When can't crystallography be trusted? The case of hexagonal YMO_3-type chromophores.

Carlo Segre

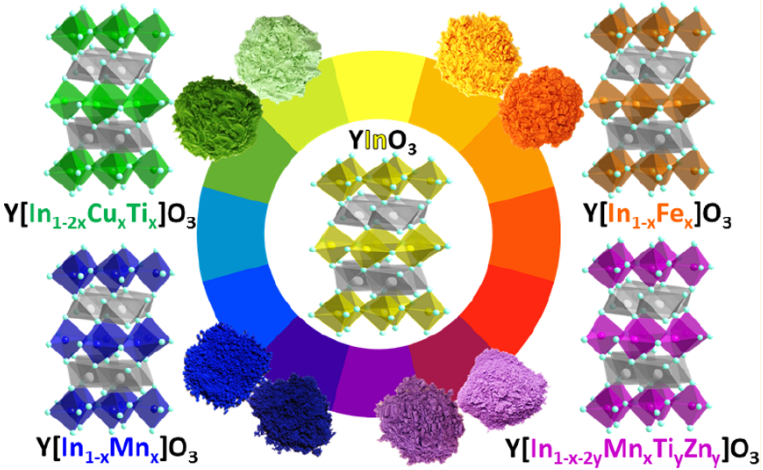
Physics Department
&
Center for Synchrotron Radiation Research and Instrumentation
Illinois Institute of Technology

September 18, 2019

Outline

- The YMO_3 chromophore system
- Long range structure of $YMn_{1-x}In_xO_3$
- Aside: An EXAFS primer
- Local structure of $YMn_{1-x}In_xO_3$
- The $YMn_{1-x}Ga_xO_3$ system
- Other cases: $LaBa_2Cu_3O_7$
- Other cases: $Zn_{1-x}Cd_xS$
- Other cases: $BaZr_xTi_{1-x}O_3$

Chromophores based on $YInO_3$



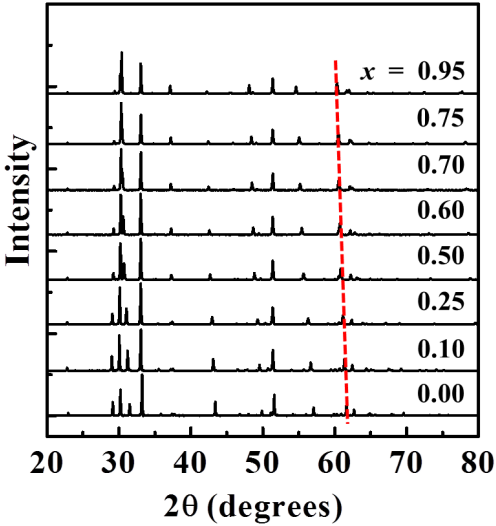
Base compound is white, dopant gives intense colors

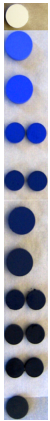
The Mn variant has commercial promise

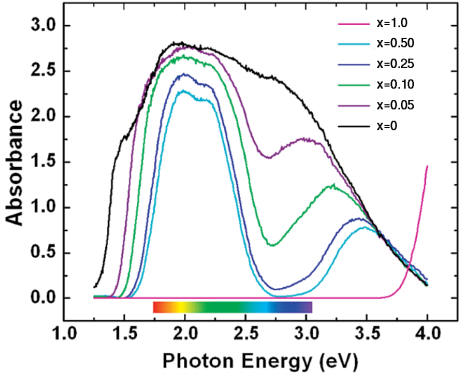
Hexagonal structure with YO_6 octahedra and InO_5 trigonal bipyramids

J. Li, S. Lorger, J.K. Stalick, A.W. Sleight, and M.A. Subramanian, *Inorg. Chem.* **55**, 9798–9804 (2016).

$YMn_{1-x}In_xO_3$ solid solution

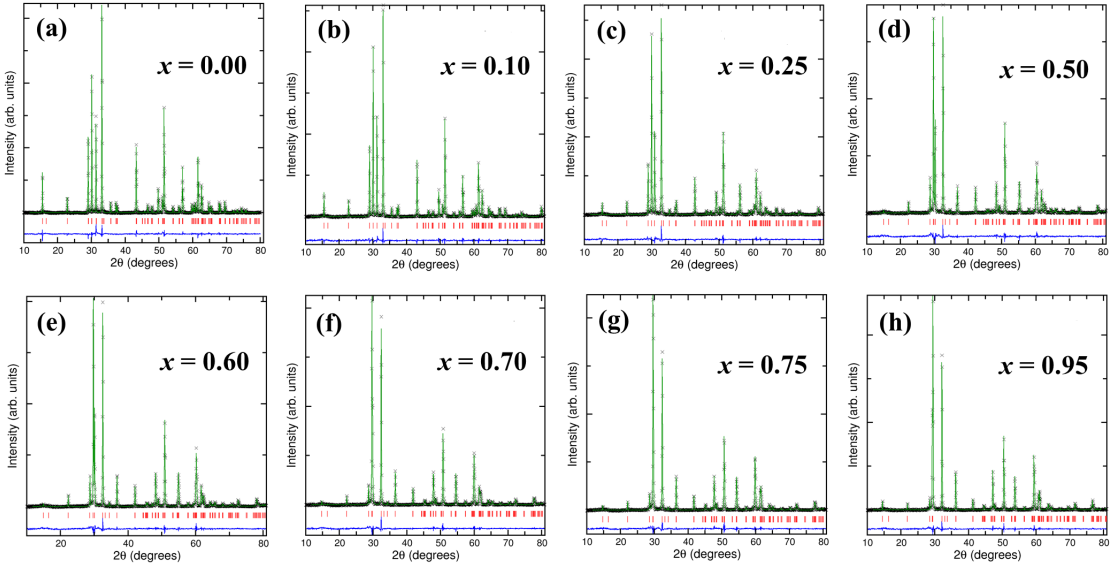




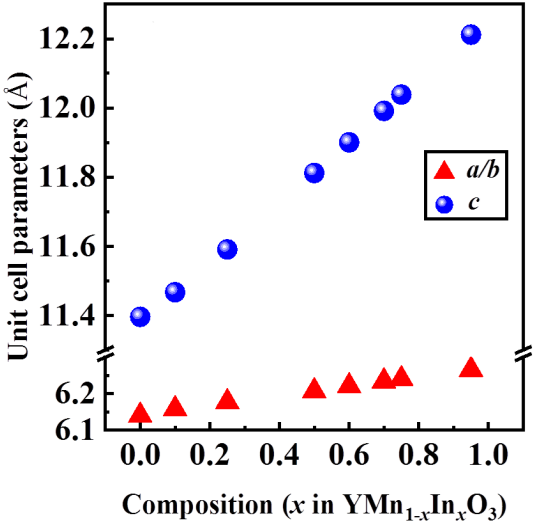


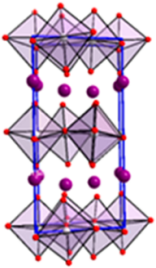
A.E. Smith, et al., *J. Am. Chem. Soc.* **131**, 17084-17086 (2009).

$YMn_{1-x}In_xO_3$ refinements



$YMn_{1-x}In_xO_3$ lattice parameters



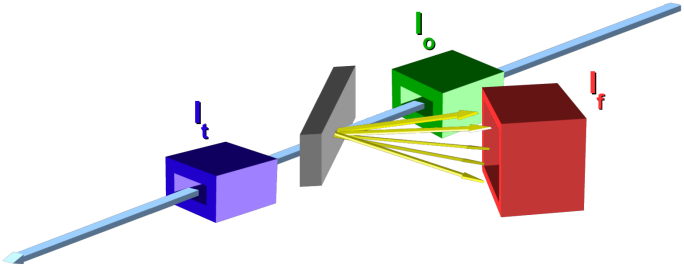


- All samples are single phase
- Lattice parameters vary linearly according to Vegard's law
- How does the local environment of the Mn and In vary?
- Hypothesis: Smooth variation in bond distances & near neighbors
- Bring on the x-ray absorption spectroscopy!

S. Mukherjee, H. Ganegoda, A. Kumar, S. Pal, C.U. Segre, and D.D. Sarma, *Inorg. Chem.* **57**, 9012–9019 (2018).

The EXAFS experiment

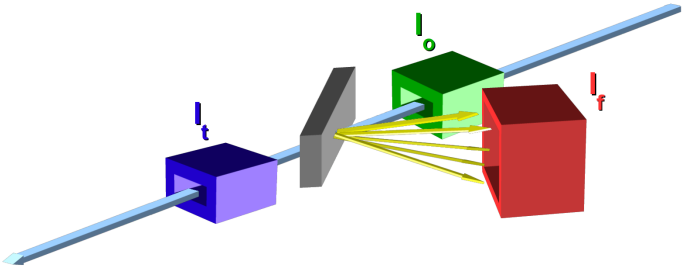
I_o = incident intensity
I_t = transmitted intensity
I_f = fluorescence intensity
$\mu(E)$ = absorption coefficient

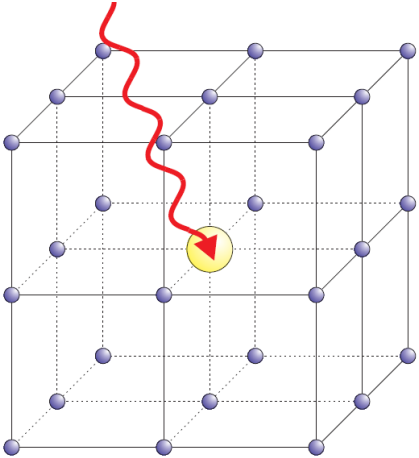


$$\mu(E) \propto \ln\left(\frac{I_o}{I_t}\right) \propto \frac{I_f}{I_o}$$

The EXAFS experiment

I_o = incident intensity
I_t = transmitted intensity
I_f = fluorescence intensity
$\mu(E)$ = absorption coefficient

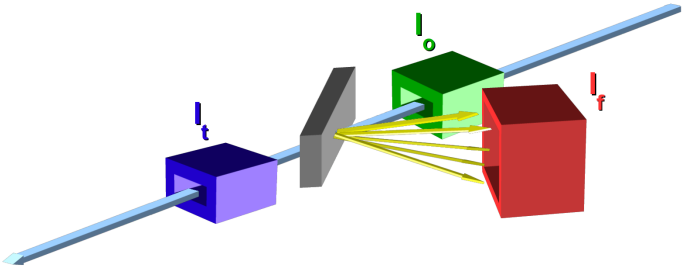


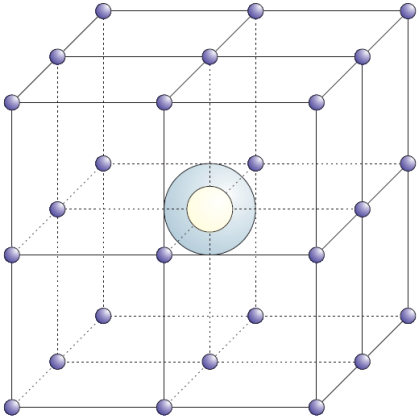


$$\mu(E) \propto \ln\left(\frac{I_o}{I_t}\right) \propto \frac{I_f}{I_o}$$

The EXAFS experiment

I_o = incident intensity
I_t = transmitted intensity
I_f = fluorescence intensity
$\mu(E)$ = absorption coefficient

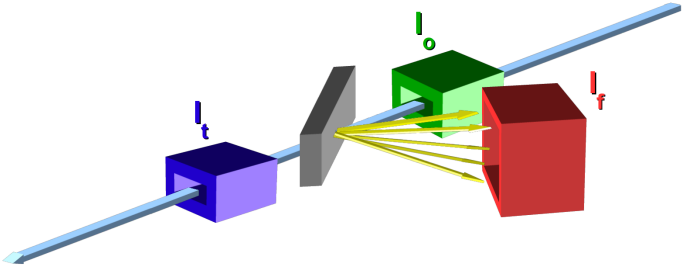


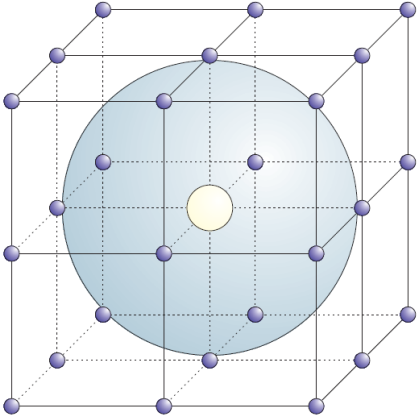


$$\mu(E) \propto \ln\left(\frac{I_o}{I_t}\right) \propto \frac{I_f}{I_o}$$

The EXAFS experiment

I_o = incident intensity
I_t = transmitted intensity
I_f = fluorescence intensity
$\mu(E)$ = absorption coefficient

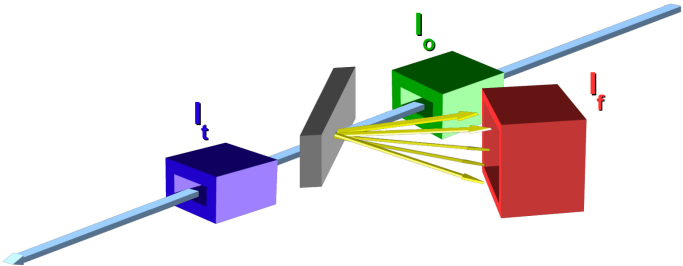


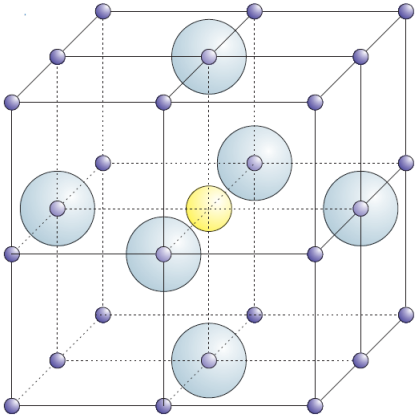


$$\mu(E) \propto \ln\left(\frac{I_o}{I_t}\right) \propto \frac{I_f}{I_o}$$

The EXAFS experiment

I_o = incident intensity
I_t = transmitted intensity
I_f = fluorescence intensity
$\mu(E)$ = absorption coefficient

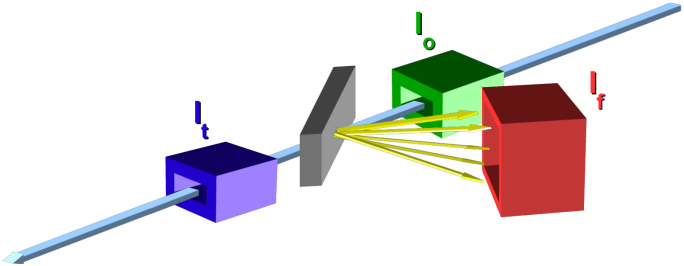


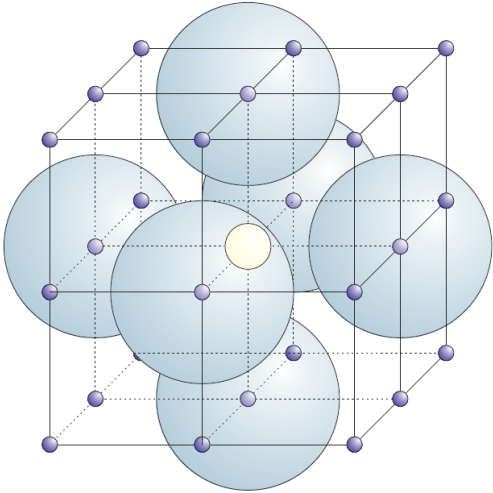


$$\mu(E) \propto \ln\left(\frac{I_o}{I_t}\right) \propto \frac{I_f}{I_o}$$

The EXAFS experiment

I_o = incident intensity
I_t = transmitted intensity
I_f = fluorescence intensity
$\mu(E)$ = absorption coefficient

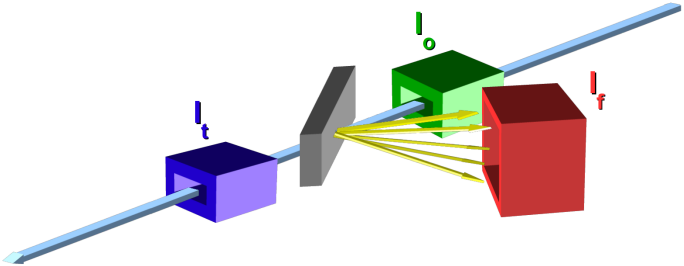


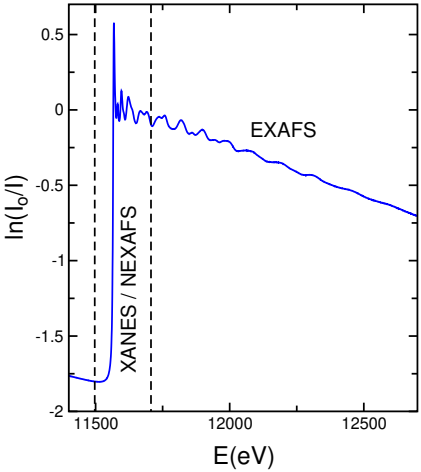


$$\mu(E) \propto \ln\left(\frac{I_o}{I_t}\right) \propto \frac{I_f}{I_o}$$

The EXAFS experiment

I_o = incident intensity
I_t = transmitted intensity
I_f = fluorescence intensity
$\mu(E)$ = absorption coefficient

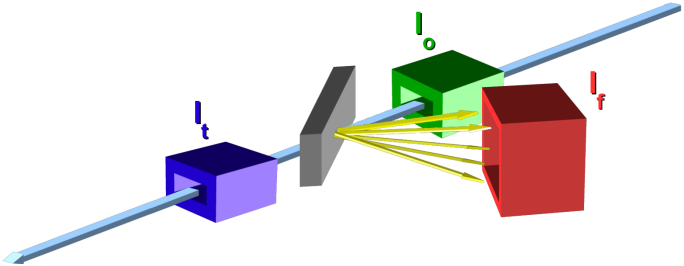


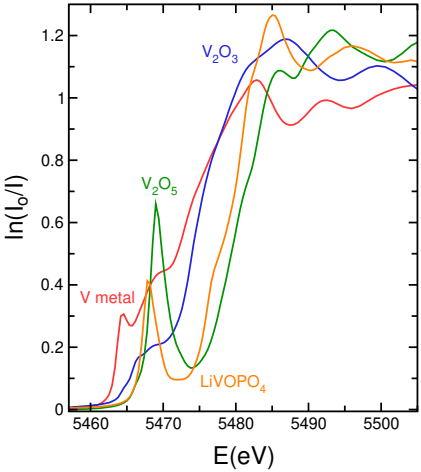


$$\mu(E) \propto \ln\left(\frac{I_o}{I_t}\right) \propto \frac{I_f}{I_o}$$

The EXAFS experiment

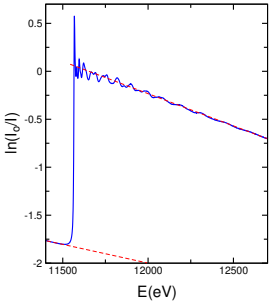
I_o = incident intensity
I_t = transmitted intensity
I_f = fluorescence intensity
$\mu(E)$ = absorption coefficient



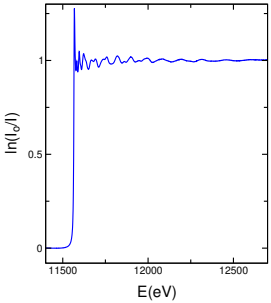


$$\mu(E) \propto \ln\left(\frac{I_o}{I_t}\right) \propto \frac{I_f}{I_o}$$

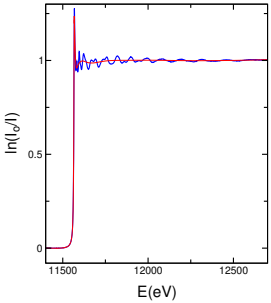
EXAFS overview



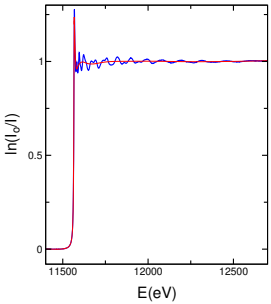
EXAFS overview



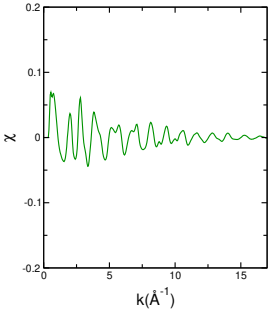
EXAFS overview



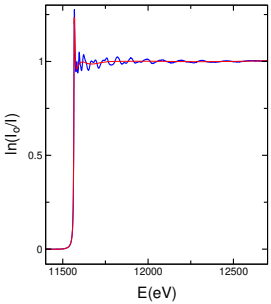
EXAFS overview



remove back-ground

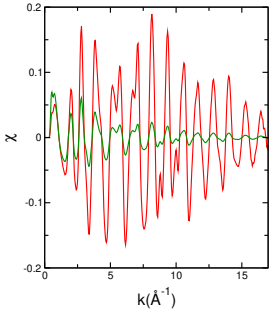


EXAFS overview

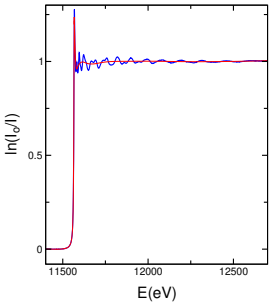


remove back-ground

apply k-weight

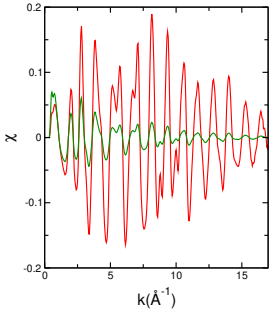


EXAFS overview

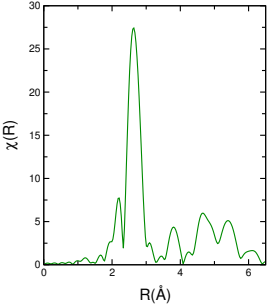


remove back-ground

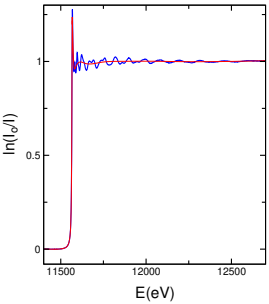
apply k-weight



Fourier Transform

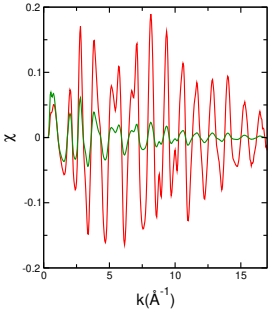


EXAFS overview



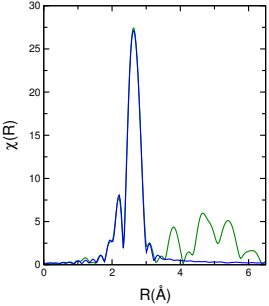
remove back-ground

apply k-weight



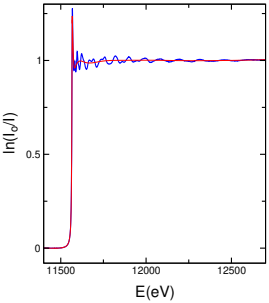
Fourier Transform

fit one



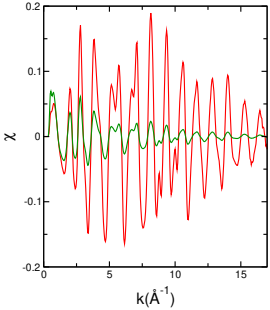
$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{k R_j^2} \sin[2kR_j + \delta_j(k)]$$

EXAFS overview



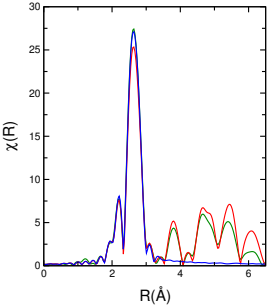
remove back-ground

apply k-weight



Fourier Transform

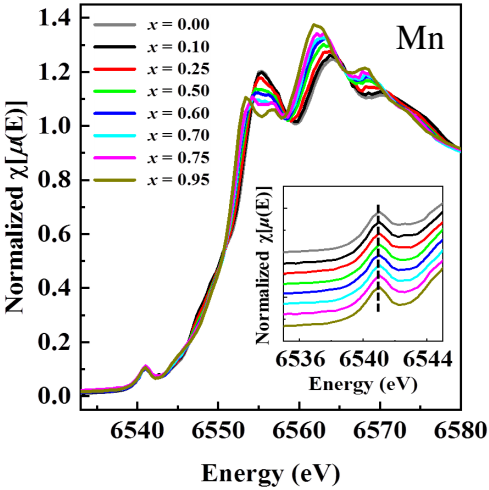
fit one or more paths

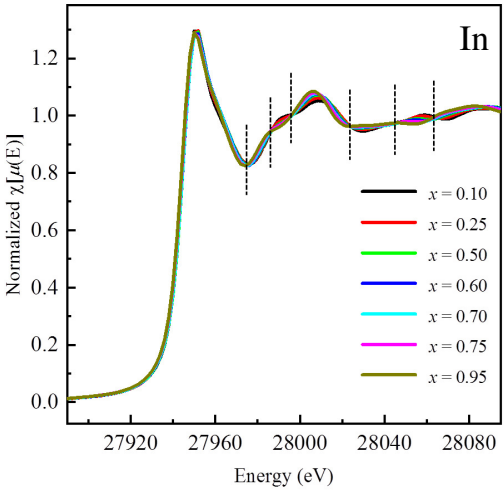


$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{k R_j^2} \sin[2kR_j + \delta_j(k)]$$

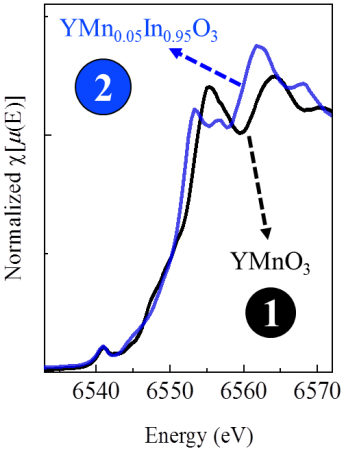
Determine Z, R, N, and σ^2 from model with computed $f(k)$, $\delta(k)$, and $\lambda(k)$

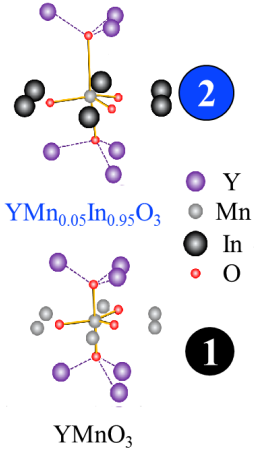
$YMn_{1-x}In_xO_3$ x-ray absorption spectroscopy

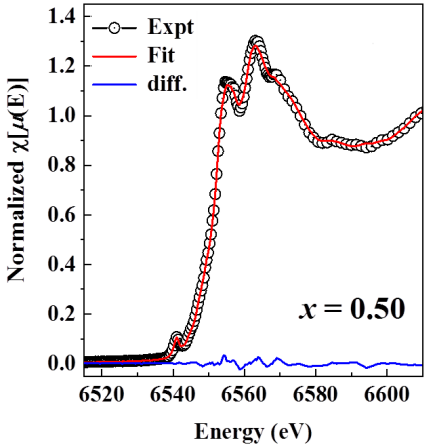




Bimodal Mn local environment fits XANES

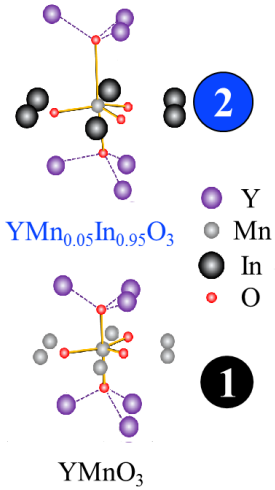


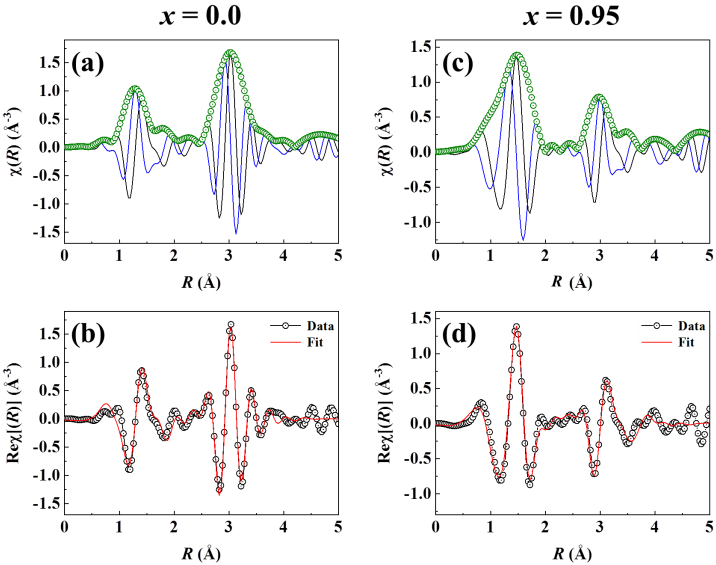




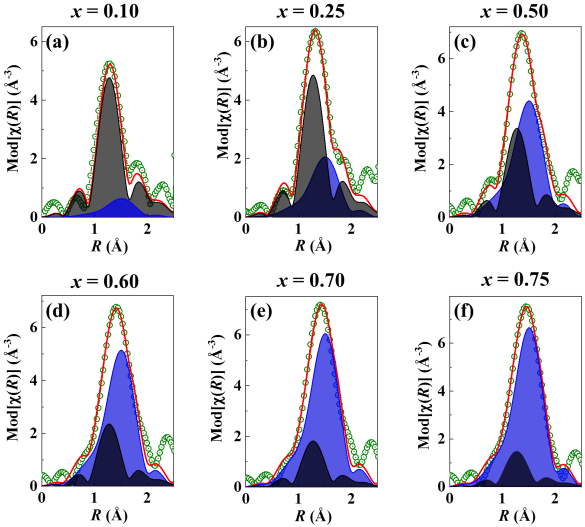
S. Mukherjee, H. Ganegoda, A. Kumar, S. Pal, C.U. Segre, and D.D. Sarma, *Inorg. Chem.* **57**, 9012–9019 (2018).

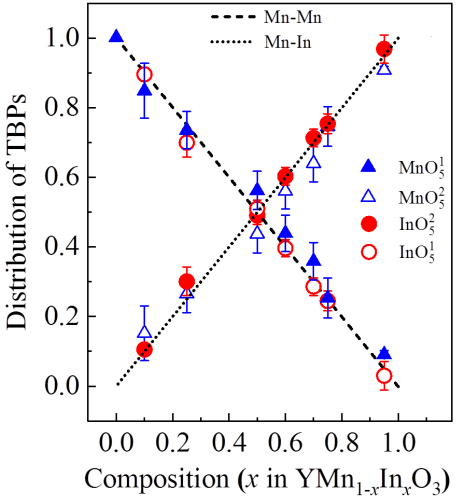
Detailed modeling on endpoint composition



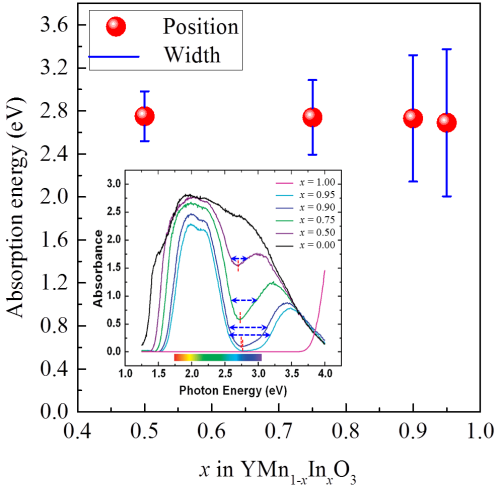


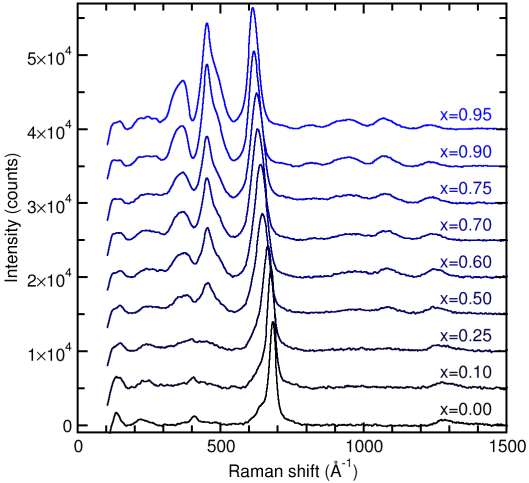
Endpoint EXAFS fits describe all samples





$YMn_{1-x}In_xO_3$ optical properties





Purple $YMn_{1-x}Ga_xO_3$ solid solution

$YGaO_3$ has same hexagonal structure

Doping with Mn gives brilliant purple colors

Is Mn in a bimodal local environment?

$YMn_{1-x}Ga_xO_3$ is more challenging, requiring careful control of temperature and time to avoid garnet impurity phase

x=0.70 x=0.80 x=0.90 x=0.95 x=0.98

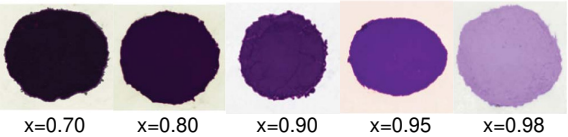
Purple $YMn_{1-x}Ga_xO_3$ solid solution

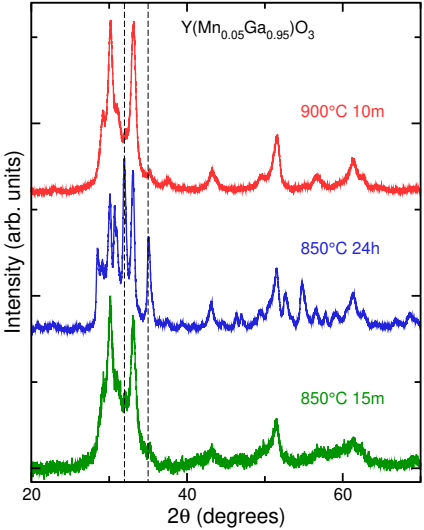
$YGaO_3$ has same hexagonal structure

Doping with Mn gives brilliant purple colors

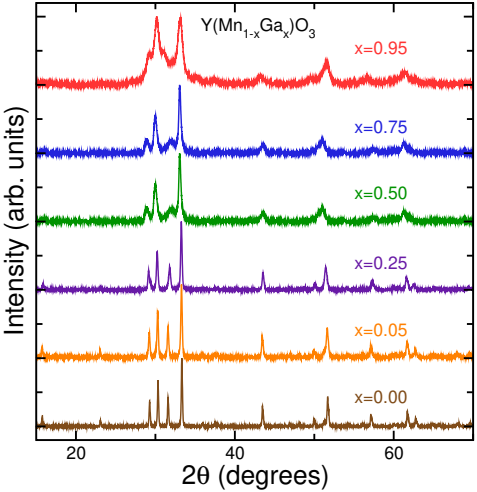
Is Mn in a bimodal local environment?

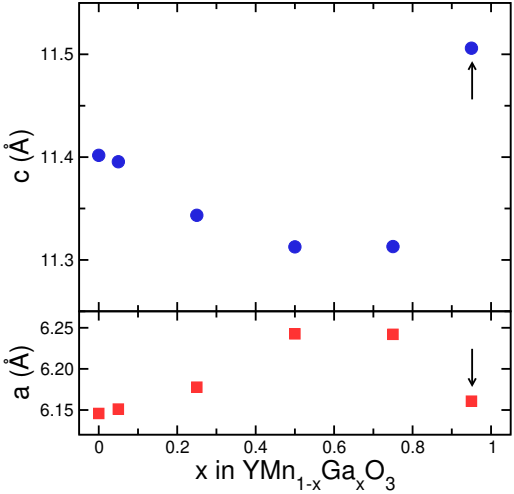
$YMn_{1-x}Ga_xO_3$ is more challenging, requiring careful control of temperature and time to avoid garnet impurity phase



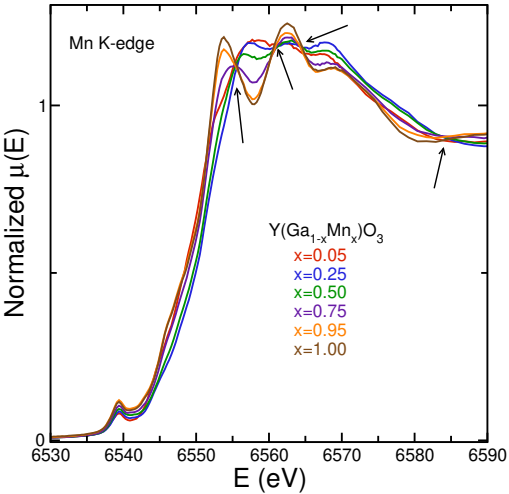


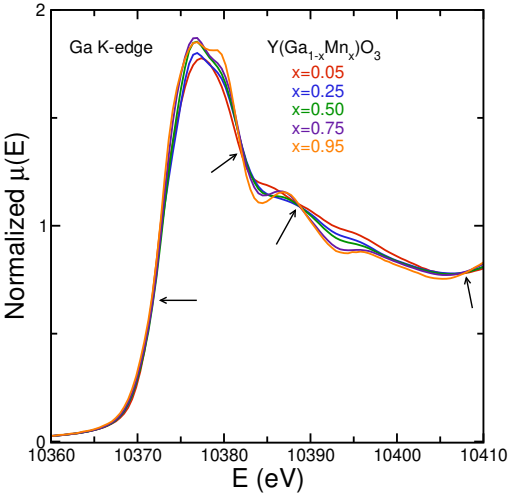
$YMn_{1-x}Ga_xO_3$ diffraction data



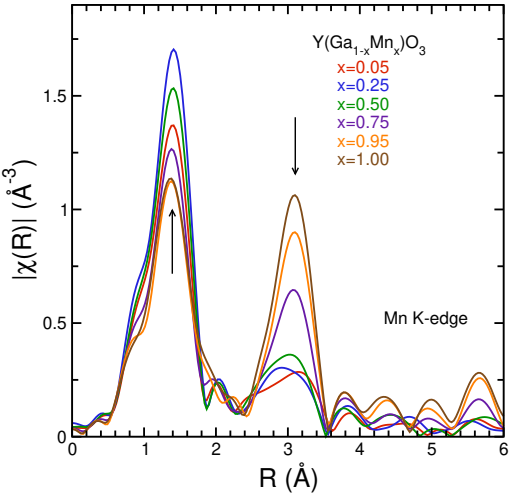


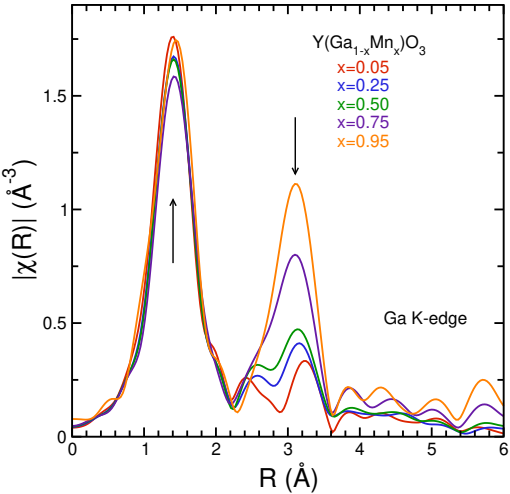
$YMn_{1-x}Ga_xO_3$ XANES





$YMn_{1-x}Ga_xO_3$ EXAFS





Where do we go from here?

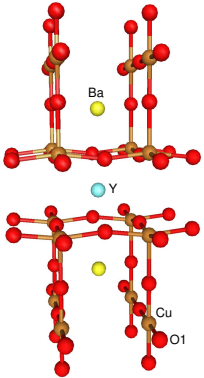
$YMn_{1-x}Ga_xO_3$ needs additional work to obtain good crystalline samples across the composition range

Bimodal environments seem to be a general property of the two systems studied so far

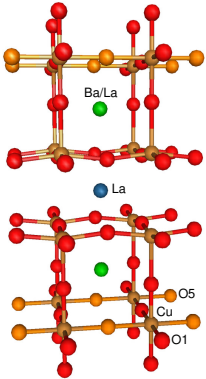
Will this bimodal environment be present in all systems based on this hexagonal structure? In other chromophore systems?

Are there any general conclusions that can be drawn for other kinds of materials?

$LaBa_2Cu_3O_{7+\delta}$: superconductivity



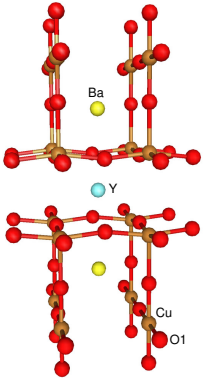
orthorhombic
$YBa_2Cu_3O_7$



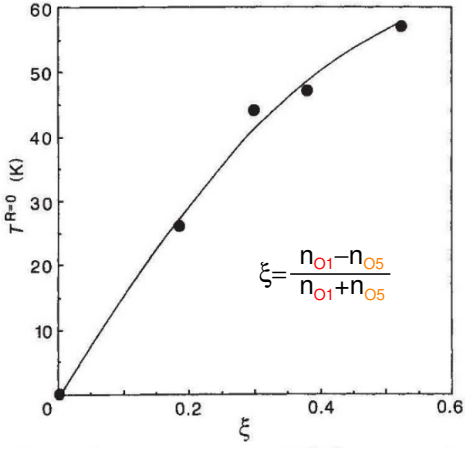
tetragonal
$La_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$

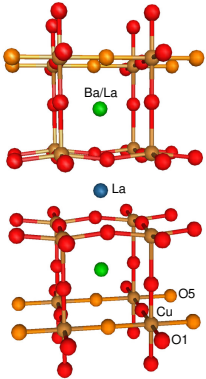
C.U. Segre, B. Dabrowski, D.G. Hinks, K. Zhang, J.D. Jorgensen, M.A. Beno, and I.K. Schuller, *Nature* **329**, 227-229 (1987).

$LaBa_2Cu_3O_{7+\delta}$: superconductivity



orthorhombic
$YBa_2Cu_3O_7$

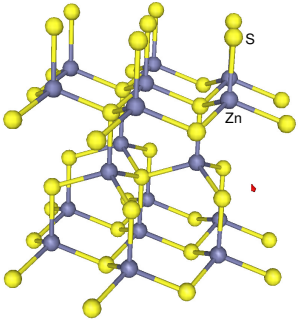




tetragonal
$La_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$

C.U. Segre, B. Dabrowski, D.G. Hinks, K. Zhang, J.D. Jorgensen, M.A. Beno, and I.K. Schuller, *Nature* **329**, 227-229 (1987).

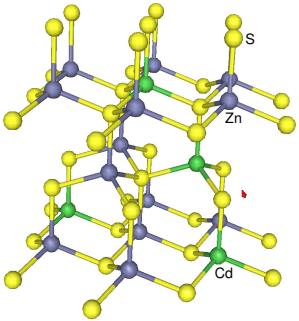
$Zn_{1-x}Cd_xS$: photoluminescence



ZnS

S. Mukherjee, A. Nag, V. Kocevski, P.K. Santra, M. Balasubramamian, S. Chattopadhyay, T. Shibata, F. Schaefers, J. Rusz, C. Gerard, O. Eriksson, C.U. Segre, and D.D. Sarma, *Phys. Rev. B* **89**, 224105 (2014).

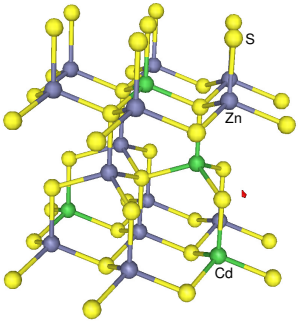
$Zn_{1-x}Cd_xS$: photoluminescence



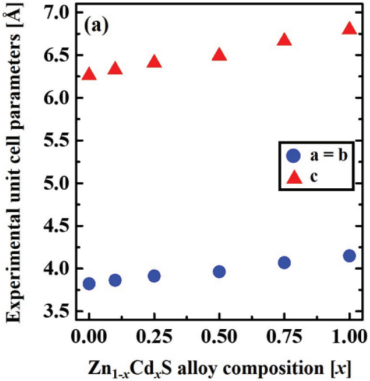
$Zn_{1-x}Cd_xS$

S. Mukherjee, A. Nag, V. Kocevski, P.K. Santra, M. Balasubramamian, S. Chattopadhyay, T. Shibata, F. Schaefers, J. Rusz, C. Gerard, O. Eriksson, C.U. Segre, and D.D. Sarma, *Phys. Rev. B* **89**, 224105 (2014).

$Zn_{1-x}Cd_xS$: photoluminescence

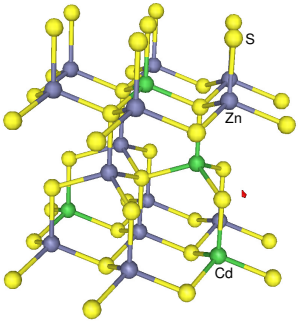


$Zn_{1-x}Cd_xS$

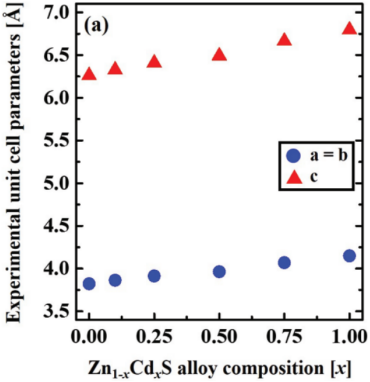


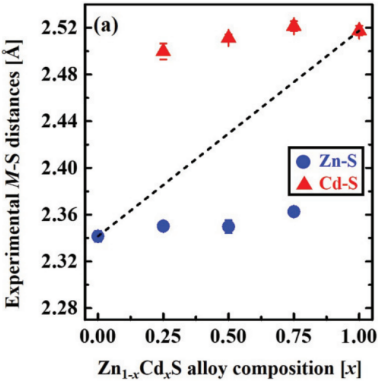
S. Mukherjee, A. Nag, V. Kocevski, P.K. Santra, M. Balasubramamian, S. Chattopadhyay, T. Shibata, F. Schaefers, J. Rusz, C. Gerard, O. Eriksson, C.U. Segre, and D.D. Sarma, *Phys. Rev. B* **89**, 224105 (2014).

$Zn_{1-x}Cd_xS$: photoluminescence



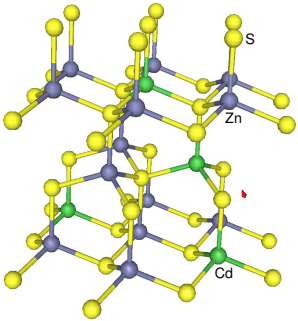
$Zn_{1-x}Cd_xS$



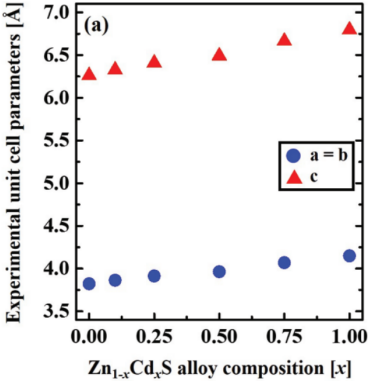


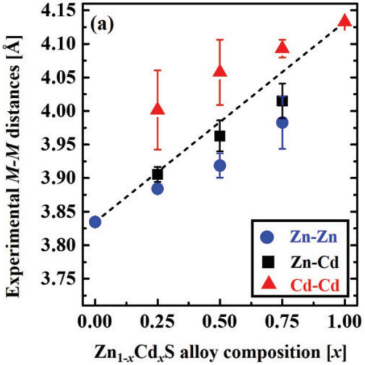
S. Mukherjee, A. Nag, V. Kocevski, P.K. Santra, M. Balasubramamian, S. Chattopadhyay, T. Shibata, F. Schaefers, J. Rusz, C. Gerard, O. Eriksson, C.U. Segre, and D.D. Sarma, *Phys. Rev. B* **89**, 224105 (2014).

$Zn_{1-x}Cd_xS$: photoluminescence



$Zn_{1-x}Cd_xS$

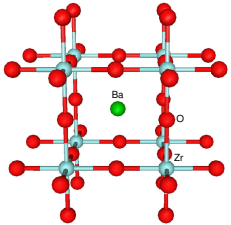




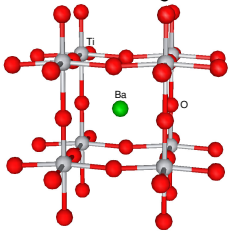
S. Mukherjee, A. Nag, V. Kocevski, P.K. Santra, M. Balasubramamian, S. Chattopadhyay, T. Shibata, F. Schaefers, J. Rusz, C. Gerard, O. Eriksson, C.U. Segre, and D.D. Sarma, *Phys. Rev. B* **89**, 224105 (2014).

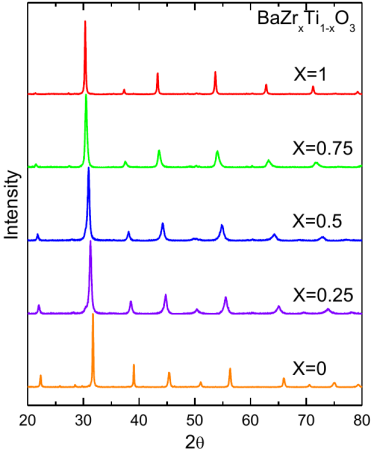
$BaZr_xTi_{1-x}O_3$: ferroelectricity

$BaZrO_3$



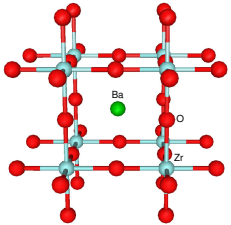
$BaTiO_3$



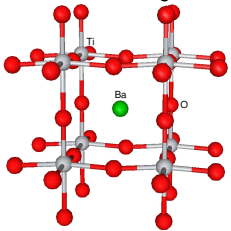


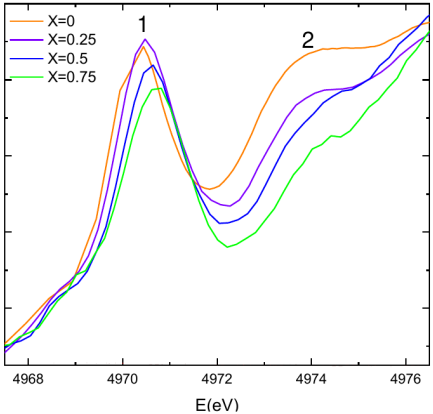
$BaZr_xTi_{1-x}O_3$: ferroelectricity

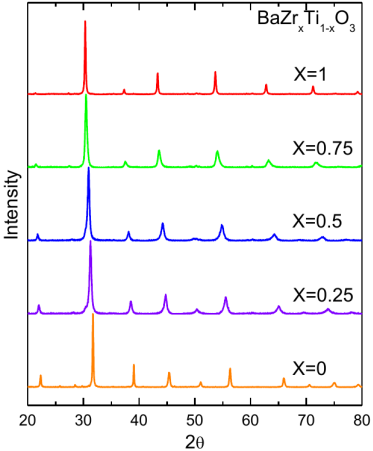
$BaZrO_3$



$BaTiO_3$

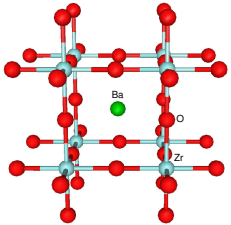




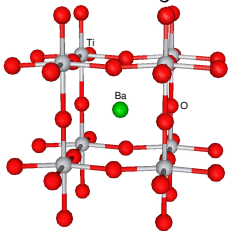


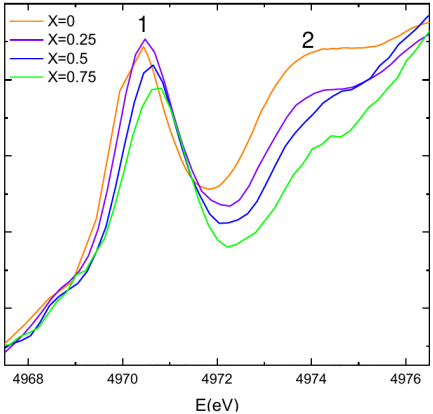
$BaZr_xTi_{1-x}O_3$: ferroelectricity

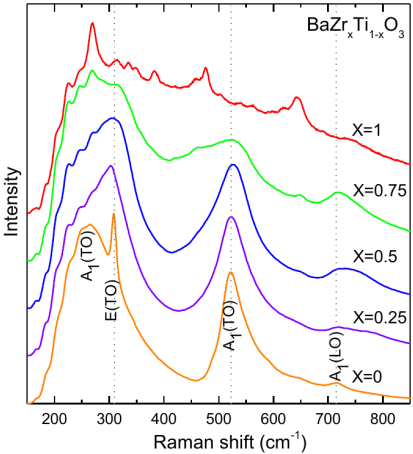
$BaZrO_3$



$BaTiO_3$







Summary

"Solid solutions" are not necessarily random

Long range structural data can be deceiving

Local structure is dominated by chemistry

Bulk properties can result from local structural inhomogeneities

A full description requires local structural measurements

Summary

"Solid solutions" are not necessarily random

Long range structural data can be deceiving

Local structure is dominated by chemistry

Bulk properties can result from local structural inhomogeneities

A full description requires local structural measurements

Thank goodness for EXAFS!

Collaborators & Acknowledgements

Huanbo Sun – Illinois Tech

Soham Mukherjee – Uppsala University

Dipankar Das Sarma – Indian Institute of Science

Duchossois Leadership Program at Illinois Tech