



## Colored oxides with hibonite structure: A potential route to non-cobalt blue pigments



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### ABSTRACT

The crystal structure of hibonite with an ideal formula  $\text{CaAl}_2\text{O}_9$  is hexagonal  $P6_3/mmc$ , isostructural with magnetoplumbite. Natural and synthetic hibonites have been widely studied for their formation, compositions, crystal structures, properties and applications. Recent increasing interest in its coloration has led to the search of inorganic pigments based on the hibonite structure. We present here the syntheses and characterization of hibonite compounds with a general formula of  $A\text{Al}_{12-x}M_x\text{O}_{19}$  ( $A = \text{Ca, Sr, RE}$  (rare earths) or any combination thereof; and  $M = \text{Ni}$  or  $\text{Ni}$  coupled with one of the following:  $\text{Ti, Sn, Ge, Nb, Ta, Sb}$ ). Bright sky-blue to royal-blue colors are induced in these oxides prepared by conventional solid state reactions, as demonstrated in the solid solutions of  $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$  ( $x = 0-1$ ) and  $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$  ( $x = 0-1$ ). The values of color coordinates  $L^*a^*b^*$  range from 64.5, -5.3, -18.5 to 57, -11.33, -30.38. Structure refinements of neutron powder diffraction data reveal that Ni preferably occupies the tetrahedral site in the hibonite structure, and magnetic susceptibility analysis confirms that this Ni is  $\text{Ni}^{2+}$ . Optical measurements further verify that the observed blue color is due to d-d transitions of tetrahedral  $\text{Ni}^{2+}$ . The preference of  $\text{Ni}^{2+}$  for the tetrahedral site is unusual because  $\text{Ni}^{2+}$  prefers the octahedral site in the spinel  $\text{NiAl}_2\text{O}_4$ . We attribute this unexpected behavior to the unusually large Al–O distances for the tetrahedral site in the hibonite structure. These blue hibonites exhibit excellent thermal stability, superior acid/base durability and better near-infrared reflectance than that of the commercial cobalt blue pigment. Our results suggest a potential route to the development of inexpensive, enduring and cobalt-free blue pigments. Synthesis and characterization methods are briefly reviewed for hibonite type of oxides, especially those with blue colors.

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Abbreviations: BSE, Backscattered Electron; EELS, Electron Energy Loss Spectroscopy; EDS, Energy-dispersive X-ray Spectroscopy; EMPA, Electron Probe Microanalysis; ESR, Electron Spin Resonance; FTIR, Fourier Transform Infrared Spectroscopy; ICP, Inductively Coupled Plasma; NMR, Nuclear Magnetic Resonance Spectroscopy; SEM, Scanning Electron Microscopy; TEM, Transmission Electron Microscopy; UV–Vis, Ultraviolet–visible; XRF, X-ray Fluorescence.

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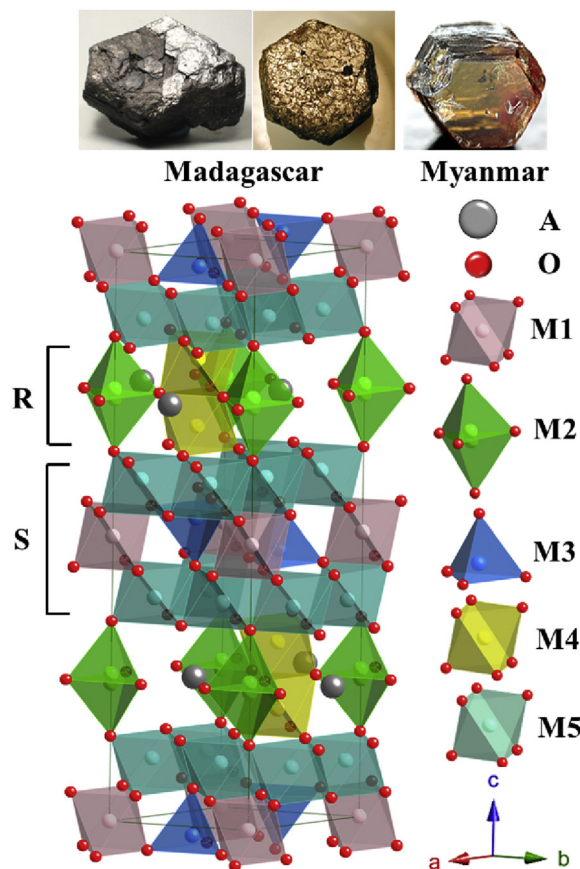
## 1. Introduction

The mineral hibonite was discovered in Madagascar by a French prospector Paul Hibon in 1953 [1,2]. The compositions and crystal structure of these naturally occurring hibonite samples were reported three years later as  $[(\text{Ca}, \text{RE})](\text{Al}, \text{Fe}^{3+}, \text{Ti}, \text{Si}, \text{Mg}, \text{Fe}^{2+})_{12}\text{O}_{19}$  with a hexagonal structure that is identical to that of the magnetoplumbite [2]. Although found primarily in high-grade metamorphic rocks from Madagascar to Siberia, Tanzania, Kenya, South India, China and Myanmar, terrestrial hibonites are rare compared with their meteoritic analogue (mostly in chondritic meteorites) that landed on earth [3,4]. The formation of metamorphic rocks was associated with high temperatures and pressure underneath the Earth's surface, and early studies on origin of meteoritic hibonite inclusions favored a vapor condensation mechanism that also required extremely high temperatures [5]. Hibonite is considered as one of the earliest condensation products from the solar nebula compared with other major CAI (Ca–Al-rich inclusion) minerals found in carbonaceous chondrite meteorites [3,5].

Research on natural hibonites has been focused on their texture, compositions, crystal structures and some physical properties, the major objective of which is to ascertain the origin of hibonite-bearing meteoritic assemblages in hope of understanding the evolution of the primitive solar nebula [3–9]. Crystal structures of synthetic hibonites have been extensively studied and determined to be isostructural with the mineral magnetoplumbite [10–18]. Although the ideal formula is  $\text{CaAl}_{12}\text{O}_{19}$ , various oxides with the hibonite structure have also been synthesized, including  $\text{PbAl}_{12}\text{O}_{19}$ ,  $\text{BaGa}_{12}\text{O}_{19}$ ,  $\text{SrAl}_{12}\text{O}_{19}$ ,  $\text{SrGa}_{12}\text{O}_{19}$  and the defect hibonite phase  $\text{La}_{2/3+8}\text{Al}_{12-8}\text{O}_{19}$  [12–18]. The hexagonal structure of hibonite  $\text{AM}_{12}\text{O}_{19}$  can be described as, along the  $c$  axis, alternating “spinel slabs” or S-blocks (similar to those in  $\beta$ -alumina) and intermediate layers or R-blocks (containing  $\text{A}^{2+}$  ions, 5-coordinated  $\text{MO}_5$  and isolated face-sharing  $\text{MO}_6$  pairs) [5,8]. As depicted in Fig. 1, the A ( $\text{A} = \text{Ca}, \text{Sr}, \text{RE}$ ) cations are in 12-fold coordination in the center of the R-blocks while the M ( $\text{M} = \text{Al}, \text{Ga}$  etc.) cations are distributed over three crystallographically distinct octahedral sites (M1, M4 and M5), one tetrahedral site (M3), and one trigonal bipyramidal site (M2). None of the three M sites with coordination number (CN) 6 have ideal octahedral symmetry. The M1 atom at the origin has ideal trigonal antiprismatic symmetry, two  $\text{MO}_6$  (M4) octahedra form a face-sharing dimer, and the  $\text{MO}_6$  octahedra based on the M5 site form a sheet perpendicular to the  $c$  axis [18]. The tetrahedral M3 cation inside the “spinel slabs” was found underbonded for  $\text{M} = \text{Al}$  [10,18]. The M2 ( $\text{M} = \text{Al}, \text{Ga}$ ) cation with trigonal bipyramidal (TBP) symmetry was reported to displace toward one of the apical oxygen atoms and hence be treated with a split-atom model [8,11,15–18]. This has been confirmed by  $^{27}\text{Al}$  NMR studies for  $\text{CaAl}_{12}\text{O}_{19}$  and  $\text{SrAl}_{12}\text{O}_{19}$  [19], and the disorder between two adjacent pseudotetrahedral sites was demonstrated to be dynamic in magnetoplumbite  $\text{BaFe}_{12}\text{O}_{19}$  at room temperature using  $^{57}\text{Fe}$  Mössbauer spectroscopy [20].

The unique structural features of hibonite make it an excellent host material to accommodate ions of various sizes, coordinations and valences. Hibonite minerals are known to occur with many impurity elements such as Mg, Ti, Si, V, Cr, Fe, Mn, Zn, Sr, Na, K and

rare earth (RE) cations [3,4,8]. Meteoritic hibonite  $\text{Ca}(\text{Al}, \text{Ti}, \text{Mg})_{12}\text{O}_{19}$  was found to emit a bright red-orange or bright blue luminescence depending on the composition [3], and substituted synthetic hibonites have been of great interest as phosphor or laser materials [21–25]. Whereas the “ideal” hibonites are colorless, natural and synthetic hibonites often display a variety of colors (Fig. 1, top): black, brownish black, reddish brown, orange, blue, green, yellow etc., as a result of the variation in occurrences and/or chemical compositions [5,26–32]. There are several studies on the pleochroism of hibonites especially the origin of the blue color [5,27–29]. The first row transition metals are responsible for the colors of many minerals, and in the case of the Blue Angel (blue hibonite-containing inclusions from the Murchison meteorite) the origin of the color has been attributed to several mechanisms: crystal field transitions within  $\text{V}^{3+}$  or  $\text{Ti}^{3+}$ , color centers and the  $\text{Fe}^{2+} \rightarrow \text{Ti}^{4+}$  charge transfer analogous to that occurring in blue sapphires [5,27,29]. The



**Fig. 1.** Polyhedral representation of hexagonal  $\text{AM}_{12}\text{O}_{19}$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{RE}$ ) with hibonite-type of structure. Twelve coordinated A atoms in gray; oxygen atoms in red;  $\text{MO}_6$  octahedra in pink (M1), yellow (M4) and cyan (M5);  $\text{MO}_5$  trigonal bipyramids in green (M2); and  $\text{MO}_4$  tetrahedra in royal blue (M3). The framework can be viewed as S-block (spinel layers) and R-block (constituted by A ions, trigonal bipyramids and face-sharing octahedra) stacking alternatively along the  $c$  axis. (Top) Images of hibonite minerals from Madagascar [1] and Myanmar [32]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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