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Effective Parameters in Synthesis and Properties of Monolithic Oxynitride Glasses Prepared by Sol-gel method

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1- Introduction

Oxynitride glasses can be formed as a result of oxygen partial replacement by nitrogen atoms in silicate or alumino-silicate glass network. According to the literature, effect of the above replacement in oxynitride glasses has been explained through the incorporation of nitrogen which results in the increment of glass transition temperature (T_g), viscosity, hardness, Young's and shear modules, refractive index, dielectric constant and decreases in thermal expansion coefficient. These results have usually been attributed to the substitution of nitrogen for oxygen atoms. The melting process of mixed oxide and nitride powders under highly reducing conditions is the commonly used method of O–N glass preparation. However, this method suffers from extremely high temperatures for melting (often exceeding 1700°C) and homogenizing the glass.

In the past years, increasing interest has focused on preparing multicomponent glass by sol-gel method, due to its lower temperature and high homogeneity. The sol-gel method is based on the hydrolysis and subsequent condensation of the metal alkoxides. Drying the obtained gel, removes the residual solvents, i.e. water and alcohols, leading to a porous dried gel. Nitridation of this porous glass precursor gel with ammonia can be utilized as an alternative method to produce homogeneous oxynitride glass without melting at lower temperature (often ≤1000°C).

The present work was aimed to obtain monolithic oxynitride glasses in the system (R_2O/RO)-SiO_2-Al_2O_3-B_2O_3 through sol-gel method.

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2- Experimental Procedure

Borosilicate glasses with composition given in Table 1, were prepared from the reagent grade chemical materials including tetraethyl orthosilicate (TEOS), aluminum-sec-butoxide, trimethyl borate barium, and potassium acetate and zinc oxide.

Table1. Composition of synthesized glasses

Glass composition	SiO_2	Al_2O_3	B_2O_3	k_2O	BaO	ZnO
GI	66	7	18	6	3	0
GII	66	15	10	6	3	0
GIII	48	30	10	2	0	10

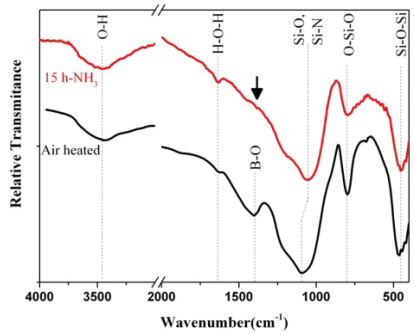
Stoichiometric amount of TEOS was dissolved in ethanol (1:4 molar ratios) and hydrolyzed by adding 1M HCl solution as a catalyst. After 2h, trimethyl borate was added and then aqueous solution of potassium or barrium and zinc nitrate were added to alkoxidessolution. To prepare zinc nitrate, zinc oxide was dissolved in diluted nitric acid. Organic citric acid was used as a chelating agent to form a stable complex with aluminum ions to improve the homogeneity of the sol. A dilute solution of Al-sec-butoxide and isopropanol (1:4 molar ratios) was added slowly to the aqueous solution of citric acid. After 24h the alkoxide and nitrate solution was mixed with chelated aluminum solution. Gelation occurred within 24h at room temperature. The gels were then dried slowly at room temperature. The porous gels were heated in flowing ammonia for different times and temperatures. The heating rate was 1°C/min.

Investigation of chemical bonding states of sintered gels was performed using ourier transform infrared spectroscopy. Micro-hardness was measured using the Vicker's micro-hardness testing method with the load of 100g for 15s. The dilatometric softening point and thermal expansion coefficient of oxide and oxynitride glasses were determined using a dilatometer. The nitrogen content of glasses was determined with oxygen nitrogen analyzer (Leco TCH-600).

3- Results and Discussion

Table 2 showes the nitrogen content of oxynitride glasses after heat treatment for various times and tempratures. The chemical composition of the glass effects the nitridation processes and the nitrogen content of glasses

were increased to 3.8% wt. by increasing soaking time of nitridation from 2h to 15h. The FTIR spectra indicated that nitrogen was chemically dissolved in the network of glass. As it can be seen in Fig. 1, a decrease in the B–O stretching band at 1405 cm^{-1}, a broadening of the Si–O stretching mode at 1088 cm^{-1} to 1500 cm^{-1}, coupled with a 5 cm^{-1} shift to a lower energy, and decrease in the intensities of O–Si–O and Si–O–Si bending mode at 800 and 460 cm^{-1}, respectively, are the important changes that have occurred in the nitridated sample.



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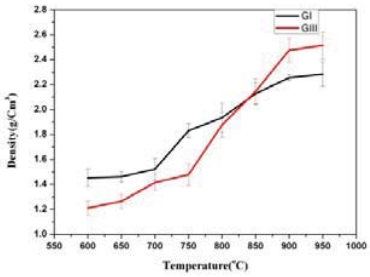
The microharness depends on sintering process on density of glass. So it can be said that the low micro-hardness of glass GIII at 750°C, is due to the incomplete sintering and its porous structure. Fig. 2 shows the bulk density variation of glasses. The microharness of this glass increases significantly with sintering temperature.

Althogh the GI glass was amorphous until 950°C, mullite was crystallized as predominant crystalline phase in GIII glass. However, the X-ray diffraction pattern of GIII glass confirmed that nitrogen had not entered the crystalline phase.



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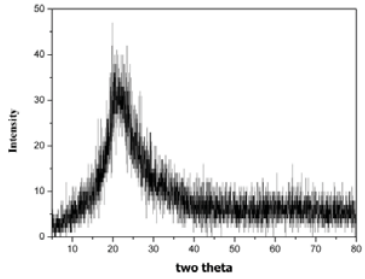

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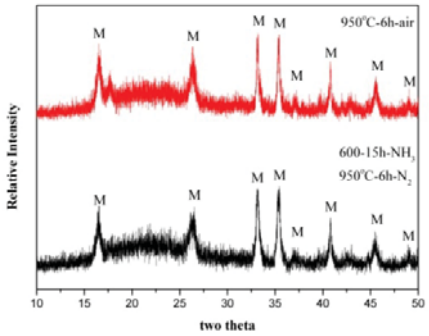

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The monolithic oxynitride glasses in SiO_2-Al_2O_3-B_2O_3 system were synthesized with sol-gel method. The chemical composition of glass effects the nitridation processes and the nitrogen content of the glasses were increased to 3.8 wt.% by increasing soaking time of nitridation from 2h to 15h. The dilatometric softening point temperature of glasses was increased approximately 25°C, their micro-hardness reached 9.76GPa and thermal expansion coefficient was decreased from 3.88×10^{-6} to 3.39×10^{-6} after nitridation process of optimal composition. The X-ray diffraction pattern of glasses confirmed that nitrogen does not enter the crystalline phase