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Density and Refractive Index Hysteresis in Compressed Silicate Glasses

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The increased refractive index of diopside and albite glass, quenched from liquidus temperatures at pressures to 50 kb, can be accurately calculated from compressibility data on the crystals at 25°C and the Lorentz-Lorenz refraction law. The results indicate that the pressure effect is locked in by 'configurational trapping' on cooling through the glass point, but thermal relaxation takes place with the thermal expansion coefficient characteristic of the applied pressure. The resulting permanent compression is therefore that predicted at 25°C and load pressure. Permanent compression of glasses at temperatures below the glass point should be that predicted at load pressure and (1) 25°C, if temperature is released before pressure, or (2) run temperature, if pressure is released before temperature, because thermal relaxation then takes place with the low-pressure thermal expansion coefficient. For SiO_2 the glass compressibility is known as a function of temperature, and the overlap field parameter ($\beta = 1.37$) can be established from other data. Refractive indices of SiO_2 glass compressed at various P and T with varying quenching cycles are consistent with the values calculated for permanent compression when $T > \sim 500$°C. At lower temperatures the compression is partly elastic and the resultant indices are thus lower than expected. In all these glasses, configurational trapping of pressure deformation is adequate to explain the permanent compression. The direct relationship of permanent compression with compressibility shows that the model of H. M. Cohen and R. Roy (1961, 1965), based on second-order structural changes at high P followed by elastic decompression, is not necessary to explain any of the existing data.

INTRODUCTION

Bridgman and Simon [1953] discovered that glasses display imperfect volume elasticity at large hydrostatic pressures and suffer permanent changes in density proportional, within limits, to the applied pressure. Because crystalline inorganic solids exhibit perfect elasticity, this effect was quite unexpected, and Bridgman and Simon established several important characteristics of the behavior of compressed glasses: (1) SiO_2 glass at room temperature has an elastic limit that must be exceeded before permanent deformation occurs; (2) both the elastic limit and the permanent compressibility decrease progressively when ions such as sodium are added to SiO_2; (3) the permanent compressibility of SiO_2 is greater at higher temperature; and (4) the density increase is achieved by folding up the vitreous network of the glass so that the Si-O bond angles are altered although the nearest neighbor Si-O distances appear to remain unchanged. The folded structures are mechanically stable at room temperature, but the original density can be restored by annealing at high temperatures. The annealing effect is similar, though opposite in sign, to the increase of density observed in annealing rapidly chilled glasses at ordinary pressure. Bridgman and Simon therefore suggested that there exists an equilibrium configuration for a glass at any temperature and that both high- and low-density metastable states, characterized by the trapping of displaced atoms behind relatively strong potential barriers, can exist.

Cohen and Roy [1961] showed that the permanent densification of SiO_2 and other glasses is accompanied by an increased refractive index, which they found to be continuously proportional to pressure at temperatures greater than 500°C. At room temperature they found a threshold pressure of about 20 kb for SiO_2 glass,

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