SPECTROSCOPIC INVESTIGATIONS OF ULTRAPHOSPHATE GLASSES IN THE SYSTEM CuO-P₂O₅

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Abstract Ultraphosphate glasses in the system CuO-P₂O₅ were prepared from 0 to 18 mol% CuO (synthesis) starting from powdery P₄O₁₀ (p.a. Merck) and fresh prepared Cu₂P₄O₁₂ in closed SiO₂ glass ampoules between 1000° and 1100°C for about 2 hours. After cooling with about 10 K min⁻¹, the ampoules were stored under paraffin oil in a desiccator and handled with exclusion of „water“. Measurements of density, chemical composition, optical and infrared spectroscopy followed. The optical spectra only show Cu²⁺, but in different positions, depending on CuO content. Cu⁺ was not found, although the glasses were melted without air contact. The different places of the copper ions in the glass structure are connected with the structure change: With increasing content of copper more Q² linked {PO₄} tetrahedra were built. This finding strongly agrees with the infrared spectra, which show an increase of Q² {PO₄} tetrahedra with increasing CuO content. The structure evolution seems to follow a binary distribution model: the (P₂O₅)ₙ specific substructure units decrease, where the CuP₂O₁₁ specific substructure units increase while the CuO content increases.

INTRODUCTION

Binary ultraphosphate glasses with elements, which are able to exist in more than one oxidation state, are of essential interest for structure investigations. This possibility opens new aspects: additional techniques can be applied, which are sensitive to electron transfers of different sources in different environments. Former structure investigations of binary ultraphosphate glasses (systems with alkali-earth oxides) used density measurements, vibrational spectroscopy, diffraction methods (X-ray: SAXS, WAXS, neutrons) and NMR [1,2,3]. In our CuO-P₂O₅ system, the optical spectroscopy can be applied additionally. In the ultraphosphate glass systems, above all with very low cation content, the cations have high distances to each of them and should not have interactions- they should occur isolated in the {PO₄}tetrahedra framework structure. This is the difference to metaphosphate glasses and systems with high cation content.
EXPERIMENTAL

As raw materials we used p.a. quality P₄O₁₀ powder and fresh prepared Cu₂P₄O₁₂. For this purpose, CuO (p.a.) and H₃PO₄ (85%, p.a.) were mixed and temperature treated at several temperature steps and times until 400°C and 24 hours. This powder was characterized by X-ray diffraction as Cu₂P₄O₁₂ completely. Together with the P₄O₁₀ both components (about 30 g together) were introduced into a SiO₂ glass ampoule of about 10 cm³ volume. After closing, the batch components were mixed intensively and melted in an electric heated oven between 1000° and 1100°C for about 2 hours, depending on CuO content. After cooling down with about 10 K min⁻¹, the glasses showed different colours, from light-blue over deep sky-blue to light and emerald green. The glass volume after melting was about one quarter to one third of the whole and mostly completely destroyed by cracks because of the different expansion coefficients between phosphate and quartz glass. In the „free“ part, condensed „P₂O₅“ was found. So, it was necessary to make chemical analyses of all glasses: Copper was determined by HPLC, and P₂O₅ with extinction method using phosphomolybdate-vanadate heteropolyacids. In the case of very low cation contents, some „H₂O“ content was found by infrared spectroscopic measurements, but not by chemical analysis, so we can assume, that this is inside the limits of the conventional chemical analysis.

Very low contents of „water“ can not be excluded, though all glass ampoules were stored shortly after cooling process in a desiccator in paraffin oil over P₂O₅.

Density measurements were done by Archimedes' method and with different pieces of the glasses. Since some small bubbles and also cracks lead to lower density values, we took the highest value in every case.

For the spectroscopic measurements, the ampoules together with the (cracked) glass had to be imbedded in a special acrylate resin and cut, grinded and polished after hardening. Otherwise, no planparallel optical polished plates could be received. This way, sometimes only very small samples resulted. The samples now were stored in hexane in the desiccator before measurements.

Optical spectroscopy was carried out by a diode-array spectrometer for very small samples in the range of 9.000 to 45.000 cm⁻¹ (about 220 to 1.100 nm), where the region between 9.000 and 17.500 cm⁻¹ was characteristic for the copper spectra. After measurements, the spectra were fitted by a peak-fit program with the computer.

Infrared spectra were measured with the BRUKER FT-IR spectrometer in the range of...
4.000 to 500 cm⁻¹, which is characteristic for the phosphates, as described in former works [2,4]. These spectra were transformed into absorbance spectra by the Kramers-Kronig procedure. The spectrum of a 33.3 mol% CuO glass composition was used to compare the spectra with the „limit“ composition „CuP₄O₁₁“ , which characterizes one of the possible substructures [5].

RESULTS AND DISCUSSION

The density measurements show an increase of density with increasing CuO content of the glasses in the region between 0 and 21.5 mol% CuO (analysis). The densities of the copper ultraphosphate glasses increase from about 2.4 to 2.6 g cm⁻³ in the investigated concentration region. This means, that the copper ions fill the spaces in the ultraphosphate framework continously, where the {PO₄} connections were lowered. The framework degradation takes place via the formation of Q² groups from Q³ groups and formation of non-bridging oxygen. In the investigated region, the density increase until 12 mol% CuO seems to be little bit stronger than after, since the network connection at low cation contents is faster than at higher contents, where the increasing number of non-bridging oxygens lead to a more loose structure.

The vibrational spectra of the „xeric“ glasses from 3 to 33 mol% CuO show 3 main complexes of bands, in accordance with [2,6]:

Complex 1 from about 1600 to 1200 cm⁻¹: It characterizes the valence vibrations of oxygens (bridging and non-bridging) against the single {PO₄} tetrahedron, which can be Q³ or Q² connected. This region is most specific for the difference of Q² and Q³ connection. The higher the energy, the higher connected are the tetrahedra. Pure P₂O₅ glass shows the highest energies with about 1450 cm⁻¹. We have no (resp. nearly no) Q² connections, except if OH groups are included in the network. When these glasses contain any „water“, the band becomes different and modifies its shape: it transforms to a band, characteristic for any content of „normal“ cations [7]. In the copper containing glasses, we find as Q³ as Q² tetrahedra in a relation, compared to the CuO content. The band maximum shifts to less than 1400 cm⁻¹, where a shoulder at lower energies occurs. At 33 mol% copper, this former shoulder is the most intense band in this system and the former band maximum decreases. At this composition, the ratio between Q³ and Q² is 1:1, like in the crystalline CuP₃O₁₂ [8]. In the whole investigated composition region, no unusual characteristics were found.

Complex 2 from about 1200 to 850 cm⁻¹: It characterizes the asymmetric valence
vibrations of different \{PO}_4\]tetrahedra against others. This region is specific for interconnections within the framework and not understood in all details. The maximum value is found in (P_2O_5) glass with the highest energy. In the 33 mol\% CuO glass, the intensity is the smallest one, but the energy of the vibration undergoes a minimum at about 12 mol\% CuO. This fact is in accordance with the findings of density behaviour.

Complex 3 from about 850 to 600 cm\(^{-1}\): It includes the symmetric valence vibrations of the \{PO}_4\]tetrahedra in the framework. Because of the relatively low intensities and its complexity, this region is not interpreted at all.

The measured spectra of the copper ultraphosphate glasses are similar to the spectra of the alkali-earth ultraphosphate systems and recommend a binary distribution of substructure units. The exact interpretation needs a band analysis, which has to be done in future works.

The optical spectra, in the region from about 9.000 to 17.000 cm\(^{-1}\) show the characteristic absorption for Cu\(^{2+}\) with a coordination number of 6 [9,10]. The glasses with less than about 11 mol\% CuO consist of 2 bands. Above this concentration, 2 further bands occur. The existence of 2 bands is result of the Jahn-Teller distortion of the ligands' field. The appearance of the double number of bands gives reason for two different positions of the Cu\(^{2+}\) ions with coordination number 6 in the framework: with less than 10...12 mol\% CuO nearly no Q\(^2\) groups exist. They are connected exclusively with Q\(^3\) groups. When the concentration of non-bridging oxygen increases with increasing CuO content, the Cu\(^{2+}\) ions prefer positions together with Q\(^2\) \{PO}_4\] tetrahedra, as known in the crystalline Cu_2P_8O_22 because of better realization of their coordination environment.

REFERENCES
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