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X-ray Raman scattering: An exciting tool for the study of matter at conditions of the Earth's interior

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Abstract. The study of minerals and melts at in situ conditions is highly relevant to understand the physical and chemical properties of the Earth's crust and mantle. Here, x-ray Raman scattering provides a valuable tool to investigate the local atomic and electronic structure of Earth materials consisting predominantly of low Z elements at high pressures and temperatures. The capabilities of x-ray Raman scattering to investigate silicate minerals, glasses, and melts are discussed and the application of the method to in situ studies of silicate melts using a hydrothermal diamond anvil cell is demonstrated.

1. Introduction

Our knowledge of the chemical composition and processes of the inner Earth has significantly improved due to in situ experiments using resistive or laser heated diamond anvil cells (DACs). To deeper understand the local structure of amorphous materials, liquids, and melts of geological relevance absorption spectroscopy is widely used. However, the most abundant elements in the Earth's crust and mantle are low Z elements such as O, Na, Mg, Al, and Si with absorption edges in the soft x-ray regime, i.e. below 2 keV. Thus, using a strongly absorbing sample environment such as a DAC hinders the application of electron energy loss or soft x-ray absorption spectroscopy (sXAS) for in situ investigations. Here, non resonant x-ray Raman scattering (XRS) [1], an energy loss spectroscopy utilizing hard x-rays as a bulk sensitive probe, opens an exciting perspective to conduct in situ studies of low and intermediate Z elements at extreme conditions to obtain similar information compared to sXAS. For example, XRS studies of the Si L-edge of silica polymorphs at ambient conditions and silica glass compressed up to 74 GPa [2] or measurements of the O K-edge in MgSiO₃ glass up to 39 GPa [3] have shown the enormous potential of the XRS method for application in geoscience.

One of the heavily discussed questions concerning the structure and chemistry of silicate melts is the dissolution of H₂O, which significantly influences its viscosity, density and thermal conductivity [4]. Of particular interest is the impact of incorporated H₂O on the degree of polymerization of such melts. So far, the local coordination of low Z elements in glasses and minerals has been studied by sXAS using quenched samples as an alternative to melts. Measurements of e.g. Si, Al, and Na K-edges were performed typically employing crystalline

reference samples for fingerprinting [5, 6]. Hitherto, in situ high pressure x-ray absorption experiments on hydrous melts were performed on samples that contained heavier elements such as iron [7]. It would be highly desirable to extend such experiments to in situ studies of low Z elements giving access to changes in local structure of the main components of silicate melts.

In this paper we prove the capabilities of the XRS technique to address exactly these problems. We present investigations on two geologically relevant model compositions, NS3 ($\text{Na}_2\text{Si}_3\text{O}_7$) and albite ($\text{NaAlSi}_3\text{O}_8$). The sensitivity of XRS to changes in the local chemical environment is discussed using measurements at the Si L- and Na K-edge and the feasibility of in situ investigations of silicate melts is demonstrated.

2. Experiment

Glasses were synthesized by melting of mixtures of oxides and carbonate. The anhydrous albite glass was annealed at 1600°C for 4 days. To enhance homogenization the melt was quenched after 2 days, crushed and re-annealed. The NS3 glass was annealed at 1300°C for 3 hours. For crystalline albite, a sample from Minas-Gerais, Brazil, was taken. All samples were measured at ambient conditions. For the in situ experiment NS3 glass was loaded together with H_2O into a hydrothermal DAC[7] using a rhenium gasket. The hydrothermal DAC was equipped with Boehler-Almax diamond anvils that provide a 70° opening angle. The temperature for the run with the hydrous NS3 melt was 600°C measured by thermocouples. The pressure was estimated to 230 MPa via the equation-of-state of H_2O and the fluid density determined from the vapor-liquid homogenization temperature. The experiments were performed at beamline ID16 of the ESRF using the multiple analyzer spectrometer for non resonant inelastic x-ray scattering [8]. The analyzer energy was set to 9.69 keV for measurements at ambient conditions of the Si L- and Na K-edge using the Si(660) reflection. In order to increase penetration depth in the highly absorbing sample environment the in situ measurements of the Si L-edge using a DAC were performed at 12.92 keV employing the Si(880) reflection. The incident energy was scanned to tune the energy loss in the vicinity of the corresponding absorption edges, i.e. 90 eV to 150 eV for Si and 1070 eV to 1100 eV for Na. An overall energy resolution of 1.5 eV and 2.4 eV at an average momentum transfer of $q = 9 \pm 0.2 \text{ \AA}^{-1}$ and $q = 12.1 \pm 0.2 \text{ \AA}^{-1}$ was obtained for the ex situ and in situ measurements, respectively. It has to be noted that at high momentum transfer not only dipole excitations contribute to the XRS spectra. Thus, for the Si L-edge also p to p and for the Na K-edge s to s, d transitions have significant spectral weight [9]. Spectra for 9 analysers were summed up, background corrected, and normalised to the integrated intensity between 100 and 130 eV (1070 eV and 1100 eV). Typical counting times were 8 hours for Si and 5 hours for Na spectra. A detailed description of the data analysis can be found in Ref. [10].

3. Results and discussion

XRS spectra of the Si L-edges of crystalline albite, albite and NS3 glass are presented in Fig. 1 (left). All spectra are characterized by a white line (A) at 108 eV energy loss, a peak structure (B) at the high energy loss tail of the white line at 115 eV, which broadens to a smooth shoulder in case of NS3, and a second broad maximum (C) at 128 eV. The general shape of the spectra is similar to the XRS spectra of crystalline SiO_2 polymorphs cristobalite and coesite, see Ref. [2]. However, there are small differences in the spectra as observed also by Farges et al. [6] for the Si K-edge. They investigated hydrous and anhydrous NS3 and albite glasses and found only subtle spectral changes suggesting small sensitivity of the Si L- and K-edges for changes in the Si-O and Si-Al-O network by H_2O incorporation. This situation changes if the influence of dissolved H_2O on the local environment of the Na cation is studied. Significant changes of the Na K-edge with increasing water content in the NS3 and albite glasses were observed [6]. Here, we demonstrate the high sensitivity of XRS spectra measured at the Na K-edge on the local coordination of Na cations in various silicate samples. The corresponding spectra are shown

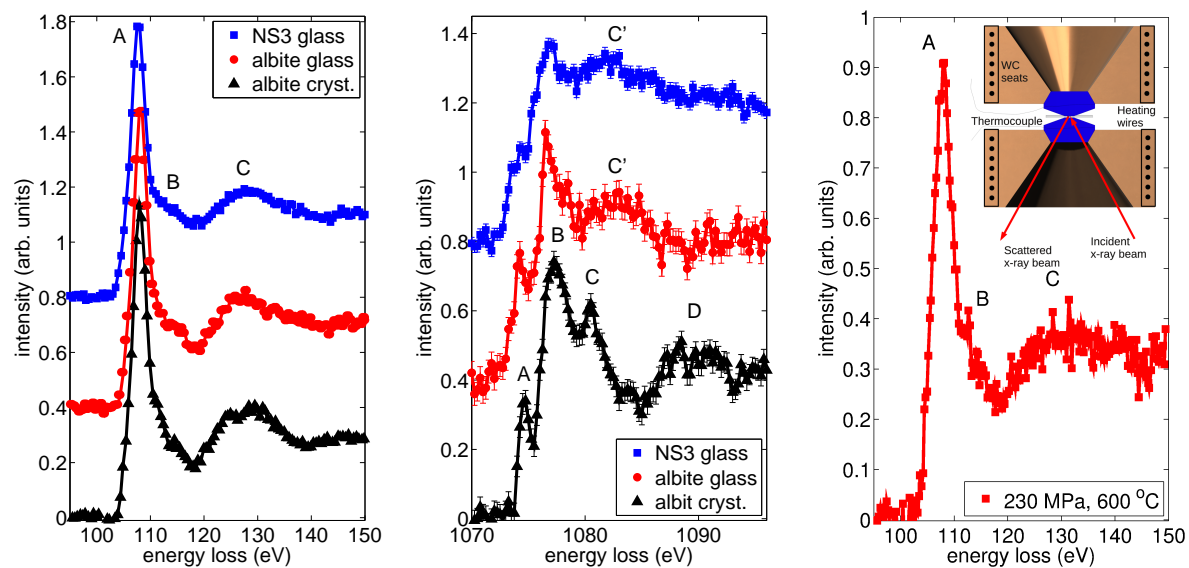


Figure 1. Left: XRS spectra measured at the Si L-edge for crystalline and glassy albite compared with results of NS3 glass. Center: XRS spectra measured at the Na K-edge for crystalline and glassy albite compared with results of NS3 glass. Right: XRS spectra measured at the Si L-edge for a hydrous NS3 melt (600°C, 230 MPa) at in situ conditions using a hydrothermal DAC as shown in the inset. The beam path through the sample and the diamond is indicated.

in Fig. 1 (center) and exhibit significant differences in shape. For crystalline albite a distinct three-peak structure is observed with prominent features A, B, and C at energy losses of 1074.6 eV, 1077.4 eV, and 1080.5 eV, respectively, followed by a broader maximum D at 1089 eV. There might be more details in this spectrum but assignment is difficult due to the statistical accuracy of the measurement (see error bars). These features are similar to those observed by Neuville et al. [5]. The intensity of Peak A is weak in sXAS measurements and related to dipole forbidden 1s to 3s transitions. This explains its strong intensity found in our spectra because of a significant contribution of non-dipole transitions in XRS for high momentum transfer. This might also affect the intensity ratio of features B and C, which is different than observed by sXAS. For the glasses the spectra show significant differences, i.e. peaks A, B shift to smaller and C to larger energy losses (denoted as C'). Features A and C' broaden whereas B sharpens. These changes are in accordance to earlier studies [5]. The broadening of spectral signatures and notably the disappearance of bump D (related to medium range order as can be inferred from FEFF calculations of Ref. [6]) are consistent with enhanced disorder in the glass. There are also considerable differences between the glass samples. All spectral features are smeared out for the partially depolymerized NS3 glass in comparison to the fully polymerized albite glass. The different intensities of peak A indicate differences in the Na coordination polyhedron. The results are in agreement with findings by Farges et al. [6] suggesting strong sensitivity of the XRS method on the local structure of Na in silicate melts. Glasses are considered to represent the melt structure close to glass transformation. However, several studies have shown that particularly the local structure may change during the cooling process even at high quench rates (e.g. Ref. [7]). Consequently, the effect of dissolved H₂O on the melt structure has to be studied at in situ conditions using a hydrothermal DAC.

The feasibility for in situ studies on hydrous silicate melt was tested using a hydrothermal DAC loaded with NS3 glass and H₂O, which formed a single-phase melt at run conditions. A

sketch of the hydrothermal DAC used in the experiment is presented in the inset of Fig. 1 (right). The x-ray beam path had to be chosen through the diamond because a highly absorbing rhenium gasket of 3 mm outer diameter and 0.125 mm height was used to enclose the melt. Although the incident and inelastically scattered x-rays had to penetrate overall 3.4 mm diamond a transmission of 30% is achieved for an x-ray energy of 12.92 keV. Such measurements are not possible with sXAS due to the very short absorption length of soft x-rays. The data collection for the spectrum of the Si L-edge of the melt took 8 hours. The obtained XRS spectrum is shown in Fig. 1 (right) and clearly emphasizes the feasibility of in situ studies of melts in a DAC using XRS. Despite the moderate quality of the result the general features (A-C) of the Si L-edge can be observed. However, much better statistics have to be aimed at to resolve the subtle changes in the spectra due to e.g. the dissolution of H₂O. Nevertheless, the experimental setup is by far not optimized yet. The size of the sample volume can be enhanced by drilling of a recess in the culet face of one anvil. For moderate pressures this recess may reach 0.1 mm in depth and 0.3 mm in diameter. This design would allow radial excitation of the sample and radial detection of the scattered radiation, and would reduce the length of the path through diamond. In situ XRS investigations focussing on the Na K-edge, which has shown much stronger spectral changes compared to the Si K-edge particularly with respect to dry and hydrous glasses [6], will provide a sensitive way to study the structural properties of hydrous melts.

Conclusion

XRS measurements of the Si L- and Na K-edge in crystalline albite, albite, and NS3 glass were performed. The Si L-edge spectra show only weak changes of spectral features, whereas the Na K-edge was found to be highly sensitive to the local environment of the Na atoms for a crystal and different glasses. Hence, the shape of the Na K-edge of the glasses allows to distinguish different degrees of polymerization and is a suitable probe for the influence of dissolved H₂O on the structure of hydrous glass. Moreover, we demonstrated the feasibility of in situ measurements on hydrous silicate melts using a hydrothermal DAC that shows the enormous potential of XRS for in situ studies of low *Z* element compounds at conditions of the Earth's interior.

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References

- [1] Schülke 2007 *Electron Dynamics by Inelastic X-ray Scattering* (Oxford University Press)
- [2] Fukui H, Kanzaki M, Hiraoka N, Cai YQ 2009 *Phys. Chem. Minerals* **36**, 171; Fukui H, Kanzaki M, Hiraoka N, Cai YQ 2008 *Phys. Rev. B* **78**, 012203
- [3] Lee SK, Lin J-F, Cai YQ, Hiraoka N, Eng PJ, Okuchi T, Mao H-K, Meng Y, Hu MY, Chow P, Shu J, Li B, Fukui H, Lee BH, Kim HN, Yoo C-S 2008 *PNAS* **105**, 7925
- [4] Mysen BO, Richet P 2005 *Silicate glasses and melts* (Elsevier)
- [5] Neuville DR, Cormier L, Flank A-M, Prado RJ, Lagarde P 2004 *Eur. J. Mineral.* **16**, 809; De Wispeleare S, Cabaret D, Levelut C, Rossano S, Flank A-M, Parent P, Farges F 2004 *Chem. Geol.* **213**, 63
- [6] Farges F, De Wispeleare S, Rossano S, Munos M, Wilke M, Flank A-M, Lagarde P 2007 *AIP Conf. Proc.* **882**, 214
- [7] Wilke M, Schmidt C, Farges F, Malavergne V, Gautron L, Simionovici A, Hahn M, Petit P-E 2006 *Chem. Geol.* **229**, 144
- [8] Verbeni R, Pylkkänen T, Huotari S, Simonelli L, Vanko G, Martel K, Henriquet C, Monaco G 2009 *J. Synchrotron Rad.* **16**, 469
- [9] Sternemann C, Soininen JA, Huotari S, Vanko G, Volmer M, Secco RA, Tse JS, Tolan M 2005 *Phys. Rev. B* **72**, 035104
- [10] Sternemann H, Sternemann C, Seidler GT, Fister TT, Sakko A, Tolan M 2008 *J. Synchrotron Rad.* **15**, 162