

HIGH DOSE NEUTRON IRRADIATION OF MgAl_2O_4 SPINEL: EFFECTS OF POST-IRRADIATION THERMAL ANNEALING ON EPR AND OPTICAL ABSORPTION—A. Ibarra (CIEMAT. Inst. Investigación Básica), D. Bravo (Universidad Autónoma de Madrid), F. J. Lopez (Universidad Autónoma de Madrid), and F. A. Garner (Pacific Northwest National Laboratory)*

OBJECTIVE

The object of this effort is to explore the origins of radiation-induced changes in physical properties of ceramic materials proposed for use in fusion reactors.

SUMMARY

Electron paramagnetic resonance (EPR) and optical absorption spectra were measured during thermal annealing for stoichiometric MgAl_2O_4 spinel that was previously irradiated in FFTF-MOTA at $\sim 405^\circ\text{C}$ to ~ 50 dpa. Both F and F+ centers are to persist up to very high temperatures (over 700°C), suggesting the operation of an annealing mechanism based on evaporation from extended defects. Using X-ray irradiation following the different annealing steps it was shown that the optical absorption band is related to a sharp EPR band at $g=2.0005$ and that the defect causing these effects is the F+ center.

PROGRESS AND STATUS

Introduction

MgAl_2O_4 is a ceramic spinel material with rather high radiation resistance, at least from the point of view of maintaining its original mechanical and elastic properties [1-4]. That resistance makes this material suitable for applications in high radiation environments such as anticipated in fusion reactors. Other environments where MgAl_2O_4 would be useful are those which require a stable ceramic matrix such as in nuclear waste containment media or as substrates for optical devices manufactured using ion implantation. This resistance to radiation has been attributed to its structural characteristics, although the reason for this behavior is not fully understood. Proposed mechanisms involve a very high recombination rate of radiation-induced point defects or a very difficult formation of dislocation loops. In any case, it seems to be related to an exceptional tolerance of this material toward a high concentration of intrinsic defects even in the absence of radiation.

One example of this tolerance is that up to 30% cation antisite disorder have been found to occur in synthetic spinel crystals, inducing a very high concentration of traps for electrons (Al^{3+} in tetrahedral symmetry sites) and holes (Mg^{2+} in octahedral symmetry sites) [5]. Another example is that MgAl_2O_4 crystals always exhibit some significant deviation from stoichiometry, i.e. the composition can be described as $(\text{MgO})(\text{Al}_2\text{O}_3)_x$ with x close to but not exactly 1.0. Thus cation vacancies, mainly of tetrahedral type, are formed to compensate for the extra charge of Al^{3+} ions [6]. After high dose neutron irradiation it has been observed that the nucleation and growth of defect clusters is greatly inhibited, whereas the number of antisite defects increases enormously, in sharp contrast to the radiation response observed in other ceramic oxides [2, 7-9].

The present work is a continuation of an experimental series in which an extensive characterization was performed on stoichiometric MgAl_2O_4 spinel specimens that were irradiated at high temperatures to very high neutron exposures (50 to 200 dpa) in the FFTF fast reactor. In previous work the effect of irradiation temperature and total dose on stoichiometric spinels has been studied, with emphasis on point defect characteristics, using characterization techniques such as optical absorption, photoluminescence, electron paramagnetic resonance, electrical conductivity and others

*Pacific Northwest National Laboratory (PNNL) is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76.

[10-12]. These specimens have also been characterized using neutron diffraction [8], as well as mechanical and elastic properties [3, 4] and electron microscopy [5, 13].

It has been observed that these irradiations induced a large increase in the optical absorption, mainly in the ultraviolet-visual range as well as in some EPR bands. Generally speaking, the optical absorption increases in intensity with dose and decreases with increasing irradiation temperature. To gain more information about the details of these radiation-induced changes, it is desirable to study the annealing behavior of the radiation effects as a function of temperature. In particular, we report in this paper the results of a detailed study of annealing effects on both the optical absorption and electron paramagnetic resonance (EPR) spectra.

Experimental Details

The specimens studied were [100] oriented stoichiometric spinel single crystals from Union Carbide Corporation, in the form of 4.8 mm diameter cylindrical pellets. The details of impurity levels, specimen fabrication and irradiation are given in [3]. The specimen was irradiated in the Materials Open Test Assembly in the Fast Flux Test Facility (FFTF/MOTA) at a nominal temperature of 405°C to a total fluence of 5.3×10^{26} n/m² ($E > 0.1$ MeV), producing ~50 dpa. After irradiation, thin slices with thickness between 0.2 to 0.5 mm were cut and polished from the cylinders. The specimens were heated to 300°C to release all charges retained in shallow traps.

Optical absorption measurements were made at room temperature with a Cary 5E spectrometer between 3300 and 200 nm. EPR spectra were obtained with a Bruker spectrometer model ESP 300E working in the X-band. Accurate values of the microwave frequencies and magnetic fields were obtained with a Hewlett-Packard HP5342A frequency meter and a Bruker ER35 M gaussmeter, respectively. All spectra were measured with a modulation frequency of 100 kHz and modulation amplitude of 0.5 Gauss.

Some low dose X-ray irradiations were also performed at room temperature through a 1 mm thick aluminium plate at about 0.5 Gy/s with a Siemens Kristalloflex 2H (tungsten anode) operated at 50 kV and 30 mA. The purpose of these irradiations was to assist in the identification of the defect types created by neutron irradiation.

Annealing was performed in air, using a conventional air-cooled oven able to reach 1200°C. The ramp rate up to the maximum temperature and down to room temperature is 10 C/min. The stabilization time at high temperature was ~30 min.

Results and Discussion

Optical Absorption Measurements

Figure 1 shows the optical absorption spectra obtained after different annealing temperatures. Before the first annealing step, the observed spectrum shows very high absorption for energies over 34,000 cm⁻¹ (4.22 eV) and a peak at around 19,500 cm⁻¹ (2.42 eV). These results are in close agreement with those of previous studies [10].

The first annealing step was made at a temperature around 400°C close to the nominal irradiation temperature of 405°C. No annealing effect should be expected at temperatures lower than the irradiation temperature. As can be observed in Fig. 1, increasing the annealing temperature from 393 to 760°C induces a significant decrease in the magnitude of the optical absorption spectra, but the decrease is not uniform for all wavelengths. Clearly, it can be observed that the intensities at absorption energies below 46,000 cm⁻¹ anneal out faster than those in the deep UV range.

