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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-SiO_2 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 Q^n species are linked together. Here, we analyze the ^{29}Si MAS NMR and Raman spectroscopic manifestations of the connectivities in seven barium silicates: Ba_2SiO_4, high-$BaSiO_3$, $Ba_4Si_6O_{16}$, $Ba_5Si_8O_{21}$, $Ba_6Si_{10}O_{26}$, high-$BaSi_2O_5$, and sanbornite (low-$BaSi_2O_5$). 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 Q^n mode frequencies ν_{Q^n} ($\pm1\sigma$) are found at 828 ($\pm$14) cm^{-1} for Q^0, 905 ($\pm$22) cm^{-1} for Q^1, 994 ($\pm$26) cm^{-1} for Q^2, and 1068 ($\pm$18) cm^{-1} for Q^3 units. Experimentally, homo-connected barium silicates show good agreement with these values, whereas the hetero-connected phases show a wider range of ν_{Q2} than of ν_{Q3} frequencies. While the ^{29}Si NMR chemical shifts of the barium silicates are in agreement with known structural trends, those measured for the Q^2 resonances remain essentially constant, which may be caused by the lattice distortion around the large Ba^{2+} 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 ^{29}Si 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 homo- 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, Ba_2SiO_4, high $BaSiO_3$, $Ba_4Si_6O_{16}$, high $Ba_5Si_8O_{21}$, $Ba_6Si_{10}O_{26}$, high $BaSi_2O_5$ and low $BaSi_2O_5$, ^{29}Si MAS NMR and Raman spectroscopies, X-ray diffraction, density functional theory calculations