The crystal structure of peprossiite-(Ce), an anhydrous REE and Al mica-like borate with square-pyramidal coordination for Al

ATHOS CALLEGARI,[1,2] FRANCA CAUCIA,[1,2] FIORENZO MAZZI,[2] ROBERTA OBERTI,[1,]* LUISA OTTOLINI,[1] AND LUCIANO UNGARETTI[1,2]

[1]CNR-CS per la Cristallochimica e la Cristallografia, via Ferrata 1, I-27100 Pavia
[2]Dipartimento di Scienze della Terra, Università di Pavia, via Ferrata 1, I-27100 Pavia

ABSTRACT

Single-crystal structure refinements are presented of the holotype of crystal peprossiite-(Ce) (Monte Cavalluccio) and of a new sample from Cura di Vetralla (Viterbo, Italy) with slightly different composition, together with new EMP-SIMS chemical analyses. These results allow us to propose a new unit formula: $[REE_{1-x-y}(Th,U)_x Ca_y](Al_3O)_{2/3}[(B_{4-z}Si_z)]O_{10}$ with $x - y + z = 1/3$ ($Z = 1$) for the peprossiite group. Lattice constants for the holotype crystal are: $a = 4.612(1)$, $c = 9.374(3)$ Å, $V = 172.6$ Å^3, $Z = 1$, space group $P\bar{6}2m$. The crystal structure was solved by Patterson methods and refined to $R_{obs} = 1.8\%$ ($R_{all} = 2.2\%$) for 706 unique reflections in the 2θ-range 6–136°. Lattice constants for the thorian peprossiite-(Ce) from Cura di Vetralla are: $a = 4.596(3)$, $c = 9.309(16)$ Å, $V = 170.3$ Å^3, and the structure was refined to $R_{obs} = 2.9\%$ and $R_{all} = 3.0\%$ for 271 unique reflections in the 2θ-range 4–80°. The topology of the tetrahedral layer and the site of the inter-layer cation (REE) in peprossiite resembles that of dioctahedral micas. The main difference lies in the presence of layers of pyramids instead of layers of octahedra typical of mica. In peprossiite, Al is coordinated by five O atoms in a nearly square-pyramidal arrangement, the base of which is formed by pairs of apical O atoms from two layers of tetrahedra related by a mirror plane. Three of these pyramids share their apical O forming Al$_3$O groups with occupancy of 2/3 according to the structure refinement. A model is proposed that explains the apparent disorder in the pyramidal layer of peprossiite by the stacking within a triple cell (with $a' = a\sqrt{3}$ and $\mathbf{a} \wedge \mathbf{a}' = 30°$) of three ordered layers randomly translated by $\pm \mathbf{a}$.