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Iron incorporation into magnesium aluminosilicate glass network under fast laser floating zone processing

N.M. Ferreira[a,b,*], A.V. Kovalevsky[b], M.A. Valente[a], N.A. Sobolev[a,c], J.C. Waerenborgh[d], F.M. Costa[a], J.R. Frade[b]

[a]Department of Physics, i3N, University of Aveiro, 3810-193 Aveiro, Portugal
[b]CICECO – Aveiro Institute of Materials, Department of Materials and Ceramic Engineering, University of Aveiro, 3810-193 Aveiro, Portugal
[c]National University of Science and Technology "MISiS", 119049 Moscow, Russia
[d]Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, 2695-066 Bobadela LRS, Portugal

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Abstract

Magnesium aluminosilicate glasses were proposed as molten electrolytes for iron pyroelectrolysis, an alternative electrometallurgical technique offering environmental and economic advantages over traditional steelmaking. This work focuses on mechanisms of iron incorporation in the glass network and related effects on physical properties. The study was performed on amorphous Fe-containing glass fibres, grown by laser floating zone in strongly non-equilibrium conditions, to retain frozen-in states characteristic for glass electrolyte at high temperatures. Up to 4 mol% content the iron cations possess predominantly 2+ oxidation state, act mostly as a network modifier and are distributed as isolated ions in the glass network. Presence of magnetic exchange interactions and paramagnetic resonance signal at $g \sim 2.0$ in the case of higher iron contents suggest progressive clustering of iron cations. The observed clustering and concomitant increase in the electrical conductivity indicate possible appearance of redox-driven hopping conductivity, acting as an electronic contribution to charge transport.

Keywords: Aluminosilicate; Laser floating zone; Iron oxide; Glass electrolyte; Molten oxide electrolysis

1. Introduction

Silicate-based glasses are finding a very broad applications range in industry and research, provided by their unique physical and chemical properties, including resistance to thermal shock, chemical durability, abrasion resistance, specific electrical transport features and spectral transmittance, deformation resistance, biocompatibility, flexibility for tuning the thermal expansion and many others [1]. Although glass-manufacturing technologies are quite mature, nowadays they are subject of continuous development, aiming at superior properties, highest technological efficiency and reduced power consumption. Magma glasses are also essentially made of silicates and that is why it is important to understand property-structure-composition relationships for these materials, which have been receiving special attention in Earth sciences [2].

Particular research efforts are directed towards deeper understanding and consequent design of electrical properties of the glasses. Silicates show reasonably high ion mobility along with high concentration of weakly-bonded mobile ions [2–5]. Therefore, they also have attracted a significant interest for potential applications as solid electrolytes in electrochemical devices, batteries, chemical sensors and smart windows [6–8]. Original prospects were proposed for magnesium aluminosilicate (MAS) glasses containing iron, as a molten electrolyte for the pyroelectrolysis process to obtain molten Fe from its oxides [9–14]. This process is considered as an alternative electrometallurgical technique for direct extraction of iron,

*Corresponding author.
E-mail address: nmferreira@ua.pt (N.M. Ferreira).

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which offers environmental and economical advantages over tradition steelmaking [9,12,15].

A specific feature of iron-containing MAS glasses is the presence of iron in two oxidation states, 2+ and 3+ [9–14]. Corresponding redox changes of iron cations in solid glasses [14,16,17] revealed a strong impact of working conditions (temperature, oxygen partial pressure) on the phase composition and on various physico-chemical properties. However, the prospects of using these results to assess the redox processes in melts during pyroelectrolysis are doubtful. Previous studies made by Ferreira et al. have demonstrated that the Laser Floating Zone (LFZ) method is a powerful processing tool for studying crystallization/vitrification mechanisms in silicate-based glasses and tuning the states of the redox-active cations [14]. The LFZ method also allows one to overcome the inherent experimental difficulties provided by harsh environments, in particular, to avoid uncertainties arising from high-temperature interaction with crucibles or other materials, since LFZ allows conditions for a self-supported molten zone. The above mentioned work [14] has shown that the crystallization process in MAS-based glasses, accompanied with separation of mullite- and cordierite-type phases, is significantly affected by the formation of nano-sized Fe-containing clusters.

In the present work, the Fe-containing MAS fibres were grown at high pulling rate providing strongly non-equilibrium conditions to prevent crystallization, and to retain the high temperature frozen-in structure of the glass electrolyte, characteristic of the pyroelectrolysis process. The iron oxidation state and local environments in the glass structure were assessed by Raman, Mössbauer and EPR spectroscopies, and by magnetization measurements.

2. Experimental procedure

Powder mixtures of MgO (Merck, +99%), Al_2O_3 (Merck, 99.5%), SiO_2 (Sigma Aldrich, 99.6%) and Fe_2O_3 (Aldrich, +99%) were prepared in the required proportions to obtain samples with nominal compositions $(100-x)$ $(Mg_{0.203}Al_{0.374}Si_{0.423}O_{1.61})$ xFe, with $x=0$, 2, 4 and 8 (mol%). A binder (PVA-Polyvinyl alcohol) was then added to the powder mixture to allow extrusion of the precursor mixture in the form of rods. These rods were used as feed and seed in the LFZ method, equipped with a continuous CO_2 Spectron SLC laser ($\lambda=10.6$ μm; 200 W) to grow dense fibres [14]. A growth rate of 200 mm/h was used to provide faster cooling. During pulling of the fibres, the seed and feed rod precursors were rotated in opposite directions to enhance the homogeneity of the target fibres.

To confirm glass/amorphous structure of the as-grown fibres, the powdered samples were characterized at room temperature by X-ray diffraction (XRD) analysis, using a Rigaku D/Max-B diffractometer system (Cu Kα, $2\theta=10$–80°, step 0.02°,exposition 2 s). Characteristic element vibrations in the samples was examined by Raman spectra through a Horiba, Jobin Yvon HR 800 UV to cross section samples at room temperature in backscattering configuration, using the 532 nm exciting line, from 100 to 1600 cm^{-1}.

A conventional constant-acceleration spectrometer and a 25 mCi ^{57}Co source in a Rh matrix were used for obtaining Mössbauer spectra at room temperature and at 4 K in transmission mode. The spectra were fitted to Lorentzian lines using a non-linear least-squares method [18]. Distributions of quadrupole splittings were fitted according to the histogram method. Further experimental details are described elsewhere [14]. Alternatively, the coordination and local environments of the iron cations in the samples were analysed by EPR spectroscopy at room temperature, using a Bruker model ESP300 E spectrometer, operating with X-band EPR spectra (9.78 GHz).

Complementary DC magnetic measurements were performed on bulk fibre samples (50–100 mg) using a vibrating sample magnetometer (VSM, Cryogenic – Cryofree). The DC magnetization was recorded on field-cooled (FC) under 0.1 T, between 5 and 300 K. Typical hysteresis curves were obtained at 5 and 300 K, for all samples in magnetic field up to 10 T in a vertical position. One also attempted to assess the impact of the iron concentration on MAS glass structure by prevailing effect on the electrical conductivity of the fibres, measured at room temperature at 100 kHz, using an Agilent 4292A Precision Impedance Analyser. To provide an appropriate electrical connection, both ends of the fibre were covered with silver paste.

3. Results and discussion

Pure and Fe-containing MAS fibres, grown by LFZ, are optically transparent and amorphous, as confirmed by XRD analysis. No crystalline phases were detected, in opposition to the fibres of similar chemical composition, pulled at lower rates [14]. The XRD patterns (Fig. 1A) show a broad hump, typical for glassy phases [19], confirming the flexibility of the LFZ method for studying crystallization/vitrification mechanisms, by controlling the nucleation process for various cooling rates.

The results of Raman spectroscopy (Fig. 1B) also confirm the amorphous nature of the as-prepared fibres, by the absence of sharp peaks, characteristic of crystalline phases formation in MAS system [14]. The shoulders at ~500 and 1000 cm^{-1} can be attributed to Si–O bond stretching and bending in SiO_4 tetrahedra [20–22]. The shift of the broadband at ~1000 cm^{-1} gives preliminary indications regarding the iron effect on the glass network, with emphasis on the formation of non-bridging oxygen upon increasing the iron concentration. In fact, 862, 906, 972 and 1056 cm^{-1} bands correspond to symmetric silicon–oxygen stretching vibrations of SiO_4 tetrahedra with respectively four, three, two and one non-bridging oxygen atoms ([20] and references therein), contributing to the shape and position of the broad ~1000 cm^{-1} peak, observed in the present work. Since Fe^{2+} cations are rather network modifiers, while Fe^{3+} can act both as network modifier and network former ([23] and references therein), an increase in iron concentration should result in the appearance of new oxygen non-bridging atoms. At the same time, the effects of Fe^{2+} on the glass structure are expected to be similar to those of Mg^{2+}, considering the similarities in ionic radii and metal–oxygen bond lengths [16]. Thus, basically the observed changes are the results of shifting the ratio between silicon and other metal