The structure of Ti-silicate glasses by Raman spectroscopy: Implications for the role of Ti in natural melts

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Introduction

The presence of Ti can have a profound influence on the physical and chemical behaviour of silicate melts. The structural role of Ti^{4+} in both natural as well as synthetic systems (i.e., glasses) has been investigated by a number of techniques. However, the existing direct and indirect data on the local structure of Ti are contradictory.

Experimental

Mixtures of analytical grade Na_2CO_3, $CaCO_3$, TiO_2 and SiO_2 were prepared, at 0.01, 0.05, 1.0, 3.4, 6.8, 10.4, 14.1 and 26.1 wt% and 0.01, 0.05, 1.0, 3.5, 7.1, 10.8, 14.7, 27.0 wt% TiO_2, along the TiO_2-Na_2SiO_3, and TiO_2–$CaSiO_3$ joins, respectively. All compositions produced clear, bubble free glass. Glasses along the TiO_2–SiO_2 join were prepared by the sol-gel method of Hayashi *et al.* (1983) rather than by flame hydolysis methods. The former produce pure solid solution glasses up to 7.4 wt% TiO_2 as opposed to ~11 wt% for the latter method. All glasses were examined optically under oil for evidence of phase separation. Crystalline rutile (Ti[6]), anatase (Ti[6]), Ba_2TiO_4 (Ti[4]), and fresnoite (Ti[5]) were also synthesized and compared to the glasses.

Raman spectra were recorded with a SPEX 1877D TRIPLEMATE Raman spectrometer with a micro-Raman attachment. All spectra were obtained on the micro-Raman system and recorded using a CCD detector and were calibrated against Ne.

Results and discussion

Results for the glasses along the TiO_2–SiO_2 join are similar to previous studies. Intense bands at ~945 and ~1100 cm^{-1} are observed in the vibrational spectra upon the addition of Ti. However, it should be noted that the presence of these bands is not definitive of Ti as they are seen in a number of Ti-free glasses upon the addition of other dopants (i.e., B). Above about 8 wt% TiO_2 the 606 cm^{-1} band of pure SiO_2 glass is observed to broaden on the high wavenumber side and intensify. These changes are concomitant with the onset of anatase formation. No bands indicative of Ti[6] are observed.

The spectra of tha alkali Ti-silicate glasses exhibit an additional band at ~842 cm^{-1} with the addition of TiO_2. This band intensifies with added TiO_2 becoming the dominant Raman band at 27.0 wt% TiO_2. The high TiO_2 wt% spectrum is very similar to that obtained from fresnoite glass but the position of the main vibrational band is midway between the equivalent band in Ba_2TiO_4 (Ti[4]) and that of the fresnoite glass and crystalline spectra. The close similarity between the high TiO_2 alkali Ti-silicate glass spectra and that of fresnoite glass would suggest similar structure with the presence of Ti[5] in addition to Ti[4] in the glasses. No evidence is observed for Ti[6].

The spectra of alkaline-earth-containing silicate glasses are more complex. The addition of TiO_2 results in the appearance of a strong band at ~846 cm^{-1} which intensifies with added TiO_2 becoming the dominant band at high TiO_2 concentrations. There are similarities between the glass spectra and those of crystalline Ba_2TiO_4 and fresnoite. The similarities again suggest the possibility of both Ti[4] and Ti[5] in the glass. However, the closer correspondence of the ~846 cm^{-1} band to Ba_2TiO_4 indicates that there is more Ti[4] in the alkaline-earth-containing Ti-silicate glasses than in the alkali Ti-silicate glasses. No evidence is observed for Ti[6].

Summary

Raman spectra of TiO_2-SiO_2, TiO_2-Na_2SiO_3, TiO_2-$CaSiO_3$, and $Ba_2TiSi_2O_8$ glasses have been

obtained. No evidence is observed for the presence of Ti[6] in the glasses except when cryptocrystalline anatase is formed. Comparison of the glass spectra with crystalline phases with differing Ti coordination suggests that the alkali and alkaline-earth glasses contain both Ti[4] and Ti[5] with a higher proportion of Ti[4] occurring in the alkaline-earth compositions.

References

Hayashi, T., Tamada, T., and Saito, H. (1983) *J. Mat. Sci.*, **18**, 3137–42.