# PRECISE DETERMINATION OF ATOM CONFIGURATION IN PARTIALLY DISORDERED SPINEL COMPOUNDS BY HARECXS

S. Matsumura, T. Soeda, M. Shimada and N.J. Zaluzec*
Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University, Fukuoka 812-8581, Japan, and *Materials Science Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA

Electron channeling enhanced x-ray spectroscopy has been being widely used to determine ordered arrangement of component atoms in multinary inorganic or metallic crystals. Recent theoretical advancements in the modeling of characteristic x-ray emission by inelastic scattering of incident electrons under dynamical diffraction conditions has achieved remarkable progress[1], and it has enabled scientists to analyze the experimental intensity of x-ray emission in precise detail. In this study, the ion configuration in magnesium aluminate spinel ($MgO{\cdot}nAl_2O_3$) has been examined by measurements of characteristic x-ray emission as a function of incident electron beam direction at high angular resolution, a technique which we have termed HARECXS (*high angular resolution electron channeling x-ray spectroscopy*). This paper reports the results and emphasizes the applicability of HARECXS to partially disordered materials.

Ion beam thinned TEM disk specimens of $MgO{\cdot}nAl_2O_3$ with compositions $n$=1.0, 2.4 and 3.0 were prepared for study after annealing at 1470 K for 2 days. HARECXS profiles were obtained in Philips EM-420T (at the ANL EM Center) operated at 120 kV with incident beam rocking between $-4\boldsymbol{g}$ and $+4\boldsymbol{g}$ ($\boldsymbol{g}$=400) orientations. The experimental results were analyzed on the dynamical scattering formulation derived by Rossouw *et al.* [1] Fifteen reflections in the 400 systematic row were included in the calculations.

Figs. 1a-c illustrate calculated HARECXS profiles of stoichiometric $MgO{\cdot}Al_2O_3$ spinel crystals with various cation arrangements. Here the parameter $k$ along the abscissa refers to the intersection of the Ewald sphere with the axis along 400 systematic reflections. $k/g_{400}$=1 corresponds to the exact Bragg condition for 400 reflection. The intensities of Mg-$K$, Al-$K$ and O-$K$ x-rays drastically change with the incident beam direction, showing characteristic HARECXS profiles depend sensitively on the ion configuration in the crystal lattice. Figs. 2a-c show experimentally obtained HARECXS profiles of $MgO{\cdot}nAl_2O_3$ with $n$=1.0, 2.4 and 3.0. The profile (2a) for $n$=1.0 looks analogous to (1a), indicating that the stoichiometric compound has a tendency to form the normal structure, where $Mg^{2+}$ and $Al^{3+}$ ions occupy preferentially the tetrahedral (IV) and the octahedral (VI) sites, respectively. In contrast, the profiles (2b) and (2c) for non-stoichiometric compounds exhibit strikingly different features. The Mg-$K$ intensity remains almost unchanged over the range $-2<k/g_{400}<2$ in (2b), while it is enhanced for $-1<k/g_{400}<1$ in (2c) in an opposite sense to (2a). This suggests that $Mg^{2+}$ ions are displaced to the VI sites with deviation from the stoichiometric composition. The simulations given in Figs. 3a-c describe quite well the experimental profiles of Figs. 2a-c, and therefore the ion configurations are consistently determined. These results are also given in terms of occupation probabilities on the IV sites in Figs. 2a-c. Here we can see that, in the stoichiometric compound, partial disordering takes place so that 60 % of $Mg^{2+}$ ions are located in the IV sites while the remaining are on the VI sites. The tendency to form the normal structure disappears in the non-stoichiometric compounds with $n$=2.4 and 3.0, as the occupation probability of $Mg^{2+}$ on the IV sites is about 1/3 or less. HARECXS has, thus, shown itself to be very useful for quantitative determination of atom configuration in crystalline materials as well as in the study of radiation-induced displacements in spinel[2], the results from which are reported in a separate paper[3].

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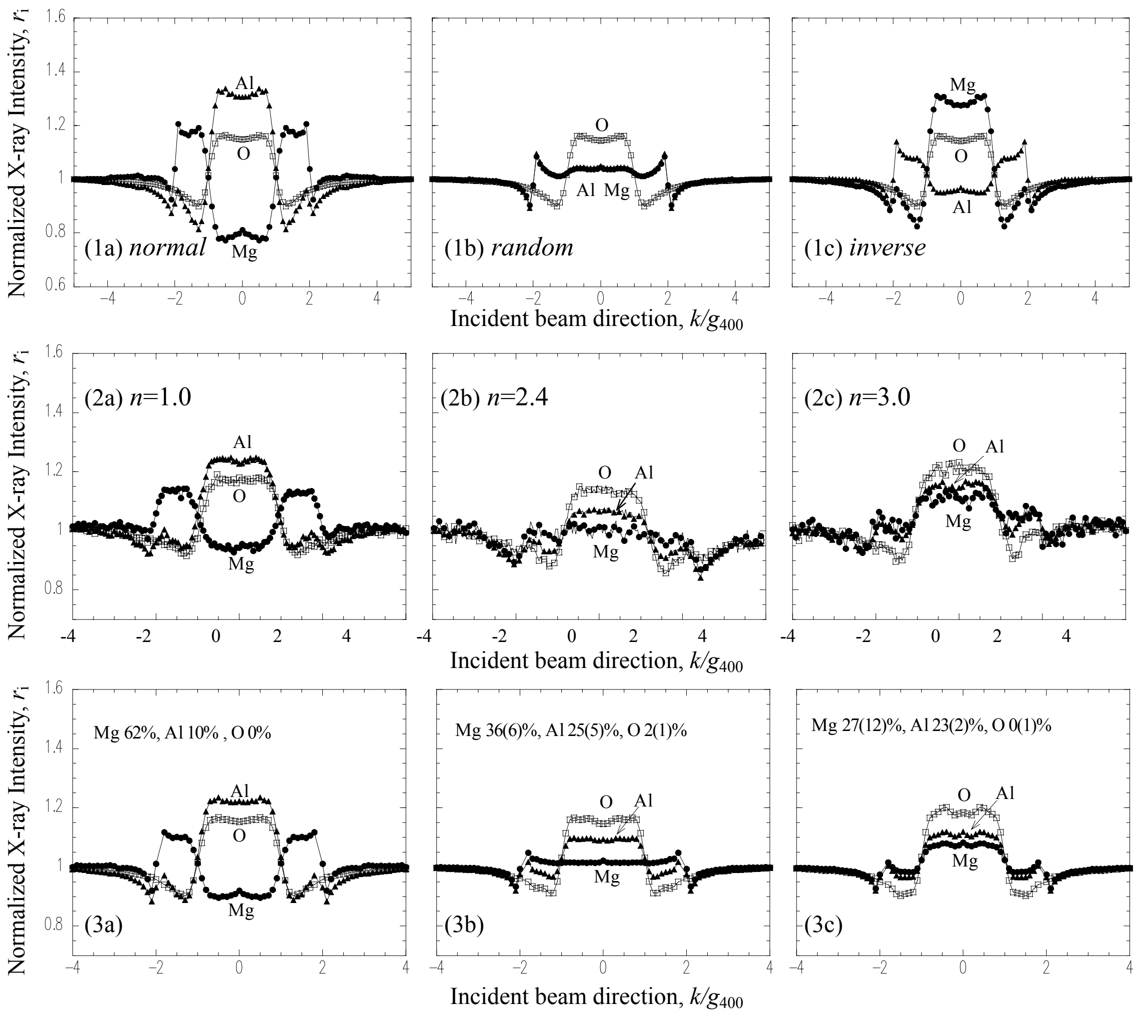


Figure 1. Calculated HARECXS profiles of stoichiometric $MgO{\cdot}Al_2O_3$ with normal (1a), random (1b) and inverse spinel structures.

Figure 2. Experimental profiles of $MgO{\cdot}nAl_2O_3$ with $n$=1.0 (2a), 2.4 (2b) and 3.0 (2c).

Figure 3. Simulation of HARECXS profiles for $n$=1.0 (3a), 2.4 (3b) and 3.0 (3c). The values inserted are the occupation probabilities on the IV sites.

References

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syo@nucl.kyushu-u.ac.jp