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Influence of Y_2O_3 on the structure and properties of calcium magnesium aluminosilicate glasses

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HIGHLIGHTS

- Calcium magnesium aluminum silicates with Y_2O_3 have been prepared.
- Density, molar volume, microhardness and chemical durability were measured and calculated.
- Determination of *Tg* and *Ts* for the samples.
- IR measurements study their structural properties systematically.
- The addition of Y_2O_3 led to increase the structure rigidity with improvement in hardness and chemical durability.

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ABSTRACT

Glasses were prepared whose composition is defined by the formula: 25CaO—20MgO—$x$$Y_2O_3$—(9–$x$) Al_2O_3—46SiO_2 mol.% ($0 \leqslant x \geqslant 3$). To investigate the relation between the structural change and compositional variation by introducing Y_2O_3 instead of Al_2O_3, the glasses were analyzed by Fourier transform Infrared (FT-IR) analysis and differential thermal analysis (DTA). The density, molar volume, hardness and the chemical durability were measured and calculated. The FTIR spectra were recorded in the spectral range from 400 to 4000 cm^{-1} and showed significant depolymerization of silicate groups and hence resulting in a net decrease of local symmetry. Introducing yttrium in the glasses increases both glass transition (*Tg*) and softening (*Ts*) temperatures. The obtained Vicker's microhardness, the density values and the chemical stability data were increased by addition Y_2O_3 instead of Al_2O_3 in the glasses. The resulting data were greatly correlated to the role played by the cations present in the glass structure.

1. Introduction

The preparation of alkaline-earth aluminosilicate glasses has been broadly investigated in the past decade; it attracted the attention and had been studied by many workers [1–4]. The system CaO—MgO—Al_2O_3—SiO_2 is one of the best understood quaternary systems in the non-metallic field, because of its application of materials based on this system [5]. The structure of yttrium and rare-earth aluminosilicate glasses had been of great interest for many years because of their technological importance and their values in understanding the basic principle of glass structure [6]. Yttrium and rare-earth aluminosilicate glasses have high elastic modulus and hardness, excellent chemical durability, high glass transition temperature (*Tg*), and relative insensitivity of *Tg* to composition variation [7].

Aluminosilicate glasses containing rare-earth and rare-earth analogue cations such as Y^{3+} and La^{3+} are interesting for a variety of technological applications, as well as for elucidating general principles of glass formation and its structure [8].

Several papers have been published reporting the effect of adding oxides of trivalent elements to silicate glasses. Y_2O_3 and La_2O_3 were added to silicate and aluminosilicate glasses, allowing to improve the alkaline durability [9] and to obtain exceptionally high glass transformation temperatures (*Tg*), high refractive indices, very low electrical conductivity and moderate thermal expansion coefficients [10].

Costantini et al. [11] studied the effect of the substitution of Y_2O_3 for CaO on the bioactivity of 2.5CaO—2SiO_2 glass. The result revealed that *Tg* and *Ts* increase with the Y_2O_3 content. The trend was explained on the basis of the increased structural rigidity when Ca^{2+} ions are substituted by Y^{3+} ions, due to the formation of stronger bonds to the oxygen. Yttrium containing aluminosilicate glasses are of technological importance in photonics, nuclear waste disposal, and as a delivery vehicle for radiation therapy.

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Their structures are also of great interest in glass science to elucidate the principles of glass formation and structures [6].

Among transition metal and lanthanide ions, Y^{3+} acts as a lanthanide ion while it definitely belongs to transition metals [12]. Historically yttrium has been grouped with lanthanides due to their similarities and co-existence in nature. Plotting physical properties of yttrium against atomic number, gives an apparent number of 64.5–67.5, placing it between the lanthanides, gadolinium and erbium. Similarities between yttrium and lanthanides in solubility and atomic radius [13].

Singh et al. [14] investigated the effect of M_2O_3 on the structural, optical and bioactive properties of the glass of composition SiO_2—B_2O_3—CaO—M_2O_3 (M = Al, Cr, Y and La). The results showed that M_2O_3 plays an important role in controlling chemical durability and bioactivity of the glasses. The Y_2O_3 containing glasses exhibit lower dissolution rate, higher density values, lower oxygen molar volume and increased optical band gap as compared to Al_2O_3 containing glasses. The aim of the work is focus to the study the effect of rare earth oxide, Y_2O_3, on the physical, chemical and the local structure of some calcium magnesium aluminosilicate glasses.

2. Experimental

2.1. Batch composition and glass preparation

The glass batches were prepared from reagent grade powders of $CaCO_3$, $MgCO_3$, Al_2O_3, Quartz (SiO_2) and Y_2O_3. The glass oxide constituents are given in Table 1. The glass batches were melted in Pt–2% Rh crucible, covered with Pt foil to minimize the evaporation, in an electric furnace with SiC heating elements at 1350–1450 °C for 3 h. Swirling the melt several times at about 30 min. intervals to obtain clear homogenous melt. The melt was cast into rods and as buttons, which were then properly annealed in a muffle furnace at 500–550 °C to minimize the strain.

2.2. Differential thermal analysis (DTA)

The thermal behavior of the finely powdered glass samples was examined using a SETARAM Labsys™ TG-DSC16. A uniform heating rate of 10 °C min^{-1} was adopted. The results obtained were used as a guide for determining the required heat-treatment temperatures applied to induce crystallization of the glasses.

2.3. Density measurements

The density of each glass sample was measured at room temperature by using Archimed's method, using Xylene as immersion solution. The density (ρ) is calculated from the equation.

$$\rho = W_{air}/(W_{air} - W_{xylene}).\rho_{xylene}$$

where W_{air} and W_{xylene} are the weight of glass sample in air and in Xylene, respectively, and ρ_{xylene} is the density of Xylene (=0.8645 g/cm^3). The arithmetic mean of three small specimens of the same sample was calculated. The accuracy of the results in triplicate measurements is ±0.001 g/cm^3. The density data were used to calculate the molar volume (V_M) given by $V_M = M/\rho$, where M is the glass molecular weight in mol.% and ρ is the density of glass.

Table 1
the compositions of the studied glass.

Glass No.	CaO	MgO	Al_2O_3	SiO_2	Y_2O_3
Y_0	25	20	9	46	–
Y_1	25	20	8	46	1
Y_2	25	20	7	46	2
Y_3	25	20	6	46	3

2.4. Microhardness measurements

The microhardness of the investigated samples was measured by using Vicker's microhardness indenter (SHIMADZU, HMV-2 Series, Japan). The eyepiece on the microscope of the apparatus allowed measurements with an estimated accuracy of ±0.5 μm for the indentation diagonals. The specimens were cut using a low speed diamond saw, dry ground using 1200 grit SiC paper and polished carefully using 6, 3 and 1 μm diamond paste to obtain smooth and flat parallel surfaces before indentation testing. At least six indentation readings were made and measured for each sample. Testing was made using a load of 100 g; loading time was fixed for all crystalline samples (15 s). The measurements were carried out under normal atmospheric conditions. The Vicker's microhardness value was calculated from the following equation:

$$H_v = A(p/d^2)\ \text{kg/mm}^2$$

where A is a constant equal to 1854.5 takes into account the geometry of squared based diamond indenter with an angle 136° between the opposing faces, p is the applied load (g) and d is the average diagonal length (μm). The microhardness values are converted from kg/mm^2 to MPa by multiplying with a constant value 9.8.

2.5. Infrared transmittance measurements

Infrared transmittance spectral measurements were carried out on powdered glass samples dispersed in KBr as a matrix material. IR measurements were performed using a Jasco spectrometer (model.FT/IR-6100), in the wave number region from 400 to 4000 cm^{-1}.

2.6. Chemical durability

The powdered method was applied to assess the chemical durability of the obtained glass. The samples were crushed in an agate mortar and then sieved using B.S. sieves to obtain particles with diameters ranging between 0.63 and 0.32 mm. The grains were washed by ethyl alcohol and then with pure dry ether 3 times and then dried. The dried sample was accurately weighed (1.0 g) in a sintered glass crucible (#4), which was then placed in 400 ml polyethylene beaker. The samples were tested in 0.1 N HCl solution; 200 ml of the acid solution was introduced into the polyethylene beaker. This quantity was sufficient to cover the sintered glass crucible. The polyethylene beaker with its contents was covered by the polyethylene cover to reduce evaporation. The chemical durability was expressed as the weight loss. The experiment was carried out at 95 °C for 1 h.

3. Results and discussion

In silica-based glasses the basic structural unit is the tetrahedral, where Si is in 4-fold coordination by oxygen (O). The Si-centred tetrahedral structural species are designated as Q^n, where Q refers to silicon atom and n denotes the number of bridging oxygens (BO) in the structural unit. The Q^4 structural species are configured in tetrahedral configuration as [SiO_2]; the Q^3 structural species form [$Si_2O_5^{2-}$] sheets; the Q^2 species result in chains where the structural unit is [SiO_3^{2-}]; the Q^1 species are [$Si_2O_7^{6-}$] dimmers; the Q^0 species are isolated [SiO_4^{4-}] monomers. The difference