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Mn^{3+} in Trigonal Bipyramidal Coordination: A New Blue Chromophore

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The development of the first known synthetic blue pigment, Egyptian blue ($CaCuSi_4O_{10}$), is believed to have been patronized by the Egyptian pharaohs, who promoted the advancement of pigment technologies for use in the arts.[1] The subsequent quest for blue pigments has a rich history linked with powerful civilizations, such as the Han Chinese [Han blue ($BaCuSi_4O_{10}$)] and the Maya [Maya blue (indigo intercalated in magnesium aluminosilicate clays)]. Currently used blue inorganic pigments are cobalt blue ($CoAl_2O_4$),[2] ultramarine ($Na_7Al_6Si_6O_{24}S_3$),[3] Prussian blue ($Fe_4[Fe(CN)_6]_3$),[4] and azurite [$Cu_3(CO_3)_2(OH)_2$].[5] All suffer from environmental and/or durability issues: Cobalt is considered to be highly toxic. Ultramarine and azurite are not stable with respect to heat and acidic conditions. Prussian blue liberates HCN under mild acidic conditions. In addition, the manufacture of ultramarine involves a large amount of SO_2 emission. Hence, the identification of intense blue inorganic pigments that are environmentally benign, earth-abundant, and durable is important but remains a challenge today. We have discovered that a surprisingly intense bright-blue color is obtained when Mn^{3+} is introduced into the trigonal bipyramidal sites of metal oxides. We have demonstrated this behavior by substituting Mn for In in hexagonal $YInO_3$ and obtaining a blue color over much of the $YIn_{1-x}Mn_xO_3$ solid-solution range, in spite of the fact that $YInO_3$ and $YMnO_3$ are white and black, respectively. We have also shown that a blue color is obtained when Mn^{3+} is introduced into trigonal bipyramidal sites in other layered oxides. We conclude that the blue color is a consequence of both the crystal field splitting associated with the trigonal bipyramidal coordination and the short apical Mn−O bonds. We expect that our results will lead to routes for the development of inexpensive, earth-abundant, environmentally benign, highly stable blue inorganic pigments.

Both $YInO_3$ and $YMnO_3$ are known in the common orthorhombic and centric form of the perovskite structure,[6,7] but they can also be readily prepared in an acentric hexagonal structure (Figure 1) that is not perovskite-related.[8,9] This hexagonal structure consists of layers of Y^{3+} ions separating layers of corner-shared MO_5 trigonal bipyramids (M = In, Mn). This structure has been of considerable recent interest because it exhibits an unusual form of improper geometric ferroelectricity accompanied by tilting of the MO_5 polyhedra.[10−12] Such ferroelectricity is compatible with M-site magnetism and therefore allows multiferroic behavior. Two detailed features of isostructural hexagonal $YInO_3$ and $YMnO_3$ are important for this work. First, their basal-plane M−O bond lengths are almost equal (2.05 Å for $YMnO_3$ and 2.1 Å for $YInO_3$). Second, the apical Mn−O distances in $YMnO_3$ (1.86 Å) are considerably shorter than those in the basal plane, while in $YInO_3$, all of the In−O bonds are roughly the same length. The crystal field splitting of the d-orbital energies in trigonal bipyramidal coordination is shown in Figure 1. Notably, the e′ → a′ energy splitting, which is the lowest-energy excitation for a d^4 cation in the cluster limit, depends sensitively on the apical M−O bond length through its influence on the energy of the d_{z^2} orbital. While the crystal field stabilization associated with a d^4 cation in trigonal bipyramidal coordination has been invoked to explain the stability of hexagonal $YMnO_3$ relative to the competing perovskite structure, trigonal bipyramidal is not a common coordination for Mn^{3+}, and we are not aware of its occurrence in compounds other than hexagonal $RMnO_3$ compounds in which R is a small rare-earth cation.[13]

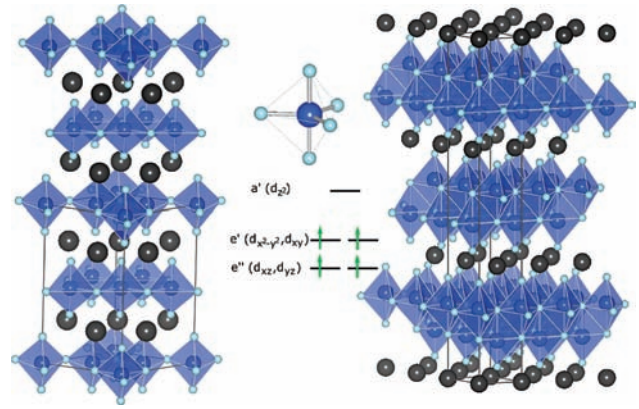

Figure 1. Structures of (left) $YMnO_3$ and (right) $YbFe_2O_4$ showing MO_5 trigonal bipyramids in blue (Mn/Fe, blue spheres; O, cyan spheres; Y/Yb, gray spheres). The $YMnO_3$ structure consists of layers of corner-shared MnO_5 trigonal bipyramids. The $YbFe_2O_4$ structure is similar but has a double layer of corner-shared FeO_5 trigonal bipyramids that share edges between the layers. Schematic energy levels for the spin-up Mn^{3+} 3d orbitals in trigonal bipyramidal coordination are shown. We note that transitions from e′ to a′ are formally dipole-allowed in this symmetry

In view of the interest in the hexagonal $RMnO_3$ phases as multiferroic materials, there have been many attempts to substitute Mn with various cations, such as Fe, Co, Ni, Cr, Ti, Ga, and Al.[14−20] The amount of substitution is always very limited before the structure converts to the perovskite structure, even for those solid-solution compositions where the end-point compound is stable in the hexagonal phase. It is thus surprising that we were able to prepare a complete single-phase $YIn_{1-x}Mn_xO_3$ solid solution (synthesis details are given in the Supporting Information) despite the fact that the size mismatch between In^{3+} and Mn^{3+} is greater than in the cases where the solid solution is more limited. We attribute this complete miscibility to the similar In−O and Mn−O basal-plane distances in hexagonal $YInO_3$ and $YMnO_3$. The large size difference between In^{3+} and Mn^{3+} is manifested only in the apical distances. A plot of unit cell edges for the $YIn_{1-x}Mn_xO_3$ solid solution is shown in Figure 2. Both the *c* lattice parameter and the *c*/*a* ratio decrease dramatically with *x* as a result of the short apical Mn−O distances.

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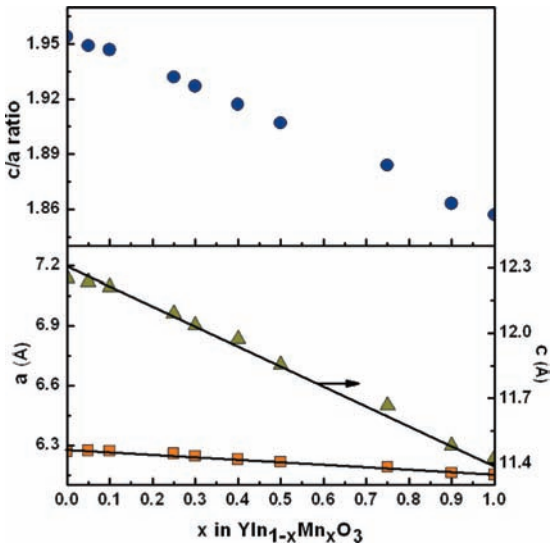

Figure 2. (bottom) Unit cell dimensions a and c and (top) the c/a ratio for the $YIn_{1-x}Mn_xO_3$ solid solution. It is clear that the similar basal-plane bond lengths in the end members lead to a weak variation of a across the solid-solution series. The c/a ratio varies strongly because of the large difference in apical In−O and Mn−O bond lengths.

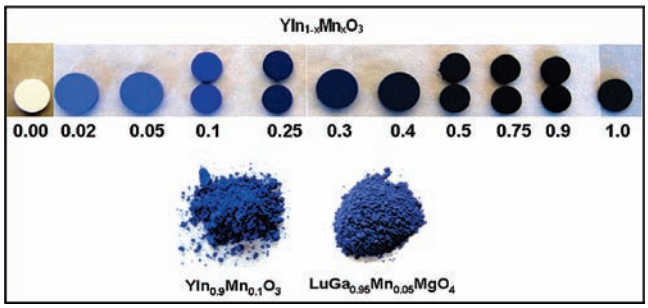

Figure 3. Colors of pellets and powders at selected compositions. The intense blue color appears at our lowest concentration of Mn doping in $YInO_3$. With increasing Mn composition, the color darkens until eventually $YMnO_3$ is found to be black (see the Supporting Information for an enlarged figure).

The blue color of the $YIn_{1-x}Mn_xO_3$ powders is evident even for very low values of x (Figure 3). To understand the origin of this blue color, we measured diffuse reflectance spectra and performed first-principles density functional theory (DFT) calculations with the LSDA+U method, which has been previously shown to give reliable results for $YMnO_3$.[11] The results of our diffuse reflectance measurements are shown in Figure 4. We see that at low doping concentrations there is a strong, narrow (~1 eV width) absorption centered at ~2 eV that absorbs in the red-green region of the visible spectrum. The absorption then decreases between 2.5 and 3 eV before a second onset near 3 eV. The absence of absorption in the 2.5−3 eV (blue) region of the spectrum results in the blue color. As the concentration of Mn is increased, the lower-energy absorption peak broadens and the higher-energy onset shifts to lower energy, consistent with the gradual darkening of the samples toward navy blue. In pure $YMnO_3$, absorption occurs throughout the entire visible region, resulting in the black color. Although we know of no precedent for a blue color arising from Mn^{3+} in trigonal bipyramidal coordination, a blue color is observed for the d^4 cation Cr^{2+} in trigonal bipyramidal coordination in [Cr(Me,tren)Br]Br.[21] To our knowledge, divalent chromium is not known in oxides.

Our DFT calculations of the densities of states and optical properties of the fully relaxed end-point compounds and selected

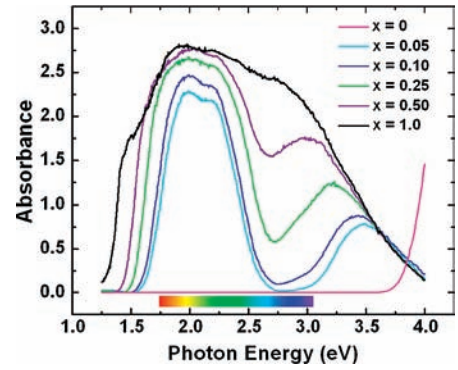

Figure 4. Diffuse reflectance spectra for the $YIn_{1-x}Mn_xO_3$ solid solution. Strong absorption in the red-green spectral region combined with relatively weak absorption in the blue region is responsible for the observed intense blue color. With increasing Mn composition, the first absorption peak broadens and the second onset shifts to lower energy, so $YMnO_3$ ($x = 1$) absorbs almost equally throughout the visible region (see the text).

intermediates (for details, see the Supporting Information) indicate that the peak at ~2 eV arises from the transition between the valence-band maximum, consisting of Mn $3d_{x^2-y^2,xy}$ states strongly hybridized with O $2p_{x,y}$ states, and the lowest unoccupied energy level, which in lightly Mn-doped $YInO_3$ is a narrow band formed from the Mn $3d_{z^2}$ state that lies in the band gap of $YInO_3$. (The absence of midgap Mn $3d_{z^2}$ states in pure $YInO_3$ leaves it colorless). Notably, in the local D_{3h} symmetry of the trigonal bipyramids, the d−d component of this transition (between symmetry labels a′ and e′ in Figure 1) is formally symmetry-allowed according to the Laporte selection rule, whereas the e″ → a′ transition is symmetry-forbidden. This results in a high transition probability and intense absorption. The strong d−d absorption here is in striking contrast to the behavior in the approximate O_h crystal field environment of perovskites, where it is formally symmetry-forbidden. In O_h symmetry, hybridization with ligands or structural distortions are required to circumvent the dipole selection rules, and d−d transitions are usually weak. Indeed, we found no blue color upon substitution of Mn^{3+} into $YGaO_3$ or $YAlO_3$ with the perovskite structure, where the Mn^{3+} would be in an environment with approximate O_h symmetry.

We assign the higher-energy peak to the onset of the transition from the O 2p band to the Mn $3d_{z^2}$ band. It should be noted that our assignments are consistent with earlier optical studies of $YMnO_3$ using second-harmonic generation[22] but that the topic has been controversial.[23] With increasing Mn concentration, our calculations indicate that the Mn 3d levels (particularly the lowest unoccupied state, corresponding to the $3d_{z^2}$ band) broaden substantially, causing the absorption peaks to become broader.

Next we investigated the structural properties of some intermediate compositions in order to determine which structural features correlate with the blue color and in turn to develop guidelines for a general search for blue compounds. Interestingly, our DFT calculations on the relaxed structures for both $Y_8Mn_2In_6O_{24}$ and $Y_8Mn_6In_2O_{24}$ units show that while the basal plane Mn−O and In−O distances in these intermediates are similar to each other and to those of the end members, the apical Mn−O and In−O distances are very different from each other, maintaining values close to those of the respective end members (see Table S5 in the Supporting Information). Since the energy of the d_{z^2} state relative to the valence-band maximum is determined primarily by the Mn−O apical bond length, this explains the lack of shift in the energy of the 2 eV absorption peak as a function of Mn concentration. If we artificially insert Mn into the $YInO_3$ structure without allowing the structure

to relax to its energy minimum, the d_{z^2} peak shifts to considerably lower energy, and the calculated absorption spectrum changes markedly.

For our single-crystal X-ray diffraction study, we focused specifically on the $YIn_{0.37}Mn_{0.63}O_3$ compound and refined the structure using the $P6_3cm$ space group of hexagonal $YMnO_3$ and $YInO_3$. The structure refined normally except for the displacement parameters for one of the apical O atoms, suggesting the presence of static disorder arising from the different In−O and Mn−O distances. Indeed, refinement of the $YIn_{0.37}Mn_{0.63}O_3$ structure with two O atoms at each apical site having occupation values fixed on the basis of the Mn/In ratio converged with shorter distances for the sites with the higher occupation. We extracted apical Mn−O distances of 1.86 and 1.89 Å and apical In−O distances of 2.05 and 2.20 Å, in excellent agreement with the results of our first-principles calculations. Violations of Friedel's law in our diffraction data confirm a polar space group. Relative to the paraelectric structure, displacements of atoms along the *c* axis, which is the polar axis, are found to be of the same magnitude as in $YMnO_3$. However, our first-principles calculations suggest that the polarization might be substantially suppressed from the values in the end-member compounds as a result of frustration of the cooperative tilting by the different sizes of the MO_5 polyhedra. This could lead to intriguing dielectric properties, which will be the subject of future work.

Finally, motivated by our findings in the $YIn_{1-x}Mn_xO_3$ system, we substituted Mn^{3+} into another structure with trigonal bipyramidal sites, the $YbFe_2O_4$ structure.[24] This structure (Figure 1) consists of layers of rare-earth cations alternating with double layers of MO_5 trigonal bipyramids. As in $YMnO_3$, the polyhedra in each MO_3 plane share corners through their basal-plane oxygen atoms; here, however, polyhedra in the second plane share edges between apical and basal oxygens with those in the first plane. As in $YMnO_3$, the topology of the layering should allow the apical bond lengths to adopt different values for the different M site cations without introducing large strain energies into the lattice. Although $YbFe_2O_4$ is not a suitable host because of its black color related to Fe^{2+}/Fe^{3+} mixed valency, there are several oxides with this structure that are transparent throughout the visible spectrum.[25] Again we found that an intense blue color is produced with 5% Mn^{3+} doping into these compounds, which include $ScAlMgO_4$, $ScGaMgO_4$, $LuGaMgO_4$, $ScGaZnO_4$, and $InGaMgO_4$. Thus, we conclude that the blue color is a general characteristic of Mn^{3+} in a trigonal bipyramidal site in oxides, provided that structural features such as layering allow for the appropriate apical Mn−O bond length.

In summary, we have shown for the first time that an intense bright-blue color occurs through most of the $YIn_{1-x}Mn_xO_3$ solid solution, in spite of the fact that the $YInO_3$ and $YMnO_3$ end members are colorless and black, respectively. The compositions as well as color are quite stable under acidic and basic conditions. We have explained the origin of the color through a detailed structural investigation and the use of first-principles DFT calculations. It has been shown that this color is a general feature of Mn^{3+} in trigonal bipyramidal coordination when the structure can accommodate the required short Mn−O apical bonds; this should be particularly favorable in layered structures. Our results suggest a route to the development of inexpensive, earth-abundant, environmentally benign blue pigments that are based on manganese.[26]

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Supporting Information Available: Details about the synthesis of polycrystalline and single-crystal samples, the X-ray diffraction procedures, and the first-principles calculations; six tables including crystallographic data and structural refinements, bond lengths, anisotropic displacement parameters, distances and polyhedral volumes after relaxation, and first-principles calculations for short apical Mn−O bonds; figures showing sample colors and powder diffraction patterns for all compositions; and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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