Environments around Al, Si, and Ca in aluminate and aluminosilicate melts by X-ray absorption spectroscopy at high temperature

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Abstract

Structural data on silicate, alumininate, and aluminosilicate melts are difficult to measure and understand at high temperature. X-ray absorption spectroscopy (XAS) performed in situ at high temperature has been used to probe the local environment of low-Z elements (Al, Si, and Ca). For fully tetrahedral network glasses, CaAl2Si4O10 (anorthite) and CaAl4O6, the modifications in the Al K-edge spectra with increasing temperature can be attributed to a structural rearrangement of the network or to an increase of fivefold-coordinated Al. For the Ca3Al2O6 composition, where Al is localized in a depolymerized tetrahedral site associated with non-bridging O atoms, XAS spectra at the Al K-edge are barely affected by temperature. Depending on the composition, Ca K-edge spectra investigated in these experiments allow us to follow changes in the distortion of the Ca sites in melts at high temperature. The structural modifications at both short and intermediate range upon melting are well shown by these XAS measurements.

Keywords: Melts, silicate, glasses, EXAFS

Introduction

Silicate, alumininate, and aluminosilicate melts are of great geological and industrial importance, as main components of glasses, ceramics, and various refractory oxides. However, the high-temperature structure of these materials is still not well established because in situ characterization is a technically challenging task. Therefore, structural information on liquids are often derived by extrapolation of the glass structure determined at room temperature, using Raman, NMR, or X-ray absorption spectroscopies, and X-ray or neutron diffraction (Mysen and Richet 2005). An important issue is thus to assess the nature of the structural modification between the glass and the liquid.

It is well known that silica glass (SiO2) is a random continuous network of corner-sharing SiO4 tetrahedra. At the vertex of each tetrahedron, an O atom (known as a bridging oxygen, BO) is involved in two Si-O bonds. As Si is partially replaced by another network former such as Al, a modifier cation (Ca2+, Mg2+, or Na+ for example) must be introduced to balance the negative charge of the (AlO4)n tetrahedra. An excess of charge-modifier oxide vs. Al2O3 oxide induces the formation of non-bridging O atoms (NBOs), which are shared between a TO4 (T = Si, Al) unit and the modifier polyhedra. Therefore, knowledge of the Al, Si, and Ca polyhedra gives a good idea of the short-range order (SRO) of the glass structure. Information at intermediate-range order (IRO) concerning the polymerization of the aluminosilicate network can also be obtained using vibrational spectroscopies (Mysen and Richet 2005).

X-ray absorption spectroscopy (XAS) is a powerful tool that was used to investigate the environment around transition elements (Ca, Mg, and Na) in glasses (Greaves et al. 1981; Ildefonse et al. 1998; Andrault et al. 1998; Neuville et al. 2003, 2004a). Advances in X-ray focusing optics and insertion devices give access to XAS spectra of light elements in different experimental conditions such as high pressure and high temperature, on the new LUCIA beamline installed at the Swiss Light Synchrotron (SLS) (Flank et al. 2006). We adapted on this beamline a homemade micro furnace in Pt-Ir10% or in Ir, developed following the design proposed by Mysen and Frantz (1992) and Richet et al. (1993), and previously used in XAS spectra of transition elements (Magnien et al. 2004, 2006). With this set-up, it is possible to measure XAS spectra of low-Z elements such as Ca, Al, and Si at high temperature on crystals, glasses, and liquids.

This study focuses on the CaO-MgO-Al2O3-SiO2 (CMAS) system, and more particularly on some important minerals found in mafic magmas, diopside (CaMgSi2O6) and anorthite (CaAl2Si2O8). To complete and understand well the role of Al in aluminosilicate melts, we have also investigated two compositions on the CaO-Al2O3 join: CaAl2O4 (CA) and Ca2Al2O6 (C3A) where Al is in tetrahedral sites, with 4 and 2 BO atoms, respectively, Q4 and Q2 (Neuville et al. 2004a), where Q4 means tetrahedral sites with n BO atoms and 4 – n NBO atoms. The CAS