

Report experiment ES-689

Introduction

Carbonatites are rare igneous rocks formed predominantly of carbonates, which have unambiguous origins in the mantle and the limit to their depth is not known. The possibility of their existence in the lower mantle [1] needs to be considered since they are direct and important participants in the mobility and long-term storage of deep carbon in the Earth [2,3]. The lower polymerization found in carbonate melts is explained by the electronic structure of the CO_3^{2-} groups, which unlike the SiO_4^{4-} tetrahedra, do not have unpaired orbitals available for covalent bonding, and hence are unable to polymerize [3]. Recently, the discovery of carbonate's high-pressure structures, characterized by the presence of CO_4^{4-} units, was reported [4, 5, 6, 7.]. They are stable at pressures and temperatures relevant for the Earth's lower mantle. This discovery has clear implications for the carbonate melt structures, indeed as an example, changes in the density and viscosity in silicate melts occur in correspondence to phase changes in the equivalent crystalline phase due to increases in coordination [8]. We therefore expect changes in the behavior of carbonate melts corresponding to phase transitions in their crystalline counterparts with an increase in coordination and close packing under compression [3]. At present, the use of glasses as analogues for melts provides the only experimental means of studying carbonate melt structures, due to technical difficulties to preserve melting in diamond anvil cell (DAC) for long periods of time. The similarity between glass and melt structures have been demonstrated by previous vibrational studies, which suggest high levels of structural similarity [9]. Recently, it has been shown that synchrotron X-Ray Raman scattering coupled with DACs provides detailed information on the pressure-induced electronic bonding changes for low-Z elements in amorphous oxides, such as for instance MgSiO_3 glass [10,11] and other molecular compounds [12]. For this reasons we decided to track the evolution of the O K-edge in carbonate glass $\text{K}_2\text{Mg}(\text{CO}_3)_2$ under compression up to 92 GPa by means of DAC and the preliminary results are shown here (Figure 1).

Experimental methods

We performed the experiments using miniature diamonds [13] of 250 and 120 μm culet size to reach pressures respectively up to 70 and 92 GPa. All diamonds' culets were perforated using a focused ion beam (FIB) beforehand at the Bayerisches Geoinstitut. The pits dig in the diamonds were roughly 10-15 μm deep and allowed the loading of a bigger sample volume inside the DAC, which dramatically increases the signal to noise ratio in the analyzer crystals. The sample was constrained in the DAC using a Rhenium gaskets initially indented down to 40 and 25 μm for diamonds culet size of 250 and 120 μm respectively. Pressure was measured using the ruby fluorescence line for pressures up to 70 GPa, where a ruby was loaded together with the sample in the 250 μm DAC, and by Raman signal for the higher pressure experiment using the 120 μm DAC.

Results

We observed clear changes on the O pre-edge at ~ 533 eV, π^* resonance, that becomes progressively less intense starting from ~ 70 GPa and almost disappears at 92 GPa, the last measured pressure point. Major changes were also observed at the O K-edge starting at about 70 GPa (Figure 1) that show a gradual transition up to the last pressure point measured, where the presence of a second oscillation in between 550-555 eV is clearly observed. These variations could reflect a change in the electrons

hybridization around the O-atoms caused by a change in polymerization between C and O, as observed in crystalline carbonates above ~ 70 GPa [7]. Moreover, the sharpening of the deep at 535 eV in between ambient pressure and 9-17 GPa could stem from the increased packing of the glass structure via atomic reorganization, without however implying changes in O bonding nor increase in the coordination environment.

We could not observe the end of the main transition because one of the two 120 μm diamonds broke in compression at pressures slightly above 92 GPa. We hence would like to continue our experiment to determine the pressure corresponding to the end of the transition and measure the O K-edge of the glass above 100 GPa using X-Ray Raman scattering spectroscopy.

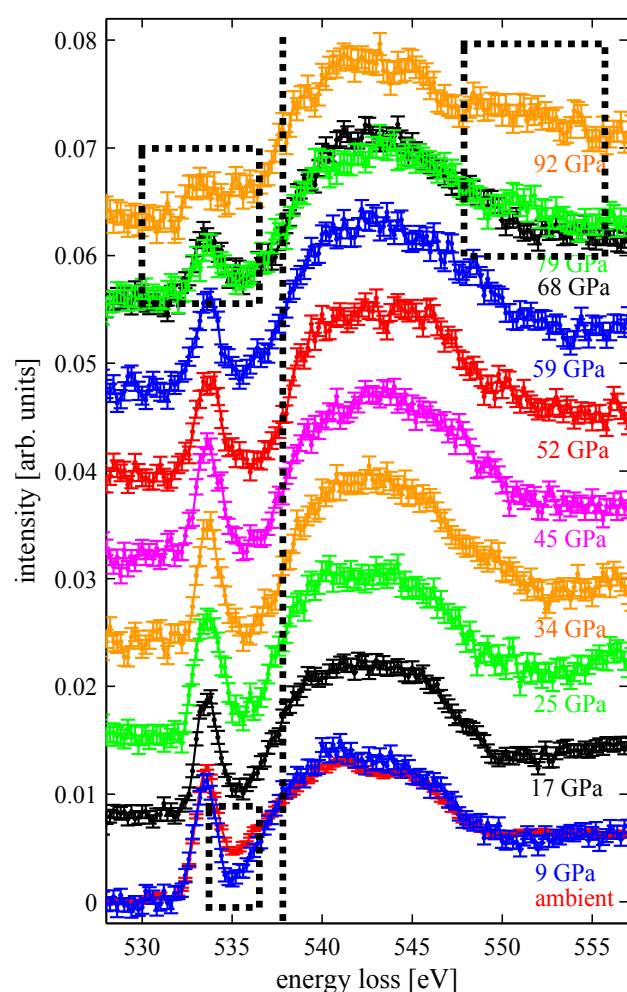


Figure 1. O K-edge data up to 92 GPa. The pre-edge region shows significant reduction in intensity at ~ 533 eV with increasing pressure, and at high pressure ($P > 60$ GPa), a new oscillation appears between 550 and 555 eV.

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