

The Lipscombite Enigma: EMPA, Micro-XANES and Single-crystal X-ray Structure Refinements of Synthetic Crystals

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The name lipscombite (pre-IMA) was originally given to synthetic hydrous iron phosphates of compositions from $\text{Fe}^{2+}_8[\text{PO}_4]_4(\text{OH})_4$ to $\text{Fe}^{3+}_{3.5}[\text{PO}_4]_4(\text{OH})_4$ and the space group $I4_722$, $a=5.37$ and $c=12.81\text{\AA}$ (Gheith 1953; Katz and Lipscomb, 1951). Subsequent studies of natural lipscombite yielded an ideal formula $\text{Fe}^{2+}\text{Fe}^{3+}_2[\text{PO}_4]_2(\text{OH})_2$ with the space group $P4_32_12$, $a=7.40$ and $c=12.71\text{\AA}$ (Cech et al., 1961; Lindberg 1962). Similarly, Chukanov et al. (2007) reported the space group $P4_32_12$ or $P4_12_12$, $a=7.242(2)$ and $c=13.125(5)\text{\AA}$ for zinlipscombite $\text{ZnFe}^{3+}_2[\text{PO}_4]_2(\text{OH})_2$. Vochten and DeGrave (1981) and Vochten et al. (1983) adopted the space group $I4_722$ [$a=5.3020(5)$ and $c=12.8800(5)\text{\AA}$] for their synthetic lipscombite, whereas Vencato et al. (1989) gave the space group $P4_32_12$, $a=7.310(3)$ and $c=13.212(7)\text{\AA}$ for another synthetic lipscombite. However, Matvienko et al. (1981) noted a clearly defined pseudo-symmetry ($a'=a/2$) in their synthetic lipscombite and reported the space group $P4_32_12$, $a=14.961(3)$ and $c=12.740(3)\text{\AA}$. In addition, several authors (Louseau et al. 1993; Dolle et al. 2005) reported synthetic lipscombite $\text{Fe}^{3+}_{1.21}(\text{PO}_4)_X$ ($X=\text{F}, \text{OH}, \text{H}_2\text{O}$) to possess the space group $I4_1/amd$, $a=5.184(1)$ and $c=13.040(5)\text{\AA}$. Similarly, Song et al. 2005 reported synthetic Ni- and Zn-bearing lipscombite to have the space group $I4_1/amd$ as well. Huminicki and Hawthorne (2002) concluded that lipscombite remains an enigma.

We have synthesized leaf-like crystals of variable colors from light pink to light green, green and dark green in the system $\text{Fe}-\text{NaH}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$ at temperatures from 160 °C and 180 °C and pH from 1 to 2. Electron microprobe analyses show that these colored varieties have an essentially uniform Fe:P atomic ratio of ~1.2. Micro-XANES Fe-K edge spectra confirmed that Fe^{3+} is the predominant oxidation state. Single-crystal X-ray diffraction datasets of our synthetic lipscombite are generally consistent with the space group $I4_1/amd$, but those of green crystals after 24-hour-long scan reveal weak reflections that are indicative of the superstructure reported by Matvienko et al. (1981). These results collectively suggest that the lipscombite series involve not only significant compositional variations involving Fe^{2+} , Fe^{3+} and vacancies and between O and OH (and possibly F and H_2O as well) but also complex order-disorder at the octahedral sites.