INTERMEDIATE GLASSES PREPARED BY MODIFICATION OF SILICA GLASS: HIGH PRESSURE TREATMENT AND FLUORINE ADDITION

By

Chia-Ying Li

A Thesis Submitted to the Graduate
Faculty of Rensselaer Polytechnic Institute
in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY
Major Subject: MATERIALS SCIENCE AND ENGINEERING

Approved by the
Examining Committee:

____
Minoru Tomozawa, Ph.D.
Thesis Advisor

____
Liping Huang, Ph.D., Member

____
Robert Hull, Ph.D., Member

____
E. Bruce Watson, Ph.D., Member

Rensselaer Polytechnic Institute
Troy, New York

November 2012
(For Graduation December 2012)

ABSTRACT

Glasses that are considered normal, such as soda-lime glass, acquire lower density when cooled at a faster rate. In contrast, anomalous glasses, such as pure silica glass, show the opposite behavior with density increasing with cooling rate. Between these two types of glasses, there are intermediate glasses, which exhibit cooling rate-independent properties such as density. Intermediate glass is expected to have unique properties and advantages over other glasses, such as absence of compaction, volume reduction experienced when a glass, e.g. a flat screen glass, is heat-treated near the glass transition temperature, reduction of residual stresses on cooling, enhanced crack initiation load, and radiation resistance.

Glass properties can be altered by high temperature/high pressure treatments. Therefore, pressurization of glass can offer a new dimension of glass processing. Additionally, doping silica glasses with fluorine or titanium can change the glass properties and serves as an alternate method to prepare glasses with specific properties. These two approaches were used to explore the possibility of making intermediate glasses.

Anomalous silica glasses were found to become intermediate glasses when heat-treated at 1.5 GPa pressure. Similar change appears to occur when 8000 ppmw F is added to silica glasses. The structural characteristics of these intermediate glasses are investigated in the present study.

To characterize some glass properties, a simple IR method using the silica structural band at ~2260 cm^{-1} that had been previously developed was used to determine the fictive temperature of silica and high silica glasses. Fictive temperature is defined as the temperature at which liquid structure froze to turn into a glass. In the present study, a similar technique using the silica structural band at ~2660 cm^{-1} was explored. This IR band is not affected by the presence of impurity hydrogen in silica glass, while the band at 2260 cm^{-1} overlaps with SiH band, which is a reaction product of silica glass and hydrogen. It was also shown that the method used to measure fictive temperature can be extended to determine the fictive pressure, the pressure at which the liquid structure froze to turn into a glass. Using this method, the structural change caused by a high

pressure/high temperature treatment and high temperature treatment can be easily distinguished.

Another aspect of high pressurized silica glasses investigated in this thesis is the depressurization structural relaxation kinetics of silica glass. Pressurized silica glasses are believed to contain high concentration of point defects, which disappear more quickly than the structural relaxation observed during the change of fictive temperatures under one atmospheric pressure. The latter is caused by changes in Si-O-Si bond angles.

Effects of fluorine addition to silica glass on the relation between the fictive temperature and mechanical properties, including elastic moduli, Poisson's ratio and hardness, are established for silica glasses doped with various amounts of fluorine. Equations are presented which allow determination of the mechanical properties as a function of both glass composition and fictive temperature. The combined effects of fictive temperature, dopant concentration, and dopant identity on the mechanical properties and structure of fluorine and titanium doped silica glasses are discussed.

Some of the unique mechanical characteristics observed in intermediate glasses based upon $CaO-Al_2O_3-SiO_2$ glass system, such as the absence of indentation size effect, were not observed in the present systems. Possible causes are discussed: High pressure silica glasses probably exhibit depressurization, in addition to fictive temperature increase, during indentation. F-doped silica glasses exhibit more anomalous mechanical properties than silica glass in spite of the normal glass behavior of density-fictive temperature relation.