

## Experiment Report Form



<b>Experiment title:</b> High pressure structural behavior of Ba <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub> polymorphs	<b>Experiment number:</b> HS-3936	
<b>Beamline:</b> ID27	<b>Date of experiment:</b> from: 16 December 2009      to: 19 December 2009	<b>Date of report:</b> 01-March-2011
<b>Shifts:</b> 9	<b>Local contact(s):</b> Dr. Pierre BOUVIER	<i>Received at ESRF:</i>

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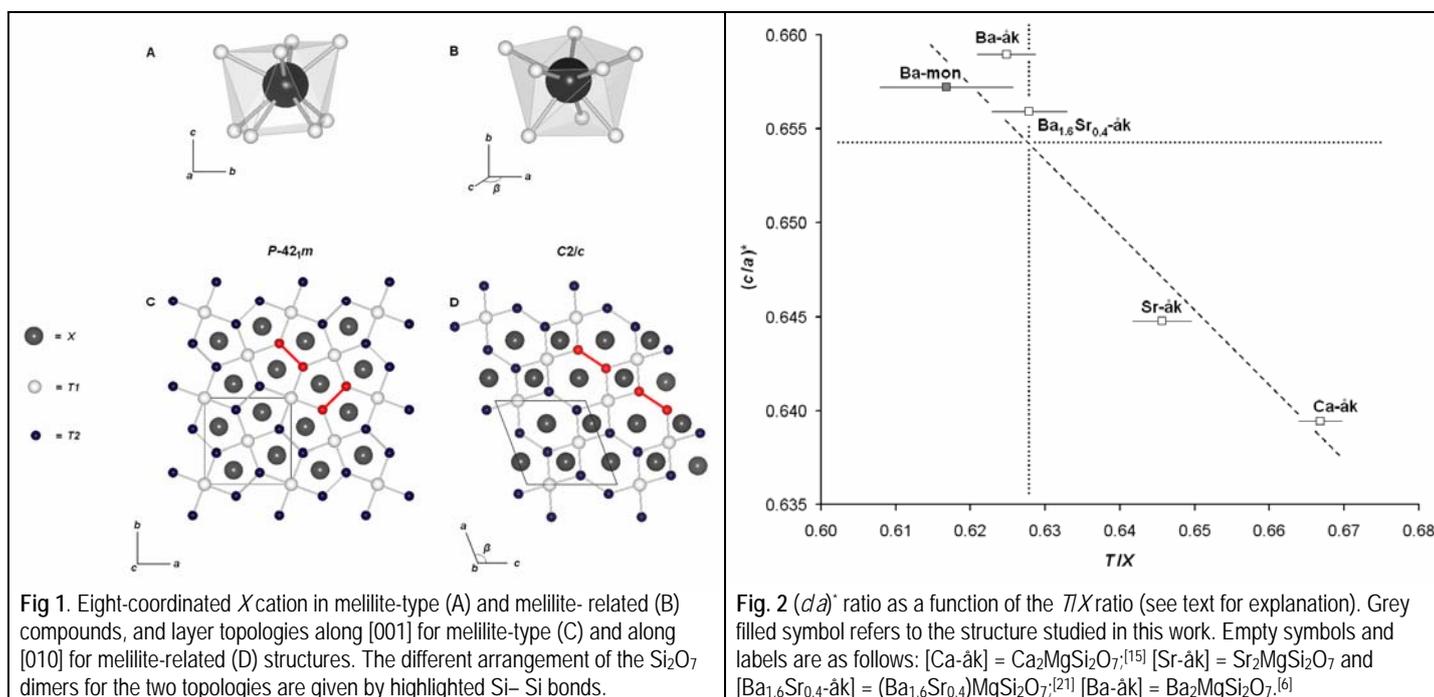
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### Report:

The monoclinic Ba<sub>2</sub>CuSi<sub>2</sub>O<sub>7</sub> (s.g. *C2/c*) is the archetype form for Ba<sub>2</sub>ZSi<sub>2</sub>O<sub>7</sub> melilite-related compounds.<sup>[1]</sup> Other silicates with this structure include Ba<sub>2</sub>CoSi<sub>2</sub>O<sub>7</sub>,<sup>[2]</sup> Ba<sub>2</sub>ZnSi<sub>2</sub>O<sub>7</sub>,<sup>[3]</sup> and Ba<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>.<sup>[4]</sup> The synthetic analogues of these materials have attracted considerable interest in different technological fields: e.g. ceramics, glasses, luminescent materials, low-dimensional magnets, etc. Suggested as structures that should not crystallize with a tetragonal melilite-type structure,<sup>[5]</sup> the above listed Mg, Co, and Cu melilite-related compounds were also solved in the *P-42<sub>1</sub>m* space group: Ba<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>,<sup>[6]</sup> Ba<sub>2</sub>CoSi<sub>2</sub>O<sub>7</sub>,<sup>[7]</sup> and Ba<sub>2</sub>CuSi<sub>2</sub>O<sub>7</sub>,<sup>[8]</sup> single crystals were successfully refined as melilite-type compounds. Although with the same stoichiometry (Ba<sub>2</sub>ZSi<sub>2</sub>O<sub>7</sub>), the monoclinic and tetragonal polymorphs exhibit substantial differences. Similarly to the extensively studied melilite-type structures, the monoclinic polymorphs consist of Si<sub>2</sub>O<sub>7</sub> dimers connected by ZO<sub>4</sub> tetrahedra to form tetrahedral sheets parallel to the *ac* plane, instead of the *ab* plane in the *P-42<sub>1</sub>m* structures. The first major difference concerns the coordination polyhedron of the barium cation, that in the tetragonal feature is a distorted square antiprism with "4 + 4" ligands, whereas in the monoclinic form it is an alternation of "5 + 3" and "3 + 5" ligand configuration (Fig. 1). However, the main difference is in the arrangement of the tetrahedral sheet topology (Fig. 1): there are only five-membered rings of tetrahedra in the tetragonal form, while four- and six-membered rings are present in the monoclinic structure. The change in the tetrahedral sheet arrangement promotes a new setting of the Si<sub>2</sub>O<sub>7</sub> dimers laying in the same layer: in the melilite-type dimers are alternatively disposed along (110) and (-110), whereas in the melilite-related compounds all the dimers are arranged along (-101). In the last decade, many studies were dedicated to assess the high- and low-temperature behavior of melilite-type structures, especially to interpret and solve the phase transition from an incommensurately modulated (IC) to a normal (N) crystal structure occurring in melilite-type compounds with calcium occupying the eight-fold coordinated site.<sup>[9-16]</sup>

On the other hand, few works have been devoted to understand the high-pressure response of melilite structures,<sup>[17-19]</sup> and no studies have been done about melilite-related compounds at non-ambient conditions. For these reasons the structural variations of synthetic  $\text{Sr}_{2-x}\text{Ba}_x\text{MgSi}_2\text{O}_7$  ( $0 \leq x \leq 2$ ) have been studied as a function of composition, pressure and temperature.<sup>[20, 21]</sup> A topological change from the tetragonal (melilite-type) to the monoclinic (melilite-related) structure along the join  $\text{Sr}_2\text{MgSi}_2\text{O}_7$  (s.g.  $P-42_1m$ ) –  $\text{Ba}_2\text{MgSi}_2\text{O}_7$  (s.g.  $C2/c$ ) occurs with  $\text{Ba} > 1.6$  apfu. The asymmetric ligand arrangement (5+3) in the monoclinic structure, compared to the tetragonal configuration (4+4), provides a more favourable coordination to large Ba atoms in the cubic site and helps to clarify the dichotomy existing for  $\text{Ba}_2\text{ZSi}_2\text{O}_7$  ( $Z = \text{Mg, Co, Cu}$ ) compounds, which have been reported in both the  $C2/c$  (solid state synthesis) and the  $P-42_1m$  (crystallization from melt) crystal symmetry. Further insights on the relationships between the two different polymorphs of  $\text{Ba}_2\text{MgSi}_2\text{O}_7$  were achieved by investigating the *in situ* high pressure and high temperature behaviour of these systems. The high pressure experiments, performed at ID27 of ESRF (France) up to  $\sim 11$  GPa, allowed to calculate the elastic moduli for the Sr melilite-type end-member and for the Ba monoclinic polymorph ( $\text{Sr}_2\text{MgSi}_2\text{O}_7$ :  $K_{T0} = 107$ ,  $K_{a=b} = 121$ , and  $K_c = 84$  GPa;  $m\text{-Ba}_2\text{MgSi}_2\text{O}_7$ :  $K_{T0} = 85$ ,  $K_a = 96$ ,  $K_b = 72$ , and  $K_c = 117$  GPa) and compare them to those reported in the literature for Ca-åkermanite. The results suggest that, although the tetragonal structure is stiffer on the whole, the compressibility of the Ba polyhedron is significantly lower in the monoclinic form. The high-temperature study of  $m\text{-Ba}_2\text{MgSi}_2\text{O}_7$  was carried out up to 1273 K. The measured thermal expansion coefficients for the unit cell edges and volume are  $\alpha_a = 8.7 \times 10^{-6} \text{ K}^{-1}$ ,  $\alpha_b = 11.0 \times 10^{-6} \text{ K}^{-1}$ ,  $\alpha_c = 8.5 \times 10^{-6} \text{ K}^{-1}$ , and  $\alpha_V = 31.1 \times 10^{-6} \text{ K}^{-1}$ , respectively. This reveals an anisotropic expansion behaviour characterized by  $\alpha_a \approx \alpha_c < \alpha_b$ . High-temperature and high-pressure data together define the well-known "inverse relationship" for both the unit cell parameters and the  $(c/a)$  axial ratio as a function of the molar volume. The combination of the high temperature/high pressure trend with the changes of the  $T/X$  dimensional misfit between the tetrahedral layers ( $T$ ) and the  $X$  interlayer, as a function of composition, suggests that the  $t\text{-Ba}_2\text{MgSi}_2\text{O}_7$  polymorph might be a metastable phase favoured by high pressure conditions (Fig. 2).

The obtained results have been reported in the following two works: "The inverse high temperature/high pressure relationship in the monoclinic  $\text{Ba}_2\text{MgSi}_2\text{O}_7$  melilite-related structure" written by M. Ardit, C. Zanelli, M. Dondi and G. Cruciani, *in press* to the Periodico di Mineralogia 79; and "Melilite-type and melilite-related compounds: structural variations along the join  $\text{Sr}_{2-x}\text{Ba}_x\text{MgSi}_2\text{O}_7$ , ( $0 \leq x \leq 2$ ) and high-pressure behaviour of the two end-members" written by M. Ardit, G. Cruciani and M. Dondi, *submitted* to the Physics and Chemistry of Minerals.



#### References:

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