IN SITU HIGH-PRESSURE X-RAY DIFFRACTION STUDY OF SYNTHETIC $Mn_2Sb_2O_7$ WITH A WEBERITE-TYPE STRUCTURE

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Several synthetic oxides including antimonates, osmates and tantalates with general formula $A_2B_2X_7$ exhibit a weberite-type structures. These structures can be described as a repeated stacking of close-packed metal layers AB_3 and A_3B, where B are the octahedrally coordinated cations and A are the larger, interstitial, cations forming eight-fold coordination polyhedra. Depending on the type of stacking sequences, different polytypes occur, including 2*M*, 4*M*, 3*T* (Yakubovich *et al*., 1993), and 6*T* (Grey & Roth, 2000) polytypes. According to Cai & Nino (2009), stabilization of a polytypic variant may be related to the relative size of the A and B cations but also pressure and temperature could play a key role. For this reason, in the frame of a doctoral study dealing with Ca and Mn antimonates, the high-pressure structural behaviour of the mineral ingersonite ($Ca_3MnSb_4O_{14}$) and of the synthetic $Ca_2Sb_2O_7$ compound, showing 3*T*- and 2*O*-weberite structures respectively, was investigated (Zanazzi *et al*., 2009; Chelazzi *et al*., 2011). In order to complete this study, an *in situ* high-pressure X-ray diffraction study has been carried out at room temperature up to 9.26 GPa on synthetic $Mn_2Sb_2O_7$ having a weberite-3*T* structure at the Bayerisches Geoinstitut, Universität Bayreuth, under the supervision of Dr. Tiziana Boffa Ballaran.

Crystals of the trigonal, weberite-type $Mn_2Sb_2O_7$ polymorph were synthesized at the Department of Earth Sciences (University of Florence). More in details, crystals were obtained by high-temperature annealing of appropriate amounts of starting materials (MnO, Sb_2O_3, Aldrich-99%). The ground mixtures were heated in platinum crucibles in air at 1100 °C for 30 days and then the sample were allowed to cool slowly in the furnace down to room temperature. The addition of $Na_2B_4O_7$ was found to be functional to increase the size of the $Mn_2Sb_2O_7$ crystals.

Two crystals of $Mn_2Sb_2O_7$ were selected on the basis of their sharp optical extinction and absence of optical twin to collect X-ray diffraction data at variable pressures. Two different Diamond anvil cells (DACs) were chosen to obtain high-pressure data: the ETH-type to measure unit-cell parameters and the Bolher-Almax DAC to collect intensity data. The choice of the Bolher-Almax DAC was due to its different design, in fact with the advent of conical diamond anvils comes the possibility of having diamond anvil cells with very large conical apertures without the drawback of obstructing materials for the incoming of outgoing beams. The conical anvils are supported by tungsten carbide seat, which provides several benefits in the data collection. For example, it circumvents the need for beryllium plates as support for the diamond anvils and the net result is the avoidance of the usual halo coming the diffraction pattern of Be and it results in better quality data also at high pressure. The DACs were loaded with a methanol-ethanol (4:1) mixture as pressure medium (Angel & Finger, 2007) and a crystal of ruby enclosed in the DAC was used to calibrate pressure with the laser-induced fluorescence technique (Mao *et al.*, 1986). Lattice parameters were collected at eight different pressures using a four-circle Huber diffractometer (MoKα radiation) operating at 50 kV and 40 mA, equipped with a point detector and SINGLE software (Angel *et al.*, 2011) allowing to use the 8-position centering method. During the centering procedure the effects of the crystal offset and diffractometer aberrations were eliminated from the refined peak positions by means of the eight-position centering.

We used the unit-cell parameters measured at various pressures to calculate the compressibility of $Mn_2Sb_2O_7$. The evolution of the unit-cell parameters normalized with respect to the room pressure exhibits a steady decrease with increasing pressure and shows no evidence of a phase transition in the investigated pressure range (Fig. 1). Thanks to the program EoS-FIT5.2 (Angel, 2000), we were able to calculate EoS parameters: V_0 = 782.7(2) Å^3, basically identical to the measured value [782.8(2) Å^3], and K_0 = 150(1) Gpa and fit the P-V

data with a Birch-Murnaghan equation of state truncated at the 2nd-order (Fig. 1). Weighted χ^2 is 1.4, maximum $\Delta\mathbf{P}$ is –0.11 GPa. The linear axial compressibilities, βa and βc, calculated using the relation for unit-cell parameters $\beta = 1/(3KT_0)$, are 2.27(2) and 2.08(2) GPa^{-1}, respectively, with relative compressions $c < a$ in the ratio 0.91:1.

The intensity data were collected at 6 different pressures using an Oxford Diffraction - Xcalibur2 diffractometer equipped with a CCD detector, operating with graphite monochromatized Mo-radiation. The intensity data were used to study the evolution of the structure of the $Mn_2Sb_2O_7$ compound with pressure, to look at the variations in bond distances and polyhedral volumes with P.

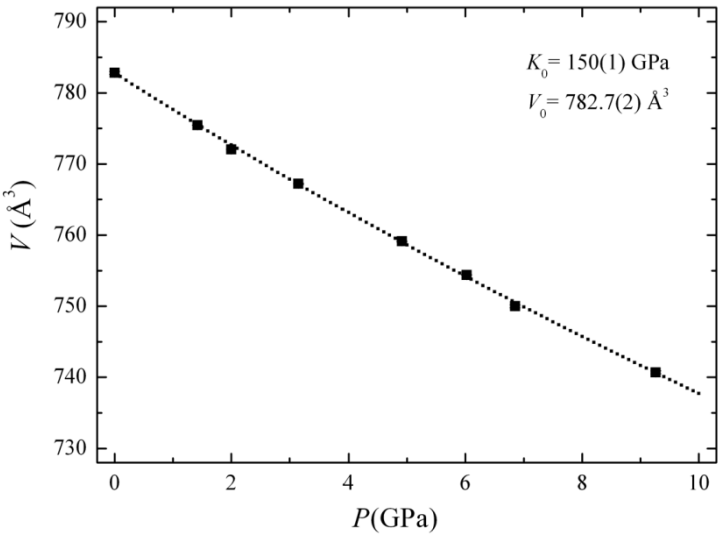

Fig. 1 - Evolution of the unit-cell volume as a function of pressure. Symbols used are larger than the errors.

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