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Synthesis, crystallization behavior and microstructure of oxynitride glass–ceramics with different modifier elements

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Abstract

M–Si–Al–O–N (M = Y, Ca, Mg) oxynitride glasses were prepared by melting batches at 1600 °C for 2 h under N_2 atmosphere in a Si–Mo-heated resistance furnace. The appropriate heat treatment temperatures were selected according to the information provided by the differential scanning calorimeter (DSC) measurement. X-ray diffraction (XRD) and scanning electron microscope (SEM) were used to study the crystallization behavior of the glass–ceramics with different modifier elements. The results indicate that for this glass system, heat treatment has an effect on volume fraction of the crystalline phases and the microstructure of the glass–ceramics, whereas the effect on the types of the crystalline phases precipitated is small.

Keywords: Oxynitride glass–ceramics; Microstructure; Crystallization

1. Introduction

Oxynitride glasses have been studied intensively because of their excellent structure and properties. In the past few years, particular interest has been focused on the M–Si–Al–O–N system, where M is magnesium [1,2], calcium [3,4] and yttrium [5–7] acting as a modifying cation. Incorporation of nitrogen into the silicate network enhances glass formation and causes an increase in properties such as density, elastic moduli, microhardness and glass transition temperature. Observed property changes for oxynitride glasses with increasing nitrogen content is consistent with a structural model in which nitrogen substitutes for oxygen and, due to the incorporation of tri-coordinated nitrogen, creates a more cross-linked glass network and structure.

As with other silicates, oxynitride glasses may be heat treated at the appropriate temperatures to crystallize as glass-ceramics and do not require the addition of nucleating agents to promote the crystallization process [6,8,9]. Many studies on crystallization of oxynitride glasses, particularly in the Y–Si–Al–O–N system [8–11], have been carried out which have been identified suitable two step heat treatments for nucleation and growth of new phases to obtain oxynitride glass–ceramics with significant increase in mechanical properties like strength and elastic modulus. The specific crystalline phases formed upon heat treatment, and the extent of their formation determined the properties of the oxynitride glass–ceramics materials [12–14].

Previous work has investigated Y–Si–Al–O–N glass–ceramics. Sainz et al. [8] have found that $YAlO_3$ was the major crystalline phase after heat treatment and Luo et al. [15] have found that $Y_2Si_2O_7$ was the major phase of Y–Si–Al–O–N glass–ceramics. The purpose of this study is to characterize the crystallization mechanism and microstructure with different modifier elements in the M–Si–Al–O–N (M = Y, Ca, Mg) glass–ceramics system.

2. Experimental procedure

2.1. Glass synthesis

A base M–Si–Al–O–N oxynitride glass was prepared with a cation composition (in eq.%) of 24M:61Si:15Al:82O:18N, where M is Y, Ca and Mg. Y_2O_3 (99.9%, A&C Rare Earth Materials Center, China), α-Si_3N_4 (99.7%, averaged particle size 0.2 um; Sinopharm Chemical Reagent Co. Ltd., China),

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Table 1
Composition (in eq.%), thermal properties, density and Vickers hardness of the oxynitride glasses.

Sample no.	Composition (eq.%)	T_g ($\pm$5 °C)	T_{c1} ($\pm$5 °C)	T_{c2} ($\pm$5 °C)	ρ ($\pm$0.01 g cm^{-3})	H_v ($\pm$0.10 GPa)
24Y18N	$Y_{24}Al_{15}Si_{61}O_{82}N_{18}$	917	1158	–	3.38	9.97
24Ca18N	$Ca_{24}Al_{15}Si_{61}O_{82}N_{18}$	861	1075	–	2.79	7.79
24Mg18N	$Mg_{24}Al_{15}Si_{61}O_{82}N_{18}$	855	1142	1216	2.83	10.43

Al_2O_3 (99.9%, Xilong Chemical Co. Ltd., China), $CaCO_3$ (99.9%, Xilong Chemical Co. Ltd., China), SiO_2 (99.9%, Xilong Chemical Co. Ltd., China), MgO (99.9%, Xilong Chemical Co. Ltd., China) were used as raw materials. Dried powders were weighed and prepared by mechanical agitation (using an attritor mill), milled in isopropyl alcohol for 24 h, and then dried again. The mixture was melted inside a silica crucible lined with BN powder at 1600 °C for 2 h under N_2 atmosphere (0.1 MPa), using a heating rate of 5 °C/min. Subsequently, the samples were first cooled with a cooling rate of 25 °C/min until a temperature of 900 °C annealing for 1 h to remove internal stresses and afterwards the samples were cooled down with furnace cooling to room temperature. Table 1 lists the nominal compositions in eq.% (equivalent percent) of these samples.

2.2. Characterization techniques

2.2.1. Density and Vickers hardness

The density (ρ) was measured by the Archimedes method, using distilled water. Vickers hardness (H_v) tests were carried out on polished glass samples using a Matsuzawa micro-hardness tester Model MXT-a 1 with a pyramid shaped diamond indenter, applying loads 9.8 N for 15 s. At least 10 measurements were taken for each sample. Indentation diagonals were measured to calculate hardness values in GPa.

2.2.2. Differential scanning calorimeter (DSC)

The differential scanning calorimeter (DSC, Netzsch 404PC, Germany) was used to determine the glass transition temperature (T_g) and crystallization temperature (T_c). About a 10 mg powder sample was placed in an alumina crucible and subjected to a heating rate of 10 °C/min from ambient temperature to 1400 °C in a flowing high purity argon environment. The experimental error on measured value was $\pm$5 °C.

2.2.3. X-ray diffraction (XRD)

X-ray diffraction (XRD) was carried out in order to analyze the crystalline phase of the samples by an X-ray diffractometer (D/max 2500 model, Rigaku, Japan) with Cu-Kα radiation (λ=1.54178 Å) operated at 40 kV and 50 mA. Data were collected from 2θ=10–80° at a scanning rate of 8 deg/min.

2.2.4. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was carried out on cut samples of glass-ceramics mounted in epoxy resin and polished to 1 μm with diamond slurries. The mirror surfaces of samples were sputtered with a gold coating and a FEI Quanta 200 scanning electron microscope was employed for observing the crystal morphology.

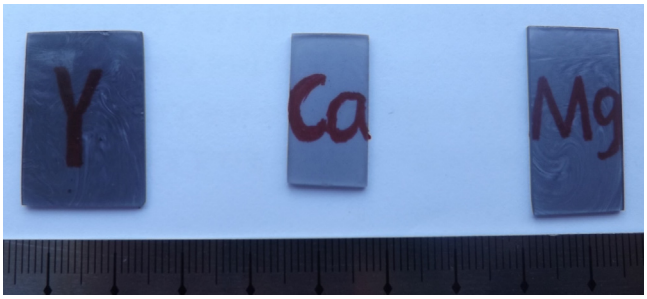

Fig. 1. Photograph of the oxynitride glass samples 24Y18N, 24Ca18N and 24Mg18N laid over the writing letters to show their transparency.

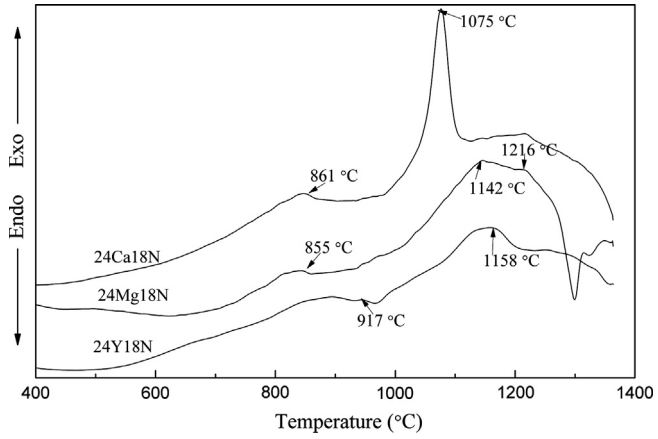

Fig. 2. DSC curves of oxynitride glass samples 24Y18N, 24Ca18N and 24Mg18N at heating rate 10 °C/min.

3. Results and discussion

3.1. Glass appearance

The appearance of the parent glasses obtained was primarily inspected by the naked eye. All the glass samples were highly homogeneous, transparent, bubble free and gray in color. The amorphous nature of these glasses was confirmed by the corresponding X-ray diffraction patterns, which did not show any crystalline phase. Fig. 1 shows fabricated glasses which are placed on a piece of written paper where the underlying letter is visible through all of them. Compared to oxide glasses, oxynitride glasses are of limited transparency, having colors varying between pale gray and almost black.