

Experiment Report Form



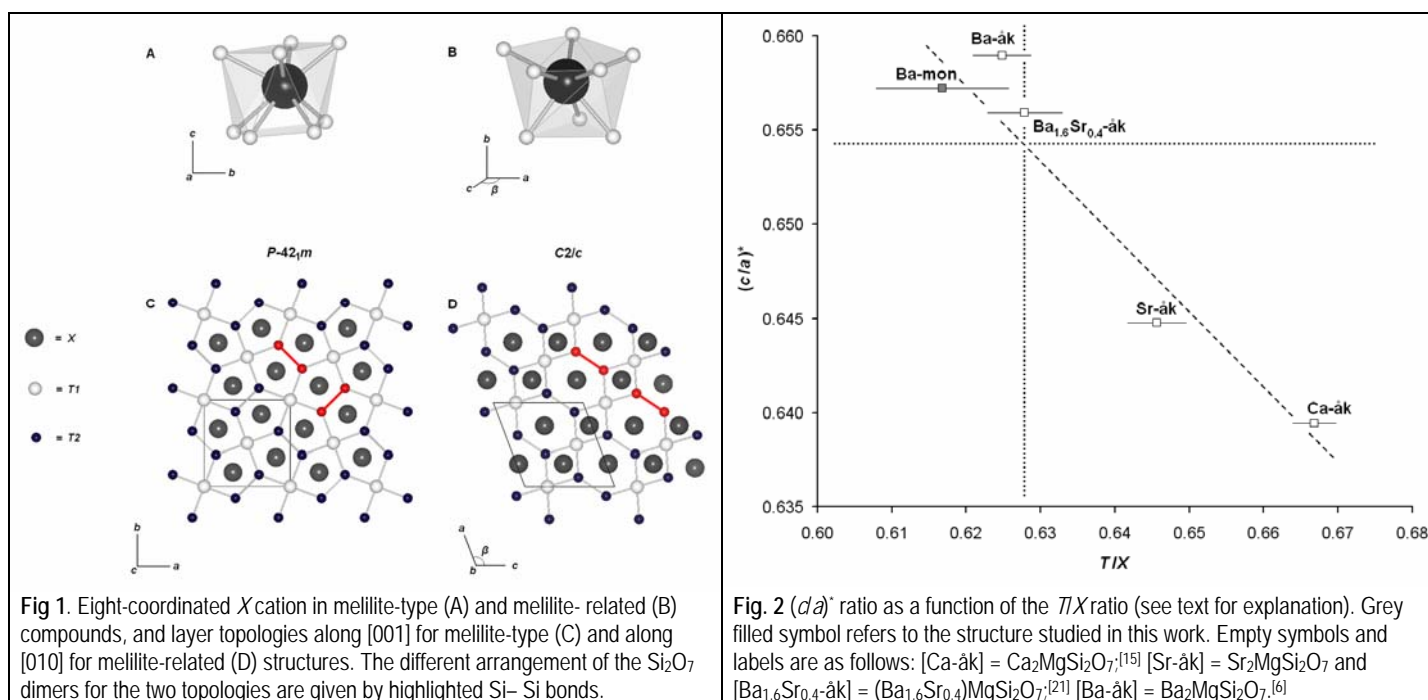
	Experiment title: High pressure structural behavior of Ba ₂ MgSi ₂ O ₇ polymorphs	Experiment number: HS-3936
Beamline: ID27	Date of experiment: from: 16 December 2009 to: 19 December 2009	Date of report: 01-March-2011
Shifts: 9	Local contact(s): Dr. Pierre BOUVIER	<i>Received at ESRF:</i>
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Report:

The monoclinic Ba₂CuSi₂O₇ (s.g. *C2/c*) is the archetype form for Ba₂ZSi₂O₇ melilite-related compounds.^[1] Other silicates with this structure include Ba₂CoSi₂O₇,^[2] Ba₂ZnSi₂O₇,^[3] and Ba₂MgSi₂O₇.^[4] 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,^[5] the above listed Mg, Co, and Cu melilite-related compounds were also solved in the *P-42₁m* space group: Ba₂MgSi₂O₇,^[6] Ba₂CoSi₂O₇,^[7] and Ba₂CuSi₂O₇,^[8] single crystals were successfully refined as melilite-type compounds. Although with the same stoichiometry (Ba₂ZSi₂O₇), the monoclinic and tetragonal polymorphs exhibit substantial differences. Similarly to the extensively studied melilite-type structures, the monoclinic polymorphs consist of Si₂O₇ dimers connected by ZO₄ tetrahedra to form tetrahedral sheets parallel to the *ac* plane, instead of the *ab* plane in the *P-42₁m* 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 Si₂O₇ 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.^[9-16]

On the other hand, few works have been devoted to understand the high-pressure response of melilite structures,^[17-19] 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.^[20, 21] 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 ~ 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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