

Out of the Blue: Inorganic Pigments Containing Mn^{3+} in Trigonal Bipyramidal Coordination Environments

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Literature Seminar

November 14, 2017

Naturally occurring inorganic pigments such as ochre, which is based on ferric oxide, have a long history and date as far back as prehistoric times.¹ The first synthetic inorganic pigment was Egyptian Blue, a calcium copper silicate that was in use 4500 years ago, but it wasn't until the 18th century that the pigment industry began to flourish.^{1,2} Since that time, new artificial pigments have been continually developed to produce the many colors we see today in paints, coatings, plastics, and inks. The global pigments market was valued at \$23 billion in 2014 and is expected to grow.³

Many pigments, however, suffer from one or more drawbacks such as chemical instability, photo instability, thermal instability, or toxicity;¹ thus there is a need to develop new pigments that are free of these issues.^{1,3} Research into inorganic pigments had slowed during the late 20th century, but an accidental breakthrough in 2009 has led to renewed interest in this area. Researchers at Oregon State were working to develop high efficiency electronic materials, when they happened to make a bright blue compound consisting of $YInO_3$ and $YMnO_3$.⁴ They found that these two oxides, which adopt an acentric hexagonal structures (Figure 1a), readily form solid solutions due to their very similar equatorial bond lengths.⁴ Similar oxides had been studied previously, but the miscibility was always very low and they reverted to their orthorhombic perovskite structure.

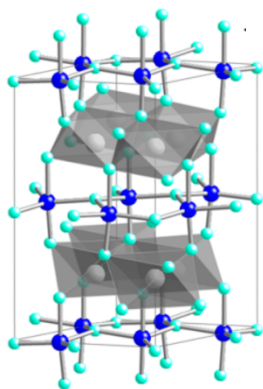


Figure 1a: Acentric hexagonal structure of $YIn_{1-x}Mn_xO_3$. The In^{3+} or Mn^{3+} ions (blue) are surrounded by five oxygen ions (teal) in a trigonal bipyramidal arrangement; also shown are the Y cations (gray).⁵

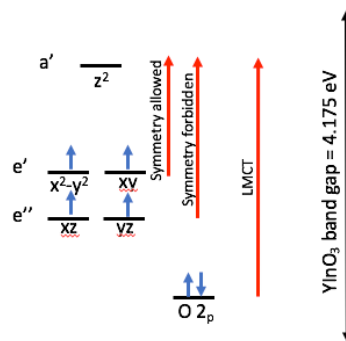


Figure 1b: Crystal field diagram for D_{3h} Mn^{3+} in a trigonal bipyramidal coordination environment. Transitions observed in the visible absorption spectrum are shown.

The manganese(III) ions in these solids adopt local trigonal bipyramidal coordination geometries, which is key to their color. The crystal field splitting diagram (Figure 1b) indicates the symmetry allowed and symmetry forbidden d-d transition.⁴ These transitions occur in the green through red region of the visible spectrum, thus giving the solids a blue color. A higher energy absorption was determined to be a ligand-metal-charge-transfer by DFT calculations.⁴ By increasing the Mn concentration, the blue pigment becomes darker.⁴ Later work was done to confirm the presence of manganese(III) by magnetic susceptibility measurements, as well as high field and frequency electron paramagnetic resonance (HFEP).^{5,6}

Different colors can be created by changing the axial bond length, which in turn alters the ligand field around Mn, and thus the energies of the transitions.⁷ For example, to produce purple

pigments, Li et al. introduced Ti^{4+} and Zn^{2+} into the In sites of $YInO_3$ to make $YIn_{1-x-2y}Mn_xTi_yZn_yO_3$.⁷ By introducing ions with smaller ionic radii than In, the axial Mn-O bond distance becomes shorter, which causes an increased crystal field splitting and shifts the absorption to higher energy.⁷ The absorption spectrum as a function of dopant levels (Figure 2a) shows that shortening the axial Mn-O bond shifts the d-d transition to higher energy due to an increase in the ligand field splitting, but shifts the LMCT peak to lower energy.⁷ These changes lead to a variety of purple shades being produced (Figure 2b).

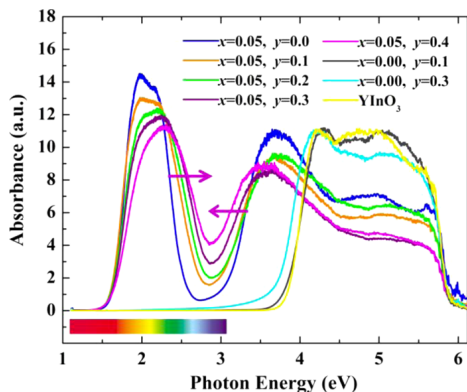


Figure 2a: DRIFTS spectra of variously doped samples of $YIn_{1-x-2y}Mn_xTi_yZn_yO_3$.⁵

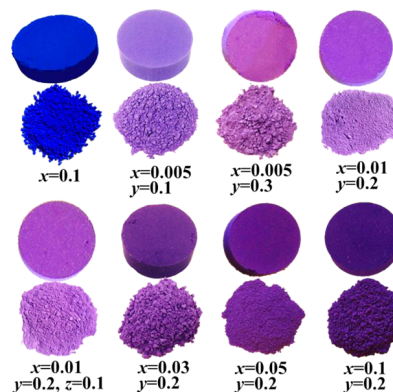


Figure 2b: Colors seen in variously doped samples of $YIn_{1-x-2y}Mn_xTi_yZn_yO_3$.⁵

One great property of these pigments is their high reflectance in the near-IR. These pigments reflect over 85% of light in this region, compared to cobalt blue (a commonly used blue pigment) which only reflects between 20-40%.⁷ The high reflectance means that these pigments reflect nearly as much heat as white pigments. This property has researchers interested in their applications for aerospace, the automotive industry, roofing, and other building coatings.⁸

Recently, blue and purple pigments have been developed in which manganese(III) ions are placed into other kinds of host materials. Saraswathy et al. developed a series of blue pigments based on $LaGa_{1-x}Mn_xGe_2O_7$, and Kim et al. developed a series of purple pigments based on $LaAl_{1-x}Mn_xGe_2O_7$.^{9,10} In these pigments, the symmetry forbidden transition is actually more intense than the symmetry allowed transition. The authors attribute this phenomenon to the long axial Mn-O bond, which causes stronger orbital mixing through spin-orbit coupling.^{9,10} Changing the dopant concentrations changes the intensities of these pigments (Figures 3a and 3b).

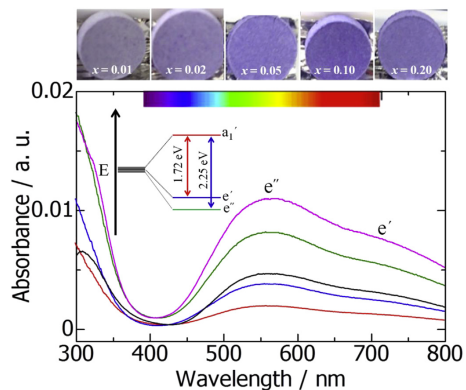


Figure 3a: Image of pigments and UV-Vis diffuse reflectance spectra for $LaAl_{1-x}Mn_xGe_2O_7$.⁶

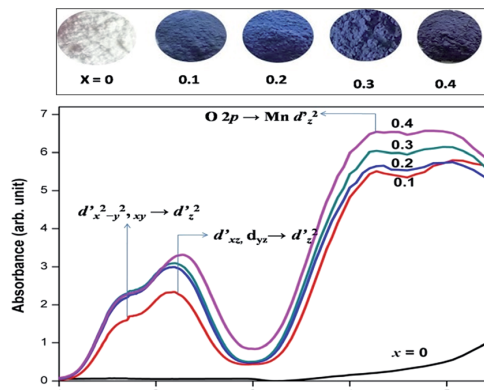


Figure 3b: Image of pigments and absorbance spectra for $LaGa_{1-x}Mn_xGe_2O_7$.⁷

Designing compounds that place Mn^{3+} in a trigonal bipyramidal coordination environment allow for the rational development of new blue and purple inorganic pigments. These pigments are chemically stable, thermally stable, non-toxic, and use earth abundant elements.^{5,9,10} Future work will undoubtedly produce new shades of colors, further increase near-IR reflectance, and lead to commercial uses.

References

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