# Exploring a Gallium-Tantalum Dual Doped Lithium Garnet

**Timothy Daniel Christopher,[1,2] Saifang Huang,[4] Peng Cao,[2,4] Zoran Zujovic,[1,3] Tilo Söhnel,[1,2,*]**

1. School of Chemical Sciences & Centre of Green Chemical Science, University of Auckland, Auckland, New Zealand
2. MacDiarmid Institute for Advanced Materials and Nanotechnology, Victoria University of Wellington, New Zealand
3. Polymer Electronics Research Centre and the NMR Centre, University of Auckland, Auckland, New Zealand
4. Department of Chemical and Materials Engineering, University of Auckland, Auckland, New Zealand

*Email: t.soehnel@auckland.ac.nz

## Introduction

- Lithium garnet oxides have been proposed as a solid-state electrolyte candidate for Li-ion electrochemical cell.
- Lithium garnets can exists in two phases, a tetragonal and a higher symmetry cubic arrangement. In 2007, a cubic phased $Li_7La_3Zr_2O_{12}$ material was reported with bulk grain lithium ion conductivity of $\sim 10^{-4}$ S cm$^{-1}$, which at the time was higher than reported tetragonal phase conductivities.[1]
- $Li_7La_3Zr_2O_{12}$ can be stabilised in the cubic phase by the elemental doping. One example of cubic phase stabilization due to substitution of $Al^{3+}$ substitution into the Li(24d) position forming a stable $Li_{6.16}Al_{0.28}La_3Zr_2O_{12}$ cubic phase.[2] Various substitution has been explored such as the substitution of $Ta^{5+}$ and $Nb^{5+}$ into the Zr(16a) position and $Ga^{3+}$ into the Li(24d) position.[3, 4, 5] Gallium doped $Li_{6.25}Ga_{0.25}La_3Zr_2O_{12}$ garnets have also reported high lithium conductivities of 1.46 x $10^{-3}$ S cm$^{-1}$.[5]
- Here we explore a new dual doped garnet series of $Li_{6.75-3x}Ga_xLa_3Zr_{1.75}Ta_{0.25}O_{12}$ (x = 0 - 0.50) and present the relationship between lithium conductivity, gallium content, lithium site occupancy and temperature.

## Diffraction Analysis

- All samples in this work were prepared via use of a pressure-less sintering technique with all pellets prepared in mother powders to avoid any contamination.
- Garnet series $Li_{6.75-3x}Ga_xLa_3Zr_{1.75}Ta_{0.25}O_{12}$, (x = 0.1 - 0 .5) exist in the cubic space group *Ia-3d*. (Fig. 1)
- Pure phase samples indicates the inclusion of Ga into the structure.

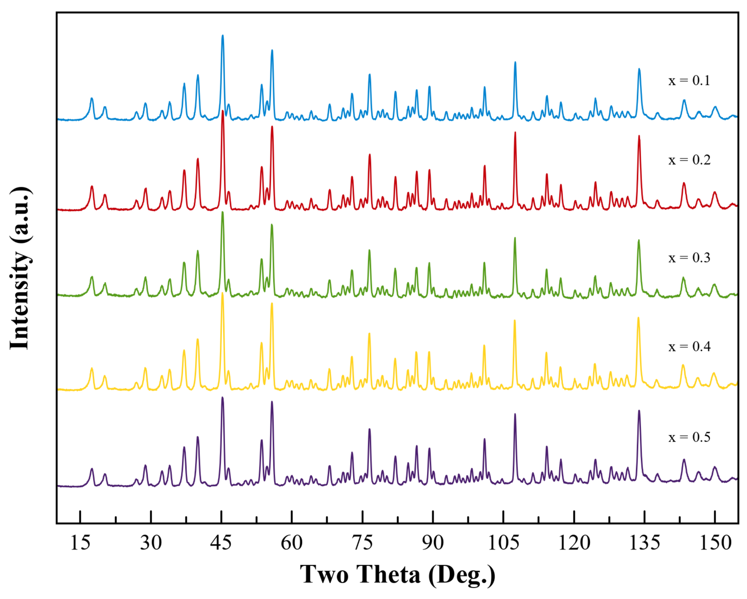


**Figure 1: Neutron diffraction data from the dual doped gallium tantalum lithium garnet oxide series $Li_{6.75-3x}Ga_xLa_3Zr_{1.75}Ta_{0.25}O_{12}$.**

- Ionic radius of $Ga^{3+}$ (62 pm) is larger than $Li^{1+}$(60 pm).
- Shift in Bragg's peaks to lower angle observed (Fig. 2) which is in agreement with Pauling's principles for ionic radii.
- Lattice constants from Rietveld refinements of XRD data sets support this increase with gallium content;

  (x = 0.1) = 12.951(2) Å & (x = 0.5) = 12.960(1) Å.

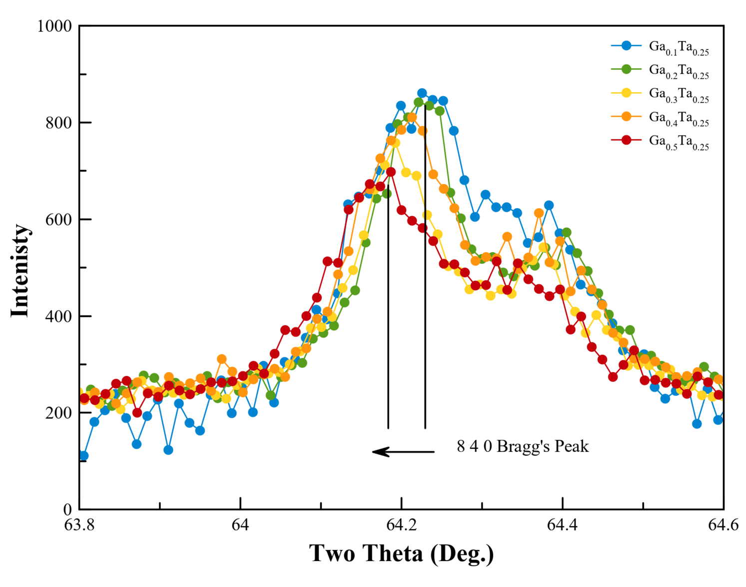


**Figure 2: Shift in (8 4 0)Bragg's reflections in the garnet series of $Li_{6.75-3x}Ga_xLa_3Zr_{1.75}Ta_{0.25}O_{12}$ x = 0.1 - 0.5 due to the incorporation of gallium into the structure which is increasing the unit cell size.**

- The lithium sites can be any of Li24d (Tetrahedral), Li48g (Octahedral) and Li96h (Octahedral Distorted).
- Only present in Li24d and 96h in dual doped system.
- Occupation of Li24d and Li96h sites fit neutron based Rietveld refinement model well. (Fig. 3)
- The exclusion of Li48g site in Rietveld modelling supported by $^7$Li NMR results.

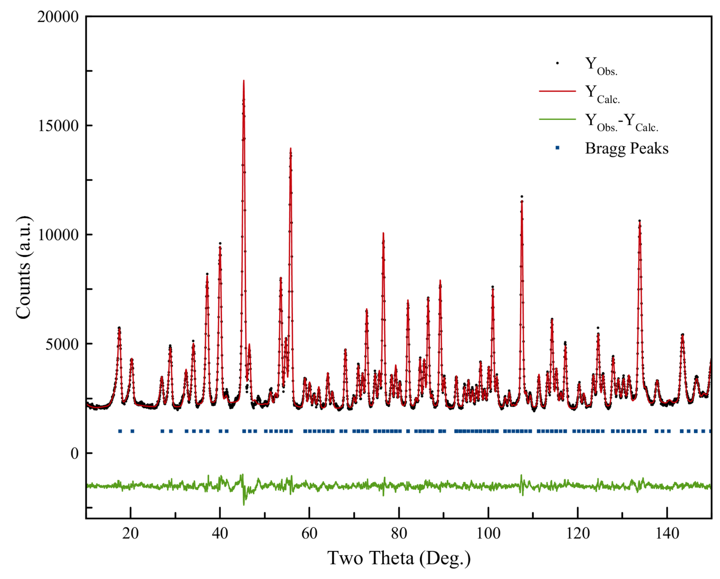


**Figure 3: Rietveld refinement of neutron powder diffraction data of gallium (x = 0.1) - tantalum (0.25) garnet oxide.**

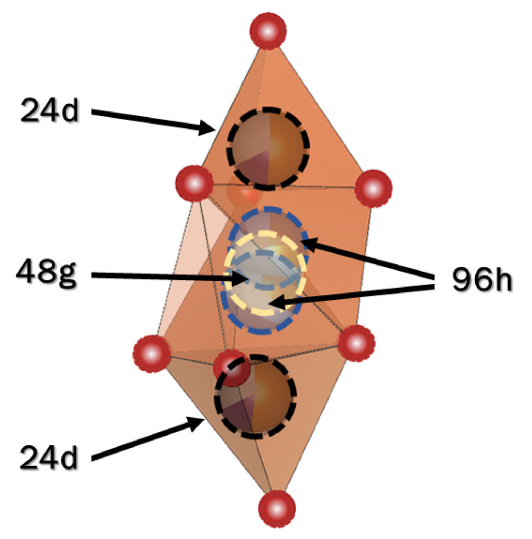


**Figure 4 : Visualization of the different lithium site within the garnet oxide. Note for this work the Li48g was not modelled in favour for the Li96h.**

- Removal of lithium due to the incorporation of gallium has a direct effect on lithium site occupancies.
- XRD and NPD refinements show gallium only present in the Ga24d sites.
- Li24d site occupancies are fairly constant with regard to gallium content.
- Li24d are partial occupied prior to gallium inclusion. With the inclusion of gallium we do not see a replacement of lithium in the Li24d sites.
- Decreasing lithium content in the Li96h sites with regard to gallium content.
- Overall gallium the co-occupies Ga24d/Li24d site and increases the number of lithium voids in the Li96h sites.

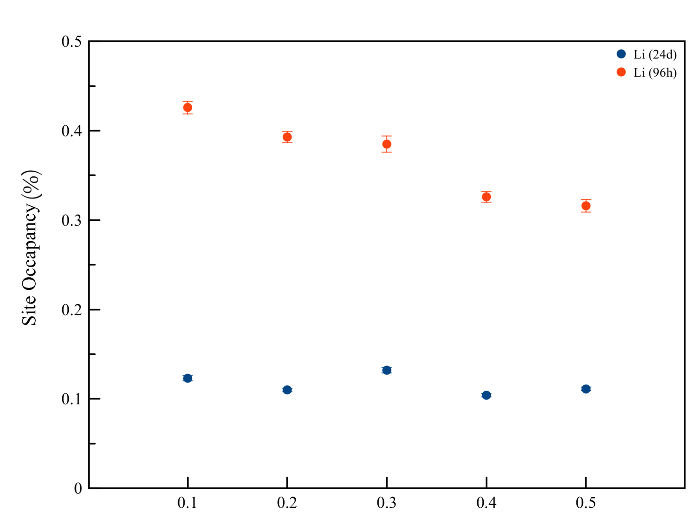


**Figure 5 : Refined lithium Li24d and Li96h site occupancies verses garnet nominal gallium content.**

## Solid-State NMR

- $^7$Li NMR spectrum shows one strong signal indicating the presence of one unique lithium environment.
- Supports the structural modelling of Li24d and Li96h. Distorted octahedral site (Li96h) lithium would be in near tetrahedral arrangement with the closest 4 co-ordinate oxygen. With a weaker interaction of the remain 2 oxygen on the opposite side of the octahedral void.
- Peaks on either side of the main signal are side-bands produced when measured at 15 kHz. Difference between main signal and side-bands is 15 kHz.
- $^{71}$Ga NMR spectrum shows one signal indicating the presence of one Ga environment. Supporting the Ga24d occupancy used in the modelling.

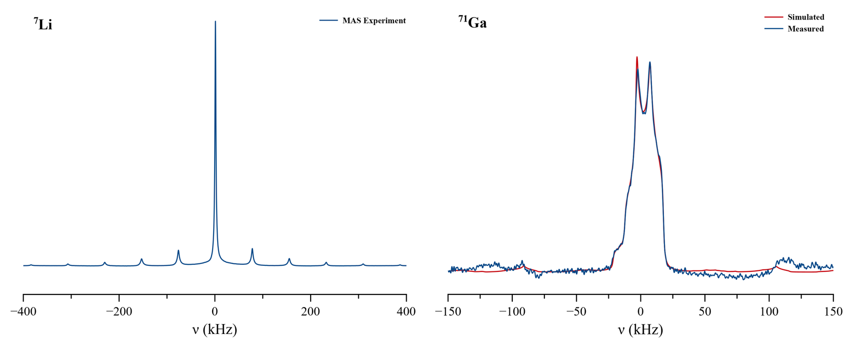

**Figure 6: Left) $^7$Li NMR MAS spectra for gallium content x = 0.5 collected at 11.74 MHz. Right) $^{71}$Ga NMR spectra for gallium content x = 0.5 collected at 11.74 T.)**

## Electrochemical Analysis

- Ionic conductivity determined by electrochemical impedance analysis of Ag/Garnet/Ag cells.
- Conductivity of the dual doped garnets increased with gallium compared to the gallium-free sample.
- Gallium content of x = 0.2 has the highest conductivity of 7.42 x $10^{-5}$ S cm$^{-1}$).
- Increase conductivity can be due to the increase number of vacancies within the material, increasing lithium mobility when compared to the gallium-free samples.

**Table 1: Ionic conductivity for the dual-doped garnet series $Li_{7-3x}Ga_xLa_3Zr_{1.75}Ta_{0.25}O_{12}$ (x = 0 - 0.5).**

| Gallium Content | Ionic conductivity $\sigma_{total}$ (S cm$^{-1}$) % |
|---|---|
| 0 | 8.86 x $10^{-6}$ |
| 0.1 | 5.04 x $10^{-5}$ |
| 0.2 | 7.42 x $10^{-5}$ |
| 0.3 | 5.62 x $10^{-5}$ |
| 0.4 | 3.63 x $10^{-5}$ |
| 0.5 | 5.92 x $10^{-5}$ |

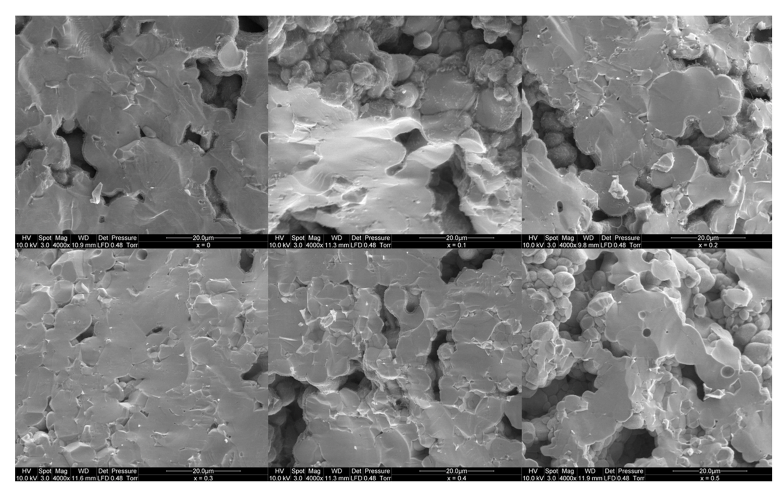

**Figure 7: Scanning electron micrographs for dual doped garnets; Top row Left to right, x = 0, x = 0.1, x = 0.2. Bottom row left to right x = 0.3, x = 0.4, x = 0.5.**

- Scanning electron microscopy to investigate pellet morphology.
- Voids still presence in some of the samples.
- Sample preparation can be improved on to reduce garnet cavitiyes and decrease grain boundaries.

## Conclusions

- Successful solid state preparation of the dual-doped gallium-tantalum lithium garnet oxide series $Li_{6.75-x}Ga_xLa_3Zr_{1.75}Ta_{0.25}O_{12}$ (x = 0 - 0.5).
- Structure determined via diffraction and supported by solid-state NMR.
- The inclusion of gallium does effect garnet ionic conductivity.
- Current preparation method can be improved.

### Acknowledgements

- Australian Government and Australian Nuclear Science and Technology Organisation (ANSTO) for beam-time and financial support.
- Maxim Adveev for experimental support with ECHIDNA high resolution neutron powder diffraction measurements.
- University of Auckland and MacDiarmid Institute for funding financial support for T. Christopher.

## References

[1] J. Awaka, N. Kijima, H. Hayakawa, and J. Akimoto, "Synthesis and structure analysis of tetragonal Li7La3Zr2O12 with the garnet-related type structure," *Journal of Solid State Chemistry*, vol. 182, pp. 2046–2052, Aug. 2009.

[2] N. Janani, C. Deviannapoorani, L. Dhivya, and R. Murugan, "Influence of sintering additives on densification and Li+ conductivity of Al doped Li7La3Zr2O12 lithium garnet," *RSC Adv.*, vol. 4, no. 93, pp. 51228–51238, 2014.

[3] R. Murugan, V. Thangadurai, and W. Weppner, "Fast Lithium Ion Conduction in Garnet-Type Li7La3Zr2O12," *Angewandte Chemie International Edition*, vol. 46, pp. 7778–7781, June 2007.

[4] V. Thangadurai, H. Kaack, and W. J. F. Weppner, "Novel Fast Lithium Ion Conduction in Garnet-Type Li5La3M2O12 (M = Nb, Ta)," *Journal of the American Ceramic Society*, vol. 86, pp. 437–440, June 2003.

[5] J.-F. Wu, E.-Y. Chen, Y. Yu, L. Liu, Y. Wu, W. K. Pang, V. K. Peterson, and X. Guo, "Gallium-Doped Li7La3Zr2O12 Garnet-Type Electrolytes with High Lithium-Ion Conductivity," *ACS Appl. Mater. Interfaces*, vol. 9, pp. 1542–1552, Jan. 2017.