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Ion beam-induced luminescence as method of characterization of radiation damage in polycrystalline materials

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ABSTRACT

The problem of information about damage build-up, intensively studied for single crystals, poses many difficulties for polycrystalline materials. The Rutherford Backscattering/Channeling (RBS/C) technique could be applied for single crystals only, but its use is excluded in polycrystalline materials. Therefore the development of a quantitative method well suited for the evaluation of damage level in polycrystalline materials is a must, and still constitutes a major challenge in materials analysis. A comparative study of damage accumulation in magnesium aluminate spinel ($MgAl_2O_4$) has been conducted using ionoluminescence (IL) and RBS/C techniques. The results obtained by both methods, demonstrate a two-step character of damage build-up process. The values of the cross-section on the damage creation in each case were estimated using MSDA model. The results presented here confirm the huge potential of the luminescence techniques for damage analysis in single- and polycrystalline samples, and ability of the IL method to perform fast, *in situ* analysis of damage accumulation process.

1. Introduction

Magnesium aluminate spinel is one of the oxides envisaged to be used as inert matrix fuel. Most of the experiments focused on studies of radiation damage in spinel were performed on single crystals, mainly because of the use of Rutherford Backscattering/Channeling (RBS/C) method. A novel concept is to use luminescence techniques as an experimental method able to collect the signal related to the disorder level, as it may be applied to both single and polycrystalline solids, is non-destructive, fast and can be easily implemented *in situ*. Recently the growing interest of the ion-beam induced luminescence (IBIL or IL – ionoluminescence) method used for material characterization is observed. The ion-induced luminescence can be directly applied for characterization of scintillating materials [1]. The luminescent signal can also be used for the control of damage induced in materials by the ion implantation [2]. Actually, two different approaches may be used for the analysis of luminescence data. The simplest one consists in the measure of decay (or increase) of luminescence peak intensities as a function of the irradiation dose [3]. This kind of analysis may lead to the assessment of the damage build-up in irradiated solids. The results obtained should thus be similar to the outcome of RBS/C analyses. Consequently, the first proof of the potential use of the luminescence techniques for studies of damage accumulation is the comparison of the kinetics of the luminescence signal (defined as peak intensity vs. irradiation fluence) with the results of RBS/C experiments.

The IL technique has been chosen to analyze the damage formation in ion-irradiated $MgAl_2O_4$ single- and polycrystals. The main aim of the study is to evaluate the potential of the luminescence technique to analyze the damage accumulation process in irradiated materials with the special emphasis to polycrystalline solids. Although damage accumulation in irradiated materials has been studied for many years now, the problem of its quantitative analysis in polycrystals is still far from being solved. This is mainly due to the fact, that quantitative measurements of damage level are mostly performed via RBS/C technique which is limited to single crystals [4]. However, in practice, such as nuclear applications, polycrystalline materials are used very frequently. It is thus

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obvious, that an experimental method able to measure the level of disorder in polycrystals is badly needed.

2. Experiments

$MgAl_2O_4$ single crystal samples (commercially available) and polycrystalline samples obtained by the hot-pressing (Astro, Thermal Technology) of magnesium aluminate nanopowder, were irradiated with 320 keV Ar^+ ions at fluencies ranging from 1×10^{12} to 2×10^{16} cm^{-2} in order to create various levels of radiation damage. All irradiations were performed at room temperature; the Ar^+ beam power density was kept below 0.1 W/cm^2 to avoid significant samples' heating during irradiation. The ionoluminescence signal (IL) was measured using a homemade system based on the use of Hamamatsu spectrometer collecting the light from a sample installed inside a target chamber of an ion implanter (Balzers MPB 202RP). A H_2^+ ion beam with the energy of 86 keV was used to excite the luminescence. The ion beam current was kept at the level of 35 μA. To avoid the influence of the carbon layer appearing on the sample surface in the result of implantation, the luminescence signal collection was realized in the inverse geometry setup (Fig. 1a). It means, the analyzing H_2^+ ion beam was directed at the angle of 45° with respect to the Ar^+-irradiated sample surface, while the optical fiber guiding the emitted light to the spectrometer was placed at the back side of the sample. The analyzing H_2^+ beam energy and angle of incidence, i.e. the penetration depth and sampling volume in the result, was selected to conform with the depth of damage created during the irradiation of the sample with Ar^+ ions of energy 320 keV, i.e. approx. 200 nm (Fig. 1b and c). Thanks to this approach, the excitation of luminescence of the spinel samples was limited to the damaged layer, avoiding the generation of signal in the unirradiated bulk part.

The RBS/C measurements were performed using 2.2 MeV $^4He^{2+}$ ion beam. The RBS/C spectra were fitted using McChasy, a Monte Carlo simulation package allowing the quantitative analysis of channeling spectra [5]. The final outcome of this analysis is the damage accumulation kinetics, i.e. the plots of the damage level vs. the irradiation fluence.

3. Results and discussion

In the result of measurements carried out a set of luminescence spectra has been recorded. The raw signal for each sample with different fluencies of Ar^+ ions was analyzed in terms of signal intensity of the selected band. Fig. 2 presents the ionoluminescence spectra recorded on the polycrystalline $MgAl_2O_4$ samples before and after irradiations with Ar^+ ions in increasing fluencies. For the sake of the clarity, the spectra of virgin sample and first few fluencies are shown. The spectra exhibit two broad bands, first of which is positioned around 400 nm (consisting in fact of a few emission bands) and demonstrating strong intensity of the ionoluminescence signal. The presence of this band is assigned to transitions from the excited states to lower energy states of the Mn^{2+} ion usually present in the synthetic spinels [6]. The second band positioned around 690 nm is much weaker and attributed to Cr^{3+} doping of the $MgAl_2O_4$ [7]. The intensity of both bands rapidly decreases with the irradiation fluence. Similar spectra were observed in the case of monocrystalline samples.

The approach used for the assessment of the radiation damage build-up in the irradiated samples was based on the analysis of the decay of the IL signal as the function of the Ar^+ ions irradiation fluence. The aim of the analysis was to compare the results obtained for monocrystalline samples using IL data with the quantitative results obtained with RBS/C technique (information on the damage level, f_D, and kinetics of the damage accumulation), so as to be able to better interpret the ionoluminescence data. The fluence of the H_2^+ ions being transferred to the sample during every second of measurements reached a value of 2.8×10^{12} cm^{-2}. It was observed, that the shape of the luminescence spectrum evolves with measurement time, likely due to the damage caused by H_2^+ ions. For that reason the raw data analyzed and presented in Fig. 3 were collected during the first full second after the beginning of IL signal generation. A part of the luminescent band (300–350 nm) appearing resistant to any changes in time of measurement (for specified Ar^+ fluence) has been chosen as the base of quantitative data analysis in each case. The integrated intensities of the selected portion of each spectrum were plotted versus the fluence of Ar^+ ions, as shown in Fig. 3. The type of analysis described above has been performed for both, mono- and polycrystalline samples.

The results of IL and RBS/C analysis were then fitted using Multi-Step Damage Accumulation (MSDA) model [8]. That allowed for the determination of damage build-up kinetics, and finally cross-section for radiation damage build-up based on the luminescence signal analysis. The results of quantitative analysis based on the luminescence (IL) signal for monocrystalline samples were subsequently compared with the results of such an analysis performed on polycrystalline samples. That way we tried to found a mutual "language" for interpretation of damage accumulation process in mono- and polycrystalline materials using luminescence data.

It is worth noting that the intensity of the luminescence signal decreases with the irradiation fluence, whereas the f_D parameter (extracted from RBS/C analysis), which describes the level of radiation damage, increases [9]. In order to compare the luminescence and channeling results it was necessary to transform the ionoluminescence data in the form similar to the RBS/C results. For that reason, the integrated intensity of the IL signal at a given fluence, I_x, was transformed into reduced values, $I_{x,red}$, defined as:

$$I_{x,red} = (I_0 - I_x)/I_0 \quad (1)$$

where I_0 is the IL signal intensity recorded for unimplanted sample.

The reduced value of IL signal mimics the behavior of the f_D parameter, i.e. it is equal to 0 for unimplanted sample and 1 for the sample with no luminescence signal recorded (Fig. 3). The proper selection of the ion energy used for the IL analysis (i.e. when the projected range of hydrogen ions used to excite the IL signal is equal to the projected range of 320 keV Ar ions used for damage creation) reduced completely luminescence originating from deep, unmodified part of the crystal. In the case studied a complete decay of the IL intensity was observed at the fluence of Ar^+ ions equal to 1×10^{14} cm^{-2}.

The results of the analysis performed for monocrystalline and polycrystalline spinel samples, as well as the MSDA fits, are presented in Figs. 3 and 4. In case of both, i.e. single- and polycrystalline samples, the changes of the reduced intensity of the IL signal with irradiation fluence exhibit a two-step character, although step 2 represents less than 5% of the signal (step 1 reaching ∼0.95). The two-step behavior of the changes of IL signal is in agreement with the RBS/C data analyzed with MSDA model (Fig. 4). However, the threshold value of the irradiation fluence in the case of IL signal is different from the RBS/C result (2×10^{13} cm^{-2} vs. 1×10^{15} cm^{-2}, respectively). These differences may be due to the fact, that RBS/C values are taken at damage peak maximum, whereas the IL data are averaged over the whole damaged layer. The values of the parameters for mono- and polycrystalline samples obtained by fitting RBS/C and IL data with the MSDA model are summarized in Table 1.

The character of the IL signal decrease (or increase in the reduced IL signal) is very similar in the case of single- and polycrystalline spinel samples (Fig. 3). That confirms the luminescence technique as the proper investigation tool, which may be used for