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Dependence of Hardness of Silicate Glasses on Composition and Thermal History

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Introduction
From an industrial point of view, it is desirable if the hardness of a glass can be predicted from its composition and manufacturing conditions.

Hardness of crystals may be calculated using a semi-empirical approach. So far, this is not possible for glasses. The aim of this study is to discuss the factors that should be taken into account in the calculation of hardness of glass.

Effect of thermal history: E-glass (aluminoborosilicate) is annealed at \( T_g \) for different durations \( T_g \rightarrow T_f \) and Vickers hardness \( (H_v) \) measured.

Effect of chemical composition
Polymerisation effect: \( \text{SiO}_2-\text{Al}_2\text{O}_3-\text{Na}_2\text{O} \) of different \( \text{Na}_2\text{O} \)-content \( \rightarrow H_v \) measured.

Modifying ion effect: \( 68\text{SiO}_2-1\text{Fe}_2\text{O}_3-8\text{A}_2\text{O}-23\text{RO} \) (A = alkali, R = alkaline earth) \( \rightarrow H_v \) measured.

Thermal History
To study the annealing effect of the E-glass on the fictive temperature \( T_f \), the heat capacity \( (C_p) \) –temperature curves are measured on the glasses annealed for various durations \( (t_a) \) at \( T_g \). \( T_f \) is determined by Moynihan’s enthalpy-matching approach.

\( H_v \) increases with duration of annealing, whereas it decreases with increasing \( T_f \). Trend is confirmed by nanoindentation on E-glass fibres \( (T_f=1166 \text{ K}) \) [Lonnroth et al., JNCS 354, 3887 (2009)].

Chemical Composition
The four \( \text{SiO}_2-\text{Al}_2\text{O}_3-\text{Na}_2\text{O} \) glasses contain different amounts of \( \text{Na}_2\text{O} \). The \( \text{Na}_2\text{O} \) excess is calculated as the amount of \( \text{Na}_2\text{O} \) that does not participate in \( \text{AlO}_4 \)-charge balancing. \( H_v \) decreases with the excess amount of \( \text{Na}_2\text{O} \), i.e., the network depolymerization degree.

Conclusions
1) Annealing lowers \( T_f \) and thereby increases the structural density of glasses. This leads to an increase of hardness.
2) For alkali ions, hardness increases with increasing ionic radius, whereas the opposite trend is observed for alkaline earth ions.
3) The structural changes of the network occurring at the atomic scale must be taken into consideration when predicting the effect of chemical composition on hardness.

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