Coordination and Oxidation State Analysis of Cobalt in Nanocrystalline LiGa$_5$O$_8$ by X-ray Absorption Spectroscopy

B Yildirim and H Riesen
School of Physical, Environmental and Mathematical Sciences
The University of New South Wales, UNSW Canberra (ADFA), Canberra, ACT 2600, Australia
E-mail: h.riesen@adfa.edu.au

Abstract The luminescence of nanocrystalline LiGa$_5$O$_8$:Co$^{2+}$ has been assigned to Co$^{2+}$ in tetrahedral sites. However, x-ray absorption spectroscopy (XAS) reveals that there is a significant fraction of cobalt ions that substitute into the lattice in the octahedral sites and, in this case, predominantly in the 3+ oxidation state.

1. Introduction

We have recently reported some persistent spectral hole-burning properties of nanocrystalline LiGa$_5$O$_8$:Co$^{2+}$ (LGO:Co) [1]. We have concluded that the hole-burning mechanism is most likely based on the photoionisation of Co$^{2+}$ ions in the tetrahedral sites and the subsequent trapping of photoelectrons by Co$^{3+}$ ions that may exist in the structure.

The Co$^{2+}$ ions replace some of the Ga$^{3+}$ ions when doped into the lithium gallate host which includes tetrahedral and octahedral sites. Macfarlane et al. [2] and Donegan et al. [3] suggested that Co$^{2+}$ ions can enter the crystal lattice in both of these sites. It has been assumed that the percentage of cobalt ions occupying octahedral sites is lower than for tetrahedral sites [2, 3].

To verify these assumptions and in order to gain a better understanding of valence and coordination state distributions of cobalt ions in LGO, XAS experiments were conducted at the Australian Synchrotron. XAS experiments were conducted in the x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) regions. XANES, in particular pre-edge transitions from 1s to unoccupied 3d states, give the most valuable information on charge distribution. In addition to the comparison of the intensities and the shifts of the XANES first derivatives with reference samples, correlating the experimental results with numerical simulations of XANES and EXAFS provide quantitative information about the coordination and oxidation states of the cobalt ions.

2. Experimental details

The XAS experiment was performed at the Australian Synchrotron. A silicon 111 monochromator with a focusing ability from 0.1x0.5 mm to 1x2 mm was used. The spectrum was measured using a well-powdered sample grinded with cellulose, the mixture was pressed into a pellet and placed in an aluminium sample holder using Kapton tape, and the calibration was performed by measuring a cobalt foil in each run.

IFEFFIT ver. 1.2.11c [4] was used for the XAS analysis and the lattice host was modeled using starting parameters from the work of Ahman et al. [5]. Two different configurations of the Co atoms, in the octahedral and tetrahedral sites in place of the Ga atoms, were considered separately and
corresponding scattering patterns were generated in ARTEMIS [6]. The same method was used for simulations of the XANES spectra in JFEFF 9.0 [7].

As Co was not only in the tetrahedral but also in the octahedral sites in this host, the fitting parameters were different for the two configurations. The best values were obtained separately and then the final EXAFS fit was obtained by merging of both the octahedral and tetrahedral peak fits. Satisfactory results were obtained when the first shell scatterings and low wave number ($k$) values were taken while the different valence states were omitted in the peak fitting.

3. Results and discussion

3.1 XANES

As a general qualitative trend, it is well established that the higher the oxidation state, the higher the energy positions for all features in XANES spectra, with a rule of thumb of 3eV per unit of oxidation state. Also, the larger the edge width, the more pronounced is the mixed valence state. In XANES studies of LGO:Co, the Co$_3$O$_4$ normal spinel has been used as a reference [8] to examine the oxidation and coordination states of cobalt in LGO since it is well known to contain both tetrahedrally coordinated Co$^{2+}$ and octahedrally coordinated Co$^{3+}$ ions in a 1:2 ratio [9].

Instead of a direct comparison of the XANES peak, we analysed the oxidation states of cobalt by a comparison of the peaks and intensities in the first derivative of the XANES spectra. The first LGO:Co peak was at 7709 eV (pre-edge) and those of its first-order derivatives at 7717 eV, 7721 eV and 7725 eV. Similarly, the first peak of Co$_3$O$_4$ was at 7709 eV (pre-edge) and those of its first-order derivatives at 7717 eV, 7722 eV and 7727 eV which were very close to the LGO:Co peaks. In Figure 1, XANES and their first derivative spectra are presented.

![Figure 1](image_url)

**Figure 1**: a) Normalised Co K-edge spectrum of LGO:Co (red), and the reference sample Co$_3$O$_4$ (blue) b) First derivative of the spectra (same colours)

The derivative peaks at 7717 eV and 7721 eV were assigned to Co$^{2+}$ and Co$^{3+}$ respectively and these peaks were also observed in [Co(NH$_3$)$_3$Cl]Cl$_2$ and [Co(NH$_3$)$_6$](SbCl$_6$) reference samples with edge energies at 7717 eV and 7722 eV respectively [10]. The shoulder on the 7717 eV peak in the first derivative spectrum of the LGO, around 7715 eV, is most probably due to the 1s to 4s transition.

The same percentage (50:50) of Co$^{2+}$ was used for both the octahedral and tetrahedral sites of the host structure for the XANES simulations by JFEFF 9.0. The Co$^{2+}$ peak was shifted around 1.6 eV on derivative peaks in simulated spectra (The simulations are not illustrated here). In the LGO:Co sample, the shift is around 0.8 eV for the prominent peak of Co$^{3+}$ with respect to Co$^{2+}$ peak position of [Co(NH$_3$)$_3$](SbCl$_6$) [10] and Co$_3$O$_4$ (marked with arrows in Figure 1b). The shift is due to existence of some Co$^{2+}$ ions in the tetrahedral sites. The Co$^{2+}$ ions in octahedral sites should be less than tetrahedrally coordinated ones since no shift was observed on the Co$^{2+}$ peak.
The Co\textsuperscript{3+}/Co\textsuperscript{2+} peak intensity ratios are around 3:2 for LGO:Co and 6:5 for Co\textsubscript{3}O\textsubscript{4} but the latter should be around 2:1. For the latter, there appears to be another peak in between the ones of Co\textsuperscript{2+} and Co\textsuperscript{3+} which could be resolved. This feature between the 2\textsuperscript{+} and 3\textsuperscript{+} peaks was assumed to be scattering from distorted octahedral sites. Taking into account the integrated intensity of this peak would increase the Co\textsuperscript{3+}/Co\textsuperscript{2+} ratio to around 2:1 for Co\textsubscript{3}O\textsubscript{4}. The distorted octahedral site was also observed in the pre-edge of Co\textsubscript{3}O\textsubscript{4}. In particular, the pre-edge of Co\textsubscript{3}O\textsubscript{4} broadens and shifts towards the edge which indicates that the cause of the broadening is more likely due to distorted Co ions in the octahedral sites.

The pre-edge peak was also observed for LGO:Co confirming the existence of Co ions in the tetrahedral sites (Figure 1). The pre-edge is most intense when the first coordination shell lacks inversion symmetry, such as in a tetrahedral symmetry, while they are also pronounced for octahedral coordination in distorted symmetries [10, 11].

3.2 EXAFS

![Figure 2](image)

**Figure 2:** Weighted Fourier transform ($k^3$ ($k$)) of Co K-edge EXAFS (red) and its fit obtained with ARTEMIS (blue) (as we are interested in first shell scattering, $R$ is taken in the range of 1-4 Å)

Different amplitude factors were used for the first shell fit to compensate for the percentage difference of octahedral Co ions which was not expected to be exactly 50:50 (in ARTEMIS, one set of scatterings from the first shell of the tetrahedrally coordinated Co and one from the octahedrally coordinated Co ions were taken for the final fit). The scatterings from the first shell lay in between 1-2 Å with Co-O bond lengths of 2.05 (±0.02) Å for the octahedral and 1.7760 (±0.005) Å for the tetrahedral configurations. The peaks from the second shell, which were mainly from the Ga atoms (Li atoms have a low scattering factor) showed two distinct peaks, the first formed by the Ga atoms closest to the octahedrally coordinated Co ion, at 2.9 Å, and the second by those further away, at 3.4 Å. All the other scatterings from the Ga atoms of the tetrahedrally coordinated Co lay between 3.4 and 3.5 Å.

4. Conclusion

From XAS measurements it follows that a significant percentage of Co ions enter the LGO lattice, indeed, also in the octahedral sites, and that both the +2 and +3 oxidation states are present. According to a XANES derivative peak analysis the Co\textsuperscript{3+}/Co\textsuperscript{2+} ratio is around 3:2 and both XANES and EXAFS spectra show that Co\textsuperscript{3+} ions exist predominantly in octahedral sites of the host structure. This result is commensurate with conclusions reached by Mössbauer spectroscopy of LiGa\textsubscript{5}O\textsubscript{8}:Fe\textsuperscript{3+} in...
which $\text{Fe}^{3+}$ enters the lattice predominantly in the Ga octahedral sites without any charge compensation requirement and is highly stable in these sites [12].

**Acknowledgements**

We would like to thank the Australian Synchrotron for access to the XAS beam line and for the provision of a travel allowance (AS093/XAS1957). BY acknowledges UNSW for a postgraduate research scholarship and for postgraduate research student support (PRSS) to attend XAFS-15.

**References**

[1] Yildirim B and Riesen H 2010 *Phys. Proc.* 3 1547-1551
[2] Macfarlane R M and Vial J C 1986 *Phys. Rev. B* 34 1
[3] Donegan J F Anderson F G Bergin F J Glynn T J and Imbusch G F 1992 *Phys. Rev. B* 45 563
[4] M. Newville 2001 *J. Synchrotron Rad.* 8 322-324
[5] Ahman J Goran Svensson G and Albertsson J 1996 *Acta Chem. Scand.* 50 391
[6] Ravel B and Newville M 2005 *J. Synchrotron Rad.* 12 537-541
[7] Rehr J J Kas J J Vila F D Prange M P Jorissen K 2010 *Phys. Chem. Chem. Phys.* 12 5503-5513
[8] $\text{Co}_3\text{O}_4$ data was downloaded from International X-ray Absorption Society (IXAS) database, http://ixs.iit.edu/database/data/Farrel_Lytle_data/RAW/Co/index.html
[9] Murakami M Yatsumoto and Y Hasegawa T 2004 *J. Appl. Phys.* 95 5330
[10] Moen A Nicholson D G Ronnnig M Lamble G M Lee J F and Emerich H 1997 *J. Chem. Soc.* 93 4071-4077
[11] Groot F De Vanko G and Glatzel P 2009 *J. Phys: Condens. Matter* 21 104207
[12] Yildirim B Stewart G and Riesen H 2012 *Proceedings of the 36th Annual Condensed Matter and Materials Meeting* 37