Harmunite CaFe$_2$O$_4$: A new mineral from the Jabel Harmun, West Bank, Palestinian Autonomy, Israel

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ABSTRACT

Harmunite, naturally occurring calcium ferrite CaFe$_2$O$_4$, was discovered in the Hatrurim Complex of pyrometamorphic larnite rocks close to the Jabel Harmun, the Judean Desert, West Bank, Palestinian Autonomy, Israel. The new mineral occurs in larnite pebbles of the pseudo-conglomerate, the cement of which consists of intensely altered larnite-bearing rocks. Srebrolodskite, magnesioferrite, and harmunite are intergrown forming black porous aggregates to the central part of the pebbles. Lamite, fluorelastadite, ye’elimite, fluoromayenite, gehlenite, tennesite, and calcioanglemite are the main associated minerals. Empirical crystal chemical formula of harmunite from type specimen is as follows Ca$_{1.011}$(Fe$^{3+}_{0.957}$Al$_{0.013}$Cr$^{3+}_{0.011}$Ti$_{0.004}$Mg$_{0.003}$)Fe$^{3+}_{0.991}$O$_4$. Calculated density is 4.404 g/cm$^3$, microhardness VH$_{MN}$ is 655 kg/mm$^2$. The Raman spectrum of harmunite is similar to that of the synthetic analog. Harmunite has been black and under reflected plane-polarized light is light gray with red internal reflections. Reflectance data for the COM wavelengths vary from ~22% (400 nm) to ~18% (700 nm).

The crystal structure of harmunite [Pnma; $a = 9.2183(3)$, $b = 3.0175(1)$, $c = 10.6934(4)$ Å; $Z = 4$, $V = 297.45(2)$ Å$^3$], analogous to the synthetic counterpart, was refined from X-ray single-crystal data to $R_1 = 0.0262$. The structure of CaFe$_2$O$_4$ consist of two symmetrically independent FeO$_6$ octahedra connected by common edges, forming double rutile-type $[[Fe_2O_4]$ chains. Four such double chains are further linked by common oxygen corners creating a tunnel-structure with large trigonal prismatic cavities occupied by Ca along [001]. The strongest diffraction lines are as follows [$d_{hkl}$, (I)]: 2.6632 (100), 2.5244 (60), 2.6697 (52), 1.8335 (40), 2.5225 (35), 2.2318 (34), 1.8307 (27), 1.5098 (19). Crystallization of harmunite takes place in the presence of sulfate melt.

Keywords: Harmunite; calcium ferrite; Raman; structure; Jabel Harmun, Palestinian Autonomy, Israel

INTRODUCTION

The new mineral harmunite CaFe$_2$O$_4$ (IMA2012-045) was discovered in pyrometamorphic larnite rocks belonging to the Hatrurim Formation (also known as the “Mottled Zone”; Bentor 1960; Gross 1977; Vapnik et al. 2007; Novikov et al. 2013). The name is given after Mt. Harmun (Jabel Harmun in Arabic language) where the rock was sampled, at the Hatrurim Formation complex situated in the Judean Desert, West Bank, Palestinian Autonomy, Israel (31°46’N–35°26’E). Type materials were deposited in the mineralogical collections of the Saint Petersburg University, Russia, catalog number 1/19518, and of the Fersman Mineralogical Museum, Moscow, Russia, catalog number 4398/1.

Natural CaFe$_2$O$_4$ was previously described from burned fossilized woody relics of siderite composition enclosed in pyrogenic iron ore in an ancient fire of the Kuzbass, Russia (Nigmatulina and Nigmatulina 2009). This mineral, which the authors called “aciculate,” has a significant Mn content (4.64–6.70 wt% MnO) and forms exsolution structures in magnesioferrite (Nigmatulina and Nigmatulina 2009). Furthermore, CaFe$_2$O$_4$ also named “aciculate,” was described from a burned dump of the Chelyabinsk coal basin by Chenskov et al. (1998). The origin of this phase is considered as anthropogenic; therefore it was not approved by the CNMNC of the IMA as a valid mineral species.

Synthetic calcium ferrite, CaFe$_2$O$_4$ is a well-known material widely used as a pigment, catalyst, thermally stable material, conductor, solid electrolyte, ceramic material, etc. (Candeia et al. 2004; Kharton et al. 2008). Its crystal structure was first reported by Hill et al. (1956) and then by Decker and Kasper (1957).

Many isotopic compounds have been reported and “calcium-ferrite type” became the common term used for structural description. For instance, Shizuya et al. (2007) has summarized related compounds having the CaFe$_2$O$_4$ structure type, based on the AB$_2$O$_3$ chemical formula ($A = Li, Na, Mg, Ca, Sr, Ba, La, and Eu; B = Ti, V, Cr, Mn, Fe, Ru, Rh, Al, Ga, In, Tl, Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Yb, and Lu$). In Nature only two phases possessing this structure type are known: xiete FeCr$_2$O$_4$ ($Bbmm$, $a = 9.462(6)$, $b = 9.562(9)$, $c = 2.916(1)$ Å) = high-pressure polymorph of chromite (Chen et al. 2008), and

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