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Accumulation and recovery of disorder in Au^{2+}-irradiated $Cd_2Nb_2O_7$

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Abstract

Cadmium niobate pyrochlore ($Cd_2Nb_2O_7$) single crystals have been irradiated at 150, 300, 450 and 600 K using 1.0 MeV Au^{2+} ions over fluences ranging from 0.01 to 3.5 ions/nm^2. The relative disorder on the Cd sublattice in the as-irradiated $Cd_2Nb_2O_7$ has been analyzed based on in situ 3.0 MeV He^+ Rutherford backscattering spectrometry along the $\langle 1\,0\,0\rangle$-axial channeling direction. The results show that the crystal can be readily amorphized under the Au^{2+} irradiation at or below 450 K; however, the relative Cd disorder tends to saturate at 600 K, and full amorphization does not occur at doses up to 5 dpa. Isochronal annealing (20 min) also has been performed at temperatures from 180 to 295 K for samples irradiated at 150 K. Thermal recovery of the disorder has been observed below room temperature.

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Keywords: Ion irradiation; Lattice disorder; Ion channeling; Pyrochlores

1. Introduction

Pyrochlore crystals exhibit a variety of interesting properties, including ionic conduction [1], catalytic activity [2] and fluorescence [3]. In addition, rare-earth titanate and zirconate pyrochlores are recognized as having a great potential for immobilization and permanent disposal of high-level radioactive nuclear wastes [4,5]. Following the successful growth of large-area $Cd_2Nb_2O_7$ single crystals at Oak Ridge National Laboratory, Rutherford backscattering spectrometry under channeling conditions (RBS/C) has been utilized [6,7] to study the disordering processes in the material. The study [7] of the disorder accumulation of $Cd_2Nb_2O_7$ at 150 and 300 K has shown a lower disordering rate at 300 K due to dynamic recovery. Considerable recovery of the disorder

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produced in $Cd_2Nb_2O_7$ at 150 K occurs during room-temperature annealing for an extended time (38 h); in contrast, the disorder produced at 300 K has been found stable at room temperature [7]. In a separate study [8], it has been revealed that high-dose ion irradiation can effectively decompose $Cd_2Nb_2O_7$ crystals; as a result, formation of gas-filled blisters takes place at or below room temperature. Further irradiation at higher doses results in blister rupture and surface exfoliation [8]. This study reports the disordering behavior in $Cd_2Nb_2O_7$ at low, ambient and elevated temperatures. In addition, the results of isochronal recovery of the Cd disorder produced at 150 K are also reported.

2. Experimental procedures

The single-crystal wafers of $Cd_2Nb_2O_7$ used in this study were grown, cut and Syton polished on the (1 0 0) plane at Oak Ridge National Laboratory [6]. Ion irradiation and in situ RBS/C experiments were performed at Pacific Northwest National Laboratory. The specimens were irradiated 60° off the surface normal at 150, 300, 450 and 600 K using 1.0 MeV Au^{2+} ions. The typical ion flux was on the order of 0.001 $Au^{2+}/nm^2/s$. A high-energy (3.0 MeV) He^+ beam was selected to improve mass resolution for the RBS/C analysis of the Au^{2+} irradiation-induced lattice disorder; the He^+ RBS/C experiment was carried out along the ⟨1 0 0⟩ axis at a scattering angle of 150°. For the Au^{2+} irradiation at 150 K, the irradiated specimens were maintained at or below the irradiation temperature during the interim technical procedures for switching Au^{2+} to He^+ and for realigning the irradiated crystal to the incident He^+ beam; RBS/C spectra were measured in situ at that low temperature. For irradiation at 300 K or higher, disorder measurements were performed at room temperature. These procedures are considered important to minimize the thermal recovery of disorder in the specimens prior to the RBS/C analysis. Subsequent to the initial RBS/C measurements, some of the low-dose areas were irradiated for a second time to achieve higher doses and a similar procedure for the disorder analysis in these areas was followed. Additional Au^{2+} irradiation at 150 K was performed in different areas of a $Cd_2Nb_2O_7$ specimen for two fluences of 0.030 and 0.037 Au^{2+}/nm^2. In situ isochronal annealing was subsequently conducted at temperatures from 180 to 270 K, with an increment of 30 K, and then at 295 K for 20 min at each temperature. The remaining disorder in the annealed specimen was determined in situ at lower than the corresponding annealing temperatures using the same ion-channeling methods. The conversion factor from ion fluence in Au^{2+}/nm^2 to dose in displacement per atom (dpa) at the depth of damage peak, which was calculated [7] based on the SRIM-97 [9] full-cascade simulations, corresponds to 1.466 under the irradiation conditions.

3. Results and discussion

The in situ RBS/C spectra for $Cd_2Nb_2O_7$ irradiated at 450 K to various Au^{2+} fluences are shown in Fig. 1, along with random and ⟨1 0 0⟩-aligned spectra from an unirradiated area. The unirradiated sample has a minimum yield of less than 4%, indicating good crystal quality prior to ion irradiation. Although the damage peaks on the

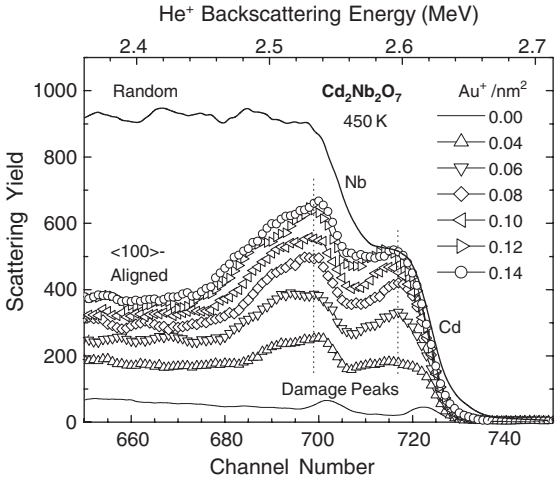

Fig. 1. A sequence of 3.0 MeV He^+ RBS/C spectra for a ⟨1 0 0⟩-oriented $Cd_2Nb_2O_7$ single crystal irradiated at 450 K with 1.0 MeV Au^{2+} ions. Also included are random and ⟨1 0 0⟩-aligned spectra from an unirradiated area.

Cd and Nb sublattices are clearly identifiable at the indicated ion fluences (Fig. 1), the RBS/C spectra for the two sublattices overlap over a range of backscattering energy. This condition does not allow for a precise analysis of the depth profiles of disorder on either of the sublattices unless a complicated deconvolution procedure or computer simulation is applied. However, evaluation of the relative disorder at the damage peak is still possible by properly subtracting the random fractions using a linear dechanneling approximation [10,11]. This has been done in this study under the assumptions of the same width of the damage profiles on the Cd and Nb sublattices (predicted by SRIM-97 [9]) and comparable dechanneling contributions from each of the sublattices (due to similar atomic numbers for Cd and Nb [12]). Additional discussion about the data analysis has been provided elsewhere [7]. Since the Nb spectra superimpose the Cd spectra (Fig. 1), a larger error bar for the relative disorder on the Nb sublattice is expected. In this report, only the Cd data for the disorder accumulation and recovery are presented and discussed.

It should be noted that although the shift in the depth of damage peaks is minimal with the increase of ion fluence at 150 K (Fig. 1), this shift to greater depths for both the Cd and Nb sublattices is apparent at 600 K for fluences higher than 2.1 Au^{2+}/nm^2 (data not shown). Similar depth shift has been observed in Au^{2+}-irradiated 6H-SiC at 550 K [13], where the shift of the damage peak was attributed primarily to thermal diffusion/migration of defects. A similar interpretation may be applicable to the depth shift in this study, i.e. Cd diffusion/migration to the Au-rich region at the elevated temperature (600 K).

The dependence of the relative Cd disorder at the damage peak on dose (dpa) or ion fluence (Au^{2+}/nm^2) is shown in Fig. 2 for Au^{2+} irradiation at various temperatures, where full amorphization corresponds to a value of unity (1.0) on the vertical scale. The solid lines in Fig. 2 are generic sigmoidal fits to the data. The results previously reported for 150 and 300 K [7] are also included in the figure for comparison. From Fig. 2, there is a general dose shift to larger values for the higher irradiation temperatures. This behavior is primarily associated

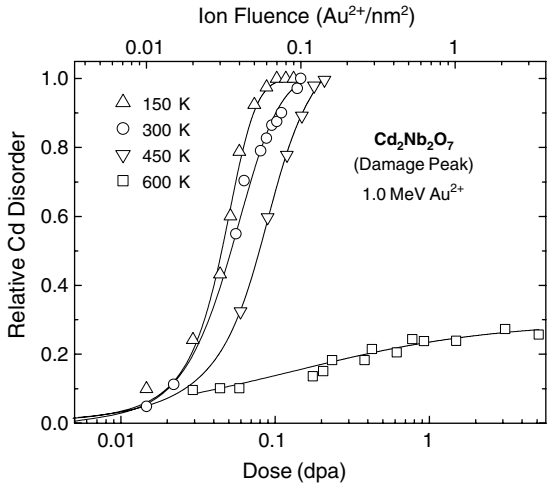

Fig. 2. Relative disorder on the Cd sublattice as a function of dose at the damage peak in $Cd_2Nb_2O_7$ irradiated at 150 [7], 300 [7], 450 and 600 K with 1.0 MeV Au^{2+} ions. The solid lines are sigmoidal fits to the data.

with the dynamic recovery during the Au^{2+} irradiation, and higher temperature leads to more dynamic recovery. Similar sigmoidal disordering behavior also has been reported for the Cd sublattice in $Cd_2Nb_2O_7$ irradiated with lighter ions (Ne^+ and Xe^{2+}) at room temperature [6]; however, the disorder accumulation curves for the lighter ions shifted to higher doses due to the ion mass (damage energy density) effect. From Fig. 2, the amorphization dose increases from 0.10 dpa at 150 K, 0.15 dpa at 300 K to 0.20 dpa at 450 K, which represent small dose values as compared to those for some other materials under similar irradiation conditions [14,15], yet a steady increase in the dose. This tendency is consistent with the TEM observations for Xe^{2+} ion irradiation of $Cd_2Nb_2O_7$ [6]. At 600 K, full amorphization does not occur at doses up to 5 dpa. The relative Cd disorder increases gradually with dose and tends to saturate at higher doses. The results suggest that the critical temperature for amorphization in $Cd_2Nb_2O_7$ under the Au^{2+} irradiation conditions is below 600 K, which is lower than the reported data (620 K) for Xe^{2+} irradiation [6]. The difference may be due to the dose-rate effect at the elevated temperatures since the ion flux in the Xe^{2+} irradiation experiment is about 17 times as high as that in this study. A

strong dose-rate effect has been observed in 4H-SiC irradiated with Al_2^{2+} ions at 450 K [16]. Additional data for temperatures between 450 and 600 K, along with model analysis of the data, are needed to better understand the disordering and amorphization behavior in $Cd_2Nb_2O_7$.

Fig. 3 shows the 20-min isochronal annealing results for $Cd_2Nb_2O_7$ irradiated to 0.030 and 0.037 Au^{2+}/nm^2 in different areas at 150 K. The relative disorder for the as-irradiated samples is reasonably consistent with the previous data [7], also shown in Fig. 2. There is a similar annealing behavior for the two fluences, featuring a gradual recovery of disorder over the temperature range. Although the recovery rate is small at the low temperatures, the results indicate that some of the recovery processes are still active below room temperature. However, distinct recovery stages are not observed. The two data points for the higher fluence at 180 and 210 K show some statistical fluctuations at the damage peak. It should be pointed out that the deviation of the data point for 0.037 Au^{2+}/nm^2 at 295 K from the fitting curve is associated with the gas blister formation that causes deformation of the local crystal structure and enhances the backscattering yield. Further irradiation with 3.0 MeV He^+ ions at room temperature resulted in a significant increase in the backscattering yield on both Cd and Nb sublattices, followed by surface exfoliation at the analyzing spot (data not shown). For the lower dose spot, similar exfoliation occurred as a result of further irradiation at room temperature. This observation is consistent with a previous report [8]. For this reason, data for higher temperature annealing are not achievable from this experiment. Again from Fig. 3, the recovered fractions at room temperature correspond to ~0.15 and ~0.20 for the fluences of 0.030 and 0.037 Au^{2+}/nm^2, respectively, which agree well with the results reported previously [7], where comparable and higher damage levels were involved.

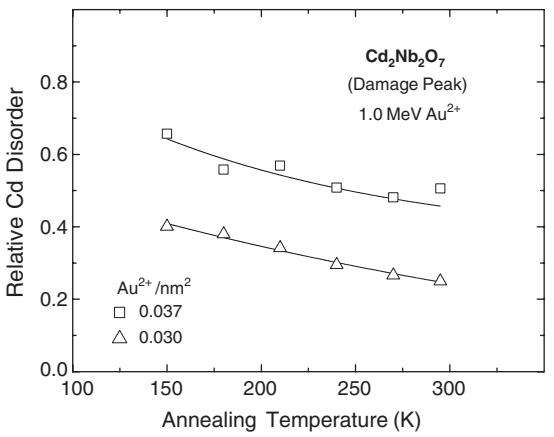

Fig. 3. Isochronal recovery (20 min) of relative disorder on the Cd sublattice at the damage peak in $Cd_2Nb_2O_7$ irradiated at 150 K to 0.030 and 0.037 Au^{2+}/nm^2 as a function of annealing temperature. The solid lines are drawn to assist the eye.

4. Conclusions

Disorder accumulation in $Cd_2Nb_2O_7$ irradiated with Au^{2+} ions at 150, 300 and 450 follows a sigmoidal dependence of relative disorder on dose. The dose required for full amorphization of the material increases from 0.10 dpa at 150 K to 0.20 dpa at 450 K. Irradiation at 600 K does not lead to full amorphization in $Cd_2Nb_2O_7$ up to 5 dpa. There is only a gradual recovery of disorder produced at 150 K over the temperatures ranging from 180 to 295 K, where distinct recovery stages are not observed.

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