Journal of Non-Crystalline Solids 499 (2018) 401–407

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Alkali metal tantalum germanate glasses and glass-ceramics formation

Cristiano Ramos da Cunha[a,*], Sérgio Alexandre Maestri[a], Bianca Paula de Sousa[a], Lia Mara Marcondes[a], Rogéria Rocha Gonçalves[b], Fábia Castro Cassanjes[a], Gaël Yves Poirier[a]

[a] Grupo de Química de Materiais, Universidade Federal de Alfenas, Campus de Poços de Caldas, Poços de Caldas, MG, Brazil
[b] Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, Ribeirão Preto, SP, Brazil

1. Introduction

Germanium oxide is a well-known glass former and has been studied due to specific properties for optical applications, such as lower melting point, viscosity and phonon energy, and higher refractive index, when compared to silica glasses [1, 2]. Tantalum oxide is of great interest for optical applications, due to a high refractive index and lower phonon energy, and also an increased rare-earth ions solubility [3, 4], as well as other transition metals, such as niobium [1, 2, 5] and hafnium [6, 7]. High concentrations of transition metals are associated with optical properties enhancement, such as band broadening and increase in quantum efficiency of emissions [1–4, 6, 7]. These improvements were attributed to alterations in the rare-earth ion neighborhood, with a replacement of the silicon atoms by the transition metal, altering the symmetry environment where the lanthanide is located. These properties can be further improved if the material is a glass-ceramic containing a crystalline phase, consisted of transition metal oxide nanocrystals [4–6, 8, 9]. Binary systems containing SiO_2 and Ta_2O_5 prepared by the sol-gel route results in materials with a high concentration of Ta and improved optical properties. However, this methodology also presents some limitations, such as difficulties for preparation of larger bulk samples and higher synthesis times related to the drying process. These limitations should be reduced by a melt-quenching preparation, but both SiO_2 and Ta_2O_5 have high melting points and are highly refractory, hence the replacement of SiO_2 for GeO_2 as the glass former. Only recently, glasses with higher tantalum oxide contents (> 10% mol) and prepared by melt-quenching were reported in the Eu^{3+} − doped and Er^{3+}/Yb^{3+} -codoped general ternary system GeO_2-Ta_2O_5-K_2O [10]. Usually, tantalum oxide is used as an enhancer for thermal and optical properties [11–13]. Also, at low concentrations, Ta_2O_5 is a glass former in a GeO_2 matrix, while at higher concentrations behaves more like a glass modifier than a glass former [14].

In this paper, we verified the glass formation ability in the ternary system $70GeO_2$-$20Ta_2O_5$-$10M_2O$; M = Li, Na, K, Rb, Cs, and we present an appropriate diagram for the glass-forming zone of the most promising ternary system, chosen for its ability to form homogeneous, transparent bulk samples. The glass samples had a fixed Ta_2O_5 content of 20% (mol), as this was reported to be the highest concentration where a glass can be formed without crystallization in a GeO_2 matrix [10]. The samples were analyzed by Differential Scanning Calorimetry (DSC) to investigate the thermal parameters and the crystallization process, aiming to verify the best conditions for obtaining transparent glass-ceramics by annealing [15]. UV-VIS-NIR spectroscopy was applied to check the absorption range and band gap energy. Raman spectroscopy and X-Ray Diffraction (XRD) were used to monitor the structural changes between glass and glass-ceramics, and also identify the crystallized phases.

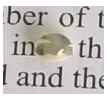
2. Experimental

The samples were prepared from starting compounds GeO_2 99,9% and Ta_2O_5 99,9% (both from Sigma Aldrich Corp.). Alkali metals were introduced by reagent grade Li_2CO_3 99%, Na_2CO_3 99,5%, K_2CO_3 99%, Rb_2CO_3 99% or Cs_2CO_3 99% (all from Vetec Química Ltda), previously dried in an oven at 105 °C for 12 h. Reagents were weighted in analytical balance for a 5 g total mass of each chosen composition, mixed and ground in an agate mortar, then melted in platinum crucible at appropriate working temperatures. All glass compositions described in this paper are batch calculations. The oxides were melted for 30 min to ensure complete elimination of CO_2 and homogeneity. The melts were quenched in a steel plate at room temperature for test samples for DSC, and steel molds pre-heated at 500 °C for preparation of larger bulk pieces for glass-ceramic formation and optical analysis. Glass forming ability was determined by preparing small samples of 3–5 g in a Pt/Au crucible, and quenched in a steel plate at room temperature from an oven at 1450 °C. DSC curves were determined in a Netzsch Calorimeter STA 449 F3 Jupiter (Selb, Germany) in bulk samples of 30–40 mg, in a Pt/Rh covered crucible from 200 °C to 1200 °C, at 10 °C/min heating rate under N_2 atmosphere. XRD was performed on powder samples in a Rigaku Ultima IV Difractometer (Tokyo, Japan), working at 40 KV and 30 mA between 10° and 70°, in continuous mode of 0,02°/s. UV-VIS-NIR absorption spectra were obtained in a Cary 7000 Agilent

* Corresponding author at: Instituto de Ciência e Tecnologia, UNIFAL, Rodovia José Aurélio Vilela, 11999 (BR 267, Km 533), Cidade Universitária, Poços de Caldas, MG CEP 37715-400, Brazil.
E-mail address: cristicunh@yahoo.com.br (C.R. da Cunha).

https://doi.org/10.1016/j.jnoncrysol.2018.07.059
Received 13 April 2018; Received in revised form 26 July 2018; Accepted 27 July 2018
Available online 02 August 2018
0022-3093/

Table 1
Characteristics of the glasses of composition $70GeO_2.20Ta_2O_5.10M_2O$; M = Li, Na, K, Rb, Cs. Temperature errors from DSC data = ± 1 °C.

Sample (M =)	Working temperature (°C)	Aspect	T_g (°C)	T_{x1} (°C)	T_{c1} (°C)	T_{x2} (°C)	T_{c2} (°C)	T_{x1}-T_g (°C)
Li	1450 ± 2		686	733	756	764	774	47
Na	1400 ± 2		726	789	808	–	–	63
K	1450 ± 2		753	828	844	980	994	75
Rb	1450 ± 2		789	846	870	–	–	57
Cs	1500 ± 2		775	847	851	1151	1172	72

Spectrophotometer in bulk polished samples, from 200 to 2500 nm. IR spectra from 2500 to 6000 nm were obtained in a Cary 630 FTIR Spectrophotometer on bulk polished samples. Raman spectra were determined in bulk polished samples from 100 to 1100 cm^{-1} in a LabRam Micro-Raman, Horiba Jobin-Yvon (Edison, NJ), operating at 632.8 nm with a He—Ne laser. Scanning Transmission Electron Microscopy (STEM) and Energy Dispersive Spectroscopy (EDS) were performed in a JEOL JEM-2200FS Field Emission Electron Microscope, configured to Ultrahigh Resolution and Acc. Voltage of 200 KeV.

3. Results

3.1. $70GeO_2.20Ta_2O_5.10M_2O$ glasses

Glass samples of composition $70GeO_2.20Ta_2O_5.10M_2O$; M = Li, Na, K, Rb, Cs were successfully obtained. These glasses will be named henceforth in this text by their alkali metal content; thus, the glass with composition $70GeO_2.20Ta_2O_5.10Li_2O$ is the lithium glass, $70GeO_2.20Ta_2O_5.10Na_2O$ is the sodium glass, and so on. Table 1 shows the synthesis parameters and their most relevant properties. Working temperatures for melting were determined by direct observation of the oxides melts (i.e. complete dissolution of all solid phases, with no bubbles and forming a homogeneous liquid). All glasses presented a clear, yellow aspect, as shown in Table 1. DSC analysis were performed in all glasses, and the obtained curves are shown in Fig. 1. These curves provide the parameters of interest T_g (glass transition temperature), T_{x1} (first peak's starting crystallization temperature), and T_{c1} (first peak's maximum height temperature) – T_{x2} and T_{c2} as T_{x1} and T_{c1}, for the second peak, if applicable. T_{x1}– T_g represents the thermal stability parameter, i.e., the temperature range where the glass is stable. Values are shown in Table 1. The presence of T_g confirms all samples as glasses. In addition, an endothermic event was observed for the lithium glass, at 1064 °C, indicating that at least one of the two detected crystalline phases melted. Endothermic events above crystallization in glasses are generally related with the melting of crystallized phases. A similar, small event can be observed around 1050 °C for the cesium glass.

3.2. $GeO_2.Ta_2O_5.K_2O$ ternary system

The ternary system of general composition $GeO_2.Ta_2O_5.K_2O$ was selected for investigation of the glass forming ability, as discussed below in Section 4.1. With the observed results, it was possible to build a ternary diagram, shown in Fig. 2. The samples were considered a glass when vitreous appearance was formed, i.e., homogeneous and transparent samples, as quenched from 1450 °C to room temperature. DRX analysis confirmed their amorphous state [10] (see also Fig. 6). Above 40% K_2O the formed glass is highly hygroscopic. Above 50% K_2O the samples were too hygroscopic to be considered viable as glasses.

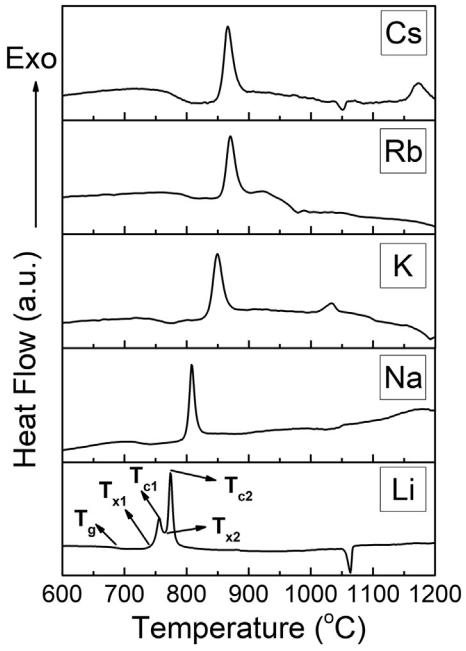


Fig. 1. DSC curves of glasses with composition $70GeO_2.20Ta_2O_5.10M_2O$; M = Li, Na, K, Rb, Cs; indicated by its alkali metal component.

3.3. Glass-ceramic formation

The system of composition $70GeO_2.20Ta_2O_5.10K_2O$ (potassium glass) was selected for glass-ceramic (GC) formation, as discussed in