NEW CRYSTALLINE ULTRAPHOSPHATES AND THEIR STRUCTURES

DÖRTE STACHEL*, ANNETT OLBERTZ*, INGRID SVOBODA⁺,
HARTMUT FUESS⁺

*Otto-Schott-Institut, Chemisch-Geowissenschaftliche Fakultät, Universität Jena,
Fraunhoferstraße 6, D-07743 Jena, Germany

⁺Strukturforschung, FB Materialwissenschaft, Technische Hochschule Darmstadt,
Petersenstraße 20, D-64287 Darmstadt, Germany

Abstract Ultraphosphates exist between the pure Q^3 connected P_2O_5 and the Q^2 connected so-called metaphosphates. They show new structure principles. Selection rules for structure connection limit the number of realizable compounds.

INTRODUCTION

Ultraphosphates and ultraphosphate glasses are polymeric phosphates between the pure phosphorus pentoxide " P_2O_5 " and the so-called "metaphosphate" composition with a ratio of cation oxide oxygens to phosphorus pentoxide of 1:1. These are the limits of concentration range, where the ultraphosphates exist. The structure of ultraphosphates was considerably unclear until the last few years. Only two types of crystalline ultraphosphates were known since 1971, namely CaP_4O_{11} and MnP_4O_{11} with a ratio of cation oxide to phosphorus oxide of 1:2¹ and $Sr_2P_6O_{17}$ and $Cd_2P_6O_{17}$ with a cation to P_2O_5 ratio of 2:3^{2,3}. These crystalline materials possess infinite layer structures with different connections between the $\{PO_4\}$ -tetrahedra. A series of ultraphosphates $M^{III}P_5O_{14}$ of the three-charged cations, namely of rare-earth elements, also were known. These ultraphosphates were of interest in laser technology^{4,5}.

Our investigations go back to 1990⁶. Above all we were interested in description of the structure of ultraphosphate glasses by means of structure investigations of compared crystalline ultraphosphates, mainly in the binary alkaline-earth ultraphosphate systems. Some new crystalline ultraphosphates were prepared and structurally identified⁷⁻¹² and also structure refinements to improve the structure interpretation were done^{13,14}.

PROPERTIES AND PREPARATION

Normally, "five-charged" phosphorus has an oxygen coordination number of four. One corner of this tetrahedron is double-bonded and not connected with other $\{\text{PO}_4\}$ tetrahedra. So, the $\{\text{PO}_4\}$ tetrahedron can be three-corner connected in maximum. The highest degree with pure Q^3 connections shows the phosphorus(V)oxide. "Metaphosphates" are purely Q^2 -connected. Between them in the ultraphosphate region, Van Wazer postulated as Q^3 , as Q^2 connections, with random distribution of small molecular units¹⁵. This thesis was of high interest, since glassy ultraphosphates are one of the stablest glasses against devitrification.

This is the reason why the preparation of the crystalline ultraphosphates takes more than one week, normally starting with metal carbonate or oxide, 85% phosphorus acid and phosphorus(V)oxide in excess. While glassy ultraphosphates are very hygroscopic materials because of their very high content of P_2O_5 , the crystalline ultraphosphates possess a higher stability against water and atmospheric influences. In this way it is possible to separate the crystals from the environed frozen-in melt by water and to dry them by methanol and acetone, additionally.

In most cases, a mixture of different ultra- and metaphosphates was obtained. The selection of pure substances only was possible by tweezers under the microscope.

STRUCTURE CONNECTION PRINCIPLES

This paper deals with crystalline ultraphosphates of the 1:2 ratio only, corresponding to the chemical composition $\text{M}^{\text{II}}\text{O} \cdot \text{P}_2\text{O}_5$ with 33,3 mole% cation(II) oxide and 66,7 mole% P_2O_5 . The ratio between Q^3 (=3-corner connected $\{\text{PO}_4\}$ tetrahedra) and Q^2 (=2-corner connected tetrahedra) is exactly 1:1. The sequence of the different tetrahedra is always $-Q^2-Q^3-Q^3-Q^2-$. This means, that in all cases two Q^3 $\{\text{PO}_4\}$ tetrahedra, respectively, connect one under the other. *This Q^3 - Q^3 connection is typically for all ultraphosphates with 1:2 stoichiometry.* At this base it is theoretically possible to create numerous structures, different in the number and the way of connections.

We found *selection principles*. The number of the connectable corners of the smallest structure unit equals the number of these bonds. That means, that the characteristic structure group of $\{2xQ^2 + 2xQ^3\}$ connects 10 bonds. As we know further, these structure units are arranged in rings of different numbers of ring members. Only some of them are stable. The minimum arrangement contains 20 bonds and consequently 2 types of rings, which members complete to 20, e.g. [10+10], [12+8], [14+6] and [16+4]. Examples for all types are given in figs. 1-4. Rings with more than 16 members and rings with less than 4 members normally are thermally unstable and consequently not to prepare by a temperature process.

Until now, only two-ring structure connections were found. Thinkable also are three- or more-ring structure units in ultraphosphates. But the discovered structures show the preferred formation of "simple" connection principles with two different ring members.

Some ultraphosphates have more than one crystalline phase. MnP_4O_{11} has [16+4] and [12+8] connections, but NiP_4O_{11} and MgP_4O_{11} have [16+4] and [14+6]. It seems to depend on the cation radius, which of the structures are preferred and which of the phase transition will be obtained.

COMPARISON TO STRUCTURE PRINCIPLES OF OTHER INORGANIC GLASS-FORMING SYSTEMS

A comparison to other types of polymer glass-forming systems shows: *Borates* have molecular structures, normally. Moreover, boron can form $\{BO_3\}$ groups as well as $\{BO_4\}$ tetrahedra. These different polyhedra connect by corners one under the other, also in the case of lower degree of connection¹⁶. *Silicates* form polymer or ring structures like phosphates. The main difference is the way of the 3- and 2-corner connection: Q^3 silicates have infinite layer structures. Increasing the Q^2 content, the infinite layers transform to broad ribbons, depending on Q^2 content. Pure Q^2 $\{SiO_4\}$ structures are single ∞ chains or rings. Never infinite layers of $Q^2\{SiO_4\}$ and $Q^3\{SiO_4\}$ tetrahedra connected one under the other, were found^{17,18}.

FIGURE 1.

[10+10]ultraphosphate $\text{Cu}_2\text{P}_8\text{O}_{22}$

FIGURE 2.

[12+8]ultraphosphate $\text{MnP}_4\text{O}_{11}$

FIGURE 3.

[14+6]ultraphosphate $\text{NiP}_4\text{O}_{11}$

FIGURE 4.

[16+4]ultraphosphate $\text{ZnP}_4\text{O}_{11}$

Ultraphosphates are a new group of crystalline substances with very new structural principles, quite different from the silicates and the borates.

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