

High resolution characterization of Y(Mn,In) Blue Chromophoric Oxides

Dr Isobel Bicket^{1,2,3}, Milenka Andelic¹, Soham Mukherjee⁴, Somnath Pal⁵, Dipankar Das Sarma⁶, Carlo U. Segre^{7,8}, Gianluigi A. Botton^{1,9}

¹Materials Science and Engineering, McMaster University, Hamilton, Canada, ²Atominstut, TU Wien, Vienna, Austria, ³USTEM, TU Wien, Vienna, Austria, ⁴Division of X-ray Photon Science, Department of Physics and Astronomy, Uppsala University, Uppsala, Sweden, ⁵MicroNano Systems, Tyndall National Institute, Cork, Ireland, ⁶Solid State and Structural Chemistry, Indian Institute of Science, Bangalore, India, ⁷Physics & Materials Science and Engineering, Illinois Institute of Technology, Chicago, USA, ⁸Center for Synchrotron Radiation Research and Technology, Illinois Institute of Technology, Chicago, USA, ⁹Diamond Light Source, Didcot, United Kingdom

Background

Throughout history, bright colours have contributed to the advancement of art and science through inspiring creativity, improving mental wellbeing, and enhancing the transfer of information. However, since many common pigments are produced using toxic materials, there has been a recent burst of interest in producing non-toxic, colourfast, long-lasting pigments for various colour treatment applications [1], led by the discovery of a durable, environmentally friendly inorganic blue pigment $Y(Mn_{1-x}In_x)O_3$ [2]. The two end compounds of this mixture, $YInO_3$ and $YMnO_3$, are white and black, respectively. Both compounds crystallize in a layered hexagonal lattice, while the intermediate compounds form a solid solution in which In and Mn occupy the same lattice sites. Mixing a small amount of Mn into the $YInO_3$ lattice results in a startling blue colour originating from absorption of other colours by electronic transitions from the Mn 3d states, including nominally forbidden d-d transitions. These transitions are made possible by the non-centrosymmetric trigonal bipyramidal (TBP) environment of O around the Mn ions [2,3].

In this study, we present a thorough characterization of the structural and spectral characteristics of $Y(Mn_{1-x}In_x)O_3$ across the full compositional range. We discuss the origin of the strong blue colour and its correlation with the crystallographic properties of this oxide material.

Methods

We use a Nion HERMES100 STEM operated at 60 keV, with an average energy resolution of 5 meV, to acquire high resolution EEL spectra across a broad range of the electromagnetic spectrum: from the mid-IR to the UV and core-loss regions. We complement our EELS results with high resolution imaging of the crystal structure using STEM, EDS, and iDPC on a double-corrected ThermoFisher Spectra Ultra STEM operated at 200 keV. JEMS enables us to visualize the crystal structure and simulate HAADF images of the various orientations we find in the STEM.

Results

In our EEL spectra, we observe several trends in the mid-IR to UV regions of the spectrum. In the mid-IR, the phonon modes redshift with more In content due to the larger relative atomic mass and size of In compared to Mn. In the visible region of the spectrum, $YMnO_3$ has strong extinction peaks arising from Mn 3d transitions (Fig. 1A), resulting in broadband absorption across the visible spectrum and a black colour in the bulk material. $YInO_3$, on the other hand, has no peaks in this spectral regime until the bandgap onset in the near-UV, resulting in a material which reflects all colours of light and appears white. In the intermediate compounds, such as $Y(Mn_{0.1}In_{0.9})O_3$, we observe a small peak around 2.2 eV and a change in the higher energy bandgap onset relative to the pure In compound. Further

increasing the Mn fraction results in stronger intensity on the 2.2 eV peak, and a new peak at 1.9 eV which redshifts to 1.7 eV and dominates the lower energy part of this spectrum. Additional extinction signal also arises near the bandgap onset, which overall shifts to lower energy and results in absorption of purple and UV light. This combination of transitions leaves only blue light to be reflected.

Through HR-STEM-EDS, we are able to identify the lattice sites occupied by Mn even in samples with low In concentration, such as $\text{Y}(\text{Mn}_{0.9}\text{In}_{0.1})\text{O}_3$ (Fig. 1B). From our EDS results, we observe that the Mn and In occupy the same lattice sites, substituting for each other in a disordered fashion, for the most part. One notable exception that we have observed is in the $\text{Y}(\text{Mn}_{0.5}\text{In}_{0.5})\text{O}_3$ oxide, wherein the Mn ions are distinctly noted to occupy specific lattice sites in a unit cell larger than former studies suggest (Fig. 1C), whereas the In ions do not show the same behaviour in this lattice. The origins of this mysterious ordering remain to be understood.

Through further analysis of our HR-STEM images, we observe an anisotropic expansion of the crystal lattice as Mn ions are replaced with the larger In ions. The lattice exhibits more expansion along the apical than the basal directions, with the *c* lattice parameter increasing by 1 Å in YInO_3 compared to YMnO_3 . We observe through selected area diffraction that in several of the intermediate compounds, the crystal lattice has a twist, likely due to the mismatch in size of the substitutional Mn and In ions. Further, using iDPC imaging, we are able to observe distinct structural features in alternating lattice planes, with a repetition matching the size of the system's unit cell (Fig. 1D).

Conclusion

In conclusion, we present a thorough characterization of the blue chromophoric oxide, hexagonal $\text{Y}(\text{Mn}_{1-x}\text{In}_x)\text{O}_3$. We examine the crystallographic and spectral characteristics of the material across the range of compositions to understand the origin of the optical properties that make this such an attractive pigment. We directly confirm the trends observed in x-ray based studies of this material and uncover evidence of Mn ions preferentially occupying unexpected sites in a larger supercell in $\text{Y}(\text{Mn}_{0.5}\text{In}_{0.5})\text{O}_3$.

Graphic:

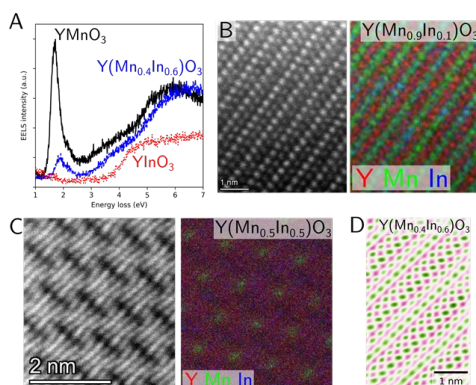


Fig. 1 A: Low-loss EELS spectra of three representative compounds spanning the compositional range. B: HR-STEM (left) and EDS (right) mapping of $\text{Y}(\text{Mn}_{0.9}\text{In}_{0.1})\text{O}_3$ along the [1-100] zone axis. C: HR-STEM (left) and EDS (right) mapping showing separation of the Mn and In lattice sites. D: iDPC image of an intermediate compound along the [1-100] axis

Keywords:

Oxide, optical, HR-STEM, HR-EELS

Reference:

- [1] Subramanian and Li, *Materials Today Advances*, 16, 2022.
- [2] Smith, et al., *J. Am. Chem. Soc.*, 131, 47, 2009.
- [3] Mukherjee, et al., *Inorg. Chem.*, 57, 15, 2018.