

Raman, crystallographic and chemical characterization of roméite-group minerals

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The roméite-group [1,2] is part of the pyrochlore supergroup and comprises some cubic oxides of $A_{2-m}B_2X_{6-w}Y_{1-n}$ formula in which Sb^{5+} predominates in the B-site. Indices m, w and n indicate vacancies in A, X and Y crystallographic sites, respectively. A-site is typically occupied by cations with ionic radii greater than 1.0 Å or H_2O , whereas X-site is usually occupied by O^{2-} , but smaller amounts of OH^- or F^- are also commonly found. Finally, Y-site is typically occupied by anions O^{2-} , OH^- or F^- ; however, large ionic radii monovalent cations ($>1.0 \text{ \AA}$) such as K^+ , Cs^+ and Rb^+ , or even H_2O can occupy it. Since the predominance of Sb^{5+} for B site is already known, the correct A and Y main occupants determine different minerals in the group and are important for the discovery of new mineral species [3]. As a source of Sb, the roméite-group minerals are economically relevant, since Sb is present in different applications, from cosmetic industry to the metal alloy production. However, only five roméite-group mineral species, namely fluorcalciroméite, hydroxycalciroméite, hydroxyferroméite, oxycalciroméite, and oxyplumboroméite have been approved by IMA. Many others can probably be discovered from possible chemical substitutions at crystallographic sites. This study analysed three different samples and determined their chemical composition by electron microprobe analysis and Raman spectra and crystal structure obtained from single-crystal X-ray diffraction. The first sample occurs in Kalugeri Hill, Babuna Valley, Jakupica Mountains, Nezilovo, Veles, Macedonia, whereas the other two occur in Prabornaz Mine, Saint Marcel, Valle d'Aosta, Italy. Sample 1 was identified as fluorcalciroméite, and samples 2 and 3 as hydroxycalciroméite. These are the first descriptions of these mineral species at the mentioned occurrences.

All samples belong to the cubic crystal system, space group $Fd\bar{3}m$, $Z = 8$, where $a = 10.2881(13) \text{ \AA}$, $V = 1088.9(4) \text{ \AA}^3$ for sample 1, $a = 10.2970(13) \text{ \AA}$, $V = 1091.8(4) \text{ \AA}^3$ for sample 2, and $a = 10.289(6) \text{ \AA}$, $V = 1089.3(19) \text{ \AA}^3$ for sample 3. The crystal structure refinements led to the convergence of R-factors of the three samples: 1) $R_1 = 0.016$. $wR_2 = 0.042$ and Goodness-of-fit = 1.176; 2) $R_1 = 0.230$. $wR_2 = 0.049$ and Goodness-of-fit = 1.095; 3) $R_1 = 0.029$. $wR_2 = 0.090$ and Goodness-of-fit = 1.338. Bond-valence calculations validated the crystal structure refinements determining the correct valences at each crystallographic site. Discrepancies observed in the Sb^{5+} bond-valence calculations were solved with the use of the proper bond valence parameters revised by Mills et al. (2009) [4]. The resulting structural formulas were $(Ca_{1.29}Na_{0.55}\square_{0.11}Pb_{0.05})_{\Sigma=2.00}(Sb_{1.71}Ti_{0.29})_{\Sigma=2.00}(O_{5.73}OH_{0.27})_{\Sigma=6.00}(F_{0.77}O_{0.21}OH_{0.02})_{\Sigma=1.00}$ for sample 1, $(Ca_{1.30}Ce_{0.51}\square_{0.19})_{\Sigma=2.00}(Sb_{1.08}Ti_{0.92})_{\Sigma=2.00}O_{6.00}(OH_{0.61}O_{0.21}F_{0.18})_{\Sigma=1.00}$ for sample 2, and $(Ca_{1.61}\square_{0.24}Na_{0.15})_{\Sigma=2.00}(Sb_{1.80}Ti_{0.20})_{\Sigma=2.00}O_{6.00}(OH_{0.48}F_{0.35}O_{0.17})_{\Sigma=1.00}$ for sample 3. The Raman spectra of all samples exhibited the characteristic bands of chemical bonds present in roméite-group minerals - the most evident one corresponded to the stretching of Sb-O bond around 510 cm^{-1} . Peaks around 1600 and 3600 cm^{-1} were observed, confirming the presence of water in the structure.

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