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 Autonoma de Madrid), F. J. Lopez (Universidad Autonoma 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 ~405°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 a 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 $(MgO)(Al_2O_3)_x$ 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

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[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 x 10^{26} n/m^2 (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 300ºC 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

<u>Optical Absorption Measurements</u>

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.

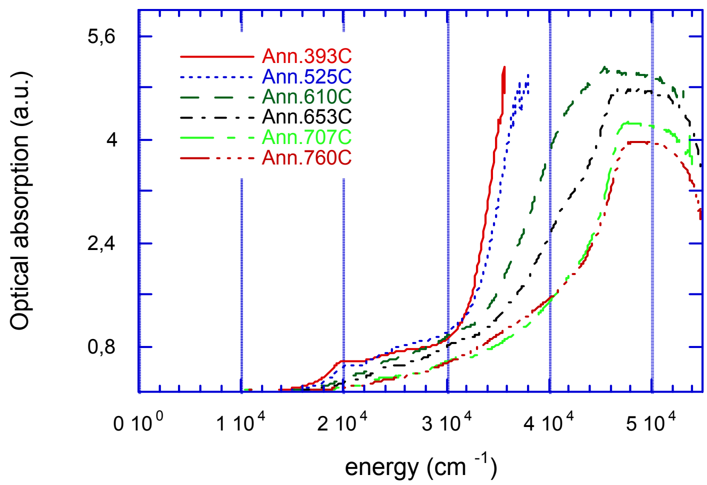

Fig. 1. Room temperature optical absorption spectra of neutron-irradiated $MgAl_2O_4$ annealed to temperatures between 400 and 760°C.

During annealing it is possible to observe that the measured optical absorption spectra are related to the presence of a number of different absorption bands. To improve the visibility of these bands Fig. 2 shows the difference spectra between the different annealing steps and the final step (after annealing at 760°C). This figure allows us to identify the optical absorption bands that are modified by the annealing process. The main annealing effect is related to the decrease of the intensity of a band around 42,000 cm^{-1} (5.21 eV). In addition, annealing of optical absorption bands at 19,500 (2.42 eV), 28,000 (3.47 eV) and 46,000 cm^{-1} (5.70 eV) was also observed.

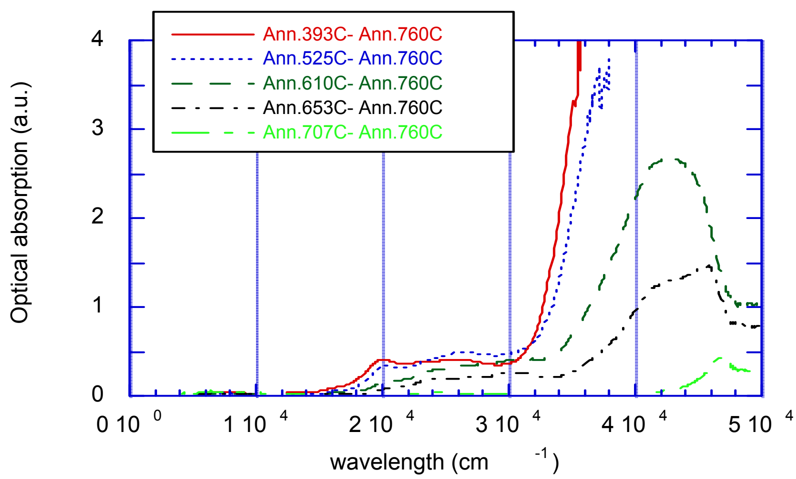

Fig. 2. Difference between the optical absorption spectra of neutron-irradiated $MgAl_2O_4$ annealed at different temperatures and the spectrum obtained after the 760°C annealing.

For temperatures higher than 760°C the specimen surface was degraded by reaction with the inner materials of the oven (mainly some kind of alumina), developing a white coating at the surface that precludes further optical measurements. This coating is now under study.

It is interesting to note that the band at 42,000 cm^{-1} has been also observed in neutron irradiated samples at lower doses and room temperature [14-17]. This band has been related to the presence of

F centers. Bands at 27,000 cm^{-1} and 18,800 cm^{-1} were also observed in these studies. These bands can be considered to be similar to those observed in this current work at 28,000 and 19,500 cm^{-1}, specially taking into account the fact that they are complex bands probably associated with defects with slightly different distorted surroundings [16, 18, 19]. Therefore, in the case of very high dose and high temperature irradiation, it seems reasonable to assume that these bands can appear at slightly different positions.

From comparison of our observed spectra with that observed in [14], it is quite clear that the relative height of the ultraviolet absorption compared with the one at 19,500 cm^{-1} is very similar, whereas the height of the bands in the region around 25,000-30,000 cm^{-1} are quite different. This suggests that the dose and temperature dependencies of the 19,500 cm^{-1} band and the ultraviolet absorption are similar, whereas the intensities of the other bands saturate at much lower doses.

Therefore, it seems that the defect responsible for absorption at 19,500 cm^{-1} is related to the defect responsible for the main ultraviolet absorption. It is also possible to observe that the annealing of the band at 19,500 cm^{-1} appears before the main annealing step since this band was not detected after the 610°C annealing. This behavior is also observed in the annealing process described in [14] but at a completely different temperature (in this work the 18,800 cm^{-1} band is only observed below 450°C. Again, this suggests that the band at 19,500 cm^{-1} is closely related to the ultraviolet bands. Taking into account that the ultraviolet bands are related to the oxygen vacancy defects (mainly F centers) it seems reasonable to relate the 19,500 cm^{-1} band to some oxygen vacancy defect, probably small clusters of two or three vacancies (giving rise to F2 or F3 defects). This proposal is further supported when taking into account that these type of defect also appears in the same energy region for Al_2O_3 or MgO [18, 20], and that they anneal out before the main F center annealing step.

At this point, it is important to note that these results suggest the presence of F centers in the irradiated material up to temperatures of 700°C. This is considered to be a very high temperature for stable F centers. For low dose, low temperature irradiations it has been found that optical bands related to V-centers anneal out for temperatures below 300°C [16, 21-23], whereas bands related to F centers usually anneal out below 500°C [14, 16, 22]. Similar results have been observed for annealing of damage produced in low-dose, low-temperature irradiations using electrons or ions [24]. Measurements of the vacancy centers during annealing made using other techniques such as positron annihilation [24] or length change [25] also provide similar information.

On the other hand, the annealing of specimens after high-dose, high-temperature irradiation shows a different behavior. From transmission electron microscopy studies it was observed that radiation-induced dislocation loops start to shrink around 725°C and completely disappear at 1200°C, whereas cavities grew slightly around 1300°C and then began to shrink with increasing annealing temperature [13]. Unfortunately, for these irradiation conditions there are no corresponding optical data.

For other irradiation conditions, such as high-dose, low-temperature irradiation, there are no neutron data, but some qualitative information can be obtained by analysing ion implantation results. In this case, the thermal annealing of radiation damage for ion implanted materials reaching the amorphization level shows that the crystallinity of the specimen recovers in a wide step starting at around 600°C and almost fully recovers by 1200°C [26]. This recovery behavior has been previously ascribed to the dissociation of defect clusters.

From these observations it can be concluded that in low-dose irradiations, vacancy centers in $MgAl_2O_4$ anneal out below 500°C in a process regulated by the mobility of point defects, whereas in high-dose irradiations, vacancy-related centers (such as the F center) can be observed at very high temperatures and their thermal stability is controlled by the thermal stability of defect clusters.

In addition to these bands, the data presented in Figs. 1 and 2, allow us to identify a band around 48,000-50,000 cm^{-1} that seems to anneal out at much higher temperatures. This band has not been previously observed in low-temperature, low-dose irradiations.

In summary, optical absorption spectrum changes induced by high-dose, high-temperature irradiation are composed of absorption bands at 50,000, 46,000, 42,000, 28,000 and 19,500 cm^{-1}. These bands anneal out at different temperatures in the range between 500 and 1000°C

EPR Results

The EPR spectra at room temperature of the irradiated specimen before the first annealing step consists of a band at g = 2.0005 ± 0.0005, as can be seen in Fig. 3. This type of band does not usually show any dependence on the orientation of the magnetic field with respect to the specimen. Band A is sharp, with a peak-to-peak width of 11 G in the derivative line. These results are in agreement with those previously published [27]. It was suggested earlier that this band could be related to F+ centers [19, 27].

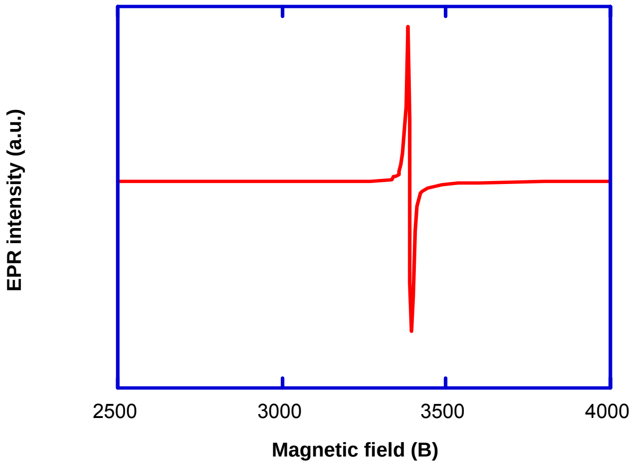

Fig. 3. Typical EPR spectrum obtained at room temperature for the neutron-irradiated $MgAl_2O_4$ specimen.

During annealing, the height of this band decreases with temperature, almost disappearing after the last heat treatment. Figure 4 shows the height of the measured band as a function of temperature. It is interesting to note that the decrease of the band takes place over the entire temperature range, and the observed behavior is similar to that observed for the 42,000 cm^{-1} absorption band.

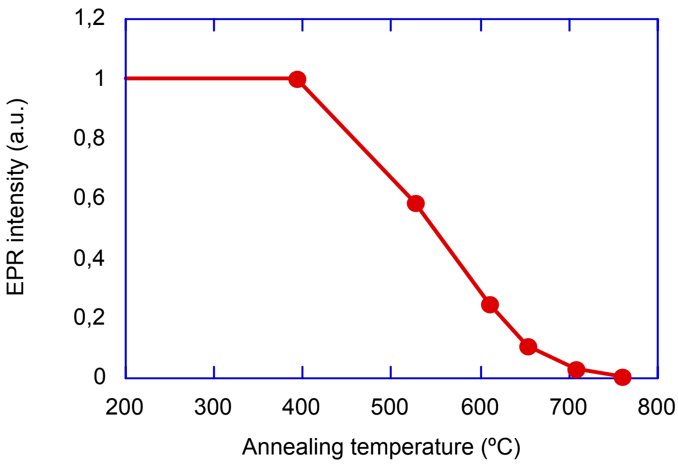

Fig. 4. Dependence on annealing temperature of the intensity of the EPR band measured in the $MgAl_2O_4$ specimen

Ionizing Radiation Effects

In order to determine if the observed annealing behavior is related to ionic or electronic effects, the samples were irradiated with X-rays after each annealing step, and the EPR and optical absorption properties were then measured both before and after the X-ray irradiation.

Before thermal annealing, no change of the spectra was found if a small level of X-ray irradiation was applied to the specimen. This is a very interesting result because before neutron irradiation, X-ray irradiation gives rise to a very characteristic and intense EPR spectra associated with the trapping of holes in cation vacancies (V-centers) [22]. The lack of this band in the optical and EPR spectra of neutron-irradiated specimens should indicate that there are no cation vacancies available, although this is unlikely taking into account that their concentration is very high even in the starting material, or that these vacancies are distorted in such a way that they cannot stabilize the holes at the cation sites. A similar mechanism has been suggested to explain the higher sensitivity to gamma irradiation of stoichiometric single crystal compared with non-stoichiometric ones [28]. This proposal is further supported by the results obtained for other neutron irradiations at lower doses and lower temperatures in which it has been observed that the V centers related optical and EPR characteristics are distorted by the irradiation and can be recovered after thermal annealing [14]. Most importantly, it should be noted that no recovery was observed in our case.

For X-ray irradiations made after annealing over 525°C there is clearly observed an increase of the absorption spectra after irradiation. In this case, as well as all the other annealing steps at higher temperatures, the dose dependence and the low temperature annealing of the ionizing radiation effect have been studied. In general, there is observed an increase of the optical absorption, mainly in the region around 37,000 cm^{-1} (4.59 eV) and also around 19,000 cm^{-1}. Figure 5 shows the increase of the optical absorption induced by different X-ray irradiations (i.e. the difference between the optical absorption spectra after and before X-ray irradiation) for the 610°C annealing step. It can be observed that the effect shows saturation behavior. The observed increase in optical absorption anneals out at temperatures below 400°C in a wide annealing step process that starts at room temperature and finishes around 400°C, similar to the annealing behavior observed for V-centers [22]. At the same time, it is observed that the previously mentioned EPR band also increases after X-ray irradiation and decreases during thermal annealing. Figure 6 shows the dose and temperature dependence of both processes for the optical absorption at 37,000 cm^{-1} and for the EPR band. It can be clearly observed that both bands behave in a similar way, indicating that they are closely related. In many papers this optical band has been related to the presence of F+ centers [14-23]. Taking this relationship into account, it can be clearly concluded, for the first time, that the observed EPR band is associated with F+ centers.

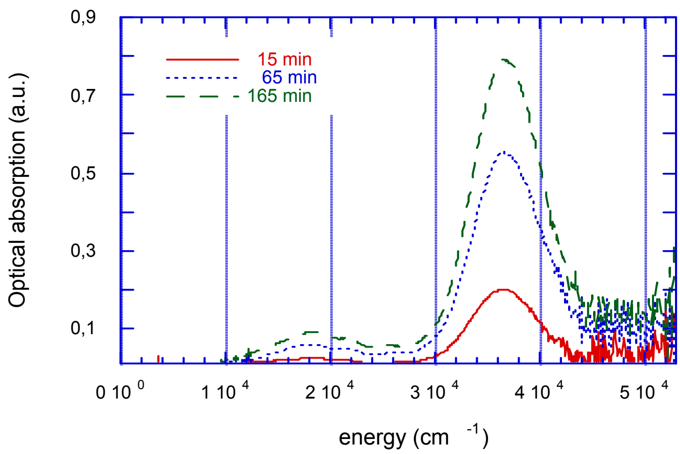

Fig. 5. Effects of different X-ray irradiations on the optical absorption spectra of neutron-irradiated $MgAl_2O_4$ specimen annealed at 610°C.

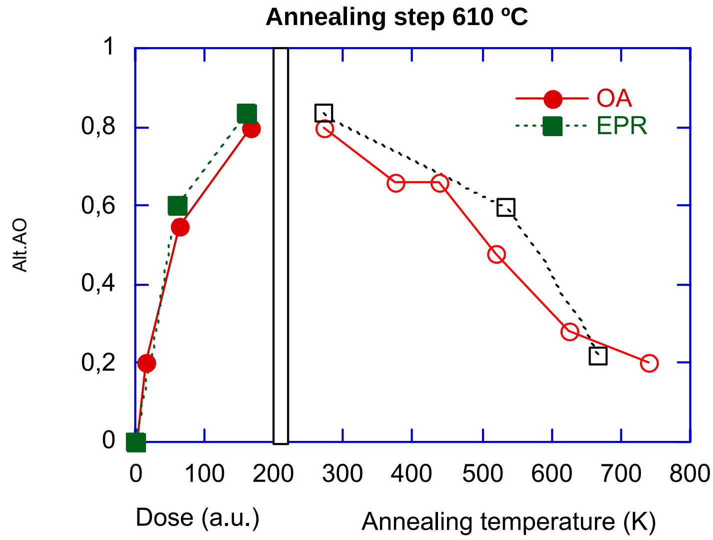

Fig. 6. Dependence on dose and thermal annealing of the X-ray effect on the neutron-irradiated $MgAl_2O_4$ specimen annealed at 610°C. (O) behavior of the optical absorption band at 37,000 cm^{-1} (□) behavior of the EPR band. Open symbols relate to the thermal annealing experiment and filled symbols relate to the dose dependence study.

Conclusions

The thermal annealing of the EPR and optical absorption characteristics of a $MgAl_2O_4$ specimen that was neutron-irradiated to 50 dpa at ~405°C has been studied. It was found that the main characteristics of both EPR and optical absorption spectra anneal out between 400 and 800°C. Both F and F+ centers are found to persist up to very high temperatures (over 700°C), suggesting the operation of an annealing mechanism based on evaporation from extended defects. It has also been demonstrated that a sharp EPR band with g=2.0005 in these irradiated specimens is related to the presence of F+ centers.

Acknowledgments

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