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

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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 different 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 [\text{Al}_4\text{Si}_3\text{O}_{10}]^{2-}. 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(311) monochromator (the spectral resolution ΔE is ~0.65 eV) 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 10⁻⁴ 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 absorption on 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).