



Structural and Optical Properties of Nanocrystalline $\text{LiGa}_5\text{O}_8:\text{Fe}^{3+}$

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Mössbauer spectroscopy results are compared with earlier optical measurements for lithium gallate doped with 5% Fe^{3+} ($\text{LiGa}_5\text{O}_8:\text{Fe}^{3+}$). Although the luminescence is attributed to Fe^{3+} ions at tetragonal sites, the results from Mössbauer spectroscopy are consistent with the majority of the Fe^{3+} ions being located at the octahedral sites.

1. Introduction

LiGa_5O_8 is an interesting host material for which photon-gated hole-burning is observed in doped Co(II). It also provides one of the rare cases where structured luminescence of doped Fe(III) has been reported, the subject of this present work.

LiGa_5O_8 is an oxide that exists in two polymorphs. The *high temperature* phase ($T > 1138$ °C) is disordered in the octahedral sites and forms an inverse-spinel system with a face-centred cubic unit cell (space group $Fd\bar{3}m$), whereas the *low temperature* phase displays 1:3 ordering of the lithium and gallium ions along the [110] direction and forms with a primitive cubic cell (space group $P4_132$) resulting in additional powder X-ray diffraction (XRD) lines (Fig. 1) [1, 2].

For both host phases of $\text{LiGa}_5\text{O}_8:\text{Fe}^{3+}$, the near-infrared (650 - 800 nm) luminescence spectrum can be assigned to the ${}^6\text{A}_1(\text{S}) \leftarrow {}^4\text{T}_1(\text{G})$ transition of Fe^{3+} ions substituting for the Ga tetrahedral (A) sites [3]. This is in accord with results reported for isostructural LiAl_5O_8 where both the Fe^{3+} luminescence and ${}^{57}\text{Fe}$ -Mössbauer spectroscopy indicated that the Fe^{3+} ions substitute for Al at the tetrahedral sites [4]. However, evidence based on the saturation magnetisation of Ga-doped LiFe_5O_8 [5] and the early electron spin resonance work of Folen (referred to in [6]) suggested that Fe^{3+} doped into LiGa_5O_8 should substitute preferentially for the Ga octahedral (B) sites. Based on their optical absorption measurements, McShera *et al.* [7] proposed that the two observations are not incompatible because the absorption, and therefore the luminescence, is much stronger for Fe^{3+} at the tetragonal sites. O'Connor *et al.* [8] later observed weaker luminescence beyond 1000 nm and attributed it to Fe^{3+} ions located at the majority octahedral sites.

In an effort to shed more light on this question, ${}^{57}\text{Fe}$ -Mössbauer spectra have been recorded for dilute concentrations of Fe^{3+} doped into LiGa_5O_8 and it is these results that are considered below.

2. Experimental details

Nanocrystalline $\text{LiGa}_5\text{O}_8:\text{Fe}^{3+}$ was prepared via a combustion reaction (at 500 - 700 °C) of nitrate salts of lithium, gallium and cobalt, with urea as the fuel. Specifically, the starting material was comprised of 2 g of $\text{Ga}(\text{NO}_3)_3 \cdot 8\text{H}_2\text{O}$, 0.122 g of $\text{Li}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, 0.8 g of urea, and an appropriate weight percentage of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ which were mixed and ground to a smooth paste with a mortar and pestle. For the low doping level of 0.6%, enriched ${}^{57}\text{Fe}$ was employed to achieve a better signal to noise ratio in the Mössbauer measurements. The combustion reaction yielded the high temperature (disordered), $Fd\bar{3}m$ phase, which was then



calcined at 900 °C for 14 hours to transform the nanocrystals to the low temperature (ordered), $P4_132$ phase.

High resolution powder XRD patterns were recorded at the Australian Synchrotron with $\lambda = 0.068818$ nm ($E_{\text{photon}} = 18.0367$ keV) which was chosen to minimise gallium K-edge absorption. The samples were packed into soda lime capillaries with a 10 μm wall thickness. Rietica v1.77 was used for a full line shape analysis and the low temperature ordered phase was modelled using starting parameters from the work of Ahman *et al.* [9]. Room temperature ^{57}Fe -Mössbauer spectra were recorded using a ^{57}Co :Rh source with sinusoidal motion whose maximum velocity was calibrated against α -Fe at room temperature.

3. Results and discussion

3.1 Synchrotron-based XRD

Powder XRD patterns are presented in Fig. 1 for ordered (1 % and 5 % Fe^{3+}) and disordered (5 % Fe^{3+}) phases of LiGa_5O_8 doped with natural Fe. The appearance of Ga_2O_3 impurity peaks for the higher Fe concentration suggests that the Fe^{3+} displaces the Ga^{3+} ions, as expected. The transformation of the lattice into the ordered primitive phase relies on the undisturbed existence of the Li ions which order in their octahedral sites. It thus follows that Fe^{3+} is stable in the Ga^{3+} sites up to these doping levels. In contrast with the case of divalent ion doping (where the cell volume jumps at around 5%) the unit cell parameter is observed here to increase smoothly with increasing Fe^{3+} concentration (where $a = 0.8203$, 0.8208 and 0.8214 nm for 0, 1 and 5 % Fe^{3+} , respectively). The unit cell expansion is due to the slightly larger ionic radius of Fe^{3+} (0.064 nm) compared with Ga^{3+} (0.062 nm) [10].

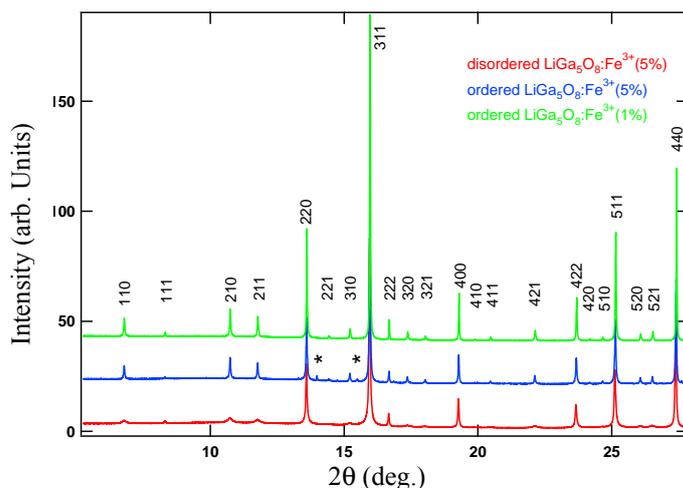


Fig. 1. Synchrotron powder XRD patterns of $\text{LiGa}_5\text{O}_8:\text{Fe}^{3+}$. The Ga_2O_3 impurity lines are indicated with (*).

3.2 ^{57}Fe -Mössbauer spectroscopy

Mössbauer spectra were recorded for $\text{LiGa}_5\text{O}_8:\text{Fe}$ with doped Fe concentrations of 0.6 % enriched ^{57}Fe (Fig. 2(a)) and 5% natural Fe (Fig. 2(b)). In each case, the prominent feature is a central broadened doublet which was fitted using a superposition of four symmetric quadrupole-split doublets. The sets of quadrupole splittings, ΔE_Q , isomer shifts, δ , and relative intensities employed for the four component doublets were very similar for the two Fe concentrations, although a larger Lorentzian line width, Γ , was needed to achieve a good quality fit in the case of the more dilute concentration ($\Gamma = 0.51$ mm/s for 0.6 % compared with 0.34 mm/s for 5 %). The weighted mean values for the quadrupole splitting and the isomer shift are summarised in the lower half of Table 1. In the case of the spectrum



for the specimen doped with 0.6 % enriched ^{57}Fe (Fig. 2(a)), an additional magnetic sextet is present which has the appearance and peak magnetic hyperfine field value (Table 1) of relaxation spectra observed elsewhere for magnetic Fe_2O_3 nanoparticles (e.g. ref. [11]). However, complex spectra observed for dilute Fe concentrations in isostructural $\text{LiAl}_5\text{O}_8:\text{Fe}$ have been attributed to slow relaxation brought about by a weak spin-spin interaction between well-separated Fe^{3+} ions that are properly incorporated into the Al sub-lattice [12]. This issue will be investigated further at lower temperatures where slower relaxation should result in a more sharply defined magnetic sub-spectrum.

Fig. 2. Room temperature ^{57}Fe -Mössbauer spectra recorded for $\text{LiGa}_5\text{O}_8:\text{Fe}^{3+}$ with (a) 0.6 % enriched ^{57}Fe , and (b) 5 % natural Fe.

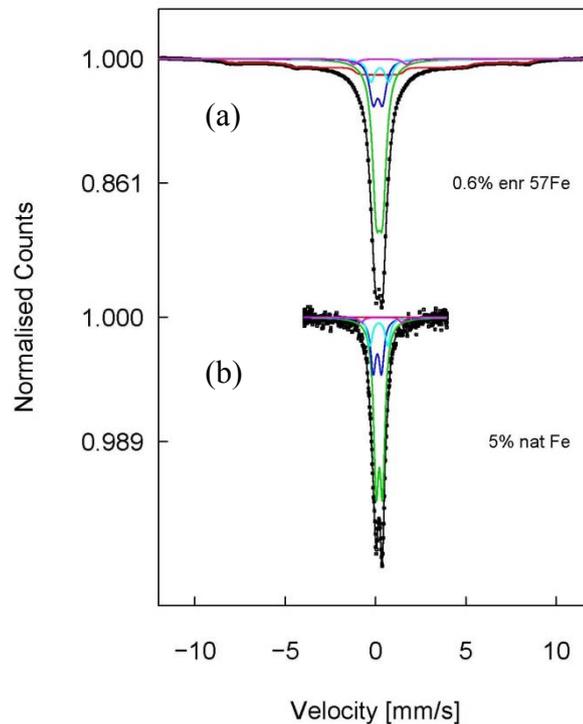


Table 1. Fitted ^{57}Fe -Mössbauer parameters for the two $\text{LiGa}_5\text{O}_8:\text{Fe}$ spectra. Theoretical point charge model (PCM) estimates of the quadrupole interaction parameters are included for ease of comparison.

	Intensity [%]	$\delta_{\alpha\text{-Fe}}$ [mm/s]	V_{zz} [10^{21} V/m ²]	η'	ΔE_Q [mm/s]	B_{hf} [T]
PCM calculations						
Ga1 (12d-site) - Octahedral, B			-2.70	0.36	0.46	
Ga2 (8c-site) - Tetrahedral, A			+0.16	≈ 0	0.03	
Ga3 (4b-site) - Octahedral, B			-2.87	≈ 0	0.48	
Experimental						
(a) ^{57}Fe 0.6% enr:						
Magnetic sextet	31.3	0.33			≈ 0	52.8 ^b
Doublet	68.6	0.30 ^a			0.53 ^a	
(b) Fe 5% nat:						
Doublet	100	0.30 ^a			0.49 ^a	

(a) Weighted mean over the four superimposed component doublets (see text)

(b) Peak magnetic hyperfine field for the relaxation broadened magnetic sub-spectrum



For Fe³⁺ in oxides, it is a useful observation that the isomer shift measured relative to α -Fe (referred to as $\delta_{\alpha\text{-Fe}}$ in Table 1) tends to fall in the sub-range of 0.17 - 0.21 mm/s for tetrahedral coordination and 0.33 - 0.37 mm/s for octahedral coordination [13,14]. From Table 1, the mean experimental isomer shift value (for the broadened doublet) is 0.30 mm/s, which sits well above the range for tetrahedral coordination and is more consistent with the majority of Fe³⁺ ions substituting for Ga at the octahedral (B) sites. Consideration of the mean experimental quadrupole splitting, ΔE_Q , leads us to the same conclusion. Point charge model (PCM) summations over nearest-neighbour O²⁻ ligands (4 and 6 for tetragonal and octahedral sites, respectively) were employed to estimate the unshielded electric field gradient (efg) tensor and the asymmetry parameter, η , at all three Ga sites. The quadrupole splitting

$$\Delta E_Q = \frac{1}{2} e Q V_{zz} \left(1 + \frac{1}{3} \eta^2 \right)^{\frac{1}{2}}$$

was then calculated using an ⁵⁷Fe quadrupole moment of $Q \approx +0.16$ b [15], and an anti-shielding factor of $(1-\gamma_\infty) \approx 10.5$ [16]. The ΔE_Q estimates are summarised in the first rows of Table 1 where it is evident that the range of 0.46 – 0.48 mm/s estimated for the octahedral (B) sites is in much closer agreement with the mean experimental value of 0.49 mm/s. By contrast, the PCM estimate for the tetrahedral (A) sites is effectively zero.

4. Conclusion

According to the ⁵⁷Fe-Mössbauer results presented here, the Fe³⁺ ions doped into low temperature phase LiGa₅O₈ enter the lattice predominantly at the Ga octahedral (B) sites. This supports the proposal of O'Connor *et al.* [8] that photoluminescence is more sensitive to the smaller population of Fe³⁺ ions in the tetrahedral (A) sites.

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