



IR absorption spectra of vitreous silica and silicate glasses: the origin of bands in the 1300 to 3000 cm⁻¹ region

A.M. Efimov, V.G. Pogareva

Vavilov State Optical Institute, St. Petersburg, Russia

efimov@ae4050.spb.edu

Introduction

The origin of particular absorption bands in the 1300-3000 cm⁻¹ region is yet disputable. For silica glasses, bands at wavenumbers less than 3000 cm⁻¹ were qualitatively assigned to the multiphonon modes of the matrix [1], these assignments being applied [2] to three bands in the 1500-2100 cm⁻¹ region of Na₂O-CaO-SiO₂ glass spectrum as well. However, five bands found [3] in this region for K₂O-CaO-BaO-SiO₂ glass spectra increase in intensity with water content, which indicates these bands to be water-related (as is the case for the known [4] 2300 to 3700 cm⁻¹ bands). Such controversy hinders understanding (i) an equilibrium between various structural sites occupied by different water-related species in glassforming melts and (ii) the actual origin of various water-related bands at wavenumbers greater than 3700 cm⁻¹ that influence greatly on the radiative heat transfer in glassforming melts and glass blocks under cooling. So, further insight into the nature of bands in the 1300-3000 cm⁻¹ region is of importance for (i) refining the industrial processes of glass melting and annealing and (ii) the better understanding of natural processes in magmas. In the given research, the parameters and origin of the IR absorption bands for Type I and III silica and (Me₂O/MeO)-SiO₂ glasses (Me being Na, K, Ca, Ba) in the 1300-5000 cm⁻¹ region are compared and discussed.

Core

To complete the domain of data for discussing, the absorption spectra of Type I and III silica glasses in the 1300-5000 cm⁻¹ region are measured using samples down

to 0.15 mm thick and processed with the dispersion analysis method based on the convolution model for the complex dielectric function. Eight bands are resolved, their frequencies being $\sim 1430, 1660, 1860, 2000, 2260, 2410, 2650,$ and 2780 cm^{-1} . The oscillator strengths of the bands coincide for samples differing in the water content, which confirms these bands to be due to the multiphonon matrix modes. Tentative assignments of the 1430, 1660, 1860, and 2000 bands to particular combination modes are proposed.

For $(\text{Me}_2\text{O}/\text{MeO})\text{-SiO}_2$ glasses, an increase in the oscillator strengths, with the water content, for bands in the $1500\text{-}2200 \text{ cm}^{-1}$ region is several times less than that for principal water-related bands in the $2300\text{-}3700 \text{ cm}^{-1}$ region. This is interpreted in terms of representing the former bands as envelopes under which spectral components due to (i) the water-related species and (ii) multiphonon matrix vibrations overlap. With an increase in the water content, it is the oscillator strengths of the water-related components alone that increase; hence the smaller rate of an increase in the total oscillator strengths of the envelopes compared to the case of water-related bands lacking the multiphonon contributions. The frequency shift of the $1540\text{-}1610, 1670\text{-}1745$ and $1800\text{-}1840 \text{ cm}^{-1}$ envelopes with the silica content of glasses is assigned tentatively to the effect of multiphonon components involving the asymmetric Si-O-Si stretch whose frequency is known [5] to be composition-dependent. The prospects of further studies into the nature of the $1300\text{-}3000 \text{ cm}^{-1}$ bands are discussed.

References

- [1] A.R. Silin', A.N. Trukhin, Point Defects and Elementary Excitations in Crystalline and Vitreous SiO_2 , Zinatne, Riga, 1985 (in Russian).
- [2] L.B. Glebov, E.N. Boulos, in: Proc. ICG 2000 Conf. "Glass in the New Millennium", Amsterdam, 2000 (on CD).
- [3] A.M. Efimov, V.G. Pogareva, A.V. Shashkin, J. Non-Cryst. Solids, 332 (2003) 93.
- [4] H. Scholze, Glass: Nature, Structure, and Properties, Springer-Verlag, N.Y., 1991.
- [5] A.M. Efimov, Glass Phys. Chem. 22 (1996) 255.