



## Article

# Nomenclature of the magnetoplumbite group

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### Abstract

A nomenclature and classification scheme has been approved by IMA–CNMNC for the magnetoplumbite group, with the general formula  $A[B_{12}]O_{19}$ . The classification on the highest hierarchical level is decided by the dominant metal at the 12-coordinated  $A$  sites, at present leading to the magnetoplumbite ( $A = \text{Pb}$ ), hawthorneite ( $A = \text{Ba}$ ) and hibonite ( $A = \text{Ca}$ ) subgroups. Two species remain ungrouped. Most cations, with valences from 2+ to 5+, show a strong order over the five crystallographic  $B$  sites present in the crystal structure, which forms the basis for the definition of different mineral species. A new mineral name, chihuahuaite, is introduced and replaces hibonite-(Fe).

**Keywords:** magnetoplumbite group, plumboferrite, chihuahuaite, hexagonal ferrite, hexagonal aluminate, mineral nomenclature, mineral classification

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### Introduction

The mineral magnetoplumbite was described by Aminoff (1925) from the Långban iron-manganese mines, Värmland County, Sweden. The formula and the topology of the crystal structure was first correctly interpreted by Adelsköld (1938). The composition of this archetypal mineral is given as ideally  $\text{Pb}[\text{Fe}_{12}]\text{O}_{19}$ . It is isostructural with  $\text{Ba}[\text{Fe}_{12}]\text{O}_{19}$  (barioferrite), a common synthetic permanent magnetic material (e.g. Pullar, 2012). They both belong to a wider family of compounds, the so-called hexagonal ferrites (or hexaferrites). The group members (Table 1) are rare as minerals, but are found in a variety of geological environments, including metasomatic skarns, high-grade metamorphic rocks (granulites), kimberlites, lherzolites, lamproites, volcanic and pyrometamorphic rocks and chondritic meteorites, altogether indicating significantly wide  $P$ – $T$ – $f_{\text{O}_2}$  stability conditions for the structure type. The minerals of the group, all possessing basic hexagonal crystal symmetry, are described by the general formula  $AB_{12}O_{19}$ , where  $A$  is a large cation ( $A^{2+}$  or  $A^{1+}$ ) and  $B$  usually represents more highly charged cations of intermediate size. In the present paper, we announce the newly approved (by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association, IMA–CNMNC) nomenclature for the magnetoplumbite group (decision 95–SM/20, Miyawaki *et al.*, 2020). It should be noted that in this context, we use the commonly accepted formulae of mineral species; the exactness of some of them might be questioned, and a future revision based on reinvestigation of type specimens is desirable.

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### Crystal structure

Many detailed studies of the crystal structure exist (e.g. Obradors *et al.*, 1985; Utsunomiya *et al.*, 1988; Moore *et al.*, 1989; Wagner 1998). It is based on an essentially closest-packed arrangement of oxygen (O) and  $A$  atoms, with  $B$  metals occupying voids. One fundamental building block,  $S$ , forms a CCP two-layer sequence,  $\cdot\text{cc}\cdot$ . A fraction of the interstitial sites is occupied by metal atoms in the same fashion as in the spinel structure, which gives an overall composition  $\{B_6O_8\}^{2+}$  of the block. A different block, denoted  $R$ , is built up of a three-layer HCP sequence,  $\cdot\text{hhh}\cdot$ . A quarter of the O atoms of the intermediate h layer is replaced by a large cation  $A$  (usually  $\text{Ba}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$  or  $\text{K}^+$  in minerals). Taking the interstitial  $B$  atoms into consideration,  $R$  is equal to  $\{AB_6O_{11}\}^{2-}$  in composition. By stacking of the blocks along the hexagonal  $c$  axis in the sequence  $\cdot\text{RSR}^*\text{S}^*$ , with a repeat of 22–23 Å, the magnetoplumbite unit cell with  $Z = 2$  is obtained (Fig. 1). Starred blocks are rotated 180° in accordance with the space-group symmetry of the crystal structure,  $P6_3/mmc$ . The  $a$  unit-cell dimension is  $\sim 5.6$  Å ( $= 4 \times$  the radius of  $\text{O}^{2-}$ ).

In the structure, the large  $A$  cation is ideally 12-coordinated to O, forming a triangular orthobicupola, at  $(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$ . The interstitial  $B$  atoms occupy five unique sites with designations  $M1$ – $M5$ . (Table 2). The five-fold coordinated  $M2$  atom, ideally located at the centre of a trigonal bipyramid ( $2b$ ), is in reality slightly displaced (split) into two statistically half-occupied, pseudotetrahedral  $4e$  sites (Obradors *et al.*, 1985). This kind of disorder is dynamic in most situations, i.e. a rapid diffusion of the metal atom takes place through the mirror plane of the bipyramid (Kimura *et al.*, 1990; Kreisel *et al.*, 1998; Du and Stebbins, 2004; Krz̄ała *et al.*, 2018). The  $M4$  coordination polyhedra are trigonally distorted octahedra that occur in pairs sharing a common face in a hematite-like arrangement, i.e. forming  $B_2O_9$  dimers.

**Table 1.** The presently valid magnetoplumbite-group minerals.

Name	Formula	Type locality	References
Plumboferrite	Pb[Fe <sub>10.67</sub> Mn <sub>0.33</sub> Pb]O <sub>18.33</sub>	Jakobsberg mine, Värmland, Sweden	Igelström (1881); Holtstam <i>et al.</i> (1995)
Magnetoplumbite	Pb[Fe <sub>12</sub> ]O <sub>19</sub>	Långban mines, Värmland, Sweden	Aminoff (1925); Holtstam (1994)
Hibonite	Ca[Al <sub>12</sub> ]O <sub>19</sub>	Esiva alluvial deposit, Madagascar	Curien <i>et al.</i> (1956); Bermanec <i>et al.</i> (1996)
Yimengite	K[Ti <sub>3</sub> Cr <sub>3</sub> Fe <sub>2</sub> <sup>3+</sup> Mg <sub>2</sub> <sup>2+</sup> ]O <sub>19</sub>	Yimeng Shan, Shangdong, China	Dong <i>et al.</i> (1983); Peng ad Lu (1985)
Hawthorneite	Ba[Ti <sub>3</sub> Cr <sub>4</sub> Fe <sub>2</sub> <sup>3+</sup> Fe <sub>2</sub> <sup>2+</sup> Mg]O <sub>19</sub>	Bultfontein diamond mine, Northern Cape, South Africa	Grey <i>et al.</i> (1987); Haggerty <i>et al.</i> (1989)
Nežilovite	Pb[Mn <sub>2</sub> <sup>4+</sup> Fe <sub>7</sub> AlZn <sub>2</sub> ]O <sub>19</sub>	Nežilovo, North Macedonia	Bermanec <i>et al.</i> (1996)
Haggertyite	Ba[Ti <sub>5</sub> Fe <sub>3</sub> <sup>3+</sup> Fe <sub>2</sub> <sup>2+</sup> Mg]O <sub>19</sub>	Crater of Diamonds State Park, Arkansas, USA	Grey <i>et al.</i> (1998)
Batiferrite	Ba[Ti <sub>2</sub> Fe <sub>8</sub> <sup>3+</sup> Fe <sub>2</sub> <sup>2+</sup> ]O <sub>19</sub>	Üdersdorf, Eifel area, Germany	Lengauer <i>et al.</i> (2001)
Barioferrite	Ba[Fe <sub>12</sub> ]O <sub>19</sub>	Mount Ye'elim, Hatrurim Complex, Israel	Murashko <i>et al.</i> (2011)
Hibonite-(Fe)*	Fe <sup>2+</sup> [Al <sub>12</sub> ]O <sub>19</sub>	Allende carbonaceous chondrite, Mexico	Ma (2010)
Gorerite	Ca[AlFe <sub>11</sub> ]O <sub>19</sub>	Hatrurim Complex, Israel	Galuskin <i>et al.</i> (2019)

\*Here renamed chihuahuaite

The total unit-cell contents for an  $AB_{12}O_{19}$  compound can thus be expressed as  $A_2[{}^{6i}(M1)_2\ {}^{5i}(M2)_2\ {}^{4i}(M3)_4\ {}^{6i}(M4)_4\ {}^{6i}(M5)_{12}]_{\Sigma 24}O_{38}$ .

The magnetic structure of magnetoplumbite can be described by the Néel model of ferrimagnetism. The spin orientation of  $Fe^{3+}$  at each site (Table 2) is a result of superexchange interaction through the  $O^{2-}$  ions. As the cation has a spin-only magnetic moment of  $5\ \mu_B$  (Bohr magnetons), the total magnetisation per formula unit would be  $(6-2-2+1+1) \times 5\ \mu_B = 20\ \mu_B$  at absolute temperature, which is in good agreement with experimental results (Kojima, 1982). Magnetoplumbite possesses a large magnetocrystalline anisotropy, which is related to a strong preference of the magnetic moments of the ions to align along  $c$ .

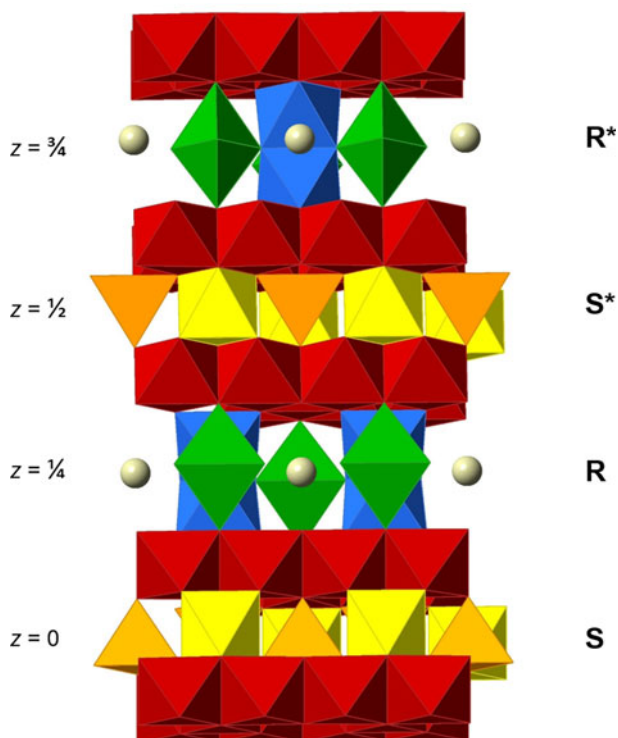
$\beta$ -alumina (diaoyudaoite), ideally  $Na[Al_{11}]O_{17}$ , is a structural derivative of magnetoplumbite (Felsche, 1968) and a common solid-state ion conductor and catalyst. The three  $O3$  atoms at  $6h$  ( $x, -x, \frac{1}{4}$ ) in the middle  $h$  layer of the  $R$  block have collapsed to a single point  $2c$  ( $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$ ), compensating for the total lower charge of the metal atoms in this compound. Consequently,  $R$  encompasses  $\{AB_5O_9\}^{2-}$  and does not contain the nominally 5-coordinated  $M2$  site. The mirror planes at  $z = \frac{1}{4}$  and  $\frac{3}{4}$  correspond to the ion conduction layer in  $\beta$ -alumina.

## Nomenclature

### Name of the group

Prior to this work, the group had not been formally approved by CNMNC. However the term 'magnetoplumbite group' is prevalent in the literature. Strunz and Nickel (2001) denominated the oxide subclass 4.CC.45 as the magnetoplumbite group, which included diaoyudaoite, plumboferrite and lindqvistite. In recent editions of Fleischer's Glossary of Mineral Species (Back, 2018) the 'plumboferrite group', covering the same group of minerals (Table 1), has been introduced. It was then in principle used as a synonym of the magnetoplumbite group.

Although plumboferrite has historical precedence over magnetoplumbite (discovered in 1881 and 1925, respectively), there are several good arguments to keep magnetoplumbite in the group name. In chemistry and materials science, the concept of magnetoplumbite (or simply 'M') type compounds for substances possessing a certain crystal structure is extremely well established (e.g. Collongues *et al.*, 1990; Pullar, 2012). It would be misleading if the mineralogical nomenclature deviated from other areas of science. The true interpretation of the composition of plumboferrite, and its close relationship to magnetoplumbite is in fact a relatively late insight (Holtstam *et al.*, 1995). Furthermore, plumboferrite is atypical in its formula and slightly different in atomic arrangement compared to other members, including positional disorder of Pb atoms and oxygen vacancies (related to  $6s^2$  lone electron-pair effects of the  $Pb^{2+}$  ion) in the region of  $z = \frac{1}{4}$  that give rise to weak superstructure reflections in X-ray diffraction data. This species is thus not ideal as an archetype for the group as a whole, although the deviations do not support it to be kept outside the group. The present choice agrees with the statement by Mills *et al.* (2009): "a group or a supergroup name can be selected contrary to the precedence rule because the name of this group (supergroup) is very firmly established in the literature."



**Fig. 1.** Polyhedral representation of the ideal magnetoplumbite-type structure viewed approximately along  $[310]$ . The  $M1$  octahedra (yellow) and the  $M3$  tetrahedra (orange) are in the central section of the  $S$  block. The trigonal bipyramidal  $M2$  positions (green), face-sharing  $M4$  octahedra (blue) and the large  $A$  atoms (grey spheres) belong to the central part of the  $R$  block. Layers of edge-sharing  $M5$  octahedra (red) are sandwiched between the cores of blocks.

**Table 2.** Properties of crystallographic sites for *A* and *B* metal atoms in magnetoplumbite-group minerals.

Site	Wyckoff position	CN	Point symmetry	Block	Magnetic spin (Fe <sup>3+</sup> )
<i>A</i>	2 <i>d</i>	12	$\bar{6}m2$	<b>R</b>	
<i>M1</i>	2 <i>a</i>	6	$\bar{3}m$	<b>S</b>	↑
<i>M2</i>	2 <i>b</i> (4 <i>e</i> )	5 (4 + 1)	$\bar{6}m2$ (3 <i>m</i> )	<b>R</b>	↑
<i>M3</i>	4 <i>f</i>	4	3 <i>m</i>	<b>S</b>	↓
<i>M4</i>	4 <i>f</i>	6	3 <i>m</i>	<b>R</b>	↓
<i>M5</i>	12 <i>k</i>	6	<i>m</i>	<b>R-S</b>	↑

CN – coordination number

**Table 3.** Classification of the magnetoplumbite group.**Magnetoplumbite subgroup, A = Pb**

Magnetoplumbite

Plumboferrite

Nežilovite

**Hawthorneite subgroup, A = Ba**

Hawthorneite

Haggertyite

Batiferrite

Barioferrite

**Hibonite subgroup, A = Ca**

Hibonite

Gorerite

**Members that do not belong to a subgroup**

Yimengite, A = K

Chihuahuaite [previously hibonite-(Fe)], A = Fe<sup>2+</sup>**Consequences**

Although the β-alumina-type minerals, presently diaoyudaite (Shen *et al.*, 1986) and kahlenbergite, K[Al<sub>11</sub>]O<sub>17</sub> (Krüger *et al.*, 2019), were included in a previous grouping, they are not part of the present nomenclature because of the requirement of isostructurality.

The mineral name hibonite-(Fe), for Fe[Al<sub>12</sub>]O<sub>19</sub> (Ma, 2010), does not fit well in this scheme as it does not belong to the same subgroup as the parent mineral, hibonite. In addition, suffixes tend to make nomenclature unnecessarily complex. Hibonite-(Fe) is thus assigned a new root name, 'chihuahuaite', after the state (estado) of Mexico where Allende, the holotype host meteorite fell in 1969 (King *et al.*, 1969). Levison modifiers may, however, be used if rare earth element (REE) dominant species are to be approved (with new root names).

Lindqvistite, Pb[Fe<sub>16</sub>Pb(Mn,Mg)]O<sub>27</sub>, is a related mineral (Holtstam and Norrestam, 1993). It has the block stacking

sequence ·RSSR\*S\*S\*· and thus a different topology than magnetoplumbite. Lindqvistite is consequently not counted as a member of the magnetoplumbite group. Galuskin *et al.* (2018) have reported closely related Ba- and K-dominant ferrites from Jabel Harmun, West Bank, Palestinian Territories. Further discoveries could motivate the creation of a supergroup, covering different stacking themes among naturally occurring ferrites.

**Subdivision**

The nomenclature is devised to be simple and flexible at the same time. The group is divided into subgroups based on composition, specifically the dominant *A*-type cation (Table 3). The rationale for this scheme is that variations in *A* atom composition tend to be less complex compared to that of *B* atoms, and information on the precise stoichiometry, including any structural vacancies at cation or anion sites that might be present, is not necessary to determine the position at the highest hierarchical level in the group.

**Definition of species**

Individual species of the magnetoplumbite group are further defined from their composition and distribution of cations over the *B*-type positions (Table 4). Monovalent, divalent, tetravalent and pentavalent cations are incorporated in the magnetoplumbite structure by charge-coupled substitutions of A<sup>2+</sup> or B<sup>3+</sup> ions (Table 5). It is evident that a large number of theoretically possible combinations of cation arrangements exist. However, studies on both minerals and synthetic materials show that most cations exhibit preferential ordering depending on their ionic size, charge and electronic configuration (Grey *et al.*, 1987; Wagner and O'Keefe, 1988; Xie and Cormack, 1990; Bermanec *et al.*, 1996; Holtstam, 1996; Nagashima *et al.*, 2010). An important trend observed is that divalent *B*-type ions strongly prefer the tetrahedrally coordinated *M3* sites (Batlle *et al.*, 1991), whereas highly charged species, like Ti<sup>4+</sup>, Mn<sup>4+</sup> and Sb<sup>5+</sup>, become enriched in the *M4* octahedra (Doyle *et al.*, 2014; Nemrava *et al.*, 2017). For compositions with a high degree of replacement of trivalent ions, divalent species also become concentrated at octahedrally coordinated sites, preferentially *M5* (Cabañas *et al.*, 1994). Some trivalent *d* cations (Cr<sup>3+</sup> and Mn<sup>3+</sup>) are ordered at the distorted *M5* octahedra (e.g. Katlakunta *et al.*, 2015; Shlyk *et al.*, 2015; Nemrava *et al.*, 2017). This behaviour is explained largely by crystal-field effects. The Fe<sup>3+</sup> cation, in cases when diluted in the compound and less abundant among *B* positions, e.g. in hibonite, is accumulated at *M2* and *M3* (Holtstam, 1996; Medina and Subramanian, 2017). Al<sup>3+</sup> in turn, when competing with other trivalent species, tends

**Table 4.** Major components at the cation sites of magnetoplumbite-group minerals. Species-defining elements are given in bold.

Mineral	<i>A</i>	<i>M1</i>	<i>M2</i>	<i>M3</i>	<i>M4</i>	<i>M5</i>
Magnetoplumbite	<b>Pb</b>	<b>Fe<sup>3+</sup></b>	<b>Fe<sup>3+</sup></b>	<b>Fe<sup>3+</sup></b> , Mn <sup>2+</sup>	<b>Fe<sup>3+</sup></b> , Ti <sup>4+</sup> , Sb <sup>5+</sup>	<b>Fe<sup>3+</sup></b> , Mn <sup>3+</sup>
Plumboferrite	<b>Pb</b>	<b>Fe<sup>3+</sup></b>	<b>Pb<sup>2+</sup></b>	<b>Fe<sup>3+</sup></b> , Mn <sup>2+</sup>	<b>Fe<sup>3+</sup></b>	<b>Fe<sup>3+</sup></b>
Nežilovite	<b>Pb</b>	<b>Al</b>	<b>Fe<sup>3+</sup></b>	<b>Zn</b>	<b>Mn<sup>4+</sup></b> , Ti <sup>4+</sup>	<b>Fe<sup>3+</sup></b> , Mn <sup>3+</sup>
Hawthorneite	<b>Ba</b>	<b>Cr<sup>3+</sup></b>	<b>Fe<sup>3+</sup></b>	<b>Fe<sup>2+</sup></b> , Mg	<b>Ti<sup>4+</sup></b>	<b>Cr<sup>3+</sup></b> , <b>Fe<sup>3+</sup></b>
Haggertyite	<b>Ba</b> , K	<b>Ti<sup>4+</sup></b> , <b>Fe<sup>3+</sup></b>	<b>Fe<sup>3+</sup></b>	<b>Fe<sup>2+</sup></b>	<b>Ti<sup>4+</sup></b>	<b>Ti<sup>4+</sup></b> , <b>Fe<sup>2+</sup></b>
Batiferrite	<b>Ba</b>	<b>Fe<sup>3+</sup></b>	<b>Fe<sup>3+</sup></b>	<b>Fe<sup>2+</sup></b>	<b>Ti<sup>4+</sup></b> , <b>Fe<sup>3+</sup></b>	<b>Fe<sup>3+</sup></b> , <b>Ti<sup>4+</sup></b>
Barioferrite	<b>Ba</b>	<b>Fe<sup>3+</sup></b>	<b>Fe<sup>3+</sup></b>	<b>Fe<sup>3+</sup></b>	<b>Fe<sup>3+</sup></b>	<b>Fe<sup>3+</sup></b>
Hibonite	<b>Ca</b>	<b>Al</b>	<b>Al</b>	<b>Al</b>	<b>Al</b>	<b>Al</b>
Gorerite	<b>Ca</b>	<b>Al</b>	<b>Fe<sup>3+</sup></b>	<b>Fe<sup>3+</sup></b>	<b>Fe<sup>3+</sup></b>	<b>Fe<sup>3+</sup></b>
Yimengite	<b>K</b>	<b>Fe<sup>3+</sup></b>	<b>Fe<sup>3+</sup></b>	<b>Mg<sup>2+</sup></b> , <b>Fe<sup>2+</sup></b>	<b>Ti<sup>4+</sup></b>	<b>Cr<sup>3+</sup></b>
Chihuahuaite	<b>Fe<sup>2+</sup></b> , Mg	<b>Al</b>	<b>Al</b>	<b>Al</b>	<b>Al</b>	<b>Al</b>

**Table 5.** Significant types of substitution in the magnetoplumbite group.

Generalised substitution	Example
<b>Homovalent</b>	
$A^{2+} \rightarrow A^{2+}$	$Pb^{2+} \rightarrow Ba^{2+}$
$B^{3+} \rightarrow B^{3+}$	$Fe^{3+} \rightarrow Cr^{3+}$
<b>Heterovalent</b>	
$2B^{3+} \rightarrow B^{2+} + B^{4+}$	$2Al^{3+} \rightarrow Mg^{2+} + Ti^{4+}$
$3B^{3+} \rightarrow 2B^{2+} + B^{5+}$	$3Fe^{3+} \rightarrow 2Mn^{2+} + Sb^{5+}$
$A^{2+} + B^{3+} \rightarrow A^{1+} + B^{4+}$	$Ba^{2+} + Fe^{3+} \rightarrow K^{+} + Ti^{4+}$
$A^{2+} + B^{3+} \rightarrow A^{3+} + B^{2+}$	$Ca^{2+} + Al^{3+} \rightarrow REE^{3+} + Mg^{2+}$
$2B^{3+} + O^{2-} \rightarrow B^{2+} + B^{2+} + \square$	$2Fe^{3+} + O^{2-} \rightarrow Pb^{2+} + Mn^{2+} + \square$

\*Describes the relation between magnetoplumbite and plumboferrite, and explains non-stoichiometry in some synthetic magnetoplumbite samples (Holtstam, 2003).

to be concentrated at M1 (Bermanec *et al.*, 1996), with the smallest octahedral volume.

### New or unaccredited mineral compositions

In the literature, analytical data are available that suggest the existence of new, yet officially unrecognised members of the group. Titanium-rich analogues of yimengite and hawthorneite (~5 Ti atoms per formula unit) were analysed by Lu and Chou (1994). Lu *et al.* (2007) have described a “Ca analogue to yimengite” or rather a Ca analogue to hawthorneite, which would fit into the hibonite subgroup. Rezvukhin *et al.* (2019) recently found yimengite with high Al (>1 atom per formula unit) contents. Sandiford and Santosh (1991) described zoned ‘hibonite’ grains with REE-rich cores ( $\Sigma REE > 0.6$  atoms per formula unit). Holtstam (1994) reported a Ti-rich magnetoplumbite sample for which Ti > Fe<sup>3+</sup> at M4 could be inferred (a possible Pb analogue to batiferite). A Mn<sup>3+</sup>-analogue to plumboferrite was detected by Chukanov *et al.* (2016). Furthermore, Chukanov *et al.* (2019) recently published analyses of a Ba-dominant analogue to nežilovite and of an Al analogue to yimengite.

From a vast amount of studies of synthetic compounds, it can be speculated that many new natural members exist with, for example:  $A = Sr^{2+}$ , REE (Ce<sup>3+</sup>, La<sup>3+</sup> etc.), Mg<sup>2+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup> or Ag<sup>+</sup> along with enrichment in the B positions (non-exhaustive list) of: Si<sup>4+</sup>, Sc<sup>3+</sup>, Ti<sup>3+</sup>, V<sup>2+</sup>, V<sup>3+</sup>, V<sup>4+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Ga<sup>3+</sup>, Ge<sup>4+</sup>, Zr<sup>4+</sup>, Nb<sup>5+</sup>, In<sup>3+</sup>, Sn<sup>4+</sup>, Te<sup>4+</sup>, Ta<sup>5+</sup> or Bi<sup>3+</sup> (e.g. Coutellier *et al.*, 1984; Morgan and Miles, 1986; Li *et al.*, 2016). The range of possible cation valences seem to be limited to 1–3 for A and 2–5 for B sites, which has implications when casting formulae of uncharacterised members of the group. Particular caution is needed for samples containing some of the divalent ionic species, as Fe<sup>2+</sup>, Mg<sup>2+</sup> and Pb<sup>2+</sup> have been shown to enter both kinds of sites. Substitutions at anion sites seem to be limited for this structure type.

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