

CESAROLITE, A POSSIBLE MEMBER OF THE BIRNESSITE GROUP OF MINERALS

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ABSTRACT

Cesarolite from type locality was investigated through EPMA and synchrotron powder diffraction studies. On the basis of these preliminary results, the relationships with the phases of the birnessite group are discussed, and the possible coexistence in the studied sample of the two rhombohedral polytypes 3R1 and 3R2 is proposed to explain the features of the X-ray diffraction pattern. A structural starting model, build up from crystal-chemical considerations, was refined for both the two polytypes through the Rietveld method.

INTRODUCTION

Cesarolite is a lead manganese oxide, defined as a new species [1] on material from Sidi Amor Ben Salem mine, Tunisia, where it was found as microcrystalline friable globular masses, with submetallic lustre and steel-gray to black colour, located in cavities in galena. A density value of 5.29 g/cm³ is reported, together with chemical data recalculated to PbMn₃O₇·H₂O. X-ray data for cesarolite, presented in PDF card 14-489 (see Table 2), were obtained [2] on material from the type locality.

Both chemical and X-ray data were presented in [3] for cesarolite from type-locality. More recently [4] the chemical formula Pb_{0.54}Mn₂O₄ was reported, together with with an hexagonal R-centered cell with $a=2.8106(1)$, $c=20.386(1)$ Å, derived from powder diffraction indexing, suggesting for cesarolite a layer-type structure related to chalcophanite.

In this study we investigated a type specimen (catalog number # 28627) preserved in University of Liège.

EXPERIMENTAL

EPMA analyses gave Al₂O₃ 0.05 %, FeO 0.14 %, PbO 40.18 %, ZnO 0.51% , MnO₂ 57.8 % sum 98.68 %. Atomic absorption spectrophotometric analyses gave PbO 39.44, ZnO 0.62, MnO 5.74, CuO 0.08, CoO 0.07, MnO₂ 51.18, H₂O 2.86. The chemical formula indicated in [4] would require PbO 40.94%, MnO₂ 59.06%. The synchrotron X-ray powder diffraction data were collected at the BM8-GILDA beamline (ESRF, Grenoble, France), with $\lambda = 0.95053$ Å, recording the diffraction effects with a Fuji Imaging-Plate (IP) detector. The sample to detector distance and the image plate tilt were calibrated with X-ray powder diffraction of standard LaB6 (NIST-SRM 660a). Data were collected up to 51.5° 2 θ , corresponding to a d-space resolution of 1.094 Å. Data were reduced with the Fit2D software .

RESULTS AND DISCUSSION

Powder pattern indexing was performed through the TOPAS-Academic program [5] obtaining two cells with distinctly high figures of merit, a monoclinic C centered cell with $a=4.875$, $b=2.813$, $c=6.993$ Å, $\beta= 103.433^\circ$, and a R centered hexagonal cell with $a=b=2.813$, $c=20.408$ Å . The

monoclinic and hexagonal cell are closely related with $\mathbf{a}_{\text{monoc}} \sim \sqrt{3} \cdot \mathbf{b}$, $\mathbf{c}_{\text{monoc}} \sim \frac{1}{3} \cdot \mathbf{c}_{\text{hex}}$. The hexagonal

cell remarkably matches that proposed by Post (1994). Both cells found for cesarolite are closely related to those reported for minerals of of the birnessite group, therefore pointing to close structural relationships with this mineral group. Phases of birnessite group have been extensively studied because they are a main constituent of oceanic Mn nodules, for their environmental interest and for polytypism [6,7]. They are properly denoted as “phyllomanganates”, as they are made up by layers of edge-sharing (Mn⁴⁺O₆) octahedra, the layers also hosting Mn³⁺ or octahedral vacancies. The resulting sheet charge deficit is restored through the insertion of interlayer cations

such as Na, K, Ca, Zn... and water molecules. A close scrutiny of the powder diffraction pattern indicated, according to [6], an hexagonal layer symmetry, with the peak positions consistent with the expected ones for a $3R$ polytype. Structural solution was therefore undertaken through the TOPAS-Academic and EXPO2004 programs, but no reasonable results were obtained, also taking into account other possible polytypes with different symmetries. The hypothesis of the possible coexistence of different polytypes, already described for birnessites [6], was therefore considered; according to [6], not only the diffraction positions for each polytype, but also the relative diffraction intensities can be reliably predicted. The only major polytypes possibly present in our sample were the $3R_1$ and $3R_2$ ones, and both their different predicted diffraction patterns could be recognized in the cesàrolite diffraction pattern. A structural solution was then attempted taking into account the possible coexistence of the two $3R_1$ and $3R_2$ polytypes: the starting positions for Mn and O_{layer} were calculated following [6], whereas Pb interlayer cations were localized through the simulated annealing process in TOPAS-Academic. The subsequent Rietveld refinement converged to $wRp=2.065\%$, $R_{\text{Bragg}}=3.7, 3.6$ for $3R_1$ and $3R_2$ polytypes, with a refined abundance ratio $3R_2/3R_1 \sim 2$. Space group and cell parameters for the two polytypes were $R\bar{3}m$, $a=2.814(1)$, $c=20.408(1)$ Å. The calculated density value for the two polytypes was 5.3 g/cm^3 , to be compared to the measured value of 5.29 g/cm^3 . The chemical formula $Pb_1Mn_{2.5}O_6$, recalculated from structural refinement, compares with $(Pb_{0.72}Zn_{0.03})_{0.75}Mn^{4+}_{2.62}O_6$ recalculated from EPMA data. The existence of $3R_1$ and $3R_2$ polytypes is also known [8] for the layered structure mineral hydrotalcite, $Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$, $R\bar{3}m$ with $a=3.046$, $c=22.772$ Å, and the coexistence of $3R_1$ and $3R_2$ polytypes in synthetic hydrotalcites [9] was hypothesized. Combined TEM, IR, TG/DTA studies could provide further insight on the interlayer content of cesàrolite, and on coexistence and stacking modalities of polytypes in cesàrolite samples.

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