

Crystal-chemistry and polytypism in lombardoite, $\text{Ba}_2\text{Mn}(\text{AsO}_4)_2(\text{OH})$

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The brackebuschite supergroup of minerals currently has about twenty members. The minerals are monoclinic with space group $P2_1/m$ ($7.5577(4) < \mathbf{a} < 7.87636(18) \text{ \AA}$; $5.97761(15) < \mathbf{b} < 6.1130(6) \text{ \AA}$; $8.7316(6) < \mathbf{c} < 9.1678(2) \text{ \AA}$; $111.785(6) < \beta < 112.930(3)^\circ$) and have general formula $\text{A}_2\text{M}^{3+}(\text{TO}_4)_2(\text{OH})$ with $A = \text{Pb, Ba, Sr, Ca}$, $M = \text{Al, Fe}^{3+}, \text{Mn}^{3+}, \text{Zn, Cu}$, $T = \text{V, As, P, S}$. Among these, the arsenbrackebuschite group include minerals having As dominant at the tetrahedral sites. Lombardoite [$\text{Ba}_2\text{Mn}^{3+}(\text{AsO}_4)_2(\text{OH})$] is thus a member of this group, described for the first time at Valletta mine, a small Fe-Mn deposit located in Valletta Valley (Canosio municipality, Maira valley, Piedmont, Italy). A crystal chemical study conducted by single crystal X-ray diffraction on Sr-rich lombardoite crystals from this locality have shown the main partitioning scheme of elements among the sites and the structural responses in terms of bond length and polyhedra geometry. Raman spectroscopy analyses on the same crystals show that chemical composition variations produce a shift of the spectra peaks wavenumber that allows distinguishing between the Ba-rich and Sr-rich members and the V-rich crystals of the solid solution. A clear relation between Sr/Ba content in lombardoite and the position of these peaks is found that allows, at first, to distinguish Sr-rich from Ba-rich samples and that could be used to calibrate the Ba-Sr content.

The diffraction studies also revealed a new polytype, having space group $C2/m$ and \mathbf{a} cell parameter four times the unit base ($27.832(2) < \mathbf{a} < 28.1443(3) \text{ \AA}$; $6.11680(10) < \mathbf{b} < 6.1476(4) \text{ \AA}$; $9.3705(4) < \mathbf{c} < 9.4391(5) \text{ \AA}$; $99.928(3) < \beta < 100.229(6)^\circ$; polytype $4M$), having \mathbf{a} along $[101]$ of the brackebuschite cell (polytype $1M$). The frequent presence of streaking in the reciprocal space along the \mathbf{a}^* direction in many of these crystals showed that this polytype must be intergrown with the polytype $1M$. In fact, both structures can be described as a different stacking of the same structural unit shifted of $\frac{1}{2} \mathbf{c}$ (brackebuschite cell). All lombardoite crystals showing the $-4M$ polytype have significant Sr amount, whereas we have observed limited solid solution of Sr in lombardoite- $1M$ and of Ba in its Sr-counterpart, aldomarinoite [$\text{Sr}_2\text{Mn}^{3+}(\text{AsO}_4)_2(\text{OH})$]. Interestingly, the cationic order of Sr in the A1 sites of the brackebuschite structure leads to a volume reduction of these polyhedra, whereas the cationic ordering of Ba in the larger A2 sites accommodates the chemical strain. This helps to reduce the strain and apparently stabilizes the polytype $4M$. The Raman signal is not sensitive to the order of the layers within the analyzed volume, making the distinction of the polytypes intergrowths with similar composition unfeasible. Observations through Transmission Electron Microscopy, have been done with the aim of characterize the micro-syntactic (crystallographically oriented) intergrowths of both polytypes.