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Silica polymorphs, glass and melt: An *in situ* high temperature XAS study at the Si K-edge

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ABSTRACT

High temperature X-ray absorption spectra at the Si K-edge were obtained for SiO_2 quartz from room temperature up to 2030 K. Important modifications are observed for the XANES spectra. These change are related to rearrangements of the SiO_4 tetrahedra beyond the short-range correlations. To interpret these spectral evolutions, SiO_2 polymorph samples were observed at room temperature and XANES calculations using FDMNES were performed. Very strong differences are shown between the different polymorphs even between α and β phases for which only small displacive angle rotations of the SiO_4 tetrahadra occurs. Therefore the quartz α to β transition could be identified at its expected temperature, 842 K. A badly defined transition toward β-cristobalite is observed between 1670 and 1940 K. The dynamics of this totally reconstructive transition was further investigated on heat treated cherts. Finally the liquid is reached around 2000 K. Many similarities were observed on SiO_2 between its glass at room temperature, β-cristobalite and liquid at high temperature.

1. Introduction

Silica polymorphs are one of the major component for Material and Earth Sciences. Even if it is a very simple system, its properties and structures can be very complex as a function of temperature and pressure. Silica, SiO_2, exists in many different phases at ambient pressure and temperature, α-quartz, tridymite, α-cristobalite, glass. All these structures are networks of corner-sharing SiO_4 tetrahedra but the structure and nature of the disorder in the high-temperature forms is still controversial [1,2]. At 847 K α-quartz evolves to β-quartz through a displacive phase transition [3]. Then prior to melting at 2000 K, β-quartz should convert to tridymite at 1140 K and then to β-cristobalite at 1743 K [4]. However due to the reconstructive nature of these two last transitions and their sluggish kinetics, only the direct transformation from β-quartz to β-cristobalite is sometime observed and its temperature estimated around 1110 K from thermodynamic calculations [5].

Si K-edge XANES spectra, from 1840 to 1900 eV, are sensitive to both the local and medium-range order around the absorbing atom, and could add constraints on the transitions mechanism and dynamics if recorded at high temperature. Recently, new developments of heating wire furnace were associated with light element X-ray absorption synchrotron beamline [6]. Using Ir heaters, temperatures from room temperature up to 2600 K can be easily obtained. Therefore α-quartz was heated up to 2030 K and the polymorphic transformations and liquid can be observed *in situ* using XANES spectroscopy at the Si K-edge.

However, Si K-edge XANES spectra are not straight forward to be interpreted. The many features present in the spectra after the absorption edge cannot be assigned to a specific atomic structure. Analogies to already known structures or calculations are needed. Therefore XANES spectra were obtained at room temperature for all the well-known polymorphs, α-quartz, tridymite, α-cristobalite,

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glass. Calculations were performed on α- and β-cristobalite, and β-quartz using their well known structures obtained from X-ray diffraction [4].

XANES spectroscopy is an excellent probe to understand the neighbors of each specific element and is especially suited to investigating disordered materials, glasses and melts [6,7] for which classical diffraction techniques are less efficient. Furthermore, comparison of these silica polymorphs with amorphous and molten silica will allow a better understanding of the local order present in the liquid and frozen into the glass.

Special attention was given to the quartz to cristobalite transition. This transition is differently observed or not at various temperatures [5,8,9]. Recently the existence of β-cristobalite nuclei has been reported around 1270 K by Brillouin spectroscopy [10]. Therefore at this *in situ* measurement was added the study of Israelian heat treated cherts sedimentary rocks of badly crystallized α-quartz for which the quartz to cristobalite transition is known to take place at low temperature too [11].

2. Experiments

SiO_2 polymorph samples are natural samples provided by J.C. Bouillard, curator of the Collection of Mineralogy of the University of Paris 6.

Spectra were recorded in fluorescence mode using a silicon drift diode detector protected by a beryllium cap, on the LUCIA beamline at SLS [12]. We used KTP(1 1 0) crystals as monochromator. Energy calibration was performed using the Al K-edge spectrum of Anorthite [6]. The heating wire setup has been described elsewhere and was adapted to the vacuum chamber of the LUCIA beamline [6]. Temperatures were measured with an optical pyrometer [6]. The sample was held at each temperature around 3 h. The beam size was 20 × 20 μm and the total sample diameter was 200 μm. XANES spectra were normalized using the Athena software [13]. Due to the high concentration of Si in the samples, a self-absorption correction was introduced. However, the self absorption correction was not always satisfactorily leading to an unrealistic intensity of the first sharp absorption peak, noted A on the figures, especially at high temperature, preventing possible comments on its intensity.

XANES calculations were performed using the FDMNES (Finite Difference Method Near-Edge Simulation) software provided by Joly [14]. The cell parameters and atomic position used in the input were taken from classical X-ray diffraction studies [4]. The calculation is based on the finite-difference method. It allows a completely free potential shape and, in particular, is not constrained to the muffin-tin approximation. The Schrödinger equation is solved in real space and in a discrete form on the node points of a three-dimensional grid based on an atomic cluster. As in most XANES calculations, the atoms are taken as neutral with orbital bases corresponding to neutral atoms. The Coulomb potential is calculated solving the Poisson equation and the energy dependent exchange-correlation potential is obtained following the Hedin and Lundqvist approach [15]. FDMNES software was used in its default status. The only input data used in this study were the atomic positions. No further normalization on the intensity was ever done on the output spectra.

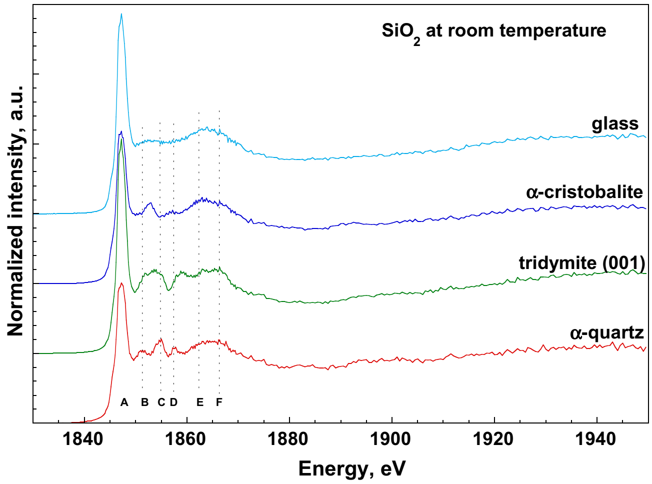

Fig. 1. XANES spectra at the Si K-edge at room temperature for SiO_2 polymorph.

3. Results

In Fig. 1 are reported all the spectra obtained at room temperature on the different well known silica polymorphs. All the spectra were recorded on fine powders with the exception of the tridymite which was oriented parallel to the *c*-axis. Many change are observed between 1840 and 1880 eV. The main resonance, *A*, on the absorption edge at 1847.1 eV does not change between the polymorphs. It is at higher energy between 1850 and 1880 eV that strong modifications are observed. The different features were label from *A* to *F* for α-quartz (see Fig. 1). This convention and their

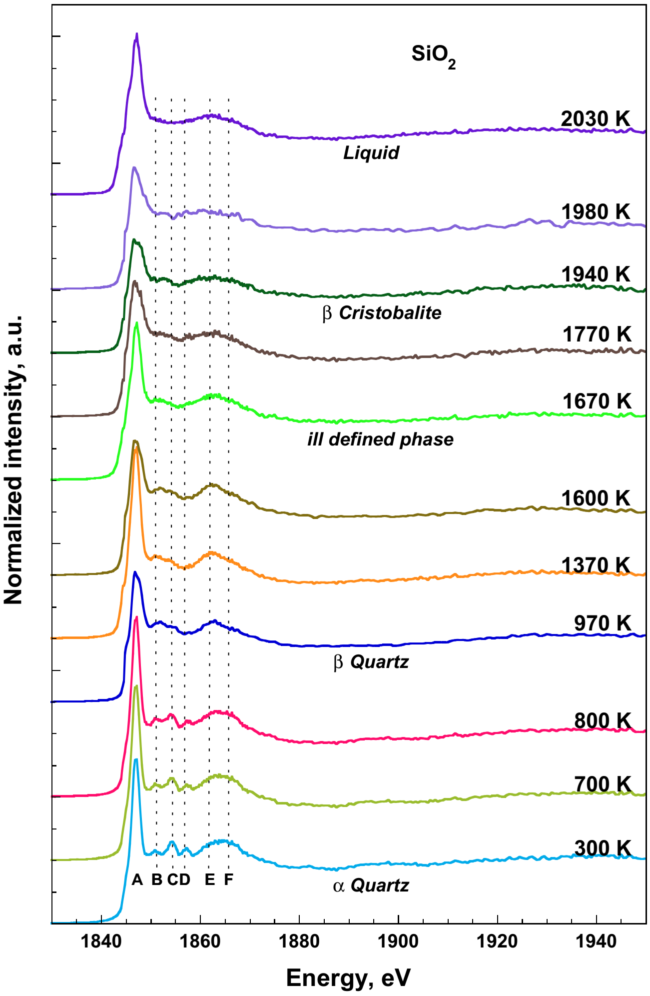

Fig. 2. Si K-edge XANES spectra for SiO_2 α-quartz brought to high temperature. Phases were assigned from calculated spectra (see text). The liquid was assigned from the thermodynamic stability field [5].