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New data on ferriakasakaite-(La) and related minerals extending the compositional field of the epidote supergroup

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Abstract: Detailed studies of ferriakasakaite-(La) including determination of chemical composition and crystal structure, infrared spectroscopy, optical characteristics in reflected light and micro-indentation hardness have been carried out on a non-metamict sample from young nosean-bearing sanidinite from the Laach Lake volcanic complex, Eifel, Germany. The chemical composition is (electron microprobe, Fe^{2+}: Fe^{3+} determined from structural data, wt%): CaO 6.74, La_2O_3 13.35, Ce_2O_3 10.58, Pr_2O_3 0.42, Nd_2O_3 0.49, Sm_2O_3, 0.34, Eu_2O_3 0.18, Gd_2O_3 0.20, ThO_2 0.43, UO_2 0.10, MgO 0.89, MnO 9.98, Al_2O_3 11.47, Fe_2O_3 7.39, FeO 4.04, TiO_2 1.32, SiO_2 29.80, H_2O (calc.) 1.49, total 99.22. The empirical formula is $(Ca_{0.68}Mn^{2+}_{0.32})_{\Sigma1.00}(La_{0.49}Ce_{0.39}Pr_{0.02}Nd_{0.02}Sm_{0.01}Eu_{0.01}Gd_{0.01}Th_{0.01}Ca_{0.04})_{\Sigma1.00}(Fe^{3+}_{0.52}Fe^{2+}_{0.04}Al_{0.34}Ti^{4+}_{0.10})_{\Sigma1.00}Al_{1.00}(Mn^{2+}_{0.53}Fe^{2+}_{0.34}Mg_{0.13})_{\Sigma1.00}(Si_{2.98}Al_{0.02})_{\Sigma3.00}O_{12.00}(OH)$. The crystal structure was solved by direct methods and refined to $R = 0.018$ based on 1259 unique reflections with $I > 2\sigma(I)$. The H atom was located. The mineral is monoclinic, space group $P2_1/m$, $a = 8.9054(1)$, $b = 5.7545(1)$, $c = 10.1037(2)$ Å, $\beta = 114.103(2)°$, $V = 472.63(1)$ Å^3. The IR spectrum confirms the presence of OH groups. Reflectance spectra of ferriakasakaite-(La) obtained in the visible range show reflectance minima at the wavelength of ~590 nm. Various epidote-supergroup minerals including ferriakasakaite-(La), allanite-(Ce), Al-dominant (at the *M*1 site) analogue of ferriakasakaite-(Ce), piemontite, piemontite-(Pb), as well as Pb-, Zn- and Cu-bearing varieties of Fe^{3+}-dominant (at the *M*1 site) analogues of piemontite and piemontite-(Pb), have been discovered in sulfide-free metasomatic rocks containing oxide/oxysalt compounds of chalcophile elements (Zn, Cu, Sb, and Pb), within the Pelagonian massif, Republic of Macedonia. Crystal chemical regularities of these minerals are discussed.

Key-words: epidote supergroup; allanite group; ferriakasakaite-(La); crystal structure; Laach Lake volcanic complex; Germany; Nežilovo; Pelagonian massif; Macedonia.

1. Introduction

Epidote-supergroup minerals rich in rare-earth elements (*REE*) are common accessory components of igneous, metamorphic and metasomatic rocks. Most *REE*-dominant epidote-supergroup minerals belong to the allanite group, which includes 15 species. Allanite-group minerals (or 'allanites' in the following) are monoclinic neso-soro silicates with the general formula $A1A2M1M2M3(Si_2O_7)(SiO_4)O(OH)$ where $A1 = Ca$, Mn^{2+} (sometimes with minor Na); $A2 = REE^{3+}$ (sometimes with subordinate or minor Ca, Pb^{2+}, Sr, Ba, Th^{4+}, U^{4+}); $M1,2 = Al$, Fe^{3+}, Mn^{3+}, V^{3+} (sometimes with subordinate or minor Cr^{3+}, Ti^{4+}, Sn^{4+}); $M3 = Fe^{2+}$, Mg, Mn^{2+} (sometimes with subordinate or minor amounts of trivalent cations, such as Fe^{3+} and/or Mn^{3+}) (Armbruster *et al.*, 2006; Mills *et al.*, 2009). The *M*1–3 cations have octahedral coordination. In all known 'allanites' the *M*2 site is Al-dominant, whereas the sites *A*1, *A*2, *M*1, and *M*3 show wide compositional variations.

The presumed Mn^{2+}-dominant analogue of ferriallanite-(La) was discovered by us in 2010 in the course of investigations of the new mineral species piemontite-(Pb)

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