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Synthesis and characterization of clinopyroxene based glasses and glass-ceramics along diopside ($CaMgSi_2O_6$)–jadeite ($NaAlSi_2O_6$) join

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Abstract

The crystallization behavior and mechanical characterization of glasses based upon the compositions along diopside ($CaMgSi_2O_6$)–jadeite ($NaAlSi_2O_6$) join has been investigated. Six glasses were obtained by the melt-quenching technique. Structural and thermal behaviors of these glasses were investigated by density and molar volume, infrared spectroscopy (FTIR) and dilatometry. The crystallization behavior of glasses was investigated by using differential scanning calorimetry (DSC). Sintering and crystallization behavior of the glass-ceramics were investigated under non-isothermal heating conditions up to temperatures of 850 °C. Mechanical characterization of glasses was investigated by using the measurement of Vickers indentation hardness and elastic constants such as Young's modulus (E), shear modulus (G), bulk modulus (K) and Poisson's ratio (ν). These data of the glasses were correlated with the structure of glasses, nature and role played by glass forming cations.

Keywords: C. Mechanical properties; C. Hardness; D. Glass

1. Introduction

Pyroxenes are major constituents of earth's crust and of the upper mantle to depths of 400 km. The general chemical formula for pyroxenes is $M2M1T_2O_6$, where M2 refers to cations in a generally distorted octahedral coordination (Mg^{2+}, Fe^{2+}, Mn^{2+}, Li^{+}, Ca^{2+}, Na^{+}), M1 to cations in a regular octahedral coordination (Al^{3+}, Fe^{3+}, Ti^{4+}, Cr^{3+}, V^{3+}, Ti^{3+}, Zr^{4+}, Sc^{3+}, Zn^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}), and T to tetrahedrally coordinated cations (Si^{4+}, Al^{3+}, Fe^{3+}). Any pyroxene belongs to either the orthorhombic or the monoclinic crystal system. Monoclinic pyroxenes are called clinopyroxenes. The chain structure of clinopyroxenes enables incorporation of various cations in their structure resulting in minerals founds in abundance in the nature, such as diopside ($CaMgSi_2O_6$), hedenbergite ($CaFeSi_2O_6$), aegirine ($NaFeSi_2O_6$), jadeite ($NaAlSi_2O_6$), spodumene ($LiAlSi_2O_6$), etc. [1].

The solid solution between diopside ($CaMgSi_2O_6$; hereafter referred as Di) and jadeite ($NaAlSi_2O_6$; hereafter referred as Jd) is a subject of relevance from petrologic as well as technological point of view. It is noteworthy that although Jd is metastable at one bar pressure and only forms at high pressure ($\geq$3 GPa), a stable solid solution exists between Di and Jd forming a C2/c monoclinic lattice and is one of the most important pseudo-binary chemical systems in petrology [2]. It is due to this reason that Di–Jd join has been an area under discussion among researchers for a considerable period of time. The binary phase diagram of Di–Jd system has been studied by Schairer and Yoder [3] at a pressure of 1 atm while many studies investigating the phase relations at high temperature and pressures in Di–Jd system have been reported [4–8]. Wood et al. [9] studied the thermo-chemistry of synthetic Di–Jd pyroxenes and found that the investigated synthetic clinopyroxenes have positive excess enthalpies of mixing. Also, it was reported that Di–Jd solid solutions are 'pseudo-ideal' near 1:1 composition at temperatures of 1000–1500 K. Recently, Abo-Mosallam et al. [2] studied the structure and crystallization behavior of glasses

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Table 1
Batch composition of glasses.

Glass		MgO	CaO	Na_2O	SiO_2	B_2O_3	Al_2O_3
Jd-0	wt.%	18.97	26.40	–	48.08	6.55	–
$CaMgSi_{1.7}B_{0.4}O_6$	mol.%	25.65	25.65	–	43.57	5.13	–
Jd-20	wt.%	15.39	21.41	2.96	48.74	6.65	4.87
$Ca_{0.8}Mg_{0.8}Na_{0.2}Si_{1.7}Al_{0.2}B_{0.4}O_6$	mol.%	21.60	21.60	2.72	45.93	5.43	2.72
Jd-40	wt.%	11.7	16.28	6.0	49.42	6.74	9.87
$Ca_{0.6}Mg_{0.6}Na_{0.4}Si_{1.7}Al_{0.4}B_{0.4}O_6$	mol.%	17.12	17.12	5.73	48.57	5.73	5.73
Jd-60	wt.%	7.91	11.01	9.12	50.12	6.83	15.01
$Ca_{0.4}Mg_{0.4}Na_{0.6}Si_{1.7}Al_{0.6}B_{0.4}O_6$	mol.%	12.11	12.11	9.09	51.44	6.06	9.09
Jd-80	wt.%	4.01	5.58	12.34	50.84	6.93	20.3
$Ca_{0.2}Mg_{0.2}Na_{0.8}Si_{1.7}Al_{0.8}B_{0.4}O_6$	mol.%	6.42	6.42	12.92	54.90	6.42	12.92
Jd-100	wt.%	–	–	15.65	51.58	7.03	25.74
$NaAlSi_{1.7}B_{0.4}O_6$	mol.%	–	–	17.27	58.57	6.89	17.27

and glass-ceramics along $(CaMgSi_2O_6)_{1-x}$–$(NaAlSi_2O_6)_x$–$(Ca_5(PO_4)_3F)_y$ where $0 \leq x \leq 30$ mol.% and $y = 7$ mol.%. He has reported that with increase in Jd content in the glasses, the polymerization in silicate glass network shifted from Q^2 to Q^3 (Q^n: degree of polymerization; n: number of bridging oxygens) and Al exists predominantly as Al (IV) species. A complete solid solution has been reported to exist between Di–Jd glass-ceramics at 1 atm pressure for the first time in literature [2]. However, to the best of our knowledge, the structure and crystallization behavior in complete series of glasses along Di–Jd join have not been reported so far in open literature. Therefore, the primary aim of this study is to investigate the structural and mechanical properties of glasses along Di_{1-x}–Jd_x (x = 0–100 mol.%) join in conjunction with their sintering and crystallization behavior. It should be noted that small amounts of B_2O_3 have been added in all the investigated glasses in accordance with substitution Scheme $0.3Si^{4+} \leftrightarrow 0.4B^{3+}$, so as to decrease the viscosity of the glass melts and tailor the flow properties of the resultant glass-ceramics which can be useful for some technological applications related with coatings on ceramic/metallic substrates [10,11]. Table 1 presents the compositions of all the investigated glasses.

2. Experimental

Homogeneous mixtures of batches (∼200 g) in accordance with glass compositions presented in Table 1 were prepared by ball milling of powders of SiO_2 (Sigma–Aldrich, purity >99.7%), $CaCO_3$ (Merck, >99.8%), Al_2O_3 (Merck, ≥98%), H_3BO_3 (Merck, 99.8%), MgO (Merck, >99.7%), Na_2CO_3 (Merck, 99.9%), and calcination at 900 °C for 1 h. The glass batch was melted in Pt crucibles at 1500 °C for 1 h, in air. Glasses in bulk form were produced by pouring the melts on preheated graphite moulds followed by annealing at 550 °C for 1 h while glass frits were obtained by quenching of glass melts in cold water. The frits were dried and then milled in a high-speed agate mill resulting in fine glass powders with mean particle sizes of 10–20 μm (determined by light scattering technique; Coulter LS 230, Beckman Coulter, Fullerton CA; Fraunhofer optical model). The experimental glass compositions as determined by X-ray fluorescence (XRF, PW 2404 X-ray Spectrometer, Phillips, Netherlands) are presented in Table 2.

Archimedes' method (by immersion in ethylene glycol) was employed to measure the apparent densities of the bulk annealed glasses which was further employed along with compositions of glasses to calculate the molar volumes and excess volumes of glasses.

Infrared spectra for the glass powders were obtained using an Infrared Fourier spectrometer (FT-IR, model Mattson Galaxy S-7000, USA). For this purpose each glass powder was mixed with KBr in the proportion of 1/150 (by weight) and pressed into a pellet using a manual press.

The elastic constants (Young's modulus (E), shear modulus (G), bulk modulus (K) and Poison's ratio (ν) of glasses were determined by ultrasonic echography. For this purpose, velocities of longitudinal (10 MHz) and transverse (4 MHz) ultrasonic waves in the investigated glass specimens were measured using piezoelectric transducers and associated electronics (ultrasonic flaw detector USD15, Krautkramer GmbH & Co., Huerth, Germany). From the longitudinal (V_l) and transverse (V_t) sound velocities, the elastic constants were calculated using the equations described in Ref. [12]. The Vickers hardness values (HMV-2000, Shimadzu, Japan) of the

Table 2
Composition of glasses (wt.%) as determined by XRF analysis.

Glass	MgO	CaO	Na_2O	SiO_2	B_2O_3	Al_2O_3
Jd-0	19.30	28.55	–	46.04	5.89	–
Jd-20	16.50	22.82	2.96	47.24	5.86	4.78
Jd-40	11.90	17.27	5.22	50.49	5.67	9.46
Jd-60	7.72	11.76	8.63	51.40	5.75	14.71
Jd-80	3.90	5.77	11.93	53.12	5.54	19.70
Jd-100	–	–	16.85	52.30	6.58	24.23