ELECTRON CHANNELING X-RAY MICROANALYSIS FOR CATION CONFIGURATION IN IRRADIATE MAGNESIUM ALUMINATE SPINEL*

S. Matsumura*, T. Soeda*, N. J. Zaluzec**, and C. Kinoshita*

*Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University 36, Fukuoka 812-8581, Japan

**Materials Science Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439

November 1999

Paper to be presented at the Fall MRS Meeting, Boston, MA, November 29 – December 3, 1999.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
ELECTRON CHANNELING X-RAY MICROANALYSIS FOR CATION CONFIGURATION IN IRRADIATED MAGNESIUM ALUMINATE SPINEL

S. MATSUMURA *, T. SOEDA *, N. J. ZALUZEC **, C. KINOSHITA *

*Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University 36, Fukuoka 812-8581, Japan, syo@nucl.kyushu-u.ac.jp
**Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

ABSTRACT

High angular resolution electron channeling x-ray spectroscopy (HARECXS) was examined as a practical tool to locate lattice-ions in spinel crystals. The orientation dependent intensity distribution of emitted x-rays obtained by HARECXS is so sensitive to lattice-ion configuration in the illuminated areas that the occupation probabilities on specific positions in the crystalline lattice can be determined accurately through comparison with the theoretical rocking curves. HARECXS measurements have revealed partially disordered cation arrangement in MgO-nAl2O3 with n=1.0 and 2.4. Most Al3+ lattice-ions occupy the octahedral (VIII) sites, while Mg2+ lattice-ions reside on both the tetrahedral (IV) and the octahedral (VIII) sites. The structural vacancies are enriched in the IV-sites. Further evacuation of cations from the IV-sites to the VIII-sites is recognized in a disordering process induced by irradiation with 1 MeV Ne+ ions up to 8.9 dpa at 870 K.

INTRODUCTION

Magnesium aluminate spinel MgO-nAl2O3 is expected to be an excellent candidate for insulators in the fusion reactors, since it exhibits strong resistance to formation of defect clusters under irradiation with high energy particles [1,2]. The stability of MgO-nAl2O3 in radiation fields is believed to come from a number of vacant sites in the spinel structure. In the ideal or "normal" structure of stoichiometric case, Mg2+ and Al3+ cations occupy 1/8 of the tetrahedral (IV) and 1/2 of the octahedral (VIII) sites, respectively, in the fcc lattice formed with O2− anions. The rest of the sites remain unoccupied as they are empty holes in the lattice. A significant number of structural vacancies are further introduced into the cation sites in the non-stoichiometric compounds with n>1. Under irradiation conditions, these empty holes and the structural vacancies are presumed to accommodate displaced lattice-ions and to suppress aggregation of defects into clusters. However, the behavior of displaced lattice-ions and vacancies in MgO-nAl2O3 under irradiation has not been conclusively confirmed by experimental measurements. Neutron diffraction [3] and nuclear magnetic resonance [4] were employed in a study of lattice-ion displacements in MgO-nAl2O3 irradiated with neutrons. These techniques disclosed the average overall behavior of structural change, but not detailed information particularly in heterogeneously damaged materials. The present authors applied a combined use of conventional electron channeling x-ray spectroscopy [5] and large angle convergent beam electron diffraction (LACBED) to this problem and succeeded in determining the lattice-ion configuration of local areas in irradiated MgO-nAl2O3 compounds [6]. This two step method is somewhat difficult and time consuming because it consists of two separate experiments and several parameters relevant to dynamical electron diffraction which must be determined. In addition, LACBED is not appropriate for use in to heavily damaged areas, since the diffraction pattern is also highly sensitive to local distortion of lattice.

To overcome the difficulties involved in the conventional electron channeling and diffraction technique, the present study examines the potential of electron channeling x-ray spectroscopy for determination of lattice-ion configuration in partially disordered MgO-nAl2O3 spinel compounds. The characteristic x-ray emission is measured precisely as a function of
incident-beam direction in the experiment, which we have termed high angular resolution electron channeling x-ray spectroscopy (HARECXS) to differentiate it from conventional electron channeling techniques [5]. The orientation dependent profiles of emitted x-ray intensity are measured and then compared to theoretical calculations [7-9] analyzed to determine the local lattice-ion configurations. In this work, the HARECXS technique is employed to investigate cation configuration in MgO-nAl2O3 with n=1.0 and 2.4 as well as disordering behavior induced by irradiation with 1 MeV Ne+ Ions at 870 K.

EXPERIMENTAL PROCEDURE

Disk specimens of MgO-nAl2O3 with n=1.0 (Union Carbide) and 2.4 (Nakazumi Crystal) were dimpled to 30μm thickness and then ion-milled with 5 keV Ar+ Ions to electron transparency. These specimens were subsequently annealed at 1470 K for 48 hours to remove lattice defects produced by ion milling and allowed to furnace cool. Single-crystalline MgO-nAl2O3 bulk crystals were irradiated at 870 K with 1 MeV Ne+ Ions to a dose of about 2 dpa (Φ=4.5 x 10^20 Ne+/m^2). The irradiated bulk specimens were mechanically thinned with a tripod polisher. The wedge shape cross sectional specimens allowed observation along Ne-Ion beam direction. Argon plasma processing [10] was performed in order to suppress the hydrocarbon contamination on the specimens during the following HARECXS measurement. Experimental data was acquired using a Philips EM420T analytical electron microscope equipped with an LaB6 electron source and an EDAX 9900 EDX system operating in the TEM mode at 120 kV. Two-dimensional angular resolution measurements of x-ray emission were carried out in a 128 x 100 pixel scan synchronized with incident beam rocking over an angular range of about 100 mrad between -4g and +4g (g=400) Bragg conditions, using customized computer control. The typical acquisition time for a complete two-dimensional scan was 18-24 hours.

RESULTS AND DISCUSSION

Fig 1 illustrates calculated HARECXS profiles of stoichiometric MgO-nAl2O3 spinel crystals with various cation arrangements. These calculations were accomplished using a computer program developed by Rossouw, et al, which takes account of dynamical scattering of incident electrons as well as the dechanneling and delocalization effects on induced x-ray emission [7,9]. Fifteen reflections in the 400 systematic row were considered in these calculations and the parameter k along the abscissa refers to the intersection of the Ewald sphere with the axis along 400 systematic reflections. In this nomenclature, 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 are given as a function of incident electron beam orientation, normalized by the values at the 5g (g=400) Bragg condition. The x-ray intensities drastically change with the beam orientation, especially in the central part of strong dynamical excitation of low order reflections. For the normal spinel structure, where the IV- and the VIII-sites are purely occupied by Mg^{2+} and Al^{3+} lattice-ions, respectively, the emission from Mg-K is suppressed, while Al-K and O-K are enhanced within the range -1<k/g_{400}<1, as shown in Fig 1(a). Outside of this range, the intensity relationship is reversed. If the cations are arranged in the inverse form, where all Mg^{2+} lattice-ions are located on the VIII-sites and Al^{3+} lattice-ions are distributed equally on both IV- and VIII-sites, the Mg emission is enhanced around the symmetric diffraction orientation and the Al signal is enhanced when -1<k/g_{400}<2, as seen in (d). For comparison, Fig 1(c) shows the case when Mg^{2+} and Al^{3+} lattice-ions occupy randomly both IV- and VIII-sites. The profiles of Mg-K and Al-K almost coincide with each other. From these figures we see that the HARECXS profiles change sensitively depending on replacement of Mg^{2+} and Al^{3+} lattice-ions between the IV- and the VIII-sites. One may conclude from Fig 1 that HARECXS would be useful for investigating ion configuration in disordered compounds.

Fig 2 presents our experimentally obtained HARECXS profiles of annealed
Fig. 1: Simulated HARECXS profiles of MgO-Al$_2$O$_3$ with various cation configuration.

(a) $P_{Mg}=1$, $P_{Al}=0$ (normal),  (b) $P_{Mg}=0.5$, $P_{Al}=0.25$,  (c) $P_{Mg}=0.33$, $P_{Al}=0.33$ (random),
(d) $P_{Mg}=0$, $P_{Al}=0.5$ (inverse). Accelerating voltage: $E=120$ kV, Foil thickness: $t=150$ nm.

MgO-nAl$_2$O$_3$ with $n=1.0$ and 2.4. The profile (2a) for $n=1.0$ looks analogous to Fig 1(a), indicating that the stoichiometric compound has a tendency to form the normal structure. In contrast, the profile (2b) for a non-stoichiometric compound with $n=2.4$ exhibits strikingly different features; for example, Mg-K signal is enhanced in the central part around the symmetric diffraction orientation, and suggests that a considerable amount of Mg$^{2+}$ lattice-ions are located on the VIII-sites. Fig 3 shows the normalized intensities $r_{Mg}$ and $r_{Al}$ plotted against $r_O$. Here one can observe that there exist approximately linear relationships of $r_{Mg}$ or $r_{Al}$ with $r_O$ around the $400$ Bragg condition, as pointed out by Anderson [8]. If the occupation probabilities of Mg$^{2+}$ and Al$^{3+}$ lattice-ions on the IV-sites are defined as $P_{Mg}$ and $P_{Al}$, then the ratios $S (=P_{Al}/P_{Mg})$ for both compounds are obtained from the relationships,

$$ r_O = \frac{1}{1-S} \cdot \frac{1}{r_{Al}} - \frac{1}{1-S} \cdot \frac{1}{r_{Mg}}. $$

Here, $L$ is the coefficient of charge density distribution in Al$^{3+}$ or Mg$^{2+}$ lattice-ions relative to O$^{2-}$ lattice-ions. Since the number of unknown parameters in this formulation is now reduced to one when $S$ is evaluated, the value of $P_{Mg}$ is easily determined by comparing the HARECXS profiles directly with the theoretical calculations. Figs. 4(a) and (b) show the calculated results corresponding to Figs. 2(a) and (b), respectively. Quite good agreements are achieved between the theoretical calculations and the experimental results, as shown in Figs. 2 and 4. Table 1 lists the occupation probabilities of cations on the IV- and the VIII-sites determined using this procedure. In the stoichiometric compound with $n=1.0$, most Al$^{3+}$ lattice-ions are located on the VIII sites, while Mg$^{2+}$ lattice-ions distribute 60\% and 40\% on the IV- and the VIII sites, respectively. Neutron diffraction has also derived comparable values of $P_{Mg}=0.763 \pm 0.02$ and $P_{Al}=0.118 \pm 0.01$ [3]. The partial disordering tendency of Mg$^{2+}$ lattice-ions has been explained...
in terms of ionic size and induced lattice strain around the IV-sites [3]. Table 1 indicates that a small amount of vacancies are also produced in the IV-sites in the stoichiometric compound. It follows that the same amount of cations should occupy empty holes of the octahedral position. The disordering tendency is more pronounced in non-stoichiometric MgO-2.4Al2O3, where 20% of Al3+ lattice-ions are located on the IV-sites and fewer Mg2+ ions remain in the IV-sites. Structural vacancies, which appear to be greater than the nominal content, are enriched in the IV-sites.

Fig. 2: HARECXS profiles of annealed MgO-nAl2O3 with n=1.0 (a) and 2.4 (b).

Fig. 3: Linear relationship between characteristic x-ray intensities around the 400 Bragg positions in the HARECXS profiles of Fig. 2.

Fig. 4: Simulated HARECXS profiles of MgO-nAl2O3 with n=1.0 (a) and 2.4 (b). Foil thickness: t=180 (a), 50 nm (b).
Table 1: Occupation numbers of Mg\(^{2+}\), Al\(^{3+}\) and vacancies on the IV-sites and the VIII-sites per unit cell in annealed MgO-\(n\)Al\(_2\)O\(_3\). The occupation probabilities on the IV-sites \((P_i)\) are also tabulated.

<table>
<thead>
<tr>
<th>Number of ions (per unit cell)</th>
<th>(n=1.0)</th>
<th>(n=2.4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Mg}^{2+})</td>
<td>8</td>
<td>3.9</td>
</tr>
<tr>
<td>(\text{Al}^{3+})</td>
<td>16</td>
<td>18.7</td>
</tr>
<tr>
<td>Vacancy</td>
<td>-</td>
<td>1.3</td>
</tr>
<tr>
<td>(\text{Total})</td>
<td>4.9 ± 0.1</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td>(\text{IV-sites})</td>
<td>3.1 ± 0.1</td>
<td>2.8 ± 0.1</td>
</tr>
<tr>
<td>(\text{VIII-sites})</td>
<td>0.61 ± 0.01</td>
<td>0.27 ± 0.01</td>
</tr>
<tr>
<td>(P_i)</td>
<td>0.10 ± 0.02</td>
<td>0.20 ± 0.02</td>
</tr>
</tbody>
</table>

Fig. 5 demonstrates HARECXS profiles obtained from a pre-peak damaged area at \(d=450\) nm and a peak-damaged region at \(d=900\) nm in a cross sectional specimen of MgO-Al\(_2\)O\(_3\) irradiated with 1 MeV Ne\(^+\) Ions at 870 K. Here, \(d\) is the depth from the irradiated surface. In this sample the calculated dose reaches about 2.0 and 8.9 dpa in the pre-peak and the peak damaged areas, respectively. Well-defined and sharp diffraction spots appeared in both regions, indicating that the spinel structure is still stable even in the peak damaged area. In contrast, the HARECXS profiles have varied significantly from that in Fig 2 (a) before irradiation. It is apparent that disordering ensues from knocked-on displacements of lattice-ions by irradiation. Table 2 summarizes the occupation numbers of Mg\(^{2+}\) and Al\(^{3+}\) lattice-ions on the IV- and the VIII-sites after 1 MeV Ne\(^+\) -Ion irradiation at 870 K. The total number of Mg\(^{2+}\) lattice-ions decreases, while Al\(^{3+}\) lattice-ions increase in the IV-sites in the pre-peak damaged area. This indicates that cations are simply replacing each other on both sites in the pre-peak damaged area. In contrast, the number of cations on the IV-sites decreases in the peak-damaged region. Mainly due to displacement of Al\(^{3+}\) lattice-ions from the IV-sites to the VIII-positions and as a result, excess vacancies are produced in the IV-sites. Neutron diffraction has suggested that a considerable amount of ions are located on unoccupied sites of the VIII-positions in MgO-Al\(_2\)O\(_3\) after neutron irradiation up to 56 dpa at 678 K [3]. Heavy Ion irradiation with 400 keV Xe\(^{2+}\) or 1.5 MeV Kr\(^+\) Ions at cryogenic temperatures [11] results in extinction of 220 reflections, which indicates removal of lattice-ions from the IV-sites. The experimental results of Heavy Ion Irradiation are qualitatively consistent with the behavior observed in the peak-damaged area. A more extended study on irradiation behavior in MgO-\(n\)Al\(_2\)O\(_3\) is in progress [12,13].

Fig. 5: HARECXS profiles obtained from MgO-Al\(_2\)O\(_3\) irradiated with 1 MeV Ne\(^+\) ions at 870 K. (a) Pre-peak damaged area \((d=450\) nm\), (b) Peak-damaged area \((d=900\) nm\).
Table 2: Cation and vacancy configuration on the IV-sites and the VIII-sites for n=1 after irradiation with 1 MeV Ne⁺ ions at 870 K. The probabilities are given in terms of the number of ions per unit cell.

<table>
<thead>
<tr>
<th>Number of ions (per unit cell)</th>
<th>Total</th>
<th>IV-sites</th>
<th>VIII-sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-peak damaged area</td>
<td>Mg²⁺ 8</td>
<td>3.0 ± 0.1</td>
<td>5.0 ± 0.1</td>
</tr>
<tr>
<td>Al³⁺ 16</td>
<td></td>
<td>3.5 ± 0.3</td>
<td>12.5 ± 0.3</td>
</tr>
<tr>
<td>Vacancy</td>
<td>-</td>
<td>1.5 ± 0.3</td>
<td>0</td>
</tr>
<tr>
<td>Peak damaged area</td>
<td>Mg²⁺ 8</td>
<td>3.0 ± 0.1</td>
<td>5.0 ± 0.1</td>
</tr>
<tr>
<td>Al³⁺ 16</td>
<td></td>
<td>2.9 ± 0.3</td>
<td>13.1 ± 0.3</td>
</tr>
<tr>
<td>Vacancy</td>
<td>-</td>
<td>2.2 ± 0.3</td>
<td>0</td>
</tr>
</tbody>
</table>

CONCLUSIONS

It has been demonstrated that the high angular resolution electron channeling x-ray spectroscopy (HARECXS) is so sensitive to lattice-ion configuration in the illuminated areas that the occupation probabilities on specific positions in the crystal lattice can be determined with sufficient accuracy. HARECXS has successfully revealed partial disordering behavior in MgOₙAl₂O₃ spinel crystals as a function of composition and irradiation with 1 MeV Ne⁺ ions at 870 K. In contrast to strong preference of Al³⁺ lattice-ions to the octahedral (VIII) sites, Mg²⁺ lattice-ions possess relatively weaker tendency to reside in the tetragonal (IV) sites. Ne⁺-Ion irradiation induces not only cation disordering but also slight evacuation of cations from the IV-sites to the VIII-positions.

ACKNOWLEDGEMENTS

The authors should like to express their gratitude to Dr. Lynn Rehn for arrangements for this collaborative work of the two groups at KU and ANL. They are also indebted to Dr. C. J. Rossouw at CSIRO for his kind offer of the efficient calculation program and invaluable comments. This research was partly supported by the US Department of Energy under contract BES-MS W-31-109-Eng-38 and by the Grant-in-Aid for scientific research from the Ministry of Education, Science, Culture and Sports, Japan and from the Japan Society of Promotion of Science.

REFERENCES

[13] T. Soeda, PhD Thesis Research, in progress, Kyushu University,