COPPER-METAPHOSPHATE GLASSES MODIFIED BY ZINC OR CALCIUM

Brázdová S.

Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice

The aim of this work was to investigate the influence of zinc and calcium ions on the structure of the phosphate glasses and their selected physico-chemical properties. Ten glasses from each of the $xZnO\text{-}(50\text{-}x)CuO\text{-}50P_2O_5$ and $xCaO\text{-}(50\text{-}x)CuO\text{-}50P_2O_5$ glass series were prepared. The amorphous character was confirmed by XRD and the chemical composition was verified by μ-XRF.

The Raman spectroscopy confirmed the presence of exclusively metaphosphate structural units (Q^2). The results also showed that zinc and calcium ions behave differently in phosphate glasses. Zinc ions interact only with non-bridging oxygens, which leads to an increase in vibration energy, therefore higher strength of the Zn-O bond than Cu-O. Calcium ions interact with non-bridging and bridging oxygen, leading to lower strength of the Ca-O bond. The coordination number of copper and zinc was found to be 4, while the coordination number of calcium was 6.

The NMR spectroscopy confirmed that all glasses are formed by metaphosphate units. At the same time, the presence of two types of structural units Q^2 was proved. The units referred to as Q^{21} are more ordered and their concentration increases with the increasing amount of zinc, resp. calcium ions in the glass. This phase separation is caused by copper.

The density of the glasses decreases in $xZnO\text{-}(50\text{-}x)CuO\text{-}50P_2O_5$ line. It causes zinc tetrahedral structures, which occupy a larger volume than copper square structures. In $yCaO\text{-}(50\text{-}y)CuO\text{-}50P_2O_5$ line, the decrease is influenced by the lower relative molecular weight of Ca3(PO3)2, higher coordination number and large octahedral structures.

The glass transformation temperature and coefficient of thermal expansion were studied by TMA. Copper and zinc metaphosphates have almost identical glass transformation temperature, in contrast to glass transformation temperature of calcium metaphosphate, higher by more than 70°C. The phase separation is reflected in nonlinear course of glass transformation temperature.