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 $\text{CaAl}_{12}\text{O}_{19}$ 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 $A\text{Al}_{12-x}M_x\text{O}_{19}$ ($A = \text{Ca}, \text{Sr}, \text{RE}$ or any combination thereof; and $M = \text{Ni}$ or Ni coupled with one of the following: $\text{Ti}, \text{Sn}, \text{Ge}, \text{Nb}, \text{Ta}, \text{Sb}$). 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 $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ ($x = 0 \sim 1$) and $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ ($x = 0 \sim 1$). 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 Ni^{2+} . Optical measurements further verify that the observed blue color is due to d-d transitions of tetrahedral Ni^{2+} . The preference of Ni^{2+} for the tetrahedral site is unusual because Ni^{2+} prefers the octahedral site in the spinel NiAl_2O_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.

Keywords: hibonite, nickel, oxides, blue pigments, neutron diffraction, optical properties

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Contents

1. Introduction.....	3
2. Materials and Synthesis	5
2.1. <i>Conventional Solid State Method</i>	5
2.2. <i>Other Preparation Methods</i>	5
3. Characterization	6
3.1. <i>Techniques Applied for Hibonites</i>	6
3.2. <i>For Ni-blue Hibonites in This Work</i>	6
4. Results and Discussion	7
4.1. <i>Colors and Phase Analyses</i>	7
4.2. <i>Crystal Structures</i>	8
4.3. <i>Optical Properties</i>	11
4.4. <i>Other Properties and Acid/Base Tests</i>	13
5. Summary	14
Acknowledgments.....	14
References.....	14

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 nature 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 $\text{La}_{2/3+\delta}\text{Al}_{12-\delta}\text{O}_{19}$ [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 β -alumina) and intermediate layers or R-blocks (containing A^{2+} ions, 5-coordinated MO_5 and isolated face-sharing MO_6 pairs) [5,8]. As depicted in Figure 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 MO_6 (M4) octahedra form a face-sharing dimer, and the 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}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}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 V^{3+} or Ti^{3+} , color centers and the $Fe^{2+} \rightarrow Ti^{4+}$ charge transfer analogous to that occurring in blue sapphires [5,27,29]. The presence of Ti^{3+} in blue hibonites has been inferred by electron spin resonance spectroscopy, Ti K-edge X-ray absorption near edge structure (XANES) spectra and X-ray and neutron structural studies [33–36]. The concentration of Ti^{3+} was found to increase with decreasing oxygen fugacity, giving rise to the growth of an absorption band that is associated with the blue color [28].

The occurrence of nickel within natural hibonites is very rare, and it is not related to the observed blue color as found in hexagonal grains of Fe-Ni metal in the core of the meteoritic hibonite inclusion [27]. Ni-substituted oxides with hibonite structure have been synthesized since early 1980s [23,37–42], and the resulting blue color has recently prompted interest in its application as inorganic pigments [43–47]. Although it is not uncommon for nickel to be utilized as a chromophore in ceramic pigments with spinel or rutile structures [48–49], the hibonite-based oxides incorporated with Ni have not been extensively investigated as potential blue pigments and the reported colors are more turquoise than blue [43–47]. The Ni-containing pigments prepared with anorthite fluxing agent and cassiterite tin buffer or from the industrial waste comprised of only ~55% hibonite phase and exhibited a very light turquoise color [44]. The color of Ni-Ti codoped hibonite samples by combustion synthesis was described as “greenish-blue, close to cyan or turquoise” [47].

Given the complexity and flexibility of the host structure, it would be of considerable interest to examine the distribution of numerous ions including Ni^{2+} substituted for Al in the $AAl_{12-x}M_xO_{19}$ ($A = Ca, Sr, RE; M = Ni$ etc.) hibonite lattice. We have previously reported on one example, $CaAl_{10}NiTiO_{19}$, where we revealed from neutron diffraction data that Ni^{2+} on the tetrahedral sites in hibonite provides a bright blue color [18]. Here we report on many more Ni^{2+} containing hibonite phases. To ensure charge neutrality of the system heterovalent substitution for Al^{3+} can be achieved combining divalent ions ($M = Ni, Mn, Fe, Co, Cu, Cr, Zn$ etc.) with tetravalent and pentavalent ions ($M = Si, Ti, Sn, Ge, Zr, V, Nb, Ta, Sb$ etc.) such that $M^{2+} + M^{4+} \rightarrow 2Al^{3+}$ or $2M^{2+} + M^{5+} = 3Al^{3+}$, and substituent ions of other valences may also be introduced to A or M site for charge compensation. We have tried coupled substitutions of various types and discovered different colors in addition to blue [50]. The details about those hibonite phases with colors other than blue will be published elsewhere. The present work is particularly devoted to syntheses and characterization of Ni-containing hibonite solid solutions $AAl_{12-2x}Ni_xTi_xO_{19}$ ($A = Ca, Sr, x = 0 \sim 1$) and $Ca_{1-x}RE_xAl_{12-x}Ni_xO_{19}$ ($RE = La, Ce, Nd, Pr, x = 0 \sim 1$) as well as compositions that display a range of blue colors. A brief review of synthesis and characterization methods will be given for hibonite type of oxides.

The Co-doped hibonites have been explored for blue pigment application [45, 51–52]. Like commercial cobalt blue ($CoAl_2O_4$), they may cause some environmental issues since cobalt is considered to be a human carcinogen. We expect that our results of hibonite-based Ni-blue will lead to routes for the development of Co-free pigments. The ultimate goal of our research is to design environmentally benign pigments with intense blue color, great durability and excellent near infrared reflectance comparable to the YInMn Blue ($YIn_{1-x}Mn_xO_3$) [53] but with less cost.

2. Materials and Synthesis

Hibonite is frequently found in meteorites and apparently forms on cooling from a liquid phase [54], and laboratory synthesis of compounds with the hibonite structure generally requires temperatures of about 1200°C or higher. There are indications that $\text{CaAl}_{12}\text{O}_{19}$ synthesis requires very high temperatures because it is actually entropy stabilized. Attempts to employ low temperature synthesis methods, such as a sol-gel precursor, still require a final temperature of about 1200°C or higher. The issue of the metastability of hibonite has been controversial, and the most recent evaluation of the situation concluded that present thermodynamic data cannot unambiguously determine whether or not hibonite is an entropy-stabilized phase, such as “FeO” [55].

2.1. Conventional Solid State Method

Hibonite compounds can be synthesized in many ways. The most convenient preparative method, especially for pigment manufacturing, would be calcination directly of the starting materials in powder or pellet form at high temperatures in air [18,44–46].

We prepared all the colored oxides with hibonite structure via conventional solid state reactions. The general formula is $A\text{Al}_{12-y}M_y\text{O}_{19}$ where A and M stand for one or more than one cations depending on charge compensation requirement. Stoichiometric amount of dried, reagent-grade Al_2O_3 ($A = \text{Ca, Sr, Ba}$), A_2CO_3 ($A = \text{Na}$), rare earths RE_2O_3 ($\text{RE} = \text{La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, Y}$), CeO_2 , Pr_6O_{11} , Tb_4O_7 , MO ($M = \text{Ni, Cu, Zn}$), M_2O_3 ($M = \text{Mn, Fe, In, Ga, Cr, Zn}$), MO_2 ($M = \text{Si, Ti, Sn, Ge, Te}$), M_2O_5 ($M = \text{Sb, V, Nb, Ta}$) and Co_3O_4 were mixed, ground and pelletized. The resulting pellets were then heated in alumina crucibles for 12 h at a range of 1300 to 1550 °C in air several times with intermediate grinding. Ramp rates were 300°C/h. Starting materials like rare earth oxides were preheated in an oven to remove moisture and carbonate content before use. To obtain pure $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ ($x = 0 \sim 1$) phases, the synthesis temperatures were 1300 ~ 1350 °C for high Ni content ($x \geq 0.4$) samples, 1400 ~ 1450 °C for low Ni content ($x < 0.4$) samples, and 1500-1550 °C for the end member $\text{CaAl}_{12}\text{O}_{19}$. Entire range of solid solutions $A_{1-x}\text{RE}_x\text{Al}_{12-2x}\text{Ni}_x\text{O}_{19}$ ($A = \text{Ca, Sr, RE} = \text{La, Ce, Pr, Nd, } x = 0 \sim 1$) were prepared in a similar way at 1400 ~ 1550 °C with longer heating time.

The M -site substitutions of $\text{CaAl}_{12-2x}\text{M}_x\text{O}_{19}$ with chromophore cations other than Ni were attempted for $M = \text{Co, Fe, Mn, Cu, Cr, V}$ and small amount of substitution resulted in colors including purplish blue, ivory, brown, creamy, pink and light turquoise, respectively. The detailed results will be published separately. Reduction of certain samples was carried out at 900 °C in 5% H_2 /95% N_2 for 5 h inside an alumina tube furnace.

2.2. Other Preparation Methods

In addition to the standard ceramic method, hibonite type of oxides have also been prepared using wet techniques through citrate-based sol-gel precursors followed by thermal decomposition at 1300 ~ 1550 °C [35,41,42], or by coprecipitation of mixed metal hydroxides and then heating at 1350 ~ 1500 °C [22]. A very recent study of $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ phases employed a combustion synthesis route, a technique that is generally not considered to be a viable commercial route [47]. Furthermore, this route still employed a final heating at 1200°C.

Single crystals are sometimes preferred for different applications such as substrates for electronics [25]. Crystal growth can be realized by floating zone method [11,12,23,26,37,39], Verneuil method [17,23,26,37,39], Czochralski technique [13] or heating the ingredients with a flux in Pt crucibles at high temperatures [15,30].

3. Characterization

3.1. Techniques Applied for Hibonites

In this article we focus on characterization of structure and various properties: color, magnetic, dielectric, and stability. Crystal structures of hibonite type of oxides have been characterized extensively by lab X-ray [8,10–17,23,30,35,39], synchrotron [41] and neutron [18,36] diffractions. Other techniques have also been employed to characterize hibonite phases. EELS in the TEM [56,57] and high-resolution solid state ^{27}Al NMR [19] were used to probe the local symmetry fingerprints for hibonite structures and local environment of Al atoms. Lattice information and defects such as dislocations were explored by TEM with electron diffraction [14,42,54]. Chemical compositions of mineral samples were normally determined by SEM equipped with EDX [32,34,36,44,51,52], EMPA [3,31,33,35], XRF [44,45,51] and even ICP with mass spectrometer [4]. The morphology, texture and elemental distribution were obtained through electron microscopic studies like SEM, TEM and BSE imaging [31,35,54]. Mossbauer [5,29,], XANES [34], FTIR/IR [24, 32,58] and Raman spectra [32,46] were utilized for obtaining additional structure information. ESR was used to make the first direct determination of Ti^{3+} [33]. Optical properties were investigated by UV-Vis-NIR spectra [24,28,32,39,44,45,47,51,52].

*List of abbreviations used above:

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.

3.2. For Ni-blue Hibonites in This Work

The calcined powders were characterized by a Rigaku Miniflex X-ray diffractometer using $\text{Cu K}\alpha$ radiation and a graphite monochromator. For lattice parameter calculation the XRD data were collected with Si as the internal standard. Powder neutron diffraction data were collected on the 32-counter high-resolution diffractometer BT-1 at the Center for Neutron Research at the National Institute of Standards and Technology. A $\text{Cu}(311)$ monochromator, yielding a wavelength of $1.5403(2) \text{ \AA}$, was employed. Collimation of $15'$ of arc was used before the monochromator, $20'$ before the sample, and $7'$ before the detectors. The samples were loaded into vanadium containers of 15.6 mm diameter and 50 mm length. Data were collected at room temperature over a 2θ range of $3\text{--}167^\circ$. Structure refinements of XRD and neutron data were carried out using GSAS-EXPGUI software [59,60]. Bond-valence analysis of the neutron structures made use of the bond-valence calculator [61].

Diffuse Reflectance data of the polycrystalline samples were measured in the visible range using a homemade UV-VIS spectrophotometer (MgO as the reference) and converted to absorbance using Kubelka-Munk equation [62]. Near-infrared reflectance data (up to 2500 nm) were collected using a Jasco V-670 Spectrophotometer. Konica Minolta CM-700d Spectrophotometer (Standard illuminant D65) was used to measure the L^* , a^* , b^* color coordinates.

Magnetic data were obtained on a Quantum Design, Physical Property Measuring System (QD-PPMS) over a temperature range of 5 to 300 K. Data were collected using the zero field cooling (ZFC) method with an applied magnetic field of 0.5T. Inverse magnetic susceptibility data were used to fit for the Curie-Weiss law. Diamagnetic corrections were made for calculating the effective magnetic moments [63].

Dielectric properties were measured on a HP Precision LCR Meter 4284A instrument with a frequency range of 20 Hz ~ 1 MHz and a temperature range of 25 ~ 250 °C. The sample pellets were sintered at a temperature slightly higher than the synthesis temperature to achieve a reasonably high density. Both sides of the pellets were smoothed with fine sand paper and coated with silver electrode. The pellets were then let dry in the oven overnight and cool to room temperature before the measurement.

4. Results and Discussion

4.1. Colors and Phase Analyses

A wide variety of substitutions were attempted on both A and M sites of the hibonite host with an ideal formula $\text{CaAl}_{12}\text{O}_{19}$. Representative colors of the resulting powders $(\text{Ca},A)(\text{Al},M)_{12}\text{O}_{19}$ are demonstrated in Figure 2. As we can see in Figure 2(a), only Co gives rise to a purplish blue color, whereas the color induced by Ni is light turquoise. However when charge compensation is achieved by adding some trivalent, tetravalent or pentavalent ions, a range of blue colors are produced in Ni-containing samples $\text{CaAl}_{12-x-y}\text{Ni}_x\text{M}_y\text{O}_{19}$ ($M = \text{Zn, Ga, In, Si, Ti, Zr, Sn, Ge, Nb, Ta, Sb, Te}$), among which the most intense blue colors are found with Ti, Ge and Nb (Fig.2(b)). In the case of $(\text{Ca},A)\text{Al}_{12-x-y}\text{Ni}_x\text{Ti}_y\text{O}_{19}$, if Ca is partially replaced by Sr the color becomes less intense and lighter, while the addition of Na helps to give a slightly darker color at low Ni content (Fig.2(c)). All the A site substitutions of $\text{Ca}_{1-x}\text{RE}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ by rare earth ions result in bright blue colors as shown in Figure 2(c).

Phase identification by X-ray powder diffraction (XRD) confirms the formation of full solid solutions of $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ ($x = 0 \sim 1$), $\text{Ca}_{1-x}\text{Sr}_x\text{Al}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ ($x = 0 \sim 1$), $\text{SrAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ ($x = 0 \sim 2$), $\text{Ca}_{1-x}\text{RE}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ ($\text{RE} = \text{La, Ce, Pr, Nd, } x = 0 \sim 1$) and $\text{Sr}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ ($x = 0 \sim 1$). Blue pellets and powders of selected solid solutions are shown in Figure 3. X-ray diffraction patterns of these two solid solutions are shown in Figure 4. The lattice parameters are calculated by whole pattern fitting of XRD data as shown in Figures 5 and 6. The increase of cell edges a , c and cell volume V is consistent with the substitution of small Ca^{2+} and Al^{3+} ions with larger La^{3+} and $\text{Ni}^{2+}/\text{Ti}^{4+}$ ions. The lattice parameters from neutron Rietveld refinement are plotted for comparison, and the discrepancy between X-ray and neutron is simply sample related. The samples for neutron experiment, darker in color, were heated for longer hours with more intermediate grindings, the relatively higher cell expansion shown by neutron

samples hence indicating higher level of Ni and Ni/Ti incorporation than samples examined by XRD.

Cell edges of solid solutions $\text{Ca}_{1-x}\text{RE}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ (RE = La, Ce, Pr, Nd, $x = 0 \sim 1$) and $\text{Sr}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ ($x = 0 \sim 1$) refined by XRD data are shown in Figure 7. The ionic radius of Sr is 1.44 Å (CN = 12), larger than that of La, 1.36 Å (CN = 12), and La is the largest among all the rare earth ions [64]. This can explain why the cell edges of Sr and La containing samples are larger than the rest of the members in the Figure 7. In addition, the Sr-bearing samples exhibit the least change in c axis with increasing level of coupled substitution (La and Ni), which could be attributed to the canceling effect of some contraction on A site and some expansion on M site. This effect however does not influence the change in cell edge a . Interestingly, the trend of c/a ratio decreases with substitution for all members in Figure 7 except for La, contrary to those in Figures 5 and 6, implying more rapid increase upon substitution along c axis than a axis for $\text{CaAl}_{12-x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ ($x = 0 \sim 1$) and $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ ($x = 0 \sim 1$) series.

Although samples of $\text{SrAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ are prepared nearly phase pure in the composition range of $0 \leq x \leq 2$, the color of the powder changes from light sky blue to turquoise above $x = 1.0$. Other rare earth containing samples $\text{Ca}_{1-x}\text{RE}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ were only made phase pure up to $x = 0.2$ under similar reaction conditions (Fig.8). It is difficult to obtain a pure hibonite phase when replacing Ca with Y, and it seems to work better with larger A ions like Sr. The M -site substitution other than Ti produced single-phase products only up to $y = 0.2$ or 0.5 for $\text{CaAl}_{12-x-y}\text{Ni}_x\text{M}_y\text{O}_{19}$ ($M = \text{Sn, Ge, Sb, Nb, Ta}$) (Fig.9). The best blue color is given by Ge or Nb containing samples, and the presence of Na helps to enhance the blue color although the sample is not a single phase.

To check the effect of Ti^{3+} on color, we prepared the $\text{CaAl}_{11.8}\text{Ti}_{0.2}\text{O}_{19}$ sample at 1450°C in air followed by heating the white powder in 5% H_2 /95% N_2 at 900°C for 5 h. The color of the powder changed to a very light turquoise blue after reduction. The resulting color would probably be more blue if the sample were treated under severe reducing conditions [28].

4.2. Crystal Structures

The complex structure of hibonite $\text{CaAl}_{12}\text{O}_{19}$ is shown in Figure 1. There are five different sites for Al: three have octahedral coordination (M1, M4, and M5), one has tetrahedral coordination (M3), and one site ideally has trigonal bipyramidal (TBP) coordination (M2). Early structural studies placed Al at the center of this TBP site, but recent studies have this Al displaced off this center along the c axis, up and down in disordered manner [11,16–18]. At high temperatures this TBP Al moves back and forth between the up and down positions. At low temperature this Al becomes trapped in one of the two positions. In addition to corner sharing of the various AlO_4 , AlO_5 and AlO_6 polyhedra, the two AlO_6 octahedra at the M4 site share a common face and the AlO_6 octahedra at the M5 site share edges to form a sheet perpendicular to the c axis. Examination of the bond valence sums (BVS) for certain atoms indicates considerable mismatch when connecting these polyhedral [18,65]. Serious underbonding for Al occurs at the M2 (2.77) and M3 (2.68) sites as well as for two O sites (1.85 and 1.87). And at the M1 site there is significant overbonding of Al (3.23). The BVS at the A site for Ca is 1.49 but becomes normal (2.09) when Ca is replaced with Sr. These poor BVS values indicating a misfit of the polyhedra is one of the factors suggesting that $\text{CaAl}_{12}\text{O}_{19}$ and some other oxides with the hibonite structure are entropy stabilized phases that are metastable at room temperature and below.

The TBP site in $\text{CaAl}_{12}\text{O}_{19}$ has much longer Al–O apical distances (2.21 Å) than Al–O basal plane distances (1.755 Å). Moving this Al atom off the ideal site along the c axis to a site with 4 equal “tetrahedral” Al–O distances has little impact on the low BVS value for Al, but it increases the BVS for the apical O from 2.02 to 2.44 [18]. Such overbonding of this O would explain the lower displacement of Al actually observed.

Another factor complicating the structures of oxides with the hibonite structure is defects related to stacking faults. The β -alumina structure has the same spinel type blocks that occur in hibonite. Intergrowth between the hibonite and the β -alumina structures has been observed and likely occurs to some extent in most hibonite compositions [66].

This article focuses on substitutions of Ni^{2+} for Al^{3+} in $\text{CaAl}_{12}\text{O}_{19}$. This substitution is charge compensated by a cosubstitution on the Ca site or the Al sites according to the formulas such as $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ and $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$. Structural analysis utilized Rietveld refinement of neutron diffraction data. Details of this procedure were previously given [18]. Results are summarized in Table 1 and cif files are provided as Supporting Information. Relative to X-ray diffraction, neutron diffraction has much greater sensitivity to Ni and Ti substitution for Al due to the scattering lengths of 10.3 fm for Ni and -3.438 fm for Ti vs 3.449 fm for Al. Also, the negative value for Ti vs the very high positive value for Ni is of great value in separating the contributions of Ni and Ti. Furthermore, the relative scattering power of O is much greater when using neutrons, and this leads to more accurate bond distances.

The analysis of $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ phases with $x = 0.5$ and 1.0 shows that 57 to 75% of the Ni^{2+} substituted enters the tetrahedral site (M3). The remainder of the Ni^{2+} is distributed over the M1, M2, and M5 sites. A statistically significant amount of Ni is not found at the M4 site. The expected increase in M3–O distances with x is observed. The refined formulas of $\text{La}_{0.49}\text{Ca}_{0.51}\text{Al}_{11.49}\text{Ni}_{0.51}\text{O}_{19}$ and $\text{LaAl}_{11.01}\text{Ni}_{0.99}\text{O}_{19}$ agree well with the intended compositions. A previous study of $\text{LaAl}_{11}\text{NiO}_{19}$ using powder X-ray diffraction reported Ni only on the tetrahedral site (M4) [41].

Structural analysis of $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ phases is much more challenging. When using X-ray diffraction, both Ni and Ti have stronger scattering powers than Al. Thus if the scattering power increases at a given M site, there is no way that this increase can be attributed to just Ni or Ti because either could cause this increase. The situation is dramatically more favorable when using neutron diffraction because the scattering lengths of all atoms present are positive with the exception of Ti, which has a negative scattering length. Thus, for $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ phases if the scattering power of a given M site decreases, this must be due to Ti substitution. If there is an increase in scattering power at a site, there must be Ni substitution at that site. There is still a complication when both Ti and Ni enter the same site, but this complication can be resolved by utilizing the results found for $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ phases where Ti is not present.

Our refinements indicate that the maximum value of x for $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ phases is close to 1.0 for samples prepared under our conditions [18]. Tables 1 and 2 summarize our results for samples with nominal x values of 0.5, 1.0, and 1.2. We find for $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ phases that the scattering power at the tetrahedral site (M3) increases rapidly with x . This indicates Ni on this site, which was anticipated based on our results for the $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ phases. For the $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ phases we found a large decrease in scattering power for the site with face-sharing octahedral, and this must be due to Ti entering this site (M4). Small amounts of Ni enter both the M1 and M5 sites. The amount of Ni on the M5 site is much greater than that on the M1 site simply because the multiplicity of the M5 site is six times greater than that of the M1 site. Our results for $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ samples with $x = 0.5$ and 1.0 indicate statistically

insignificant amount of Ni on the M4 site, and this is apparently also true for $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ phases.

An X-ray diffraction study on $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ phases also concluded that Ni went mainly to the M3 site and that Ti went mainly to the M4 site [47]. However, the site occupancies were inferred, not actually refined. The occupancies of Ni and Ti given often do not agree well with our findings using neutron diffraction. This X-ray diffraction study did not detect the presence of Ni on the M1 and M5 sites, which we show is readily detected using neutron diffraction.

The M1–O distance and the average of M5–O distances increase by about 0.01 Å with Ni substitution, consistent with significant amount of Ni^{2+} substitution on the M1 and M5 sites. The average M3–O distances increase by about 0.03 Å due to the much greater Ni substitution at the M3 site. This distance increase would be even greater if it were not for the fact that this site has larger M3–O distances than expected when this site is occupied by Al only. The average M4–O distance also increases by about 0.03 Å as Ti^{4+} enters the M4 site. Although Ti^{4+} is larger than Al^{3+} , this increase in average distance is in part due to an increase in the difference between the two different M4–O distances. This difference is 0.10 Å in $\text{CaAl}_{12}\text{O}_{19}$ and increases to 0.19 Å with the Ni/Ti substitution. The smaller M4–O distance actually decreases by 0.02 Å as the average M4–O distance increases by 0.03 Å (Table 1). Average distances are expected to increase as the individual distances of a polyhedron become more scattered. The M4–M4 distance increases from 2.60 to 2.79 Å as Ti enters this site. This can be considered as consequence of the increased cation-cation repulsion as a 4+ cation enters this site with face-shared octahedra. The three short M2–O distances related to the triangle of the TBP unit increase from 1.755 to 1.783 Å with the substitution on the M2 site, which is mostly Ti. At the same time the short apical M2–O distance decreases from 2.027 to 1.895 Å. Thus, this TBP site becomes more tetrahedral like.

The distribution of Ni and Ti over the five M sites is far from random with factors other than coordination number playing important roles. Studies of NiAl_2O_4 with the spinel structure indicate a preference of Ni^{2+} for the octahedral sites [67], which would be expected based on the crystal field stabilization of Ni^{2+} in an octahedron and relative sizes of Ni^{2+} vs Al^{3+} [64]. Disorder with increasing temperature moves much of the Ni to the tetrahedral sites [67]. The preference of Ni^{2+} for the tetrahedral M3 site in $\text{CaAl}_{12}\text{O}_{19}$ can be attributed to the longer than normal Al–O distances at the M3 site. These long distances cause displacement factors to be high for this site (Table 1). The actual displacements are anharmonic, as we have previously shown, because an ellipsoid is not compatible with a tetrahedral site [18]. Small amounts of Ni substitute on all the M1, M2, and M5 sites as expected from our results on $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ phases. Substitution of Ti for Al on the tetrahedral site is not expected because this coordination for Ti is very rare in oxides. Substitution of Ti on the M1 site is unfavorable because Al at this site is significantly overbonded, and the addition of Ti to this site would further aggravate this situation. The location of Ti^{4+} is very much influenced by the M–M repulsive interaction that occurs whenever octahedra share faces or edges. Since this M–M distance tends to be shorter for face sharing than for edge sharing, one might expect that Ti would favor the M5 site over the M4 site. But the opposite occurs. There are two reasons for this preference of Ti. Each octahedron based on M5 shares four of its edges with other M5 octahedra, but the M4 based octahedra share only one face. Secondly, the M4–M4 distance is not constrained and can readily expand as Al is replaced by Ti. In fact, this M4–M4 distance across the face expands so much as Ti enters that it

becomes essentially the same as the M5–M5 shared edge distance. Thus, the repulsive M–M interaction on the M5 site is about four times stronger than for the M4 site. Therefore, the M4 site is very strongly preferred over the M5 site for Ti^{4+} . TBP coordination is well established for Ti^{4+} in compounds such as $\text{YCu}_{0.5}\text{Ti}_{0.5}\text{O}_3$ [68]. Thus, substitution of Ti^{4+} into the M2 where there is no M–M interaction can be expected.

The repulsive M4–M4 interaction in the face-shared octahedra causes an overall expansion of the O3–M4–O3–M4–O3 face-share unit along the c axis. Thus, the expansion along the c axis is more pronounced in the $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ series than in the $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ series where no Ti is present (Table 1). The a axis expansion is also slightly greater in the $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ series than the $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ series. This can be attributed to the greater concentration of Ni in the M5 site in the $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ series. The layer associated with M5 cations is under tension, which causes any expansion to be mainly perpendicular to the c axis. In the case of $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ series, the large A site where Ca ions locate may provide extra room to accommodate the change upon La substitution and result in an expansion along a axis that is smaller than expected.

4.3. Optical Properties

The optical spectra of blue hibonite samples are shown in Figure 11 for the solid solutions $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ ($x = 0 \sim 1.2$) and $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ ($x = 0 \sim 1$). Unlike white $\text{CaAl}_{12}\text{O}_{19}$ ($x = 0$) powders that exhibit negligible absorption across the entire visible range, strong absorption centered around 600 nm, in the orange region of the visible spectrum, is detected for all Ni-containing samples. This intense absorption is actually a collection of four peaks arising from d-d transitions of Ni^{2+} in tetrahedral coordination. Two of these peaks are spin-allowed. The two weaker peaks are unusually intense considering that they are spin-forbidden [44,47]. The weak peak at ~710 nm has been attributed to Ni^{2+} in octahedral coordination [47].

In the case of $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ (Fig. 11a), a peak arising from an O-to-Ti charge transfer tails into the visible region, but is too weak to have a significant impact on color. There is also a small increase in absorption with increasing x in the low energy region tailing into the infrared range. This feature could be expected if a small amount of the Ti were present as Ti^{3+} . These small increases in absorption in the high and low energy regions of the visible spectrum do not occur in the $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ series (Fig. 11b) because no Ti is present. In both series, the absence of absorption in the 500 ~ 430 nm (blue) region of the spectrum is responsible for the observed blue color.

Different shades of color are barely distinguishable when they are visually similar. The subtle alteration in color, however, can be differentiated and quantified using CIE $L^*a^*b^*$ color space through the hue (color), the chroma (vividness/dull-ness) and the brightness. A unique color can be described precisely by 3-dimensional color coordinates L^* , a^* and b^* . The vertical axis L^* gives the brightness from 0 (black) to 100 (white). The value of a^* shows colors from green to red (- to +) and b^* from blue to yellow (- to +) with neutral gray values at $a^* = 0$ and $b^* = 0$. Measured chromatic coordinates of two representative solid solutions $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ ($x = 0 \sim 2$) and $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ ($x = 0 \sim 1$) are illustrated in Figure 12, and those of selected powder samples are given in Table 3. The blue color of all our samples is clearly indicated by the negative b^* values range from -16.78 to -30.38. Notice the compositions of $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ in the range $x = 1 \sim 2$ are not phase pure, and the increasing amount of impurity is accompanied by an undesirable color change from royal blue to dark turquoise. For sake of comparison, the L^* ,

a^* and b^* values of commercial Co-blue, NiAl_2O_4 spinel and one of our Co-bearing samples are also listed in Table 3.

As shown in Figure 12, both solid solutions demonstrate continuous decrease of L^* , a^* and b^* values with Ni content till $x = 0.5$. Beyond this point, the brightness L^* keeps dropping till $x = 1$ for both series, while the trend is reversed for the blue component of the $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ series leaving the most negative b^* value (-30.38) at $x = 0.5$. In the case of $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$, all three coordinates decline till $x = 1$, after that both L^* and a^* start to flatten out and b^* moves towards +b (yellow) direction while the color is shifting from royal blue to dark turquoise. The best blue color therefore is given by $x = 1$ in the Ti-containing samples ($b^* = -28.44$). Although the values of a^* associated with red(+)/green(-) hue display the least variation, the overall movement of these data points, in a 2-dimensional color space, is heading towards blue and green region with increasing amount of Ni.

Table 3 contains couple of samples discussed in section 4.1, and some other compositions that failed to produce decent blue colors such as $\text{CaAl}_{10}\text{TiNi}_{0.5}\text{Zn}_{0.5}\text{O}_{19}$. As stated by Bermanec et al [69] divalent transition metal ions such as Zn^{2+} and Mg^{2+} exhibit unusual preference for the tetrahedral coordination in hibonite type of structures whereas Ni^{2+} show large octahedral crystal field stabilization energy. When substituting Ni^{2+} and Zn^{2+} simultaneously into the hibonite host lattice, it might be more favorable for Zn^{2+} to occupy the tetrahedral site, resulting in less tetrahedral Ni^{2+} and hence worse blue color [69]. This also seems to be true for coupled substitution with Ni and Si. In general, Ti-containing samples show better blue colors than their Sn-containing counterparts given the same Ni concentration, and similar conclusion was drawn based on Co-bearing hibonite pigments [51]. For a complex composition like $\text{Ca}_{0.5}\text{La}_{0.5}\text{Al}_{11}\text{M}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$, better blue coloration was achieved when the trivalent M was In^{3+} instead of Ga^{3+} .

The values of blue component b^* manifested by our Ni-containing hibonite samples are still not as negative as those exhibited by commercial Co-blue and other Co-bearing pigments [51,52]. The initial evaluation performed by The Shepherd Color Company concluded that our Ni-containing hibonite pigments are likely to provide a cost benefit in the blue color space due to their low cost and high concentration of aluminum trioxide. Additional tests are in progress regarding Acid/Base resistance, weatherability and more.

Besides color, another desired property of pigments is the ability to reflect heat due to rising energy costs. Near infrared (NIR) energy contributes to ~52% of the total solar radiation absorbed by earth as heat. White pigments like TiO_2 can reflect more than 80% of NIR radiation, leading to less NIR absorption, less heat build-up and hence less cooling expense. However, NIR-reflecting pigments with various colors, including dark colors, are in high demand for cool pigment applications. Our NIR measurements in the range of 700 ~ 2500 nm show some peculiar features of reflectance for all hibonite samples prepared in this work (Fig.13). Generally, the total NIR reflectance is inversely proportional to Ni content incorporated in the host material. Despite compositional variation, the spectra of our samples exhibit 3 peaks and 3 valleys over the entire range of measurement, with the peak positions centered near 500 nm, 1000 nm and 1500 nm, respectively. The peak width gradually broadens with wavelength such that the narrowest peak locates in the highest energy end and vice versa. The observed reflectance defined by the valleys and peaks range from 40 to 95% across the NIR region. Although not as good as the YInMn blue, the blue hibonite pigment still reflects more NIR radiation than Co-based pigment especially near 1500 nm as shown in Figure 14. Better NIR reflectance and lower

cost than Co-blue makes this hibonite pigment a potential candidate for many applications where solar heat reflection and energy-saving properties are desired.

4.4. Other Properties and Acid/Base Tests

Magnetic susceptibility measurements for $\text{LaAl}_{11}\text{NiO}_{19}$, $\text{Ca}_{0.5}\text{La}_{0.5}\text{Al}_{11.5}\text{Ni}_{0.5}\text{O}_{19}$ and $\text{CaAl}_{11}\text{Ti}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$ samples were made to verify the oxidation state of Ni^{2+} in the structures. Temperature dependence of magnetic susceptibility (χ) and inverse magnetic susceptibility ($1/\chi$) are shown in Figure 15. Curie-Weiss law was implemented to determine the effective magnetic moment of nickel. Tetrahedrally coordinated Ni has two unpaired electrons and its spin-only magnetic moment (μ_s) equals $2.83 \mu_B$. However, effective magnetic moment (μ_{eff}) usually observed for Ni^{2+} is higher, in a range of $2.9 \sim 3.9 \mu_B$, due to an orbital angular momentum contribution, which frequently occurs for 3rd row late transition metal cations [70]. This spin-orbit coupling has been observed in Ni-bearing oxides with hibonite structure based on previous optical studies [44,47].

Curie and Weiss constants were calculated from the slope and the intercept of linear region of $1/\chi$ vs. temperature plot. Effective magnetic moments were derived from experimentally determined Curie constants. Calculated magnetic moments, Curie and Weiss constants of $\text{LaAl}_{11}\text{NiO}_{19}$, $\text{Ca}_{0.5}\text{La}_{0.5}\text{Al}_{11.5}\text{Ni}_{0.5}\text{O}_{19}$ and $\text{CaAl}_{11}\text{Ti}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$ are given in Table 4. Diamagnetic correction for μ_{eff} was applied [71]. As we can see, all samples show paramagnetic behavior in the measured temperature region ($5 \sim 300$ K). Weiss constants of all compounds are not significantly different from zero and they are negative, suggesting a weak antiferromagnetic interaction. The experimental moments are in reasonable agreement with the moments expected from high-spin Ni^{2+} , hence +2 oxidation state for nickel is confirmed. $\text{LaAl}_{11}\text{NiO}_{19}$ has higher concentration of Ni^{2+} and more negative Weiss constant value comparing to $\text{Ca}_{0.5}\text{La}_{0.5}\text{Al}_{11.5}\text{Ni}_{0.5}\text{O}_{19}$ and $\text{CaAl}_{11}\text{Ti}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$ due to stronger nickel-nickel interactions.

Dielectric properties have been widely investigated for hexaferrites with the magnetoplumbite structure. Arora A. and co-authors studied dielectric properties of co-substituted *M*-type barium hexaferrites $\text{Ba}_{1-x}\text{La}_x\text{Na}_x\text{Fe}_{10}\text{CoZnO}_{19}$, showing that dielectric constant (κ) decreases and dielectric loss ($\tan \delta$) increases with the increasing of La-Na content [72]. Dielectric properties of Ni-containing hibonite materials however have never been reported.

Dielectric measurements were made for $\text{CaAl}_{11}\text{Ti}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$ and $\text{CaAl}_{10}\text{TiNiO}_{19}$ compounds at frequencies of 1, 10, 100, 500, 750 kHz and 1 MHz and in the temperature range $25 \sim 250^\circ\text{C}$. Temperature dependence curves of κ and $\tan \delta$ for $\text{CaAl}_{11}\text{Ti}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$ and $\text{CaAl}_{11}\text{Ti}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$ are illustrated in Figure 16 and Figure 17, respectively. Frequency dependence of their κ and $\tan \delta$ are given in Figure 18.

The compositions are insulators and dielectric measurements reveal relatively low dielectric constants. The κ values decrease with the increase of applied temperature and frequency for both samples. In the case of $\text{CaAl}_{11}\text{Ti}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$ $\tan \delta$ decreases with increasing temperature and frequency, while $\tan \delta$ for $\text{CaAl}_{10}\text{TiNiO}_{19}$ is relatively constant at all studied temperatures and frequencies. Theoretical values of κ (κ_{th}) were calculated according to Subramanian et al [73] and compared with experimentally determined values. The κ_{th} of $\text{CaAl}_{10}\text{TiNiO}_{19}$ equals 9.70, which is in good agreement with the experimental value. The $\kappa_{\text{th}} = 9.33$ for $\text{CaAl}_{11}\text{Ti}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$ and it is somewhat smaller than the experimentally measured values of compound.

To check stability of blue hibonite samples under rigid basic and acidic conditions, a series of experiments were performed. The lab tests were carried out using the following acids and base:

HCl, HNO₃, CH₃COOH and NaOH, for selected samples like CaAl₁₀TiNiO₁₉ and LaAl₁₁NiO₁₉. We weighed powders of our samples and mixed them with small amount of 50 ~ 60% diluted acid/base. The powders were then stirred for ~12 h, washed with DI water to remove residue acid/base from the solid, and dried in the oven overnight. XRD was performed to check the phase purity after acid/base exposure. For all our blue hibonite samples, no significant change was found based on XRD patterns and sample colors before and after the experiment. Powder XRD patterns of CaAl₁₁TiNiO₁₉ and LaAl₁₁NiO₁₉ before and after acid/base treatment are shown in Figure 19.

Stability with respect to temperature, acid and base is very crucial for pigment performance. Commercial blue pigments like ultramarine (Na₇Al₆Si₆O₂₄S₃), Prussian blue (Fe₄[Fe(CN)₆]₃) and azurite [Cu₃(CO₃)₂(OH)₂] are not stable under acidic conditions [53]. Our Ni-containing hibonites are promising for applications like highly durable and cost-effective blue pigments.

5. Summary

In this work, a range of blue colors including sky-blue and bright royal-blue are successfully produced by cation substitution on both A and M sites in hibonite-based oxides AM₁₂O₁₉ in presence of Ni²⁺ ions. A is one or two of the following elements: Ca, Sr, Ba, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, Na; and M is one or more of the following elements: Al, Ni, Ga, In, Ge, Si, Ti, Sn, Zr, Nb, Ta, Sb, Te). Detailed synthesis and structural, optical, magnetic, dielectric characterization are presented for two representative solid solutions: CaAl_{12-2x}Ni_xTi_xO₁₉ ($x = 0 \sim 1$) and Ca_{1-x}La_xAl_{12-x}Ni_xO₁₉ ($x = 0 \sim 1$).

Due to big difference in neutron scattering lengths, incorporated Ni²⁺ and Ti⁴⁺ ions are successfully located in the hibonite lattice through Rietveld refinements. Optical spectra reveal an intense absorption band that broadens with increasing Ni content. Origin of the observed blue color is attributed to the allowed d-d transition of Ni²⁺ on tetrahedral sites. Recorded CIE L*a*b* color parameters of our blue samples manifest exclusively large negative values for blue component b*. Ni-containing blue hibonites in this work show better reflectance than Co-blue in the near-infrared region suggesting potential “Cool Pigments” applications.

In this article, we also provide a brief review on synthesis and characterization of hibonite related oxides with colors, especially those with blue colors.

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Table 1. Rietveld refinement results of neutron powder diffraction.¹⁾

Composition	La _{0.5} Ca _{0.5} Al _{11.5} Ni _{0.5} O ₁₉	LaAl ₁₁ NiO ₁₉	CaAl ₁₁ Ti _{0.5} Ni _{0.5} O ₁₉	CaAl ₁₀ TiNiO ₁₉	CaAl _{9.6} Ti _{1.2} Ni _{1.2} O ₁₉
χ^2	2.00	1.32	1.67	1.23	1.94
R _{wp} (%)	5.25	4.10	4.68	3.85	4.92
R _p (%)	4.06	3.34	3.86	3.12	3.84
$a = b$ (Å)	5.5750(1)	5.5906(1)	5.5837(1)	5.6024(2)	5.6049(2)
c (Å)	21.952(1)	22.009(1)	21.995(1)	22.138(2)	22.160(2)
V (Å ³)	590.87(1)	595.73(1)	593.87(1)	601.73(1)	602.88(1)
Al2, z	0.2390(4)	0.2399(2)	0.2608(2)	0.2643(2)	0.2656(3)
Al3, z	0.0284(2)	0.0273(1)	0.0280(1)	0.0273(1)	0.0271(1)
Al4, z	0.1904(2)	0.1894(1)	0.1900(2)	0.1889(7)	0.1870(8)
Al5, x	0.1670(4)	0.1673(2)	0.1672(2)	0.1676(2)	0.1677(3)
Al5, z	0.8917(1)	0.8921(1)	0.8919(1)	0.8930(1)	0.8931(1)
A, ²⁾ U_{iso} (Å ²)	0.0096(8)	0.0092(4)	0.022(1)	0.029(2)	0.026(2)
Al1, U_{iso} (Å ²)	0.007(2)	0.002(1)	0.005(1)	0.005(1)	0.005(1)
Al2, U_{iso} (Å ²)	0.008(5)	0.003(1)	0.003(2)	0.004(3)	0.004(3)
Al3, U_{iso} (Å ²)	0.0059(8)	0.0042(5)	0.0038(5)	0.0041(4)	0.0065(6)
Al4, U_{iso} (Å ²)	0.008(2)	0.003(1)	0.002(1)	0.003(2)	0.007(6)
Al5, U_{iso} (Å ²)	0.0031(6)	0.0054(4)	0.0041(4)	0.0049(3)	0.0060(4)
Ni(Al1) Occ. ³⁾	0.026(9)	0.053(9)	0.028(7)	0.049(8)	0.050(8)
Ti(Al2) Occ.	-	-	0.056(3)	0.064(3)	0.067(3)
Ni(Al2) Occ.	0.023(7)	0.015(5)	0.010(3)	0.012(3)	0.020(3)
Ni(Al3) Occ.	0.188(8)	0.283(7)	0.180(5)	0.234(5)	0.245(5)
Ti(Al4) Occ.	-	-	0.191(6)	0.408(6)	0.445(6)
Ni(Al4) Occ.	0.016(8)	0.010(8)	0.0	0	0
Ni(Al5) Occ.	0.005(4)	0.053(5)	0.016(3)	0.065(3)	0.075(4)
La(Ca) Occ.	0.492(26)	1	-	-	-
Refined FOR. ⁴⁾	La _{0.49} Ca _{0.51} Al _{11.49} Ni _{0.51} O ₁₉	LaAl _{11.01} Ni _{0.99} O ₁₉	CaAl _{11.01} Ti _{0.49} Ni _{0.50} O ₁₉	CaAl _{10.13} Ti _{0.94} Ni _{0.93} O ₁₉	CaAl _{9.95} Ti _{1.02} Ni _{1.03} O ₁₉
A–O3×6, Å	2.7914(1)	2.7990(1)	2.7952(1)	2.8042(1)	2.8055(1)
A–O5×6, Å	2.689(2)	2.674(1)	2.708(1)	2.725(1)	2.728(2)
Al1–O4×6, Å	1.886(2)	1.895(1)	1.883(1)	1.892(1)	1.894(1)
Al2–O1, Å	2.444(9)	2.417(5)	2.443(6)	2.552(5)	2.576(8)
Al2–O1, Å	1.960(8)	1.974(5)	1.969(6)	1.918(5)	1.895(8)
Al2–O3×3, Å	1.774(3)	1.771(2)	1.765(2)	1.777(2)	1.783(3)
Al3–O2, Å	1.862(4)	1.866(3)	1.854(3)	1.860(3)	1.855(4)
Al3–O4×3, Å	1.807(2)	1.828(1)	1.815(1)	1.824(1)	1.823(2)
Al4–O3×3, Å	1.961(4)	1.986(2)	1.978(3)	2.009(8)	2.039(2)
Al4–O5×3, Å	1.869(3)	1.863(2)	1.874(2)	1.868(7)	1.851(2)
Al5–O1, Å	1.851(4)	1.870(2)	1.858(2)	1.874(2)	1.878(3)
Al5–O2, Å	1.969(4)	1.953(2)	1.970(2)	1.956(2)	1.955(3)
Al5–O4×2, Å	1.978(2)	1.971(1)	1.982(1)	1.979(1)	1.981(2)
Al5–O5×2, Å	1.838(2)	1.853(2)	1.835(1)	1.854(1)	1.855(2)
Al2–Al2, ⁵⁾ Å	0.48(2)	0.44(1)	0.47(1)	0.63(1)	0.68(1)
Al4–Al4, ⁶⁾ Å	2.62(1)	2.67(2)	2.64(2)	2.71(3)	2.79(2)
A, BVS ⁷⁾	-	2.65	1.45	1.40	1.39
Hibonite phase ⁸⁾	97%	95%	99%	98%	98%

Notes:

- 1) All refined in space group P6₃/mmc. Ca at 2d (1/3, 2/3, 3/4), Al1 at 2a (0, 0, 0), Al2 and O1 at 4e (0, 0, z), Al3, Al4 and O2 at 4f (1/3, 2/3, z), Al5, O4 and O5 at 12k (x , $2x$, z), O3 at 6h (x , $2x$, 1/4). Octahedral sites: Al1, Al4 and Al5; TBP site: Al2; tetrahedral site: Al3. Details of the Rietveld refinements are in Supporting Information.
- 2) A = La, Ca. Atomic displacement parameters are constrained to be the same for atoms at the same site. Anisotropic atomic displacement values are available for calcium and oxygen atoms in cif files (Supporting Information).
- 3) Ni(Al1) means Ni at the site of Al1 and so forth. Occ. stands for site occupancy.

- 4) Refined formulas, as opposed to nominal compositions.
- 5) Distances between two split sites of TBP Al₂.
- 6) Distances between two adjacent Al₄ sites in face-sharing AlO₆ octahedra.
- 7) BVS stands for bond valance sum [61].
- 8) Impurity phases for La-containing samples are: Al₂O₃, LaAlO₃, NiAl₂O₄; for Ti-containing phases are: TiO₃, CaTiO₃, NiAl₂O₄.

Table 2. Average bond distances ($\text{\AA}$) from neutron refinements.

Refined composition	A–O	M1–O	M2–O	M3–O	M4–O	M5–O	M4–M4	M2dis ¹
$\text{La}_{0.49}\text{Ca}_{0.51}\text{Al}_{11.49}\text{Ni}_{0.51}\text{O}_{19}$	2.740	1.886	1.945	1.821	1.915	1.909	2.62	0.242(16)
$\text{LaAl}_{11.01}\text{Ni}_{0.99}\text{O}_{19}$	2.737	1.895	1.941	1.838	1.925	1.912	2.67	0.221(10)
$\text{CaAl}_{12}\text{O}_{19}$	2.745	1.879	1.934	1.804	1.916	1.906	2.595	0.185(11)
$\text{CaAl}_{11.04}\text{Ti}_{0.48}\text{Ni}_{0.49}\text{O}_{19}$	2.752	1.883	1.941	1.825	1.926	1.910	2.64	0.237(11)
$\text{CaAl}_{10.14}\text{Ti}_{0.95}\text{Ni}_{0.93}\text{O}_{19}$	2.765	1.892	1.960	1.833	1.939	1.916	2.71	0.315(10)
$\text{CaAl}_{9.95}\text{Ti}_{1.02}\text{Ni}_{1.03}\text{O}_{19}$	2.767	1.894	1.964	1.831	1.945	1.918	2.79	0.341(14)

1. Displacement of M2 from the ideal TBP site in $\text{\AA}$.

Table 3. L^* , a^* , b^* values of selected hibonite samples with blue colors.

Compositions	L^*	a^*	b^*
$\text{Ca}_{0.5}\text{La}_{0.5}\text{Al}_{11.5}\text{Ni}_{0.5}\text{O}_{19}$	57	-6.5	-30.38
$\text{LaAl}_{11}\text{NiO}_{19}$	46.8	-3	-23
$\text{CaAl}_{11}\text{Ti}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$	65.47	-11.1	-22.76
$\text{CaAl}_{10}\text{TiNiO}_{19}$	49.59	-14.72	-28.44
$\text{SrAl}_{11}\text{Ti}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$	66.07	-10.39	-21.17
$\text{SrAl}_{10}\text{TiNiO}_{19}$	65.12	-11.46	-18.53
$\text{SrAl}_{9.6}\text{Ti}_{1.2}\text{Ni}_{1.2}\text{O}_{19}$	62.94	-12.12	-17.86
$\text{SrAl}_8\text{Ti}_2\text{Ni}_2\text{O}_{19}$	52.31	-17.99	-10.34
$\text{Ca}_{0.5}\text{Ce}_{0.5}\text{Al}_{11.5}\text{Ni}_{0.5}\text{O}_{19}$	57.35	-12.37	-27.43
$\text{Ca}_{0.5}\text{Pr}_{0.5}\text{Al}_{11.5}\text{Ni}_{0.5}\text{O}_{19}$	58.59	-13.03	-22.7
$\text{Ca}_{0.5}\text{Nd}_{0.5}\text{Al}_{11.5}\text{Ni}_{0.5}\text{O}_{19}$	59.87	-12.15	-24.46
$\text{La}_{0.5}\text{Sr}_{0.5}\text{Al}_{11.5}\text{Ni}_{0.5}\text{O}_{19}$	63.51	-10.98	-23.48
$\text{CaAl}_{11}\text{Sn}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$	67.51	-9.68	-20.26
$\text{CaAl}_{11}\text{Ge}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$	55.19	-13.77	-22.54
$\text{CaAl}_{11.4}\text{Nb}_{0.2}\text{Ni}_{0.4}\text{O}_{19}$	57.59	-13.63	-26.83
$\text{CaAl}_{11.4}\text{Sb}_{0.2}\text{Ni}_{0.4}\text{O}_{19}$	67.23	-10.49	-18.72
$\text{CaAl}_{11.4}\text{Ta}_{0.2}\text{Ni}_{0.4}\text{O}_{19}$	64.83	-12.02	-19.27
$\text{Ca}_{0.5}\text{La}_{0.5}\text{Al}_{11}\text{Ga}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$	66.28	-10.46	-18.73
$\text{Ca}_{0.5}\text{La}_{0.5}\text{Al}_{11}\text{In}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$	58.81	-11.73	-26.96
$\text{CaAl}_{10}\text{TiNi}_{0.5}\text{Zn}_{0.5}\text{O}_{19}$	54.46	-13.4	-16.78
$\text{Ca}_{0.5}\text{Na}_{0.5}\text{Al}_{10.5}\text{TiNi}_{0.5}\text{O}_{19}$	54.85	-15.91	-24.97
$\text{Ca}_{0.4}\text{Sr}_{0.6}\text{Al}_{10.8}\text{Ti}_{0.6}\text{Ni}_{0.6}\text{O}_{19}$	66.42	-10.89	-19.85
$\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Al}_{10}\text{TiNiO}_{19}$	50.73	-14.17	-25.93
$\text{Ca}_{0.75}\text{La}_{0.25}\text{Al}_{11.25}\text{Ti}_{0.25}\text{Ni}_{0.5}\text{O}_{19}$	66.69	-11.12	-19.72
$\text{Ca}_{0.5}\text{La}_{0.5}\text{Al}_{11}\text{Ti}_{0.25}\text{Ni}_{0.75}\text{O}_{19}$	56.22	-10.66	-26.83
$\text{CaAl}_{11.8}\text{Co}_{0.2}\text{O}_{19}$	64.17	-4.66	-20.22
NiAl_2O_4	63.14	-15.72	-16.06
Shepherd Co Blue	43.51	-4.46	-44.39

Table 4. Calculated magnetic moments μ_{eff} , Curie and Weiss constants of $\text{LaAl}_{11}\text{NiO}_{19}$, $\text{Ca}_{0.5}\text{La}_{0.5}\text{Al}_{11.5}\text{Ni}_{0.5}\text{O}_{19}$ and $\text{CaAl}_{11}\text{Ti}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$ samples.

Compound	Temperature range (K)	Curie constant	Weiss constant (K)	μ_{eff} (without diamagnetic correction)	μ_{eff} (with diamagnetic correction)
$\text{LaAl}_{11}\text{NiO}_{19}$	250-300	1.70	-8.78	3.53	3.70
$\text{Ca}_{0.5}\text{La}_{0.5}\text{Al}_{11.5}\text{Ni}_{0.5}\text{O}_{19}$	250-300	1.64	-5.19	3.47	3.64
$\text{CaAl}_{11}\text{Ti}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$	250-300	1.59	-4.10	3.41	3.58

Figure 1. Polyhedral representation of hexagonal $AM_{12}O_{19}$ ($A = \text{Ca, Sr, RE}$) with hibonite-type of structure. Twelve coordinated A atoms in gray; oxygen atoms in red; MO_6 octahedra in pink (M1), yellow (M4) and cyan (M5); MO_5 trigonal bipyramids in green (M2); and 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].

Figure 2. Colors resulted from a variety of substitutions for the hibonite host with an ideal formula $\text{CaAl}_{12}\text{O}_{19}$. (a) $\text{CaAl}_{12-x}\text{M}_x\text{O}_{19}$ ($M = \text{Cr, Mn, Fe, Ni, Co, Cu, Ti, V}$); (b) $\text{CaAl}_{12-x-y}\text{Ni}_x\text{M}_y\text{O}_{19}$ ($M = \text{Zn, Ga, In, Si, Ti, Zr, Sn, Ge, Nb, Ta, Sb, Te}$); (c) $\text{Ca}_{1-x}\text{A}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ ($A = \text{Sr, La, Ce, Pr, Nd, Gd, Y}$) and $\text{Ca}_{1-x}\text{A}_x(\text{Al/Ni/Ti})_{12-x}\text{O}_{19}$ ($A = \text{Sr, Na}$).

Figure. 3 A series of color photographs of blue pellets and powders according to the following two solid solutions: (left) $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ ($x = 0 \sim 1.2$), and (right, inside box) $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$.

Figure 4. A series of X-ray powder diffraction patterns for the (top) $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ ($x = 0.1 \sim 1.2$), and (bottom) $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ ($x = 0 \sim 1$) solid solutions.

Figure 5. Cell edges of solid solution $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ ($x = 0 \sim 1.2$) refined by X-ray and neutron powder diffraction data. Estimated uncertainties are smaller than the plotted point size.

Figure 6. Cell edges of solid solution $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ ($x = 0 \sim 1$) refined by X-ray and neutron powder diffraction data. Estimated uncertainties are smaller than the plotted point size.

Figure 7. Cell edges of solid solutions $\text{Ca}_{1-x}\text{RE}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ ($x = 0 \sim 1$) and $\text{Sr}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ ($x = 0 \sim 1$) refined by X-ray powder diffraction: 1. RE = La; 2. RE = Ce; 3. RE = Pr; 4. RE = Nd; 5. $\text{Sr}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ ($x = 0 \sim 1$). Estimated uncertainties are smaller than the plotted point size.

Figure 8. XRD patterns of $A_{1-x}\text{RE}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ ($x = 0.2$). From bottom to top: 1. $A = \text{Ca}$, $\text{RE} = \text{La}$; 2. $A = \text{Ca}$, $\text{RE} = \text{Ce}$; 3. $A = \text{Ca}$, $\text{RE} = \text{Pr}$; 4. $A = \text{Ca}$, $\text{RE} = \text{Nd}$; 5. $A = \text{Ca}$, $\text{RE} = \text{Sm}$; 6. $A = \text{Ca}$, $\text{RE} = \text{Eu}$; 7. $A = \text{Ca}$, $\text{RE} = \text{Gd}$; 8. $A = \text{Ca}$, $\text{RE} = \text{Tb}$; 9. $A = \text{Ca}$, $\text{RE} = \text{Dy}$; 10. $A = \text{Ca}$, $\text{RE} = \text{Ho}$; 11. $A = \text{Ca}$, $\text{RE} = \text{Er}$; 12. $A = \text{Ca}$, $\text{RE} = \text{Tm}$; 13. $A = \text{Ca}$, $\text{RE} = \text{Yb}$; 14. $A = \text{Ca}$, $\text{RE} = \text{Lu}$; 15. $A = \text{Sr}$, $\text{RE} = \text{La}$; 16. $A = \text{Sr}$, $\text{RE} = \text{Ce}$; 17. $A = \text{Sr}$, $\text{RE} = \text{Pr}$; 18. $A = \text{Sr}$, $\text{RE} = \text{Nd}$; 19. $A = \text{Ba}$, $\text{RE} = \text{La}$.

Figure 9. XRD patterns of $\text{CaAl}_{12-x-y}\text{Ni}_x\text{M}_y\text{O}_{19}$ (For $M = \text{Ti, Ge and Sn}$, $x = 0.5$, $y = 0.5$; For $M = \text{Nb, Ta and Sb}$, $x = 0.4$, $y = 0.2$). The composition for Na is $\text{Ca}_{0.5}\text{Na}_{0.5}\text{Al}_{10.5}\text{Ni}_{0.5}\text{TiO}_{19}$.

Figure 10. Neutron Rietveld fits of (a) $\text{LaAl}_{11}\text{NiO}_{19}$ (Phase 1, ~95%). Impurity phases include: Phase 2, LaAlO_3 ; Phase 3, Al_2O_3 ; Phase 4, NiAl_2O_4 . (b) $\text{CaAl}_{10}\text{NiTiO}_{19}$ (Phase 1, ~98%). Impurity phases include: Phase 2, TiO_2 ; Phase 3, CaTiO_3 ; Phase 4, NiAl_2O_4 .

Figure 11. Diffuse reflectance spectra of solid solutions (a) $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ ($x = 0 \sim 1.2$) and (b) $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ ($x = 0 \sim 1$).

Figure 12. The CIE $L^*a^*b^*$ color coordinates for solid solutions (a) $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ ($x = 0 \sim 2$) and (b) $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ ($x = 0 \sim 1$). Estimated uncertainties are smaller than the plotted point size.

Figure 13 NIR reflectance spectra of selected Ni-containing hibonite solid solutions. (a) $\text{CaAl}_{12-2x}\text{Ni}_x\text{Ti}_x\text{O}_{19}$ ($x = 0.5, 1.0, 1.2$); (b) $\text{Ca}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ ($x = 0.0, 0.1, 0.3, 0.5, 0.7, 1.0$); (c) $\text{Sr}_{1-x}\text{La}_x\text{Al}_{12-x}\text{Ni}_x\text{O}_{19}$ ($x = 0.0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.0$); (d) $\text{Ca}_{0.5}\text{RE}_{0.5}\text{Al}_{11.5}\text{Ni}_{0.5}\text{O}_{19}$ (RE = La, Ce, Nd, Pr) and $\text{Sr}_{0.5}\text{La}_{0.5}\text{Al}_{11.5}\text{Ni}_{0.5}\text{O}_{19}$.

Figure 14. NIR reflectance spectra of selected Ni-containing hibonite samples. Commercial Co-blue pigment and TiO_2 are included for comparison.

Figure 15. Magnetic susceptibility (χ) and inverse magnetic susceptibility ($1/\chi$) vs. temperature of (1) $\text{LaAl}_{11}\text{NiO}_{19}$; (2) $\text{Ca}_{0.5}\text{La}_{0.5}\text{Al}_{11.5}\text{Ni}_{0.5}\text{O}_{19}$ and (3) $\text{CaAl}_{11}\text{Ti}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$. 1 emu (cgs units) = 10^{-3} A m^2 (SI units).

Figure 16. (a) Temperature dependence of (a) dielectric constant κ and (b) dielectric loss $\tan \delta$ for $\text{CaAl}_{11}\text{Ti}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$ hibonite sample.

Figure 17. (a) Temperature dependence of (a) dielectric constant κ and (b) dielectric loss ($\tan \delta$) for $\text{CaAl}_{10}\text{TiNiO}_{19}$ hibonite sample.

Figure 18. Frequency dependence of (a) dielectric constant κ and (b) dielectric loss ($\tan \delta$) for $\text{CaAl}_{11}\text{Ti}_{0.5}\text{Ni}_{0.5}\text{O}_{19}$ and $\text{CaAl}_{10}\text{TiNiO}_{19}$ hibonite samples.

Figure 19. XRD patterns of (a) $\text{CaAl}_{11}\text{TiNiO}_{19}$ and (b) $\text{LaAl}_{11}\text{NiO}_{19}$ hibonite compounds before and after exposure of various acids (HNO_3 , CH_3COOH , HCl) and base (NaOH).