STRUCTURE INVESTIGATIONS OF BINARY PHOSPHATE GLASSES

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Abstract Structure investigations were performed on several glass series of $x\text{MeO} \cdot (1-x)\text{P}_2\text{O}_5$ with Me = Mg, Ca, Zn and x ranging from 0 to 0,5 using modern structure sensitive methods, like ^{31}P MAS NMR, IR spectroscopy, x-ray scattering. As reference sample new well defined polymer crystalline ultraphosphates were used. The results are presented on example of the glass system $\text{ZnO-P}_2\text{O}_5$.

INTRODUCTION

While the structure of silica glasses is well known for phosphate glasses doesn't exist a sufficient structural model. The structure concepts of these glasses predominantly base on the theory of van Wazer.¹ It describes a monotonous change of glass structure and properties in dependence on composition as a result of a continuous distribution of structure units in glass. However, discontinuous changes of composition-property-relations which were found in phosphate glasses can't be explained by this model. The main part of investigations confines to glasses containing higher amounts of network modifier than phosphorus pentoxid. About the concentration range between 0 and 50 mol % network modifier oxide, the so called ultraphosphate range, there are only few publications. The reasons are probably the evaporation of phosphorus pentoxide during melting and difficult handling because of the hygroscopic behaviour of this and the glasses.

The aim of our investigations was to study the structure of ultraphosphate glasses by combination of independent, structure-sensitive methods, like ^{31}P - NMR, IR-spectroscopy and X-ray diffraction. A comparison of new well defined crystalline ultraphosphates with their corresponding glasses should give information about

structural similarities and differences.

The investigations were performed on several glass series of $x \text{ MeO} \cdot (1-x) \text{ P}_2\text{O}_5$ with $\text{Me} = \text{Mg}, \text{Ca}$ and Zn and x ranging from 0 to 0,5. All glasses were prepared using "water-poor" technique of sealed, evacuated SiO_2 glass tubes.²

RESULTS AND DISCUSSION

The structure units of phosphate network can be classified by the Q^n terminology, where n is the number of bridging oxygens in a PO_4 group. As metal oxide (MeO) is added to phosphorus pentoxide (P_2O_5), the phosphate structural groups convert from Q^3 to Q^2 then to Q^1 and finally to Q^0 . According to van Wazer, the structure of P_2O_5 glass is solely formed by Q^3 groups. Ultraphosphates consist of statistically distributed Q^3 and Q^2 groups. Metaphosphate is formed by Q^2 .¹

^{31}P -NMR spectroscopy gives information about the kinds of the PO_4 tetrahedra in crystalline materials and glasses. In the $\text{ZnO-P}_2\text{O}_5$ system, the number of Q^3 groups

FIGURE 1. Change of the amount of Q^3 and Q^2 groups with increasing ZnO content

continuously decreases with increasing ZnO content, whereas the number of Q^2 groups increases (fig.1). Other Q^n groups don't occur in the region between P_2O_5 and $\text{Zn}(\text{PO}_3)_2$ composition. These results confirm the theory of van Wazer.

For glass structure, not only the knowledge of kind and number of characteristic polyhedra are

important but also its interconnection. By help of X-ray scattering, it was possible to determine atom distances and coordination numbers of the atoms. Furthermore, this method gives information about the intermediate range order of glass by evaluation of the main diffraction peak. The position of maximum and full widths half maximum of this peak reflect the distance between characteristic repetitive arrangements of atoms and their range of periodicity.³

In the $\text{ZnO-P}_2\text{O}_5$ system, the average range of periodicity of these characteristic units is

0,9 nm. The good agreement of the scattering curves of the crystalline compounds of this system with the corresponding glass indicates a similar structure of crystal and glass.⁴

FIGURE 2. The smallest structure unit of $\text{ZnP}_4\text{O}_{11}$

Information about the short and intermediate range order of crystal and glass are also obtained by IR spectroscopy. It was found that the IR spectrum of a crystalline compound in

the range of valence vibrations can be described by a minimal number of stretching vibrations calculated from the crystallographically non-equivalent PO_4 tetrahedra of the crystal structure. These tetrahedra are connected to form the smallest structure unit. The interconnection of these units forms the crystal structure. The smallest structure unit of zinc ultraphosphate $\text{ZnP}_4\text{O}_{11}$ is shown in figure 2.⁵

In the $\text{ZnO-P}_2\text{O}_5$ system, the IR spectra of the investigated glasses correspond with the related crystals. This suggests that the kinds of structure units and their interconnection within a characteristic range is nearly the same.⁶ An example is given in figure 3 for crystalline $\text{ZnP}_4\text{O}_{11}$ and the corresponding glass.

FIGURE 3. IR spectra of crystalline zinc ultraphosphate $\text{ZnP}_4\text{O}_{11}$ and the related glass

The IR spectra of zinc phosphate glasses show typical changes in the region from 0 to 50 mol % ZnO . With the help of factor analysis, 3 spectroscopic components were

found. They are identical with the spectra of P_2O_5 glass (0 mol % ZnO), ZnP_4O_{11} glass (33 mol % ZnO) and metaphosphate glass (50 mol % ZnO). The proportions of the components in the spectra of the glasses were calculated and are given in table 1 together with the theoretical portion calculated from the analyzed ZnO content.⁷ In the range from 0 to 33 mol % the glass structure is formed by the structure elements of P_2O_5 glass and ZnP_4O_{11} glass. Whereas, in the region from 33 to 50 mol% it consists of structure units of ZnP_4O_{11} glass and metaphosphate glass.

TABLE 1 Composition of the glasses investigated ($ZnUP=ZnP_4O_{11}$, $ZnMP=Zn(PO_3)_2$)

ZnO- content [mol%]	theoretical content [mol%]			calculated content [mol%]		
	P_2O_5	ZnUP	ZnMP	P_2O_5	ZnUP	ZnMP
0	100	0	0	100	0	0
4,7	86	14	0	91	9	0
10,4	69	31	0	84	16	0
5,0	55	45	0	69	31	0
19,1	42	57	0	53	47	0
24,6	26	74	0	16	84	0
30,3	9	91	0	10	90	0
32,0	4	96	0	11	89	0
32,4 c	3	97	0	3	97	0
39,4	0	63	37	0	69	31
43,4	0	40	60	0	14	86
50,0	0	0	100	0	0	100

A binary distribution model for the $ZnO-P_2O_5$ system was developed from these results (figure 4). It can also be applied for the other investigated systems $MgO-P_2O_5$ and $CaO-P_2O_5$.

SUMMARY

In summary, the structure of a glass with stoichiometric composition solely contains the structure elements of the related crystalline compound. By contrast, in the

concentration range between two compounds, the glass structure consists of two structure units given by the two limiting compounds. The structural difference between glass and crystal is determined by its order, not by its structure elements.

FIGURE 4. Binary distribution model for the ZnO-P₂O₅ system

ACKNOWLEDGMENT

We thank Dr. P. Losso for ³¹P-NMR-, Dr. K. Meyer for IR- and Dr. G. Walter for the X-ray scattering measurements. For financial support, we kindly thank the Deutsche Forschungsgemeinschaft.

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