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Young's modulus, Vickers hardness and indentation fracture toughness of alumino silicate glasses

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Abstract

A wide range of alumino silicate glasses with different network modifier ions (Li, Mg, Na, Ca, Zn, La, Ba, Sr, and Pb) was prepared. The glasses were studied with respect to their mechanical properties: Poisson's ratio, Young's modulus, Vickers hardness and indentation fracture toughness. These properties were mostly affected by the field strength of network modifier ions. All determined properties increase with increasing field strength of the network modifier ions. The mixed modifier alumino silicate glasses with zinc and magnesium show a positive deviation from linearity with two maxima. Lanthanum containing glasses show larger values of mechanical properties for higher lanthanum concentrations. For magnesium alumino silicate glasses the mechanical properties get smaller with increasing SiO_2 concentration; an effect of the magnesium concentration is not observed. Furthermore, if up to 9 mol% MgO is replaced by MgF_2 the mechanical properties are not significantly affected. Compared to models predicting Young's moduli of all studied glass compositions, significant deviations are found.

Keywords: C. Mechanical properties; C. Hardness; D. Glass

1. Introduction

The mechanical properties of alumino silicate glasses are of great importance due to their numerous industrial applications, e.g. as chemically strengthened cover glasses in personal electronic devices [1], as glass for glass fiber reinforced composite materials [2], as scaffolds for bone repair [3] and for modern design purposes [4]. Recently, they have also been proposed as bulk laser materials [5,6] for high power applications. So in recent years, many models have been developed to theoretically describe the relationship between the properties and the composition of these glasses. There are commonly accepted calculation models for hardness [7] and elastic modulus [8,9], but as shown in this article, values calculated using these models differ considerably from the measured values.

Studies on the glass structure of alumino silicates with magic-angle spinning nuclear magnectic resonance (MAS-NMR) techniques [10] and molecular dynamic simulations (MD) [11,12] show that the aluminum is mostly incorporated into the glass network as $[AlO_4]^-$ tetrahedra which act as network forming species. The negative charge of $[AlO_4]^-$ tetrahedra is compensated by positively charged cations. As the formation of Al–O–Al linkages is energetically less favorable than Si–O–Al linkages, these Al–O–Al linkages scarcely occur [13] (Al/Al avoidance principle). The principle is put into perspective by investigations on Si/Al ratios much smaller than unity [14]. In peralkaline or metaluminous compositions, the ratio of aluminum to network modifier is smaller than 1. For these glasses it is assumed that *all* aluminum units form tetrahedra with 4/2 bridging-oxygen. The remaining concentrations of network modifier ions form non-bridging-oxygen sites by splitting up the Si–O–Si bridges. Hence, the average number of bridging-oxygen per network forming $[SiO_4]$ and $[AlO_4]^-$ tetrahedron BO/T can directly be calculated from the chemical composition and is a simple measurement of the connectivity and rigidity of the glasses.

Crack resistance of glass is an important mechanical property. Cook and Pharr [15] stated a lack of generality in indentation-cracking behavior due to the complexity and diversity of the indentation cracking patterns. They showed that shape and

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Table 1
Chemical compositions of the studied samples, the hereof calculated values of the mean number of bridging oxygen per network forming unit, and Poisson's ratio, ν, Young's-moduli, E, Vickers hardness, H_v, and indentation fracture toughness, K_c.

Sample	Composition (mol%)			BO/T	ν	E (GPa)	H_v (GPa)	K_c (MPa m$^{1/2}$)
	M_xO_y MF_z	Al_2O_3	SiO_2		±0.02	±3	±0.2	±0.05
Pb	20 PbO	20	60	4	0.249	77	5.58	0.59
Zn	20 ZnO	20	60	4	0.256	97	6.85	1.18
Ca	20 CaO	20	60	4	0.257	100	6.79	0.94
Li	20 Li_2O	20	60	4	0.227	83	6.18	1.01
Na	20 Na_2O	20	60	4	0.200	72	5.96	0.57
La	9 La_2O_3	21	70	3.89	0.254	103	6.95	0.97
BaMg	10 BaO; 10 MgO	20	60	4	0.250	88	6.67	0.85
CaMg	10 CaO; 10 MgO	20	60	4	0.260	95	7.02	0.97
SrMg	10 SrO; 10 MgO	20	60	4	0.251	93	6.79	0.92
ZnMg	10 ZnO; 10 MgO	20	60	4	0.249	99	7.00	1.07
Mg	20 MgO	20	60	4	0.255	102	7.15	1.16
Mg30	30 MgO	10	60	3.5	0.254	96	7.48	0.95
Mg45	45 MgO	5	50	2.67	0.281	104	7.35	0.92
Mg37	37 MgO	13	50	3.37	0.268	107	7.85	0.99
Mg15	15 MgO	14	71	3.98	0.241	91	7.34	1.08
Mg20OH	20 MgO	20	60	4	0.253	101	7.27	1.06
La20	20 La_2O_3	20	60	3.2	0.285	102	7.22	0.74
La15	15 La_2O_3	15	70	3.4	0.266	94	7.12	0.75
La16	16 La_2O_3	24	60	3.56	0.278	115	7.18	0.82
La25	25 La_2O_3	25	50	3	0.300	110	7.64	0.74
La12	12 La_2O_3	28	60	3.86	0.283	94	7.32	0.76
Zn03Mg17	3 ZnO; 17 MgO	20	60	4	0.260	102	7.42	1.75
Zn05Mg15	5 ZnO; 15 MgO	20	60	4	0.260	102	7.33	1.44
Zn15Mg05	15 ZnO; 5 MgO	20	60	4	0.260	100	7.13	1.46
Mg-F1.5	18.5 MgO; 1.5 MgF_2	20	60	4	0.258	96	7.08	1.07
Mg-F3	17 MgO; 3 MgF_2	20	60	4	0.258	103	7.17	1.09
Mg-F9	11 MgO; 9 MgF_2	20	60	4	0.247	98	7.08	1.10

sequence of a crack were strongly affected by the material parameter Young's modulus divided by hardness E/H. According to Yamane and Mackenzie [16], the resistance of a glass to deformation during indentation is a result of three distinct processes: plastic (shear) flow, densification and elastic deformation. With detailed investigations [16–19] of the densification vs. shear contribution of the indentation a better understanding of the deformation mechanism was reached. According to Kato [20] a clear correlation between the crack resistance and Vickers hardness, fracture toughness or "brittleness" cannot be found. But glasses with a larger densification around the indentation show higher crack resistance. Rouxel et al. [21,22] ascertained that the resistance of glasses toward corner cracks is related to Poisson's ratio ν. The authors distinguish between resilient glasses ($0.15 < \nu < 0.20$), semi-resilient glasses ($0.20 < \nu < 0.25$), easily damaged glasses ($0.25 < \nu < 0.33$) and highly resilient glasses ($0.33 < \nu$). Investigations on the compositional dependence of mechanical properties show deviations from linearity within mixed modifier oxide glasses. Both positive [4,23–25] and negative [4,22,26–28] deviations were found.

In this article, a simple correlation between field strength of the network modifier ions and the (measured) values for Young's modulus, Vickers hardness and indentation fracture toughness is demonstrated. For this a large variety of alumino silicate glasses with different network modifier ions has been studied. Furthermore, the influence of network modifier concentration, the addition of fluorine and the effect of mixed modifiers oxides were studied.

2. Experimental procedures

The glasses were prepared from reagent grade raw materials. The raw materials used were SiO_2 (Sipur A1, Bremthaler Quarzitwerk, Germany), Al_2O_3 (Pengda Munich, Germany), MgO (Merck, Germany), ZnO (Heubach, Germany), Li_2CO_3 (Sigma-Aldrich, USA), $La_2O_3 \cdot H_2O$ (Laborchemie Apolda, Germany), $BaCO_3$ (Reachim, USSR), $CaCO_3$ (Merck, Germany), $SrCO_3$ (Ferak, Germany), $PbCO_3$ (Merck, Germany), Na_2CO_3 (Merck, Germany), and MgF_2 (Chemiewerk Nünchritz, Germany). For the preparation of all the samples magnesium oxide and aluminum oxide were used except for the sample Mg20/OH which was prepared from magnesium carbonate hydroxide and aluminum hydroxide. The chemical compositions of the glasses calculated from the batch composition are summarized in Table 1. For alkali and alkaline earth alumino silicate glasses, the molar composition is 20 mol% network modifier oxide, 20 mol% Al_2O_3 and 60 mol% SiO_2. For the lanthanum, magnesium and zinc magnesium containing glasses, other chemical compositions have also been prepared.