

Supplementary Information - Evaluation of the effect of site substitution of Pr doping in the Lithium  
garnet system  $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$

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Comparative XRD patterns before and after densification via high temperature N<sub>2</sub> heat treatments, showing increased phase degradation as Pr content increased. Additionally, in figure S1a an XRD pattern is shown after storage in an Ar glove box for 1 week.

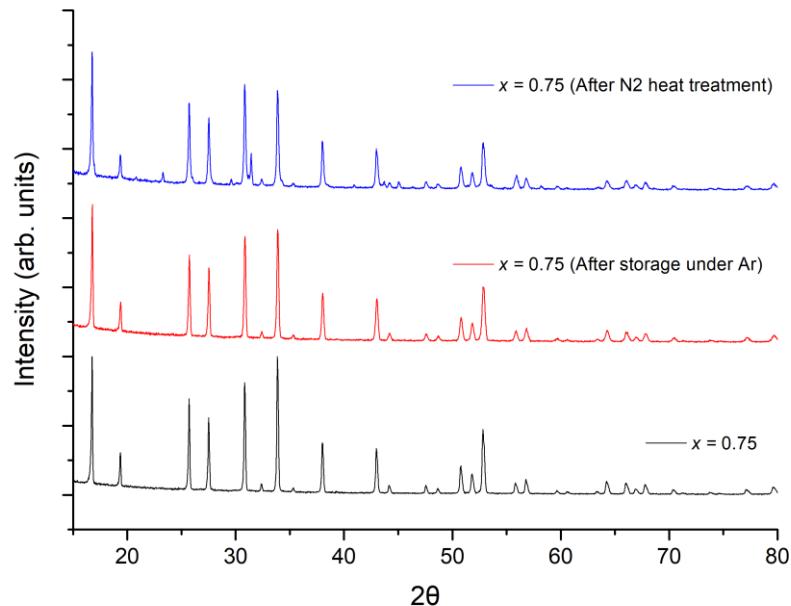


Figure S1a. XRD patterns for  $\text{Li}_{5.75}\text{La}_3\text{Nb}_{1.25}\text{Pr}_{0.75}\text{O}_{12}$  freshly synthesised, after storage in a Ar glove box for 1 week and after the high temperature N<sub>2</sub> treatment, the latter of which shows phase degradation.

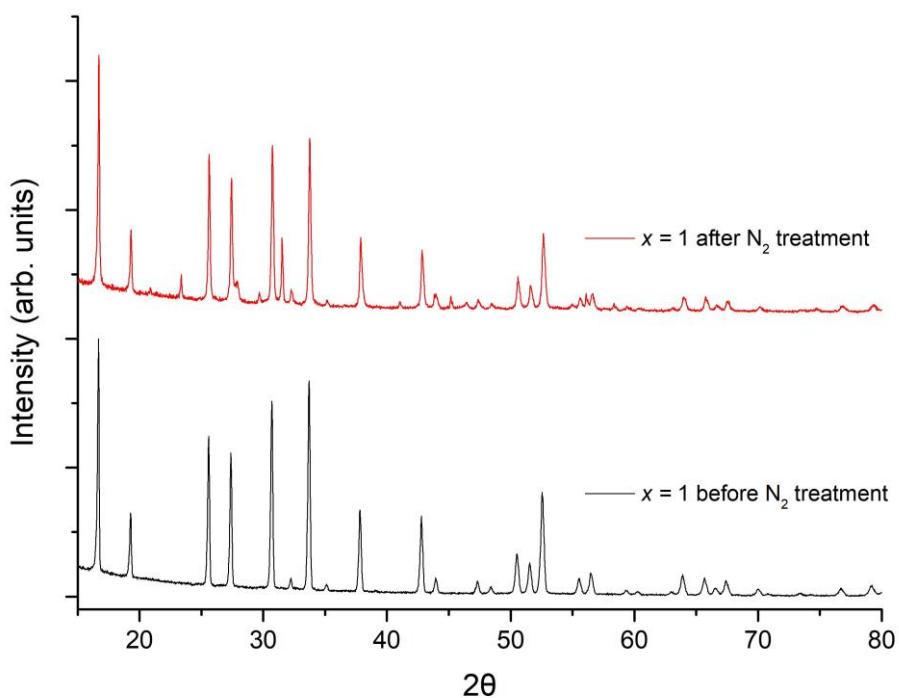


Figure S1b. XRD patterns for  $\text{Li}_6\text{La}_3\text{Nb}_1\text{Pr}_1\text{O}_{12}$  freshly synthesised and after the high temperature N<sub>2</sub> treatment, the latter of which shows more severe phase degradation than  $x = 0.75$

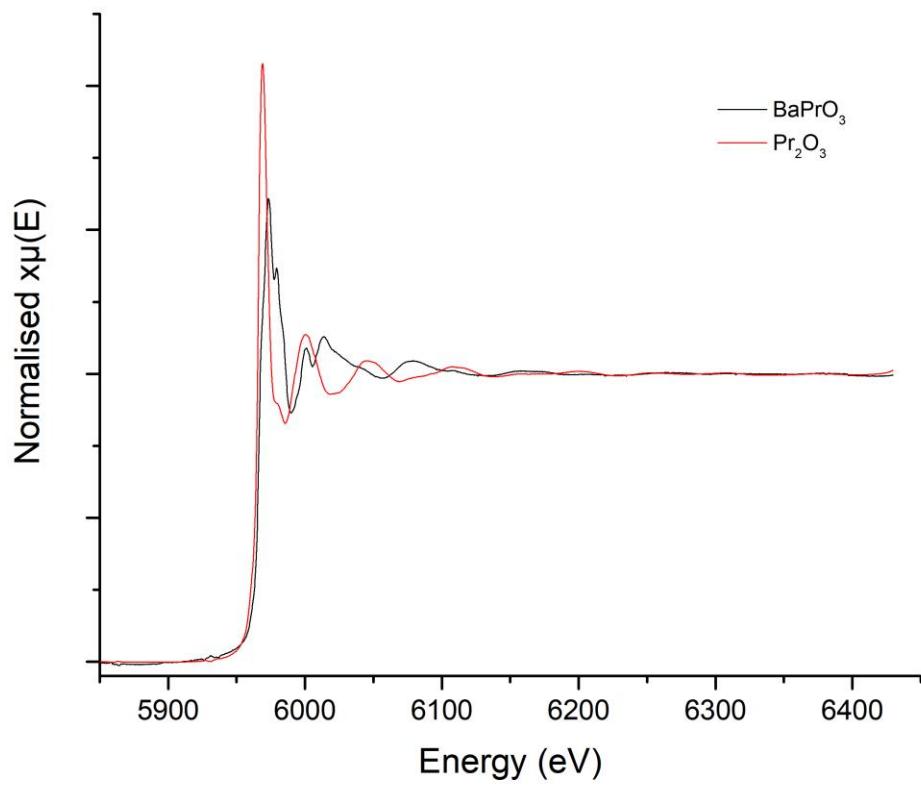


Figure S2. XANES spectra of reference samples  $\text{Pr}_2\text{O}_3$  and  $\text{BaPrO}_3$  overlaid.

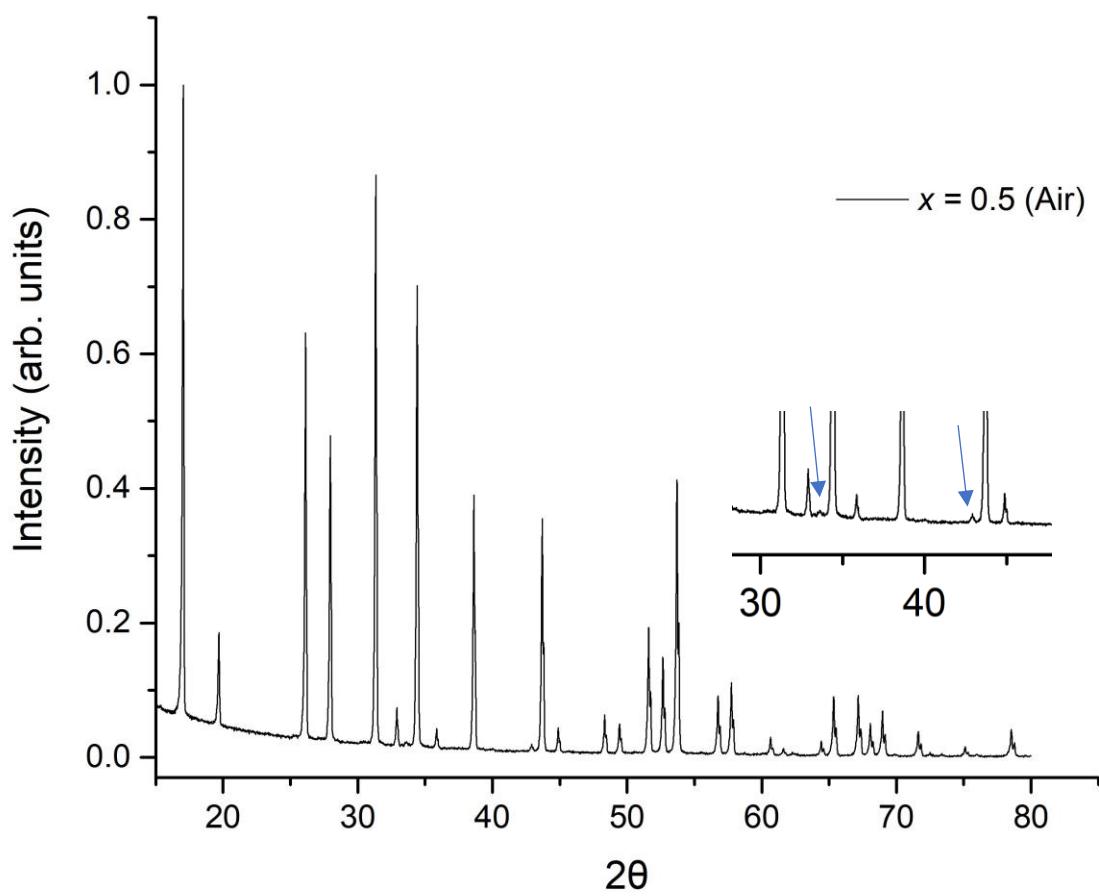


Figure S3. Example XRD of La site doping ( $x = 0.5$  synthesised in air) showing small  $\text{Li}_3\text{NbO}_4$  impurity, marked additionally with arrows in the magnified inlay. This impurity was noted for all air-based synthesis and in some  $\text{H}_2$  synthesised phases.

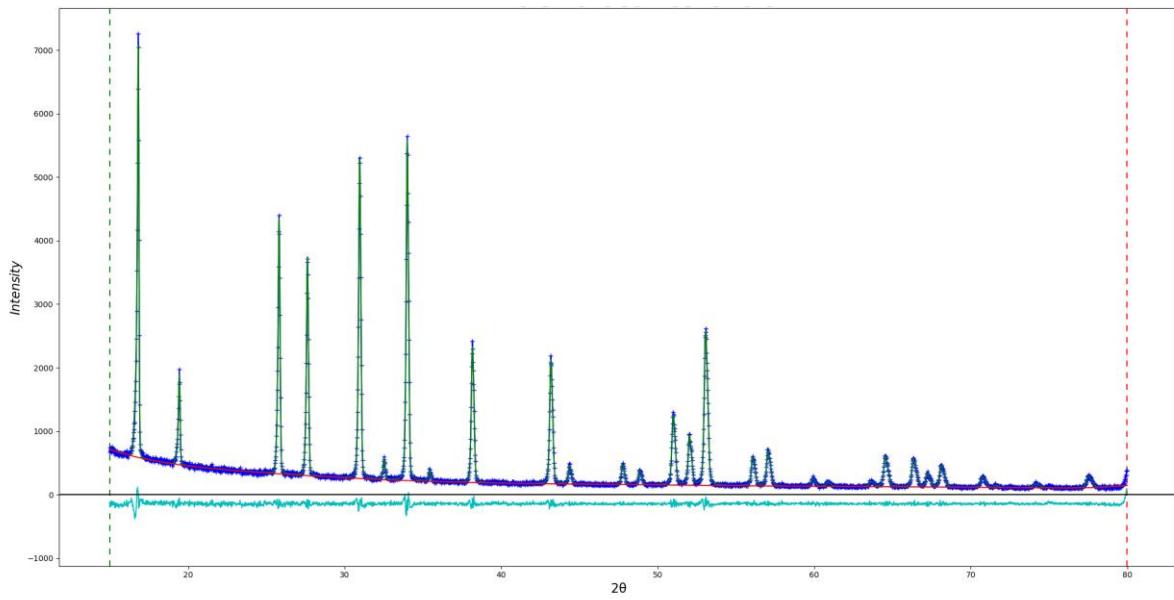


Figure S4. Example Rietveld refinement of Pr LLNO garnet materials. The above example is of  $\text{Li}_{5.5}\text{La}_3\text{Nb}_{1.5}\text{Pr}_{0.5}\text{O}_{12}$

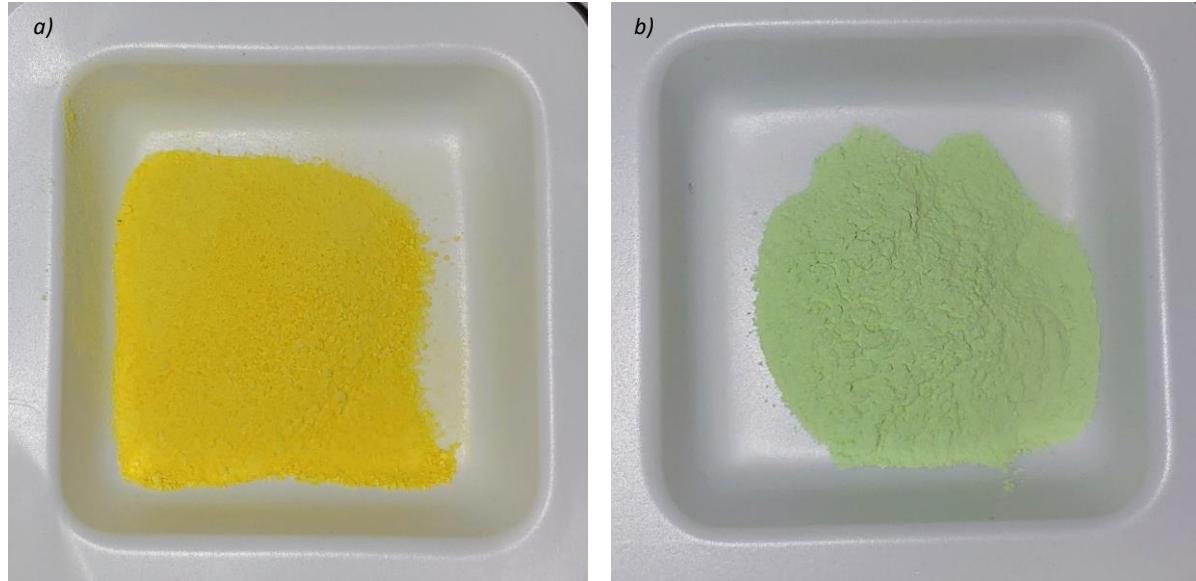


Figure S5. Powder colours of lithium garnet phases where a) is  $\text{Li}_{5.25}\text{La}_3\text{Nb}_{1.75}\text{Pr}_{0.25}\text{O}_{12}$  and b) is  $\text{Li}_5\text{Pr}_{2.5}\text{La}_{2.5}\text{Nb}_2\text{O}_{12}$  synthesised under 5%  $\text{H}_2$