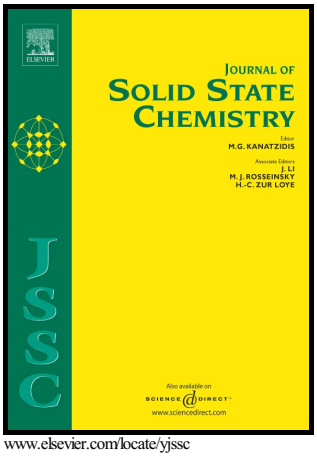

www.elsevier.com/locate/yjssc

Determination of Cation Distribution in the $Fe[Li_{1/2}Fe_{3/2}]O_4$–$LiFeTiO_4$–$Li[Li_{1/3}Ti_{5/3}]O_4$ System: Mixed Nature of Solid Solution and Superlattice

Kazuhiko Mukai, Yuichi Kato, Hideyuki Nakano

PII: S0022-4596(16)30508-4
DOI: http://dx.doi.org/10.1016/j.jssc.2016.12.025
Reference: YJSSC19644

To appear in: *Journal of Solid State Chemistry*

Received date: 16 November 2016
Revised date: 27 December 2016
Accepted date: 28 December 2016

Cite this article as: Kazuhiko Mukai, Yuichi Kato and Hideyuki Nakano Determination of Cation Distribution in th $Fe[Li_{1/2}Fe_{3/2}]O_4$–$LiFeTiO_4$–$Li[Li_{1/3}Ti_{5/3}]O_4$ System: Mixed Nature of Soli Solution and Superlattice, *Journal of Solid State Chemistry* http://dx.doi.org/10.1016/j.jssc.2016.12.025

Determination of Cation Distribution in the $Fe[Li_{1/2}Fe_{3/2}]O_4$–$LiFeTiO_4$–$Li[Li_{1/3}Ti_{5/3}]O_4$ System: Mixed Nature of Solid Solution and Superlattice

Kazuhiko Mukai*, Yuichi Kato, Hideyuki Nakano

Toyota Central Research & Development Laboratories, Inc., 41–1 Yokomichi, Nagakute, Aichi 480–1192, Japan

*Tel.: +81-561-71-7698. Fax: +81-561-63-6948. e1089@mosk.tytlabs.co.jp

Abstract

The solid solution technique is one of the oldest but most powerful methods in the search for advanced materials. Hume-Rothery rules regarding solid solutions are well established for alloys, but little is known about oxides. In this study, we focused on the spinel oxides of $Fe[Li_{1/2}Fe_{3/2}]O_4$–$LiFeTiO_4$–$Li[Li_{1/3}Ti_{5/3}]O_4$ to clarify their cation distribution, which necessitates other rules for substitutionally ordered/disordered solid solutions. Here, the chemical formula of the spinels is represented as $Li_{1/2+x/2}Fe_{5/2-3x/2}Ti_xO_4$ with $0 \le x \le 5/3$. Synchrotron radiation X-ray diffraction measurements indicated two types of 1:3 cation order at the octahedral site over the wide x range; i.e., the cation order between one Li^+ ion and three Fe^{3+} ions at $0 \le x \le 1$ and the cation order between one Li^+ ion and three Ti^{4+} ions at $1 < x \le 1.55$. Rietveld refinements indicated that the formation of the cation order at $1 < x \le 1.55$ is achieved by a combination of $1 \times (Li^+_{1-x1-y1}Fe^{3+}_{x1}Ti^{4+}_{y1})$ and $3 \times$