ($n = 4$), while the remaining modifications, in all probability, belong to the second. These structures are analogous to the corresponding silicate structures. It is known that the interatomic distances in SiO_4 and PO_4 tetrahedra differ from one another by only about 5%; the great similarity in the structures of phosphates and silicates has already been noted (^{1}).

Fig. 2. I.r. spectrograms of aluminum phosphates: a—modification (A); b—modification (C); v—modification (G)

Figure 2: Fig. 2. I.r. spectrograms of aluminum phosphates: a—modification (A); b—modification (C); v—modification (G)

Aluminum phosphates have still been investigated rather little; however, already from the works of d' Yvoire (^{5}) it is evident that this is a very extensive class of compounds, and the application to it of the concepts and nomenclature developed in the study of silicate structures may facilitate further work.

Numerous studies of berlinite ($AlPO_4$) and its polymorphic transformations (^{6}) have shown that AlO_4 tetrahedra can enter into a lattice consisting of PO_4 tetrahedra, forming structures similar to aluminosilicates. It is possible that some of the minerals described below belong precisely to this class of compounds, which by analogy should be called aluminophosphates.

We investigated two minerals obtained by heating a solution of alumina in phosphoric acid to 400-600° and separated from the lower modifications (A) formed simultaneously. The composition of these minerals corresponds to the stoichiometric formula $Al_2O_3 \cdot 3P_2O_5$.* Their X-ray diffraction patterns, obtained with CuK_α radiation using a nickel filter, are given in Fig. 1, and the infrared spectra, recorded from pressed pellets, in Fig. 2.

The mineral with principal lines 3.81, 3.34, and 3.01 kX is identified from its X-ray diffraction pattern as the modification (C) synthesized by d' Yvoire. Most characteristic of this mineral, for the method of preparation used here, is crystallization in the form of acicular spherulites, as well as spherical formations with a characteristic extinction pattern in the form of a rotating cross (Fig. 3). Fragmental grains with wavy extinction are often encountered, as are twins of intergrowth and penetration. Plates with gray interference color occur, in the form of elongated hexagons and parallelograms, with positive elongation and extinction along the long diagonal. The refractive indices are $N_g \sim 1.606$, $N_p \sim 1.591$.

The characteristic line of the second mineral—5.62 kX—is located in the small-angle region, where considerable experimental errors are possible. Therefore, on the basis of the X-ray diffraction pattern it cannot be stated with certainty whether this mineral is identical with modifications (B) or (D), in which the interplanar spacings for the most intense lines have values of 5.48 and 5.46 Å, respectively. Under the microscope this mineral, which we shall designate as modification (G), is represented by aggregates composed of shapeless fragments up to $60\,\mu$ in size. Individual fragments have wavy extinction. Plates in the form of parallelograms with positive elongation are encountered. The refractive indices are $N_g \sim 1.500$, $N_p \sim 1.438$. The differential thermal-analysis curve of this compound shows no effects up to 1200°. After heating to 1050° for two hours, the mineral partially decomposes.

Fig. 3. Types of crystallization of modification (C). Crossed nicols. 270×

Figure 3: Fig. 3. Types of crystallization of modification (C). Crossed nicols. 270×

Fig. 2. I.r. spectrograms of aluminum phosphates: **a**—modification (A); **b**—modification (C); **v**—modification (G).

From a comparison of the infrared spectrograms (Fig. 2) of modifications (A), (C), and (G), it is evident that the last has a much greater similarity to modification (A), both in the position and in the character of the absorption peaks. Hence it should be assumed that modifications (G), like modifications (A),

* All chemical analyses were carried out by Z. Ya. Selivanova.

is characterized by a structure consisting of isolated rings of PO_4 tetrahedra. It is not identical to the structure of modifications (B) or (D), which, according to the studies of d' Ivoire (4), have a chain structure.

At the same time it was found that the (A)-modification of $Al_4(P_4O_{12})_3$ reacts with KCl, forming compounds which, apparently, should be regarded as potassium aluminophosphates. In our experiments the reaction proceeded with an excess of KCl for 2–6 hours at 900°. The melt was cooled together with the muffle, and then leached with hot water. The insoluble residue was transferred to a filter, dried, and examined.

Fig. 3. Types of crystallization of modification (C). Crossed nicols. 270×

It proved that this residue consisted of a mixture of different crystals which, according to their characteristic refractive index, should be divided into two groups.

Crystals with the higher refractive index constitute a homogeneous substance. Among them there occur very perfect forms of crystallization. This is a biaxial mineral with refractive indices $N_g \sim 1.573$; $N_p \sim 1.558$. Chemical analysis of this mineral gave the following results: P_2O_5 –60.93-59.51%; Al_2O_3 –18.80-19.87%; K_2O –21.20%, which approximately corresponds to the stoichiometric ratio $K_2O \cdot Al_2O_3 \cdot 2P_2O_5$, or $KAlP_2O_7$.

X-ray photography of a single crystal showed that the mineral belongs to the monoclinic system. Determination of the parameters of the crystal lattice from oscillation X-ray photographs without aligning the crystal gave the following results: $\beta = 122°30'$; $a = 7.31$ kX; $b = 9.74$ kX; $c = 9.09$ kX. With 4 molecules of $KAlP_2O_7$ in the unit cell, the calculated specific gravity is 2.93, which is close to the experimentally determined value.

The phase with the low refractive index is represented by crystals of irregular form with a large number of polysynthetic twins (Fig. 4a). The refractive indices of this phase vary within rather broad limits: $N_g = 1.495$-1.485; $N_p \sim 1.460$-1.475.

Fig. 4. Types of crystallization of the low-refractive phase of potassium aluminophosphates: a –phase (C), obtained by slow cooling; b –phase (B), obtained by quenching

Figure 4: Fig. 4. Types of crystallization of the low-refractive phase of potassium aluminophosphates: a –phase (C), obtained by slow cooling; b –phase (B), obtained by quenching

Since the birefringence of this phase is not very large, it may be assumed that it is a mixture of isomorphous solid solutions of variable composition. The elongation of the crystals is negative. The mineral is biaxial, has straight extinction, and apparently belongs to the rhombic system. In hydrochloric acid this phase dissolves readily even in the cold. Chemical analysis gave (in wt.%): P_2O_5 –61.82-59.85; Al_2O_3 –9.16-7.50; K_2O –30.40; Cl –0.81. This approximately corresponds to the stoichiometric formula $3\text{-}4.5K_2O \cdot Al_2O_3 \cdot 5\text{-}6P_2O_5$.

X-ray photographs of these minerals were taken in a camera with a copper anticathode and an ionization counter without a filter. It should be noted that the intensity of individual lines of the low-refractive phase varies from one X-ray photograph to another.

The X-ray pattern of the phase with high refraction, corresponding to the formula $KAlP_2O_7$, coincides with the X-ray pattern obtained for a compound of this composition by d' Ivoire ((5), p. 1233). This compound was first synthesized by Uvrar (7), who, in addition, synthesized a compound with the stoichiometric formula $3P_2O_5 \cdot 2Al_2O_3 \cdot 3K_2O$, crystallizing in the form of monoclinic plates.

The reaction yield, both total and in terms of the content of individual phases, proved variable in different experiments. Experiments involving rapid cooling of the melt (900°—water) shed some light on the mechanism of the reaction of $Al_2O_3 \cdot 3P_2O_5$ with molten KCl. In this case the composition of the insoluble residue differed substantially from that obtained upon slow cooling: the content of the phase with high refraction, which on slow cooling was 60-80%, became very small. The phase with low refraction was represented by large elongated crystals, up to 1-2 mm in size. Polysynthetic twins were not observed at all. The birefringence of these crystals is lower than that of the same phase obtained by slow cooling, and the refractive indices varied within much narrower limits: $N_g \sim 1.486 \div 1.483$; $N_p \sim 1.474 \div 1.477$.

Fig. 4. Types of crystallization of the low-refractive phase of potassium aluminophosphates: *a* –phase (C), obtained by slow cooling; *b* –phase (B), obtained by quenching.

Apparently, as the temperature decreases this mineral enters into secondary reactions and undergoes recrystallization, possibly with formation of a mixture of solid solutions of variable composition. It should be noted, however, that the principal lines on the X-ray pattern of the low-refractive phase obtained by quenching (2.83; 4.14; 3.16; 3.03 kX) do not coincide with the lines on the X-ray pattern of the low-refractive phase obtained by slow cooling.

It will be possible to establish the exact chemical formula of these compounds and assign names to them, on the basis of the nomenclature proposed above, only after their structures have been determined by X-ray analysis. For the time being we propose to call this group of compounds potassium aluminophosphates, assigning the following indices to the individual phases: to the compound $KAlP_2O_7$ –(A), to the phase with a low coefficient of refraction obtained by quenching –(B), to that obtained by slow cooling of the melt –(C), and to the compound of composition $3K_2O \cdot 2Al_2O_3 \cdot 3P_2O_5$ –(D).

The principal lines on the X-ray pattern of potassium aluminophosphate (C) (intensities are given on a five-point scale): 6.46 Å–2; 3.97 Å–5; 3.48 Å–3; 3.43 Å–3; 3.35 Å–1; 3.18 Å–3; 2.90 Å–2; 2.77 Å–1; 2.70 Å–1; 2.60 Å–1; 2.281 Å–3; 2.227 Å–2; 2.11 Å–1.

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Note: Figure translations are in progress. See original paper for figures.