Journal of Non-Crystalline Solids 500 (2018) 417–421

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

The effect of alkaline-earth substitution on the Li K-edge of lithium silicate glasses

Cedrick O'Shaughnessy[a,*], Grant S. Henderson[a], Benjamin J.A. Moulton[a,b], Lucia Zuin[c], Daniel R. Neuville[d]

[a] Department of Earth Sciences, University of Toronto, Canada
[b] Departamento de Física, Universidade Federal de São Carlos, Brazil
[c] Canadian Light Source Inc, 44 Innovation Boulevard, Saskatoo, Canada
[d] Laboratoire des Géomatériaux, CNRS-Institut de Physique du Globe de Paris, France

ARTICLE INFO

Keywords:
XANES
Silicates
Glasses
Lithium
Alkaline-earth

ABSTRACT

We present the first Li *K*-edge XANES study of a varied suite of lithium silicate (LS) and lithium alkaline-earth silicate (LMS) glasses. The LS series contains three glasses with compositions LS4 (20 Li_2O–80 SiO_2), LS2 (33 Li_2O–67 SiO_2) and LS1.5 (40 Li_2O–60 SiO_2) and the LMS series is comprised of four glasses of compositions 20 Li_2O–20 M_2O–60 SiO_2 where M = Mg, Ca, Sr and Ba. The spectra were compared to those of known salts and minerals, particularly to lithium metasilicate (Li_2SiO_3) and lithium carbonate (Li_2CO_3). Crystalline lithium metasilicate has a sharp, strong intensity absorption edge whereas the lithium silicate glasses all have a weak intensity edge feature, similar to that of lithium carbonate (Li_2CO_3). The intensity of the edge is governed by the existence of a 2*p* electron and can be correlated with the ionicity of the Li—O bond. Therefore, the bonding environment in LS glasses differs considerably from their crystalline counterparts. The area of the absorption edge peak increases with the lithium content of the LS glasses. As for the LMS glasses the edge peak changes drastically depending on the alkaline-earth present. The peak area of the LMS glasses decreases with increasing charge density (Z/r^2) from barium to magnesium. The area of the absorption edge peak in the LS glasses is larger than that of the LMS glasses. Thus, the addition of alkaline-earth elements to lithium silicate glasses modifies the glass network differently depending on the specific element, which in turn creates an altered lithium bonding environment as evidenced by their Li *K*-edge XANES spectra.

1. Introduction

Lithium is a very important element in the cycling of volatiles in magmatic settings and can be strongly isotopically fractionated in both silicic differentiates and the resulting gas condensates [1]. The structure of lithium silicate glasses has been studied for many years because both lithium metasilicate and disilicate glasses are exceptional examples of homogeneous nucleation [2, 3, 4–6]. Homogeneous nucleation is preferred to heterogeneous nucleation when attempting to control physical properties of glass ceramics for industrial purposes due to a more uniform distribution of crystals [6]. Heat-resistant ceramics are typically multicomponent systems which include both Li_2O and MgO in significant quantities (~10 wt%) [7,8]. Similarly, a class of phosphate-bearing glass-ceramics containing lithium disilicate as the main crystalline phase has been established as a biomaterial in dental applications [9]. Additionally, lithium-bearing silicate glasses are an important component in a variety of industrial applications: nuclear waste glasses [10] and in ion-conducting glasses [11,12] which contain a minimum of 3.5 wt% Li_2O.

Lithium is a difficult element to probe as it is nearly invisible to X-ray diffraction (XRD). Therefore, element-specific probes, such as, X-ray absorption near-edge structure (XANES) spectroscopy are an excellent tool to determine the bonding environment of elements in amorphous materials [13]. Many Li *K*-edge XANES spectroscopy studies have been performed on a variety of Li-bearing compounds including battery components, salts and minerals [14–18]. Additionally, some of these materials have also been probed using X-ray Raman Spectroscopy and their spectra reveal similar features for the Li *K*-edge [19,20].

In this study, we probed the Li *K*-edge of seven (7) glasses and two standard compounds in order to assess structural changes in the glasses. The two series (lithium silicate and lithium alkaline-earth silicate) enable us to explore the effect of lithium content and alkaline-earth

* Corresponding author.
E-mail address: c.oshaughnessy@mail.utoronto.ca (C. O'Shaughnessy).

https://doi.org/10.1016/j.jnoncrysol.2018.08.028
Received 5 July 2018; Received in revised form 15 August 2018; Accepted 23 August 2018
Available online 12 September 2018

substitution on the lithium-bearing silicate glasses.

2. Methods

2.1. Glass synthesis

A variety of lithium silicate (LS4 (20 Li_2O–80 SiO_2), LS2 (33 Li_2O–67 SiO_2) and LS1.5 (40 Li_2O–60 SiO_2)) and lithium alkaline-earth silicate (20 Li_2O–20 M_2O–60 SiO_2 named LiM where M = Mg, Ca, Sr and Ba) were synthesized using a melt-quench technique. The samples were prepared by combining the stoichiometric amounts of Li_2CO_3, MCO_3 and SiO_2 to make approximately 100 g batches. The mixtures were then calcined at 900 °C for 24 h to remove the CO_2. The mixtures were placed in Pt crucibles and heated to 200 °C above their respective melting temperatures for 1 h and were then quenched by placing the bottom of the crucible in water. Following the first quench, samples were then mechanically crushed in a mortar and pestle and a second melt-quench cycle was performed. All samples were stored in a desiccator or 100 °C furnace to avoid interaction with atmospheric H_2O. The glass samples were analyzed using the electron microprobe at IPGP with a Camebax SX50. The lithium content was calculated using the difference method and the abundances are reported in wt% in Table 1. The densities of the LS glasses were measured using a Berman density balance and their values are consistent with previously published data [21,22]. Additionally, all samples were analyzed using Raman spectroscopy to verify that the samples had not undergone crystallization. Two crystalline standards were used to compare to the glasses, lithium metasilicate crystal and lithium carbonate. The spectra of these standards are described in detail in O'Shaughnessy et al. [15]. The lithium metasilicate crystal was synthesized by recrystallizing a lithium silicate glass sample prepared as outlined above, whereas the lithium carbonate was a high purity powder (> 99%).

2.2. X-ray Absorption Near-Edge Structure (XANES) Spectroscopy

We performed the Li *K*-edge (54.7 eV) XANES measurements at the Canadian Light Source Inc. (CLS), Saskatoon, Canada using the variable line spacing-plane grating monochromator (VLS-PGM) beamline [23,24]. The spectra were collected in fluorescence yield (FLY) due to its sampling of a large volume of space which renders it more sensitive to the bulk of the sample compared to the total electron yield (TEY) [13,15,17,25,26]. The microchannel plate detector is mounted at 90° to the incident beam with the sample at 45° to the incident beam which negates self-absorption effects [27]. The beamline slits were opened to 50 mm × 50 mm with a resolution E/ΔE > 10,000 and the pressure in the experimental chamber was maintained below 10^{-7} torr for all measurements [17]. The spectra were collected in the range of 35–75 eV. The fluorescence signal was normalized to the incoming intensity (I_0), measured by a Ni mesh located upstream of the sample chamber. A two-step polynomial background correction was performed on the pre-edge region (~ 35–58 eV) and post-edge region (~ 65–75 eV) and the spectra were normalized to their maximum intensity (as in [15]). All edge positions are calculated by using the maximum intensity of a specific peak and are reported as such in eV with an error of ± 0.05 eV (Fig. 2). In order to compare the values of the edge positions in our samples to those of previously published data we calibrated the value of the main absorption edge of LiCl by shifting its value to 60.8 eV as reported in the experiments of Tsuji et al. [16] following the procedure of Wang and Zuin [17] and O'Shaughnessy et al. [15]. The data presented in this paper was collected during the same beamtime as LiCl and the spectra were shifted accordingly. Additionally, the peak positions for lithium metasilicate and lithium carbonate are also taken from O'Shaughnessy et al. [15] to compare to the values of the lithium glass samples. The peaks have been labeled by their relative positions and not by the specific electronic interaction as in O'Shaughnessy et al. [15]. The spectra of the previously studied minerals show many features which were labeled and these labels have been used for the spectra of the glass samples in this study O'Shaughnessy et al. [15]. The spectra of reference standards are in agreement with previous XANES studies [14,16,17]. In order to determine the area of the absorption edge peak (peak A, in the glass samples) the spectra were area normalized and two hinge-points were determined (using positions obtained from the first derivative) to calculate the area underneath the spectra (as graphically depicted in Fig. 1).

Table 1
Electron microprobe analysis of lithium-bearing glasses.

Sample	SiO_2	Li_2O	MgO	CaO	SrO	BaO
LS1.5	75.17 (6)[a]	24.83	–	–	–	–
LS2	79.97 (9)	20.03	–	–	–	–
LS4	88.99 (7)	11.01	–	–	–	–
LiMg	71.97 (5)	11.93	16.13 (7)			
LiCa	67.73 (9)	11.21	–	21.13 (5)		
LiSr	57.45	9.52	–	–	32.98 (8)	
LiBa	49.63 (7)	8.22	–	–	–	42.23 (7)

[a] The abundances are reported in wt% and the standard deviation is in parentheses.

3. Results

3.1. Lithium silicate glasses (LS)

The lithium silicate glasses display almost identical spectra with small differences in peak positions and relative intensities (Fig. 2 and Table 2). The spectra have three main features peaks A, C and G. Peak A is similar to peak p in Li_2CO_3 which has been described in previous studies [14,16]. The positions of peak A (~60 eV) for the lithium silicate glass samples are listed in Table 2 and its position shows no compositional variation. The position of peak A in lithium metasilicate is located at higher energy than for the equivalent peak in the glasses. The highest intensity peak in all three glass samples is peak C located at ~63 eV (Table 2). Finally, peak G is located at ~67 eV (for the LS glasses) and is almost identical in shape, position and intensity in all three samples (Fig. 2 and Table 2).

3.2. Lithium alkaline-earth silicate glasses (LMS)

The LMS glasses also have three main features but their shape and positions show a large amount of variability depending upon the

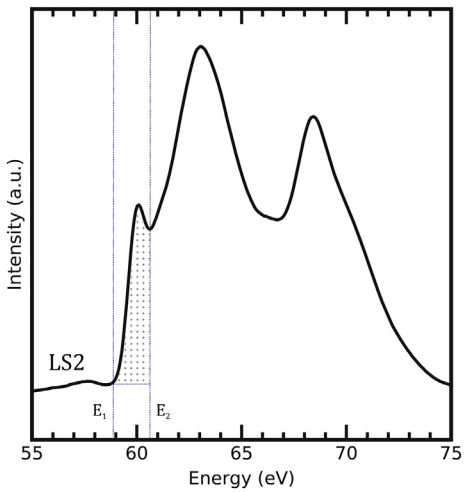

Fig. 1. Graphical depiction of the area calculation of the main peak of the lithium glasses using two hinge-points and a trapezoidal method.