Rietveld Refinement of Solid Solutions of La_2TiO_5 and $La_4Ga_2O_9$

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Orthorhombic (Pnam) La_2TiO_5 and monoclinic ($P2_1/c$) $La_4Ga_2O_9$ were found to form solid solutions in the whole concentration range. Samples of $La_2Ti_{(1-x)}Ga_xO_{(5-x/2)}$ with x = 0.00, 0.20, 0.50, 0.70, 0.90, 0.95 and 1.00 were prepared by solid state reaction of oxides at 1300 °C in air (fired and remixed several times for 60 h, until no change).

Structure of La_2TiO_5 has already been known, while $La_4Ga_2O_9$ was found in this study to be isostructural with $Y_4Al_2O_9$, $Eu_4Al_2O_9$ and $Pr_4Ga_2O_9$, and was successfully refined from the $Y_4Al_2O_9$ model.

Laboratory data in the range of 10-120 °2θ were used for an unrestrained Rietveld refinement (TOPAS). Results were consistent and showed random replacement of Ti^{4+} by Ga^{3+} ions in the solid solutions, coupled with oxygen vacancies, most probably preferably occurring at one site. Vacancies at this site are not ordered till x = 0.90 and the structures up to this composition are orthorhombic, obeying Vegard's law. Increase of a and c and decrease of b was explained considering ionic radii and shifts of ions towards the vacant site.

Ordering of the oxygen vacancies on one oxygen site at x = 0.95 and 1.00 causes doubling of the unit cell and lowering of the symmetry to monoclinic. In pure $La_4Ga_2O_9$ (x = 1.00) the total population at this site reaches 0.5 and the ordering (1 full : 1 empty) produces the superstructure. The structural relationship between the end members (orthorhombic and the other monoclinic) was also clarified by finding the transformation matrix between the two.

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