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Graţianite, $MnBi_2S_4$, a new mineral from the Băiţa Bihor skarn, Romania

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Abstract

The new mineral graţianite, $MnBi_2S_4$, is described from the Băiţa Bihor skarn deposit, Bihor County, Romania. Graţianite occurs as thin lamellae, intimately intergrown with cosalite and bismuthinite, or as flower-shaped blebs within chalcopyrite, where it is associated with cosalite and tetradymite. Graţianite displays weak to modest bireflectance in air and oil, respectively, and strong anisotropy. The mean empirical composition based on 20 electron probe microanalyses is: $(Mn_{0.541}Fe_{0.319}Pb_{0.070}Cu_{0.040}Cd_{0.009}Ag_{0.001})_{\Sigma 0.980}(Bi_{1.975}Sb_{0.018})_{\Sigma 1.993}(S_{4.008}Se_{0.012}Te_{0.007})_{\Sigma 4.027}$, corresponding to the ideal formula $MnBi_2S_4$. Graţianite crystallizes in the monoclinic system (space group $C2/m$). Single-crystal X-ray studies of material extracted by the focused ion beam-scanning electron microscopy (FIB-SEM) technique, and carried out on the MX2 macromolecular beamline of the Australian Synchrotron determined the following cell dimensions: $a = 12.6774(25)$ Å, $b = 3.9140(8)$ Å, $c = 14.7581(30)$ Å, $\beta = 115.31(3)°$, $V = 662.0(2)$ Å^3, and $Z = 4$. The six strongest X-ray reflections and their relative intensities are: 3.448 Å (100), 2.731 Å (77), 2.855 Å (64), 3.637 Å (55), 3.644 Å (54), and 3.062 Å (51).

Graţianite is the monoclinic analog of berthierite ($FeSb_2S_4$), garavellite [$Fe(Bi,Sb)_2S_4$] and clerite [$Mn(Sb,As)_2S_4$] (Nickel-Strunz class 02.HA.20). It is isostructural with synthetic sulfides and selenides in the $MnBi_2S_4$–$MnSb_2S_4$ and $MnBi_2Se_4$–$MnSb_2Se_4$ series, and with grumiplucite ($HgBi_2S_4$) and kudriavite, [$(Cd,Pb)Bi_2S_4$], ^{3}P members of the pavonite homologous series. The mineral is named for Graţian Cioflica (1927–2002), formerly Professor in Mineralogy and Ore Deposits at the University of Bucharest, Romania.

The Băiţa Bihor skarn, like others within the same belt, is geochemically complex. The availability of Cu, Zn, and Pb, but also Ag, Bi, Mo, and B, as well as a wide range of minor elements, has created an environment allowing for crystallization of an unusually diverse range of discrete minerals. Graţianite is part of the peculiar associations of Bi–Pb-sulfosalts and Bi-chalcogenides that are genetically related to Au-enrichment. This study demonstrates the versatility of FIB-SEM techniques for in situ extraction of small volumes of well-characterized material, coupled with single-crystal X-ray analysis using synchrotron radiation, for the characterization of new minerals.

Keywords: Graţianite, new mineral, bismuth-manganese-sulfosalt, Băiţa Bihor, pavonite homologous series