CHEMISTRY LETTERS, pp. 1711-1714, 1987.

Improvement of Mechanical Properties of Metaphosphate Glass by Addition of Chromium Oxide

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The mixed alkaline earth metaphosphate glasses containing various amounts of Cr_2O_3 were prepared, and their mechanical properties were measured. With the addition of Cr_2O_3, Young's modulus was improved from 60 to 120 GPa, Vickers hardness from 4 to 8 GPa, and toughness from 0.6 to 1.1 MPa $m^{1/2}$. This improvement was attributed to the change of glass structure from the linear chain and/or ring structure of metaphosphate glass to the three dimensional structure.

Although phosphate glasses are being used widely for various industrial applications because of their good characteristics, such as low melting,[1)] high thermal expansion,[2)] high optical transmission[3)] and large glass-forming ability,[4)] phosphate glasses generally have poor chemical durability[5,6)] and weak mechanical properties[7)] when they are compared with silicate glasses. In glass science, however, it is well-known that a physical property of glass can be improved by introducing another kind of cations to the glass composition.

In the previous paper,[8)] it was reported that the chemical durability of metaphosphate glass was improved greatly by adding a large amount of chromium oxide. In the present paper, the effect of the addition of chromium oxide to metaphosphate glass on the mechanical properties is reported. As will be described later, the Young's modulus of over 120 GPa has been achieved in a metaphosphate glass containing the mixture of three kinds of alkaline earth oxides and 30 mol% chromium oxide. This value has been rarely achieved by oxide glasses.

The starting materials for making glass were the reagent grade $Mg(H_2PO_4)_2$, $Ca(H_2PO_4)_2$, $Ba(PO_3)_2$, and Cr_2O_3. They were mixed so as to yield the compositions shown in Fig.1 and melted in a Pt-Rh crucible placed in an electric furnace at

1400-1500 °C for 1 h. The melt was cast into a steel mold. After annealed for 30 min at 500-700 °C depending on glass composition, a cube with the edge length of 3-5 mm was cut from the glass block for measuring the sound wave velocities by means of the cubic resonance method reported previously.[9] The Young's modulus, bulk modulus, shear modulus and Poisson's ratio were calculated from the density and the sound wave velocities. The density were determined by using the Archimedes method.

The hatched area in Fig.1 presents the glass-forming region. The maximum amount of Cr_2O_3 dissolved in the system of metaphosphate glass was found to be about 30 mol% at the ratio MgO/(CaO + BaO)= 1. Clearly the glass-forming region was enlarged by mixing different kinds of alkaline earth ions.

The variation of Young's modulus is shown in Fig.2 as a function of the amount of chromium oxide added to the $2MgO{\cdot}CaO{\cdot}BaO{\cdot}4P_2O_5$ glass. The Young's modulus increased almost linearly with increasing Cr_2O_3 content, and attained to the highest value of about 120 GPa. This value is nearly equal to the value of 121 GPa

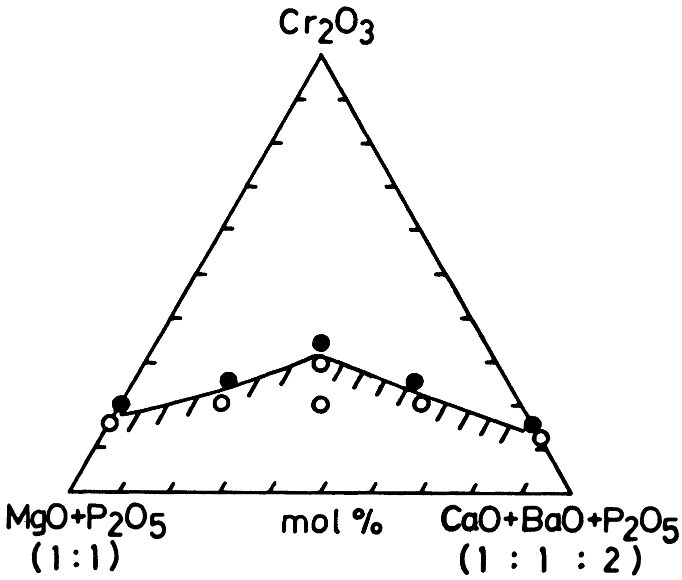

Fig.1. Glass-forming region in the Cr_2O_3-MgO-CaO-BaO-P_2O_5 system : ○ = glass, ● = crystal.

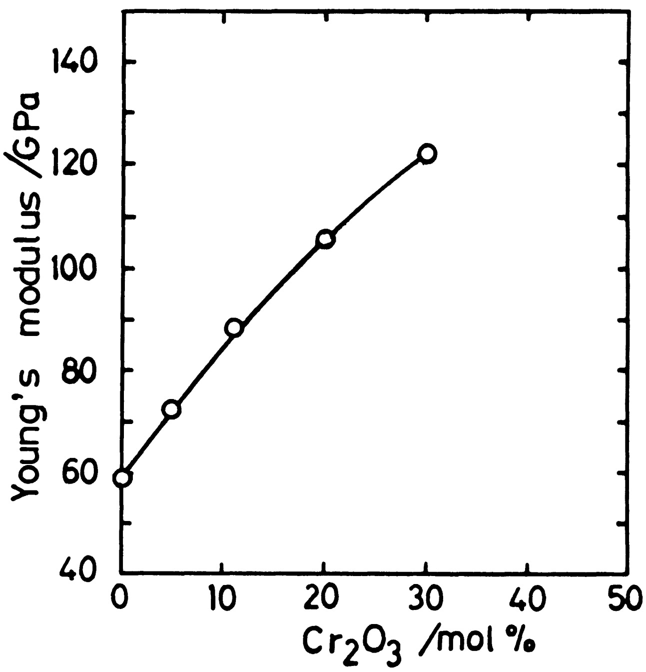

Fig.2. The variation of Young's modulus as a function of chromium oxides added to the $2MgO{\cdot}CaO{\cdot}BaO{\cdot}4P_2O_5$ glass.

Table 1. Elastic properties of the glasses in the Cr_2O_3-MgO-CaO-BaO-P_2O_5 system

Glass composition/mol%					Density	Modulus /GPa			Poisson's
Cr_2O_3	MgO	CaO	BaO	P_2O_5	$g \cdot cm^{-3}$	Young's	Bulk	Shear	ratio
0	25.0	12.5	12.5	50.0	2.862	59.0	40.6	23.5	0.258
5	23.8	11.9	11.9	47.4	3.005	72.4	47.8	29.0	0.248
10	22.5	11.2	11.2	45.1	3.185	88.3	57.0	35.6	0.242
20	20.0	10.0	10.0	40.0	3.393	105.7	73.5	41.9	0.260
30	17.5	8.7	8.7	35.1	3.535	122.0	83.8	48.5	0.257

reported by Makishima et al.[10] for a glass in the Y_2O_3-TiO_2-Al_2O_3-SiO_2 system, the highest among those of silicate glasses.

Other elastic moduli and Poisson's ratio are listed in Table 1 for the glasses having the ratio MgO/(CaO + BaO)= 1.

The structure of alkaline earth metaphosphate glasses is considered as follows:[11] PO_4 tetrahedra are bonded to adjacent tetrahedra by bridging oxygen atoms, forming chains. Neighbouring polyphosphate chains are then linked together by cross bonding between the metal cations and two non-bridging oxygen atoms of each PO_4 tetrahedron. The P-O-P bond between PO_4 tetrahedra is generally much stronger than the cross bond between chains via the

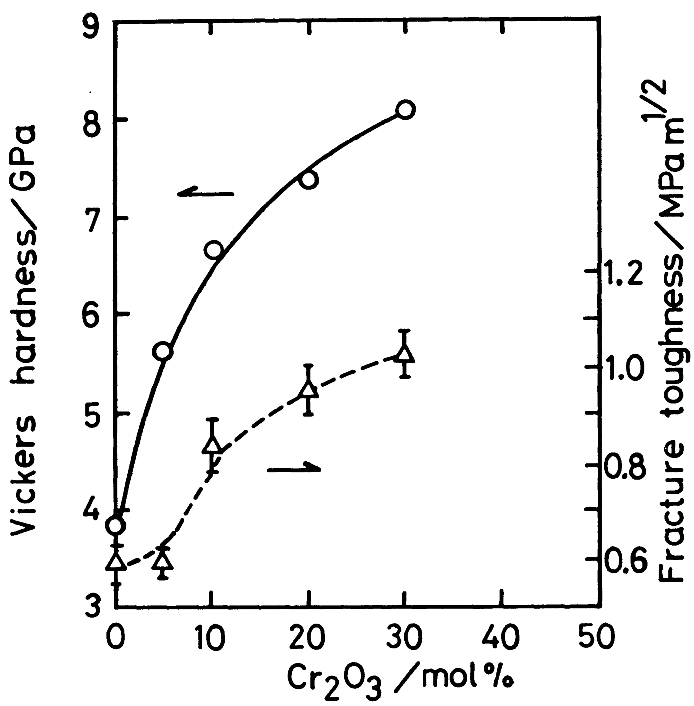

Fig.3. The variations of Vickers hardness and fracture toughness as a function of chromium oxides added to the $2MgO \cdot CaO \cdot BaO \cdot 4P_2O_5$ glass.

metal cation.[11] Trivalent cations (M^{3+}) added to glass structure occupy the sites between the polyphosphate chains, strengthening the cross bonding between the chains. The high field strength of M^{3+} also affect the highly polarized P=O bonds in PO_4 tetrahedra, and may form MPO_4 structural units as proposed for BPO_4 or $AlPO_4$. With high chromium concentrations, the average length of the polyphosphate chain is reduced and this tightening or compaction of glass structure brings in the increase in density and elastic moduli.

Such a tightening of glass structure should give considerable effects on hardness and toughness. The hardness of glass was measured on the same glasses used for the sound wave velocity measurement by using a Vickers hardness tester with 100 g load for 15 s. The fracture toughness was obtained by the indentation fracture method[12] with 1 kg load for 15 s. The results are plotted in Fig.3, which shows an increase in both hardness and toughness with increasing Cr_2O_3 content, as expected. The variation of hardness with Cr_2O_3 content was approximately similar to that of elastic moduli.

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(Received May 28, 1987)