Ca neighbors from XANES spectroscopy: A tool to investigate structure, redox, and nucleation processes in silicate glasses, melts, and crystals

MARI A RITA CICCONI1,* , DOMINIQUE DE LIGNY1, TAMires M. GALLO2, AND DANIEL R. NEUVILLE3

1Departm ent Werkstoffwissenschaften, Lehrstuhl für Glas und Keramik, Universität Erlangen-Nürnberg, Martensstrasse 5, D-91058 Erlangen, Germany
2CNPEM/LNLS, Brazilian Synchrotron Light Laboratory, Campinas, São Paulo 13083-100, Brazil
3Institut de Physique du Globe de Paris, CNRS, Géomatériaux, Sorbonne Paris Cité, 1, rue Jussieu, F-75238 Paris, France

ABSTRACT

In this study, Ca K-edge X-ray absorption spectroscopy (XAS) has been employed to study the Ca structural role in a set of silicate glasses. For the first time the accurate analysis of the Ca pre-edge peak has been performed, providing information about the different Ca local environments, and on its structural role.

This approach was tested on Ca-aluminosilicate glasses (CAS system) with constant SiO2 content (50 and 76 mol%), ranging from percalcic to peraluminous domains. In alkali-earth aluminosilicate glasses Al and Si are network formers in a large range of compositions, whereas calcium should act either as network modifier and charge compensator. The results obtained show a different Ca behavior as a function of Al content, which in turn is related to the Al local environment. For example, we observe changes in the pre-edge peak centroid energies depending on the changes in the role of Ca as a network modifier (Al = 0 mol%) to charge compensator (aluminosilicate join) to a more complex role in the peraluminous domain, depending on the fraction of \( [4][5][6] \)Al. This approach was further applied to study Fe-bearing glasses and a diopside (CaMgSi2O6) composition at different temperatures. It was possible to correlate the variations occurring in the Ca pre-edge peak centroid positions with both redox state and crystal nucleation mechanism.

Keywords: Calcium, XAS, glass structure, redox, nucleation

INTRODUCTION

Calcium is a very important element in Earth and materials sciences. It can be found in all natural processes, i.e., mechanisms of sedimentation, magmatic processes, redox mechanisms, nucleation, and growth crystallization mechanisms (Magnien et al. 2008; Neuville et al. 2008, 2014) and that implies that calcium plays a key role in the formation of materials. The structure of calcium aluminosilicate glasses is of great interest for technological or geological applications. These glasses are attractive materials due to their highly refractory nature and their excellent optical and mechanical properties (Lines et al. 1989; Wallenberger and Brown 1994). They can also be considered as frozen approximations of melts, for which a detailed knowledge of the structure is needed to better constrain the modeling of magmatic processes. The phase diagram CaO-Al2O3-SiO2 (CAS) investigated for the first time by Rankin (1915) is very important for glasses, glass-ceramics, ceramics, concrete, and Earth sciences. In the CAS system Ca can play different roles as a function of the Al2O3 content. Ca can act as network modifier (NM) or as charge compensator (CC) depending upon what role Al plays in the glass. The CAS system is remarkable because glasses from pure SiO2 to calcium aluminate can be synthesized using normal quench rates (10°/s), contrary to alkali or Mg aluminosilicate glasses (Neuville et al. 2008). Moreover, recently Hehlen and Neuville (2015) have demonstrated a change in the role of Ca as a function of chemical composition by investigating changes in the VV/VH Raman signature. Here we investigate the Ca environment using X-ray absorption spectroscopy at the Ca K-edge (4038.5 eV).

EXPERIMENTAL METHODS

Ca K-edge X-ray absorption near edge structure (XANES) spectra were obtained at the soft X-rays spectroscopy (SXS) beamline at the Brazilian Synchrotron Light Laboratory, LNLS (electron energy of the storage ring is 1.37 GeV). The SXS beamline equipped with a Si(111) monochromator (the spectral resolution \( \Delta E \)) had a focused beam of 2.5 mm² spot size, and the spectra were recorded in total electron yield (TEY) detection mode, with the sample compartment pressure at 10⁻⁸ mbar. Measurements were done with sample surfaces normal to the beam. The pre-edge peak region was scanned in 0.1 eV (±0.015) steps, whereas the edge region was scanned in 0.25 ev (±0.03) energy steps, and the energies were calibrated using a Ti foil. XANES spectra were reduced by background subtraction with a linear function and then normalized for atomic X-ray sensitivity using the average absorption coefficient of the spectral region from 4100 to 4300 eV. The threshold energy was taken as the first maximum of the first derivative of the spectra, whereas the main peak positions were obtained by calculating the second derivative of the spectra. In addition to the position of the main edge, particular attention has been given to the analysis of the pre-edge peak. This small feature is attributed to the transition of the Ca 1s electron to the unoccupied Ca 3d⁰ 2p hybridized states. The intensity of the components of the pre-edge peak is thus related both to quadrupole transitions and to the p-like components of the \( e_g \) orbitals (Bianconi et al. 1978; de Lazaro et al. 2007). XANES normalization and pre-edge extraction have been carried out following previous work made on iron by Cicconi et al. (2015 and references therein). After the background subtraction the pre-edge peaks have been fitted by a sum of pseudo-Voigt (pV) functions. The centroid position of the pre-edge peak represents the energy position of the deconvoluted components weighted by their integrated area.