A theoretical and experimental investigation of hetero- vs. homo-connectivity in barium silicates

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Abstract

Barium silicates may be found in contact aureoles and are used in several important technologies (e.g., LEDs). The BaO-SiO2 system stabilizes 13 crystalline phases with different silicate tetrahedral and connectivity profiles. Aside from phases composed of a single structural unit (isolated or homo-connected tetrahedra), one encounters the relatively rare case of hetero-connected tetrahedra in which varying proportions of several Q4 species are linked together. Here, we analyze the ²⁹Si MAS NMR and Raman spectroscopic manifestations of the connectivities in seven barium silicates: Ba₂SiO₅, high-BaSiO₃, Ba₂Si₂O₆, Ba₅Si₃O₁₄, Ba₅Si₆O₂₆, high-BaSi₂O₅, and sanbornite (low-BaSi₂O₅). The structures and purity of these phases were confirmed by Rietveld refinement. From a Raman spectroscopic database of 144 predominantly homo-connected crystalline silicates, the mean Q4 mode frequencies νQ4 (±1σ) are found at 828 (±14) cm⁻¹ for Q4, 905 (±22) cm⁻¹ for Q3, 994 (±26) cm⁻¹ for Q2, and 1068 (±18) cm⁻¹ for Q1 units. Experimentally, homo-connected barium silicates show good agreement with these values, whereas the hetero-connected phases show a wider range of νQ4 than of νQ3 frequencies. While the ²⁹Si NMR chemical shifts of the barium silicates are in agreement with known structural trends, those measured for the Q4 resonances remain essentially constant, which may be caused by the lattice distortion around the large Ba²⁺ cations. To complement and rationalize experimental measurements, first-principles calculations at the density functional theory level have reproduced measured frequencies within a mean absolute deviation of <7 cm⁻¹. Our work highlights how the results provided by ²⁹Si NMR and Raman spectroscopies and ab initio calculations can be combined to rationalize the structure of complex systems. The present findings also shed light on the vibrational modes that may be used to track bond lengths in situ at extreme conditions and the behavior of hetero- vs. hetero-connectivity, revealing clear implications for evaluating silicate glasses and melts where hetero-connectivity is the rule rather than the exception.

Keywords: Barium silicates, Ba₂SiO₅, high BaSiO₃, Ba₅Si₆O₂₆, high Ba₅Si₄O₁₄, Ba₅Si₆O₂₆, high BaSi₂O₅, and low Ba₂SiO₄. ²⁹Si MAS NMR and Raman spectroscopies, X-ray diffraction, density functional theory calculations

Introduction

During the last decade, the study of barium silicates is of particular interest because of their applications in different fields. For example, barium silicate-based ceramics are used as solid-oxide sealant materials (e.g., Namwong et al. 2010), erasable-writable optical storage devices (Lin et al. 2019), and, when doped with rare-earth elements, as light-emitting diode materials (Xiao et al. 2009; Chen et al. 2015). Barium silicates are built of SiO₄ tetrahedra, the fundamental building blocks of almost all silicate minerals and liquids (Liebau 1985). The remarkable stability of SiO₄ tetrahedra through the transition from the solid into the liquid state is central to understanding and predicting the properties of silicate crystals, glasses, and melts. The modified random network model of silicate liquids describes them as having two entangled substructures: one constructed from interconnected silica tetrahedra and one comprised of ill-defined modifier-oxygen polyhedra (MO₄, where M = K, Ba, etc.) (cf. Greaves 1985). A silicon tetrahedron may be connected to up to four additional tetrahedral units. Connectivity is defined by the number of Si-O-Si bonds found around a central tetrahedron and described using the Qₙ species notation, where n is the number of bridging oxygen (BO) atoms shared between tetrahedra and 4–n is the number of non-bridging oxygen (NBO) atoms bound to M cations (cf. Calas et al. 2006). Most crystalline silicates are built from a single Qₙ species, whereas silicate liquids and glasses have two or more Qₙ species that are assumed to be randomly linked. Sanbornite, low-Ba₂SiO₄, is an uncommon mineral composed