



Review paper

Issues associated with the development of transparent oxynitride glasses

Sharafat Ali^{a,*}, Bo Jonson^a, Michael J. Pomeroy^b, Stuart Hampshire^b

^aDepartment of Built Environment and Energy Technology, Linnæus University, SE-351 95 Växjö, Sweden

^bMaterials and Surface Science Institute, University of Limerick, Ireland

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Abstract

Oxynitride glasses and glass ceramics are increasingly recognized as potential materials in specialist applications in modern industrial sectors. Oxynitride glasses have superior mechanical, rheological and optical properties to their oxide glass counterparts. Properties of these glasses can be tailored by changes in nitrogen content and additions of various alkaline-earth and or rare-earth elements. In contrast to oxide glasses, oxynitride glasses are difficult to prepare which adds to production costs. Furthermore, they contain impurities in the form of elemental silicon and silicides, have poor oxidation resistance in air above their glass transition temperatures and have poor transparency in the visible region. This article reviews the above issues in relation to the potential applications of these glasses.

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1. Introduction

Studies of oxynitride glasses over the last few decades have demonstrated that the addition of nitrogen to silicate glasses significantly affects the physical properties. For example, with

increasing nitrogen content, hardness, Young's modulus, strength, toughness, refractive index, viscosity and glass transition and crystallization temperatures all increase, while the thermal expansion coefficient decreases [1–11]. Oxynitride glasses have attracted interest because mechanical, rheological and optical properties can be tailored by changing composition, especially nitrogen content and various alkaline-earth or rare-earth modifying ions. Oxynitride glasses were first discovered as grain boundary phases in silicon

*Corresponding author. Tel.: +46 470708991; fax: +46 470 708756.
E-mail address: sharafat.ali@lnu.se (S. Ali).

nitride based ceramics. Since the ambient and high-temperature behavior of the ceramics is markedly governed by the chemistry of the intergranular glass phases, studies of bulk oxynitride glasses became important [12–14].

Oxynitride glasses have been prepared in a number of M-Si-O-N systems (with M=Na, Li, Mg, Ca, Sr, La, Y, Al), M-Si-Al-O-N systems (where M includes Li, Mg, Ca, Ba, RE, Y and M^I-M^{II}-Si-(Al)-O-N systems (where M^I-M^{II} modifiers: Na-Ca, RE-Mg, La-Y, Mg-Li, Mg-Cs, Mg-Ba, La-Er, Mg-Y). Conventionally, oxynitride glasses have been synthesized by heating appropriate powder mixtures of modifier oxide(s) and nitride compounds in crucibles and in an Ar or N₂ atmosphere [1,6,15–25]. More recently, more nitrogen rich glasses with N content up to 18–20 at.% have been produced by incorporating the modifier as a metal or metal hydride in reaction mixtures rather than metal oxides as normally used with silicon or aluminum nitride as the nitrogen source [26–31].

In extensive studies of various M-Si-Al-O-N systems (M=Mg, Ca, Y, Nd) [2,7,8,11,12,15], the properties of glasses with fixed cation ratios were measured and showed, unambiguously, the effect of changes in nitrogen:oxygen ratio on properties. Glass transition temperature (T_g), viscosity, micro-hardness, elastic moduli, resistance to devitrification, refractive index, dielectric constant and a.c. conductivity all were seen to increase systematically while coefficient of thermal expansion (CTE) decreased with increasing N:O ratio for glasses with different cation ratios. These effects are known to be due to the increased cross-linking within the glass structure as 2-coordinated bridging oxygen atoms are replaced by 3-coordinated nitrogen atoms.

Although the increase in properties with nitrogen content has clear advantages, it is more complicated to prepare oxynitride glasses than pure oxide glasses. Nitrogen containing glasses cannot be prepared from oxide melts using atmospheric nitrogen as nitrogen source [32]. Instead, nitrogen must be added as a nitrogen containing compound which is soluble in the oxide/silicate melt. In this way, the transfer of nitrogen atoms from the solid into the liquid state is quite rapid, and recombination of individual nitrogen atoms to form N₂ molecules (with consequent gaseous loss) is minimized, depending on what other components are present. Melting must be carried out in pure nitrogen containing a sufficiently low oxygen partial pressure during melting to avoid oxidation of glass forming components [30]. Nitrogen-containing silicate glasses are generally less transparent than their counterpart oxide glasses and are often grey or black and translucent only in thin sections, due to inclusions of other phases. This poor transparency in the visible region is the main obstacle to the utilization of oxynitride glasses in optical applications. The opacity of oxynitride glasses has been investigated [17,33,34], but no significant progress has so far been made toward the production of fully transparent glasses with high nitrogen contents. The most common reasons for the diminished transparency are precipitation of silicon and silicides [32,34].

In principle, nitrogen-rich glasses are thermally less stable in the presence of oxygen, that is, more prone to be oxidized,

than their oxygen rich counterparts [35–38]. Above the glass transition temperature, oxynitride glasses are in a non-equilibrium state and, in an oxidizing environment, oxidation and crystallization take place in this temperature range. Their low oxidation resistance limits high temperature uses of oxynitride glasses in air.

This article reviews the issues associated with the synthesis cost, impurities, transparency and oxidation resistance of oxynitride glasses especially in the alkaline earth –Si-O-N systems.

2. Preparation of oxynitride glasses

Oxynitride glasses can be prepared in a number of ways:

- (a) By nitridation of a base glass or melt:

In this method, the base glass is treated with nitrogen and/or ammonia gas at an appropriate temperature for extended periods of time. The amount of nitrogen incorporated by using this method is limited. Mulfinger was the first to investigate to study the incorporation of small amounts (< 0.5 wt%) of N into silicate glasses, by bubbling ammonia through soda-lime-silica melts [39].
- (b) By melting metal oxides, silicon dioxide and nitride compounds:

Oxynitride glasses have conventionally been synthesized by melting mixtures of glass modifier metal oxides, SiO₂, Al₂O₃ and Si₃N₄/(AlN), yielding glasses with nitrogen contents up to typically ca. 30 eq.% (N content in equivalents; eq.% N = (3[N]x100)/(3[N]+2[O]), where [N] and [O] are the atomic concentrations of N and O respectively) [10,11,15]. Glasses prepared by this route are the ones that have been studied most.
- (c) By melting pure metal, silicon dioxide and silicon nitride:

This synthesis method is quite new and has enabled the preparation of oxynitride glasses with significantly higher concentrations of nitrogen up to 65 eq.% as well as modifier additives [26–31]. In this synthesis route, the modifier is introduced as a metal or metal hydride instead of metal oxide and the mixture is melted under a N₂ atmosphere.
- (d) By sol-gel:

Oxynitride glasses have also been prepared at lower temperatures by using sol-gel techniques [40–42]. Oxide gels can be converted to oxynitride gels by treatment with flowing anhydrous ammonia at temperatures in the upper part of the range 400–1100°C. Brinker and Haaland [40] synthesized dense, colorless and homogeneous glasses with up to 2 eq.% nitrogen in the Na-Al-Ba-Si-O-N system, and Rajaram and Day [43] produced glasses in the M-Na-P-O-N system (M=alkaline earth element) with nitrogen contents up to 25 eq.%.

2.1. Difficulties associated with oxynitride glass melting

The main difficulties encountered in the preparation of oxynitride glasses are: (i) relatively high melting temperatures,

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