



	Experiment title: CRYSTAL STRUCTURE OF NEW MICROPOROUS MIXED OCTAHEDRAL-PENTAHEDRAL TETRAHEDRAL (OPT) FRAMEWORK METALLOSILICATES	Experiment number: CH-2148
Beamline: BM1B	Date of experiment: from: 05/05/2006 to: 09/05/2006	Date of report: <i>Received at ESRF:</i>
Shifts: 12	Local contact(s): Dr. EMERICH Herman	

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Report:

Microporous mixed octahedral-pentahedral tetrahedral (opt) framework metallosilicates are a new class of interesting materials with possible application as acid and oxidation catalysts, ion-exchanger and molecular sieves[1]. With respect to zeolites, in which Si and heteroatoms (e.g., Al, B, Ga, Ti, Ge, etc.) are tetrahedrally coordinated, the OPT materials contain polyhedra with mixed coordination. In particular, the SiO₄ tetrahedra can be interconnected with five-, six- and even seven-coordinated metal ions (Ti, Zr, V, Y, lanthanides, etc.) [1]. During the experiment several data collections have been carried out on four new materials with chemical formulae: a) Na_{1.08} K_{0.5} Bi_{1.14} Si₃O_{8.5} 1.78H₂O; b) Bi₂ Si₃ O₉; c) Na Nb Si₂ O₇ 2H₂O; d) Na_{2.8} K₂ Ce₂ Si₁₂ O₃₀ 4H₂O.

The aim of the experiment was to determine the unit cell parameters, space group and the crystal structure of these new materials.

Experimental

Powder diffraction data were collected at the SNBL station B (BM1B) whose very high resolution powder diffractometer is equipped with six detectors and Si (111) analyzer crystals before them. The powder patterns were collected from 1 to 50° 2-theta; the wavelength employed was set to 0.79959 Å. An effective step size of 0.005 ° was used in rebinning the continuous-mode-collected data. The counting time was optimized for each data collection in order to collect with good counting statistics the very weak reflection at high angle.

Results

In the case of the compound listed as a) and b), these materials are the first examples of bismuth mixed OPT framework silicates reported until now. The crystal structure of the first one (sketched in Fig. 1a) was determined using a non-conventional B 1 1 *m* space group and a unit cell parameter a = 6.821, b = 22.395, c = 6.842 Å and β = 113.97° obtained by ITO computer program [2]. The crystal structure of the compound was found strictly related to the previously reported lanthanide silicate AV-20[3], which is in turn linked to the monoclinic polytype of the calcium silicate hydrated tobermorite 11Å. However several differences were

found between them, particularly in the distribution and coordination of extraframework cations likely caused by the larger sodium content determined in our compound.

Concerning the bismuth silicate with chemical formula $\text{Bi}_2\text{Si}_3\text{O}_9$ the X-ray diffraction patterns showed a significant presence of quartz. Nevertheless using the reflection list (excluding quartz peaks) obtained from the high resolution pattern an hexagonal unit cell with the following parameters: $a = 6.845\text{\AA}$ and $c = 9.414\text{\AA}$ ($M_{(20)} = 130$, $F_{20} = 292$) has been determined by TREOR[4]. A structure with similar parameters and space group $P6_3/m$ has been reported for a bismuth-germanate, with the chemical formula $\text{Bi}_2\text{Ge}_3\text{O}_9$ [5]. The crystal structure refinement has been carried out starting from the coordinates given for this compound. The presence of quartz has been taken into account by a multiphase structure refinement in the Rietveld analysis. In this structure the stacking of tetrahedral and octahedral sheets gives rise to small cages (Fig. 1). X-ray diffraction analysis does not show any organic or water molecules inside these cages, in line with the slight weight loss (ca. 0.4%) observed in thermogravimetric analysis.

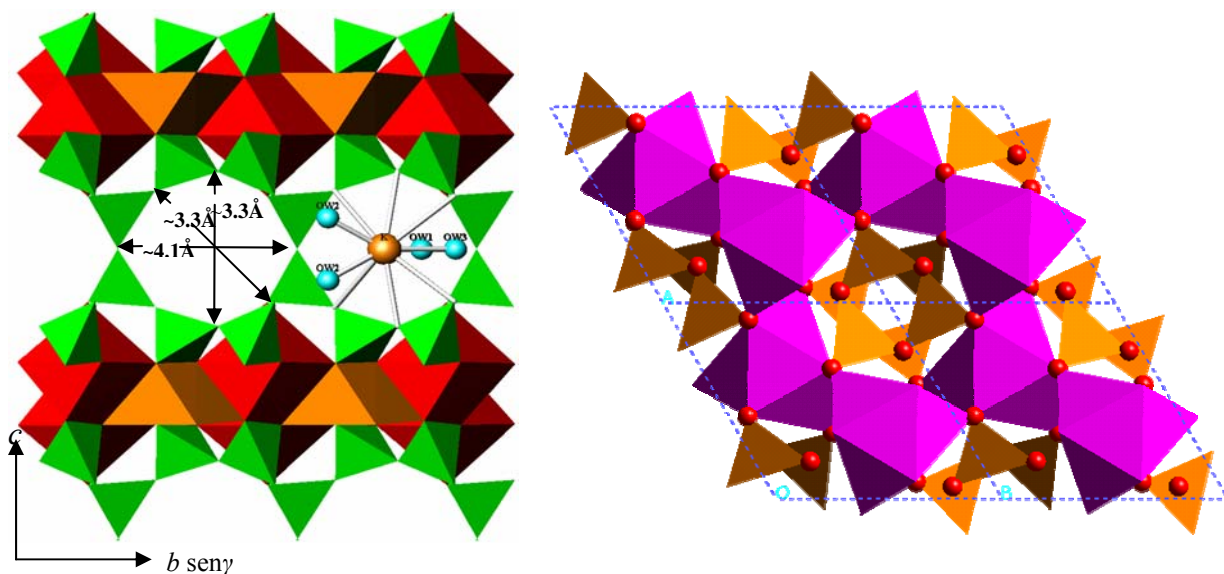


Fig. 1: Polyhedral structures of the bismuth silicates: $\text{Na}_{1.08}\text{K}_{0.5}\text{Bi}_{1.14}\text{Si}_3\text{O}_{8.5}\cdot 1.78\text{H}_2\text{O}$ viewed along the [100] (left), and $\text{Bi}_2\text{Si}_3\text{O}_9$ viewed along the [001] (right). The channel dimensions, calculated considering the ionic radius of oxygen equal to 1.35\AA , are indicated. The extraframework content is also shown as spheres.

Concerning the niobium silicate with general formula $\text{Na Nb Si}_2\text{O}_7\cdot 2\text{H}_2\text{O}$, although the high resolution data allowed a better understanding of the orthorhombic unit cell, already found using laboratory data, but with the b parameter half respect to that obtained by high resolution data ($a = 13.610(5)$, $b = 23.630(9)$, $c = 9.115(6)$ \AA), the space group is still ambiguously. A careful inspection of the reflection indexes seems to indicate the $h00 = 2n+1$ as the unique systematic absence all the attempt to solved the crystal structure of this compound in the $P2_122$ space group failed. We concluded that other systematic absences are present, but they are not resolvable by powder diffraction, even in high resolution conditions: new syntheses are in progress with the aim to produce large single crystals. Finally, an orthorhombic unit cell with parameters $a \approx 7.30$, $b \approx 7.27$ e $c \approx 15.06$ \AA was found for the compound $\text{Na}_{2.8}\text{K}_2\text{Ce}_2\text{Si}_{12}\text{O}_{30}\cdot 4\text{H}_2\text{O}$. Unfortunately, an extended research using these parameters indicated that the crystal structure has been already solved in the $Pnma$ space group [6].

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