

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

BENJAMIN J.A. MOULTON<sup>1,2,\*</sup>, EDUARDO O. GOMES<sup>3</sup>, THIAGO R. CUNHA<sup>1,2</sup>, CARSTEN DOERENKAMP<sup>4</sup>,  
LOURDES GRACIA<sup>3,5</sup>, HELLMUT ECKERT<sup>4,6</sup>, JUAN ANDRÉS<sup>3</sup>, AND PAULO S. PIZANI<sup>1,2</sup>

<sup>1</sup>Universidade Federal de São Carlos, Departamento de Física, Rod. Washington Luis, Km 235 13565-905 São Carlos, SP, Brazil

<sup>2</sup>CERTEV — Center for Research, Technology, and Education in Vitreous Materials, Department of Materials Engineering, Federal University of São Carlos, 13565-905 São Carlos-SP, Brazil

<sup>3</sup>Departament de Química Física i Analítica, Universitat Jaume I, 12071, Castelló de la Plana, Spain

<sup>4</sup>Institute of Physics in São Carlos, University of São Paulo, São Carlos, SP 13566-590, Brazil

<sup>5</sup>Department of Physical Chemistry, University of Valencia (UV), 46100 Burjassot, Spain

<sup>6</sup>Institute of Physical Chemistry, Westfälische Wilhelms-Universität Münster, Corrensstrasse 28/30, 48149, Münster, Germany

### ABSTRACT

Barium silicates may be found in contact aureoles and are used in several important technologies (e.g., LEDs). The BaO-SiO<sub>2</sub> 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<sup>n</sup> species are linked together. Here, we analyze the <sup>29</sup>Si MAS NMR and Raman spectroscopic manifestations of the connectivities in seven barium silicates: Ba<sub>2</sub>SiO<sub>4</sub>, high-BaSiO<sub>3</sub>, Ba<sub>4</sub>Si<sub>6</sub>O<sub>16</sub>, Ba<sub>5</sub>Si<sub>8</sub>O<sub>21</sub>, Ba<sub>6</sub>Si<sub>10</sub>O<sub>26</sub>, high-BaSi<sub>2</sub>O<sub>5</sub>, and sanbornite (low-BaSi<sub>2</sub>O<sub>5</sub>). 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<sup>n</sup> mode frequencies  $\nu_{Q^n}$  ( $\pm 1\sigma$ ) are found at 828 ( $\pm 14$ ) cm<sup>-1</sup> for Q<sup>0</sup>, 905 ( $\pm 22$ ) cm<sup>-1</sup> for Q<sup>1</sup>, 994 ( $\pm 26$ ) cm<sup>-1</sup> for Q<sup>2</sup>, and 1068 ( $\pm 18$ ) cm<sup>-1</sup> for Q<sup>3</sup> units. Experimentally, homo-connected barium silicates show good agreement with these values, whereas the hetero-connected phases show a wider range of  $\nu_{Q^2}$  than of  $\nu_{Q^3}$  frequencies. While the <sup>29</sup>Si NMR chemical shifts of the barium silicates are in agreement with known structural trends, those measured for the Q<sup>2</sup> resonances remain essentially constant, which may be caused by the lattice distortion around the large Ba<sup>2+</sup> 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<sup>-1</sup>. Our work highlights how the results provided by <sup>29</sup>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<sub>2</sub>SiO<sub>4</sub>, high BaSiO<sub>3</sub>, Ba<sub>4</sub>Si<sub>6</sub>O<sub>16</sub>, high Ba<sub>5</sub>Si<sub>8</sub>O<sub>21</sub>, Ba<sub>6</sub>Si<sub>10</sub>O<sub>26</sub>, high BaSi<sub>2</sub>O<sub>5</sub> and low BaSi<sub>2</sub>O<sub>5</sub>, <sup>29</sup>Si MAS NMR and Raman spectroscopies, X-ray diffraction, density functional theory calculations