Factors Affecting Anti-site Disorder in the $Al_{1-x}Ga_xFeO_3$ System

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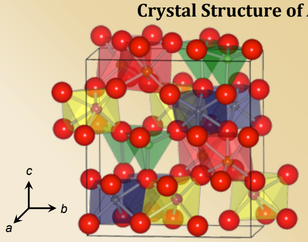
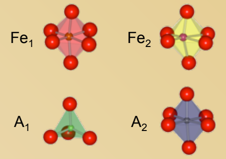
Abstract

The $Al_{1-x}Ga_xFeO_3$ system ($0 \le x \le 1$) was systematically studied using X-ray absorption near-edge spectroscopy (XANES) to examine changes in the metal coordination number (CN) due to composition, synthetic method and annealing temperature.[1,2] These materials possess coupled ferrimagnetic and piezoelectric properties, with potential applications in new multifunctional devices such as ultra-sensitive magnetic field sensors.[3] While changes in composition, synthetic method and annealing temperature have been shown to affect anti-site disorder, and thus material properties in the $Al_{1-x}Ga_xFeO_3$ system, these three factors have not been compared in a single study until now. $Al_{1-x}Ga_xFeO_3$ was synthesized via a citrate sol-gel method (SG), a co-precipitation method (CP), and a ceramic method (CM), and annealed at multiple temperatures. The XANES spectra show that Al and Fe have octahedral site preferences, while Ga has a tetrahedral site preference.[1,2] With increasing annealing temperature, the average Al CN was found to increase while the average Fe CN was found to decrease. The CP method also showed the largest variability in metal CN with composition and annealing temperature, relative to the SG and CM methods.

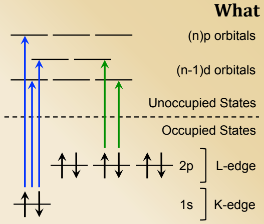
Crystal Structure of $Al_{1-x}Ga_xFeO_3$



-Orthorhombic ($Pna2_1$)[4-6]
-10 Crystallographic Sites
-4 Cation Sites; 6 Anion Sites



What is XANES?



Core electrons of a specific atom are excited into unoccupied states

K-edge excitations:
1s → (n-1)d transition (Pre-edge)
1s → (n)p transition (Main edge)

$L_{2,3}$-edge excitations:
2p → (n)s and (n-1)d transitions

XANES provides information on both charge and CN of the absorbing atom

Experimental

Synthesis:

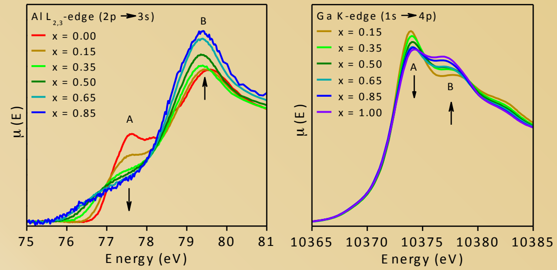
Co-precipitation Method[2]	Citric Sol-gel Method[2]	Ceramic Method[1]
Al + Ga_2O_3 + Fe_2O_3	$Al(NO_3)_3$ + $Ga(NO_3)_3$ + $FeCl_3$	Al_2O_3 + Ga_2O_3 + Fe_2O_3
↓	↓	↓
Dissolve in 12.1M HCl at 80°C while stirring	Add Citric Acid + Ethylene Glycol + Water	Grind in mortar, pellet at ~6 MPa
↓	↓	↓
Cool to ~25°C, titrate 14.8 M NH_4OH to form precipitate	Stir and heat at 80°C - 100°C until solvent is gone	Anneal at 1350°C for ~3 days; air quench
↓	↓	↓
Filter and decompose at 800°C for ~12 hours	Grind and decompose at 600°C for ~12 hours	Grind in mortar, pellet at ~6 MPa
↓	↓	↓
Grind, pellet and anneal between 1000°C and 1350°C for ~40 hours; air quench	Grind, pellet and anneal between 900°C and 1350°C for ~40 hours; air quench	Anneal at 1350°C for ~3 days; air quench

XANES:

Al $L_{2,3}$-edge (Fluorescence Yield), Canadian Light Source (CLS):
Beamline: Variable Line Spacing Plane Grating Monochromator (VLS PGM, 11ID-2)
Calibration: Al metal foil, 72.55 eV[7]

Ga K- and Fe K-edge (Transmission), Advanced Photon Source (APS):
Beamline: Pacific National Consortium/X-ray Science Division Collaborative Access Team (PNC/XAS-CAT, 20-BM)
Calibration: Ga metal, 10367 eV[7]
Fe metal, 7112 eV[7]

The Effect of Composition on Metal CN



Al $L_{2,3}$- and Ga K-edge of $Al_{1-x}Ga_xFeO_3$:
-Feature A: Al/Ga CN = 4 -Feature B: Al/Ga CN = 6

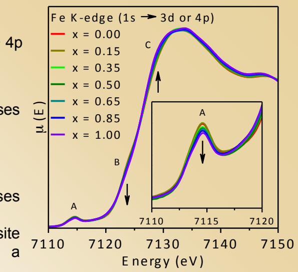
With increasing values of x (Ga):
-The intensity of feature A decreases and the intensity of feature B increases

This indicates that:
-The average CN of Al and Ga increases with x
-Al has an octahedral site preference at high values of x
-Ga has a tetrahedral site preference at low values of x

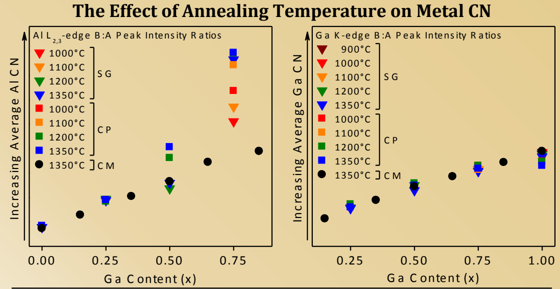
Fe K-edge of $Al_{1-x}Ga_xFeO_3$:
-Feature A (pre-edge): 1s → 3d
-Features B & C (main-edge): 1s → 4p

With increasing values of x (Ga):
-Pre-edge intensity remains low
-Features A and B intensity decreases and feature C intensity increases

This indicates:
-Fe remains mostly 6-coordinate
-The average Fe CN decreases slightly with increasing x
-Al and Fe have an octahedral site preference, while Ga has a tetrahedral site preference

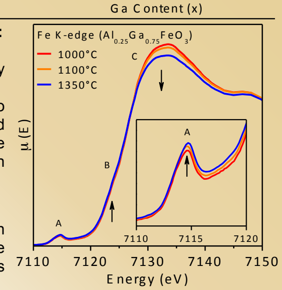


The Effect of Annealing Temperature on Metal CN

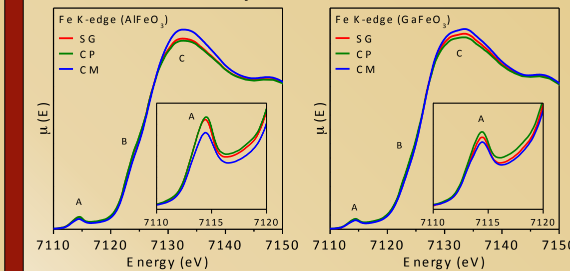


With increasing annealing temperature:
-The average CN of Al increases
-The average CN of Ga is largely unaffected by annealing temperature
-The average CN of Fe was found to decrease, as seen by the increased intensity of feature A and B, and the decreased intensity of feature C in the Fe K-edge spectra.

This indicates:
-Anti-site disorder increases with increasing annealing temperature due to Al and Fe exchanging sites with each other



The Effect of Synthetic Method on Metal CN



In both spectra, the order of pre-edge (feature A) intensities, from highest to lowest, is CP > SG > CM. Greater pre-edge intensity correlates with more Fe in the tetrahedral site.

This indicates:
-The CP method results in the greatest amount of anti-site disorder, followed by the SG and CM methods, respectively
-**Why?** Cation mobility is not inhibited by a polymeric or oxide network, which favours greater anti-site disorder during synthesis

-The SG method has an intermediate amount of anti-site disorder
-**Why?** Polymer network inhibits ion mobility, but not as significantly as the oxide network in samples prepared via the CM method

-The CM method has the least amount of anti-site disorder
-**Why?** The constant breaking of metal-oxygen bonds and long cation diffusion path lengths are thought to inhibit metal site exchange

Conclusions

The effect of composition on metal CN in $Al_{1-x}Ga_xFeO_3$:

Metal	Al	Ga	Fe
Low x	Mix of 4- and 6-coordinate	Mostly 4-coordinate	Mostly 6-coordinate
High x	Mostly 6-coordinate	Mix of 4- and 6-coordinate	Mostly 6-coordinate (more than at low x)

-The tetrahedral site preference of Ga inhibits anti-site disorder for high values of x

Anti-site disorder increases with increasing annealing temperature:
-Al displaces Fe from the octahedral sites into the tetrahedral site
-Ga remains mostly unaffected by annealing temperature due to its strong tetrahedral site preference

Synthesis can have a significant effect on anti-site disorder:
-The CP method results in the greatest amount of anti-site disorder, followed by the SG and CM methods, respectively
-The CP method has no long range network binding the ions resulting in greater ion mobility during synthesis, and thus more anti-site disorder
-The polymeric or oxide network inhibits ion mobility in the SG and CM methods

References

[1] Walker, J.D.S.; Grosvenor, A.P. *J. Solid State Chem.* **2013**, *197*, 147. **[2]** Walker, J.D.S.; Grosvenor, A.P. *Inorg. Chem.* **2013** (Submitted). **[3]** Eerenstein, W.; Mathur, N.D.; Scott, J.F. *Nature* **2006**, *442*, 759. **[4]** Momma, K.; Izumi, F., *J. Appl. Crystallogr.* **2008,** *41*, 653. **[5]** Bouree, F.; Baudour, J. L.; Elbadraoui, E.; Musso, J.; Laurent, C.; Rousset, A. *Acta Crystallogr., Sect. B: Struct. Sci* **1996**, *B52*, 217. **[6]** Arima, T.; Higashiyama, D.; Kaneko, Y.; He, J. P.; Goto, T.; Miyasaka, S.; Kimura, T.; Oikawa, K.; Kamiyama, T.; Kumai, R.; Tokura, Y. *Phys. Rev. B: Condens. Matter* **2004**, *70*, 064426. **[7]** Thompson, A.; Attwood, D.; Gullikson, E.; Howells, M.; Kim, K.-J.; Kirz, J.; Kortright, J.; Lindau, I.; Pianetta, P.; Robinson, A.; Scofield, J.; Underwood, J.; Vaughan, D.; Williams, G.; Winick, H., *X-ray Data Booklet*. Third ed.; Lawrence Berkeley National Laboratory: Berkeley, 2009.

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