



in Rb-silicate glass and liquid to 1400 °C

F. Seifert*; **E. Paris****; **D.B. Dingwell***; **A. Mottana*****;
C. Romano****; **I. Davoli*******

*Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

**Dipartimento di Scienze della Terra, Università di Camerino, I-62032 Camerino, Italy

***Dipartimento di Scienze Geologiche, Terza Università di Roma, I-00146 Roma, Italy

****Dipartimento di Scienze della Terra, Università di Roma "La Sapienza", I-00185 Roma, Italy

*****Dipartimento di Matematica e Fisica, Università di Camerino, I-62032 Camerino, Italy

Abstract

In-situ high-temperature XANES spectra at the Ti-K edge demonstrate that the coordination number of Ti in $\text{Rb}_2\text{TiSi}_4\text{O}_{11}$ in the glassy, supercooled and stable liquid regimes remains essentially unchanged at a mean value close to 5 up to a temperature of 1400 °C. A slight increase in the intensity of the pre-edge peak with temperature can be taken as evidence for a minor decrease in the average coordination number of Ti (from ca. 5.0 in the glassy state to ca. 4.75 at 1400 °C).

Introduction

Most studies of melt structures have been performed on their quenched equivalents, i. e. glasses and assumed that these structures represent that of the melt near the glass-transition temperature (cf. Mysen, 1988). A limited temperature range (on the order of several tens of degrees) is accessible for such studies by changing the quench-rate (Dingwell and Webb, 1990). For covering a wider temperature range, in particular into the region of stable liquids, *in-situ* techniques have to be used instead. Such studies are rare, mostly because of methodological difficulties. It has been shown, however, that the main structural features such as the topology of the network remains unchanged with temperature in fully polymerized melts such as GeO_2 (Seifert et al., 1981) and that, in depolymerized melts, only rather subtle changes occur, such as in the connectivity of SiO_4 tetrahedra (i.e. the distribution of Q-species) via disproportionation reactions of the type $\text{Q}^3 = \text{Q}^4 + \text{Q}^2$ (Brandriss and Stebbins, 1988; Mysen and Frantz, 1992; Seifert et al.,

1981). Furthermore, minor coordination changes of Si and Al have been found (e.g. Poe et al., 1992 a, b).

It is the purpose of the present note to describe *in-situ* measurements on a $\text{Rb}_2\text{TiSi}_4\text{O}_{11}$ glass and melt via Ti-K-edge XANES in the temperature range of 25 to 1400 °C. This composition has been chosen as a result of a general comparison of $\text{X}^{n+}_{2/n}\text{TiSi}_4\text{O}_{11}$ glasses (where X is Li, Na, K, Rb, Cs, Ca, Sr, Ba, and Al) (Dingwell et al., 1993). This melt is expected, for reasons to be discussed below, to have an intermediate coordination number of Ti between 4 and 6 and therefore to be susceptible to variation with temperature. The need of *in-situ* spectroscopic data for explaining anomalous macroscopic properties in Ti-bearing melts has been emphasized recently by Lange and Navrotsky (1993).

Experimental

Starting materials for the preparation of a glass of $\text{Rb}_2\text{TiSi}_4\text{O}_{11}$ composition were powder mixtures of SiO_2 (99.95), TiO_2 (99.8) and Rb_2CO_3 (99) which were fused and homogenized at 1400°C in air in a MoSi_2 box furnace in a Pt crucible and then poured onto a steel plate for cooling. An analysis is provided by Dingwell et al. (1993)

The X-ray absorption of the glass and liquid sample has been measured at temperatures between 25 and 1400 °C in a high-temperature cell (Seifert et al., 1993) at the PWA line of the National Synchrotron Radiation Facility, Frascati, Italy, at the Ti K-edge (4966 eV) using a (111) channel-cut Si monochromator with an energy resolution of 1 eV, at steps of 0.2 eV. The powdered glassy starting material was pressed into a Pt mesh (mesh size ca. 0.3 mm) and this mesh was then mounted between two MgO blocks held together by Pt wires. The MgO blocks were drilled in such a way as to ensure unattenuated passage of photons. This assembly was then inserted into a horizontal Pt-wound tube furnace. The surface tension of the melt was sufficient to keep a film of appropriate thickness suspended vertically for the period of the measurements (several hours). Temperature was measured and controlled by a Pt-Pt90Rh10 thermocouple and held constant to $\pm 1^\circ\text{C}$. Between individual scans, temperature was allowed to equilibrate for ca. 30 minutes. A Ti metal foil (EXAFS Materials, 4966.0 eV) was used for energy calibration at room

temperature. Experimental XANES data have been reduced by subtraction of background and normalisation of the spectra at the absorption edge.

Results and Discussion

Fig. 1 shows a (normalized) comparison of the spectra obtained. It should be noted that all spectra except the room temperature spectrum are in the region of the relaxed (stable or metastable) liquid, i.e. above the glass transition temperature T_g which, for this composition, lies between 550 and 600 °C (Takahashi et al., 1977). At these elevated temperatures rapid structural relaxation and consequently an equilibrium structural state are assumed. The overall shape of the absorption spectra is nearly independent of temperature, although with increasing temperature a general broadening of the features just above the edge can be observed, as well as increasing noise. The most important result is, however, that the relative height of the pre-edge peak only varies marginally with temperature, from 45% (normalized) height at room temperature (corresponding to a structural state near T_g at 550 - 600 °C) to 52 - 53 % at the highest temperature employed. We therefore conclude that the overall structure of the melt shows little change with temperature. In detail, however, we observe a systematic temperature dependence: although the variation in pre-edge intensity with temperature is not much larger than the mean standard deviation of the individual determinations, a trend of increasing pre-edge height with temperature is apparent from the data (Fig. 2).

It has been shown (Waychunas, 1987; Paris et al. 1993; Dingwell et al., 1993) that the height of the Ti^{4+} pre-edge is inversely correlated with coordination number (CN) of titanium. It is also clear however, that appreciable ranges are observed at a given coordination number, most likely related to varying degrees of distortion of the polyhedra. The intensity of the pre-edge peak changes from 1 - 29 % for CN = 6 to 40 - 45 % for CN = 5 to 57 - 84 % for CN = 4 in the crystalline state. A least-squares fit on the variation of pre-edge intensity as a function of coordination number has been obtained (Paris et al., 1993). Applying this relationship for crystalline standards to the present liquid data, the *average* coordination number of Ti in the $Rb_2TiSi_4O_{11}$ glass is close to 5.0, and the change in pre-edge height reported in Fig. 2 then corresponds to a decrease in *average* coordination number on the order of 0.25 in the temperature range between T_g and

1400 °C. Such a decrease of CN with temperature may be expected on very general crystal chemical grounds; what is surprising, however, is that the magnitude of this effect is so small. It should be emphasized that, given the lack of energy resolution in the XANES absorption spectra, we would not be able to distinguish between a fivefold and a mixed 4+6-fold coordination of titanium, i.e. we cannot determine the width of the distribution curve of coordination numbers which may also change with temperature.

Given the ranges of pre-edge intensity at constant coordination numbers, the subtle variation with temperature could, in principle, also reflect a change of site distortion at constant coordination number. We favour, however, for the large variations resulting from chemical substitution a variation in average coordination number. This is because of the large variations in the volume per oxygen attributed to titanium in these melts which is evident from the density data for these melts (Dingwell, 1992).

Acknowledgements: We thank Prof. Emilio Burattini and his PWA staff for assistance in the operation. Financial support from Fonds der Chemischen Industrie, Frankfurt; CNR, Rome (CT92.00799.CT05) and Vigoni exchange programme of CRUI and DAAD is gratefully acknowledged.

References:

- /1/ Brandriss, M.E.; Stebbins, J.F.:
Effects of temperature on the structure of silicate liquids: ²⁹Si NMR results. *Geochimica et Cosmochimica Acta* 52 (1988) p. 2659-2669.
- /2/ Dingwell, D.B.:
Density of some titanium-bearing silicate liquids and the compositional dependence of the partial molar volume of TiO₂. *Geochimica et Cosmochimica Acta* 56(1992) p. 3403-3407.
- /3/ Dingwell, D.B.; Paris, E.; Seifert, F.; Mottana, A.; Romano, C.:
An X-ray absorption study of Ti-bearing silicate glasses. (submitted to *Physics and Chemistry of Minerals*) (1993)

- /4/ Dingwell, D.B.; Webb, S. L.:
Relaxation in silicate melts. *European Journal of Mineralogy* **2** (1990) p. 427-449.
- /5/ Lange, R.A.; Navrotsky, A.:
Heat capacities of TiO₂-bearing silicate liquids: Evidence for anomalous changes in configurational entropy with temperature. *Geochimica et Cosmochimica Acta* **57** (1993) p. 3001-3011.
- /6/ Mysen, B.O.:
Structure and Properties of Silicate Melts. Elsevier (1988) 354 pp.
- /7/ Mysen, B.O.; Frantz, J.D.:
Raman spectroscopy of silicate melts at magmatic temperatures: Na₂O-SiO₂, K₂O-SiO₂ and Li₂O-SiO₂ binary compositions in the temperature range 25-1475°C. *Chemical Geology* **96** (1992) p. 321-332.
- /8/ Paris, E.; Romano, C.; Mottana, A.; Seifert, F.; Dingwell, D.B.:
Ti K-edge XANES study of crystalline Na₂TiSiO₅ and the systematics of pre-edge intensity versus coordination number. (submitted to *Physics and Chemistry of Minerals*) (1993)
- /9/ Poe, B.T.; McMillan, P.F.; Angell, A.; and Sato, R.K.:
Al and Si coordination in SiO₂-Al₂O₃ glasses and liquids: A study by NMR and IR spectroscopy and MD simulations. *Chemical Geology* **96** (1992a) p. 333-349
- /10/ Poe, B.T.; McMillan, P.F.; Coté, B.; Massiot, D.; Coutures, J.P.:
SiO₂-Al₂O₃ liquids: in-situ study by high-temperature ²⁷Al NMR spectroscopy and molecular dynamics simulation. *Journal of Physical Chemistry* **96** (1992b) p. 8220-8224.
- /11/ Seifert, F.; Mysen, B.O.; Virgo, D.:
Structural similarity between glasses and melts relevant to petrological processes. *Geochimica et Cosmochimica Acta* **45** (1981) 1879-1884.
- /12/ Seifert, F.; Paris, E.; Dingwell, D. B.; Davoli, I.; Mottana, A.:
A high-temperature device for in situ measurement of X-ray absorption spectra. *Condensed Matter and Materials Comm.* **1** (1993) (in press)

/13/ Takahashi, K.; Mochida, N.; Yoshida, Y.:

Properties and structure of silicate glasses containing tetravalent cations. *Journal of the Ceramic Society of Japan* **85** (1977) p. 330-340.

/14/ Waychunas, G.A.:

Synchrotron radiation XANES spectroscopy of Ti in minerals: Effects of Ti bonding distances, Ti valence, and site geometry on absorption edge structure. *American Mineralogist* **72** (1987) p. 89-101.

Figure captions

Fig. 1

XANES spectra of $\text{Rb}_2\text{TiSi}_4\text{O}_{11}$ melt and glass, normalized to the maximum height of the absorption edge. Note the general similarity of the topology of the spectra.

