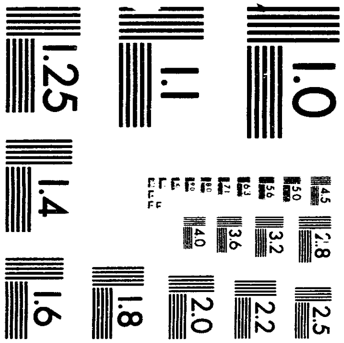
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EFFECT OF TEMPERATURE AND RECOIL-ENERGY SPECTRA ON IRRADIATION-INDUCED AMORPHIZATION IN $Ca_2La_8(SiO_4)_6O_2$

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Effect of temperature and recoil-energy spectra on irradiation-induced amorphization in $Ca_2La_8(SiO_4)_6O_2$

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Single crystals of $Ca_2La_8(SiO_4)_6O_2$ have been irradiated with different ions/energies in an *in situ* study of the effects of temperature and recoil-energy spectra on irradiation-induced amorphization. The dose for compete amorphization increases with temperature in two stages. The low-temperature stage (below 250 K) has an activation energy of 0.01 ± 0.003 eV and is believed to be associated with simultaneous close-pair recombination. The high-temperature stage (above 250 K) has an activation energy of 0.13 ± 0.02 eV and may be associated with irradiation-enhanced defect mobility. The critical temperature for amorphization increases from ~360 K for 0.8 MeV Ne^+ to ~710 K for 1.5 MeV Kr^+. At 15 K, the amorphization dose is ~0.36 dpa and is independent of recoil-energy spectra. The amorphization dose increases more rapidly with temperature for Ne^+ due to the larger fraction of mobile defects produced by the low energy recoils. The temperature dependence is similar for 1.0 MeV Ar^+, 1.5 MeV Kr^+, and 1.5 MeV Xe^+.

1. Introduction

A recent study of polycrystalline $Ca_2Nd_8(SiO_4)_6O_2$ doped with ^{244}Cm [1,2] indicates that irradiation-induced amorphization in this material occurs directly within the collision cascade of the heavy recoil nuclei (Pu) emitted during alpha decay of Cm and that the fully amorphous (bulk) state is reached at a dose equivalent to about 0.3 dpa. However, in another study of polycrystalline $Ca_2Nd_8(SiO_4)_6O_2$ [3], He^+ ion irradiations at room temperature (up to 0.46 dpa) and Ar^+ ion irradiations at elevated temperatures (up to 14.5 dpa) produce no loss of crystallinity. In order to understand this behavior and to contribute to the basic understanding of irradiation-induced amorphization in complex silicates, a systematic study of ion-beam-induced amorphization in single crystal $Ca_2La_8(SiO_4)_6O_2$ has been undertaken as part of a larger collaborative effort, which includes other orthosilicates [4,5], to investigate the effect of topological complexity on irradiation-induced amorphization. This paper expands on previous results [6] and addresses the effects of temperature and recoil-energy spectra on irradiation-induced amorphization in $Ca_2La_8(SiO_4)_6O_2$.

2. Experimental procedures

The single crystals of $Ca_2La_5(SiO_4)_6O_2$ were grown from a stoichiometric melt by the Airtron Corp. and have been characterized (JCPDS Card 29-337) as having the hexagonal apatite ($P6_3/m$) structure with lattice parameters: $a_o = 0.9651(3)$ nm and $c_o = 0.7151(2)$ nm. Specimens with [001] orientations were cut as thin sections from the crystals and prepared as TEM specimens by Ar^+ ion milling. The irradiations were carried out at the HVEM-Tandem Facility at Argonne National Laboratory. This facility consists of a modified Kratos/AEI EM7 high voltage electron microscope (HVEM) and a 2 MV tandem ion accelerator [7]. All irradiations were performed 5 to 10° off the zone axis of the oriented specimens. Irradiations with 0.8 MeV Ne^+ and 1.5 MeV Kr^+ ions over the temperature range from 15 K to 773 K were performed to investigate the temperature dependence of amorphization. Additional irradiations were performed at 300 K with 1.0 MeV Ar^+ and at 15 K and 300 K with 1.5 MeV Xe^+ ions to investigate the effects of recoil-energy spectrum on irradiation-induced amorphization. The displacements generated per ion as a function of depth in the electron transparent thickness (~200 nm), as shown in Fig. 1, were calculated using TRIM-90 (full cascades) [8], a specimen thickness of 200 nm, and an assumed displacement energy of 25 eV. The displacement dose (dpa) for complete amorphization was calculated at a depth of 100 nm (center of thin region).

3. Results and discussion

The progression of the amorphization process during irradiation of the single crystal $Ca_2La_8(SiO_4)_6O_2$ specimens was followed in the electron transparent thickness of the specimens by *in situ* transmission electron microscopy and selected area electron diffraction. At low doses, a diffuse halo associated with the presence of amorphous material appeared in the electron diffraction patterns. The intensity of this diffuse halo increased with increasing dose, while the intensity of the diffraction maxima from the remaining crystalline material decreased and eventually disappeared at the dose for complete amorphization. This evolution of the amorphous state is shown in Fig. 2 for 1.5 MeV Kr^+ ion irradiations at 300 K.

The effects of temperature on the fluence for complete amorphization of $Ca_2La_8(SiO_4)_6O_2$ under 0.8 MeV Ne^+ and 1.5 MeV Kr^+ ion irradiations are shown in Fig. 3. At 15 K, the dose for complete amorphization is 0.32 and 0.38 dpa for the 0.8 MeV Ne^+ and 1.5 MeV Kr^+ irradiations, respectively, indicating that within experimental error (±10%) the amorphization dose is independent of recoil-energy spectra at this temperature. For both ions (Fig. 3), the dose for complete amorphization increases with temperature in two stages. The first stage (Stage I, 15 to 250 K) is probably associated with a close-pair recombination process within the cascade. By 250 K, the Stage I annealing process is completed. Above 250 K (Stage II), the dose for complete amorphization increases at a different rate with temperature; this increase may be associated with irradiation-enhanced defect mobility. The more rapid increase in amorphization dose with temperature for Ne^+ is probably due to the larger fraction of mobile defects produced by the low energy recoils, as discussed below. At 423 K, only partial amorphization could be produced under Ne^+ irradiation to 15 dpa. Irradiation with Kr^+ to 4.4 dpa at 773 K produced no observable amorphization.

The effects of temperature on amorphization can be described by an activation energy, E_a, associated with each annealing stage that decreases the average amorphous volume produced per cascade [6]. Under the conditions employed in this study, irradiation at elevated temperatures decreases the rate at which the amorphous fraction, f_a, accumulates at a constant ion flux. Although other amorphization mechanisms may be active, it is assumed, both for simplicity and based on previous work [1,2], that amorphization occurs directly within the collision cascade for this material. In the absence of annealing, the rate of direct-impact amorphization (per unit time) is given by the expression:

$$df_a/dt = \phi\sigma\,(1 - f_a) \qquad (1)$$

where ϕ is the ion flux, σ is the cross section for direct amorphization, and the term $(1 - f_a)$ accounts for the decrease in crystalline material available for amorphization (i.e., the probability that the ion will penetrate undamaged material). Generally, the effect of simultaneous thermal annealing is taken into account by adding a term, $(-f_a/\tau)\exp(-E_a/kT)$, to the above equation [9]; however, this leads to a solution that predicts incomplete amorphization at elevated temperatures, a maximum value of f_a that decreases with increasing temperature, and significant post-irradiation recrystallization at these temperatures (all contrary to the experimental results observed in this study, as well as in another study [5]). If the effect of temperature is assumed to decrease only the incremental volume of amorphous material produced per ion by thermally-enhanced in-cascade annealing or some other irradiation-enhanced annealing process, then df_a/dt may be written as

$$df_a/dt = (\phi\sigma - \tau^{-1}\exp[-E_a/kT])\,(1 - f_a) \qquad (2)$$

where τ is a time constant, E_a is the activation energy for the annealing process, and the term $\tau^{-1}\exp[-E_a/kT]$ accounts for the temperature dependent decrease in amorphous volume produced per collision cascade. Integration of this expression, along with the appropriate boundary conditions ($f_a = 0$ at $t = 0$), yields an expression of the form:

$$f_a = 1 - \exp[-\phi\sigma t + (t/\tau)\exp(-E_a/kT)]. \qquad (3)$$

At elevated temperatures, the relationship between time and temperature to achieve the same level of damage (same f_a) as defined by the time, t_o, at T = 0 K can be expressed as

$$\ln(1 - t_o/t) = \ln(1/\phi\sigma\tau) - E_a/kT. \qquad (4)$$

Since the ion flux is a constant in this study and the displacement dose is proportional to the ion fluence, ϕt, the above expression can be rewritten as

$$\ln(1 - D_o/D) = \ln(1/\phi\sigma\tau) - E_a/kT \qquad (5)$$

where D_o is the dose for complete amorphization at 0 K for a single annealing process. Equation 5 is similar to the expression derived by Morehead and Crowder [10]; however, in their model, D_o/D in Eq. 5 would be replaced by $(D_o/D)^{1/2}$ or $(D_o/D)^{1/3}$.

By applying the above model (Eq. 5) to the data in Fig. 3, the activation energy, E_a, can be determined from an Arrhenius type plot of $\ln(1 - D_o/D)$ versus $1/kT$. The amorphization dose, D_o, at T = 0 K associated with Stage I annealing is 0.36 and 0.32 dpa for Ne^+ and Kr^+ ions, respectively. The characteristic dose, D_o, for Stage II annealing (amorphization dose at 0 K under the conditions of complete Stage I recovery at 0 K) is estimated to be 0.52 and 0.80 for the Ne^+ and Kr^+ irradiations, respectively. The results of this analysis, along with a linear fit, are shown in Fig. 4. The activation energies determined for each stage are nearly identical for both the Ne^+ and Kr^+ irradiations, consistent with the presence of similar irradiation-produced defects, although the relative concentrations are different. The activation energy determined by linear regression for Stage I annealing is 0.01 ± 0.003 eV, and the activation energy determined for Stage II annealing is 0.13 ± 0.02 eV. These values are considerably less than the activation energy for thermal recrystallization (3.1 eV) previously determined for fully amorphous $Ca_2Nd_8(SiO_4)_6O_2$ [11]. These activation energies, however, are similar in magnitude to activation energies previously reported for irradiation-enhanced epitaxial recrystallization in other materials [9,12].

In addition to the activation energy, the critical temperature, T_c, above which complete amorphization does not occur ($D = \infty$), can be determined from the linear fit to the data in Fig. 4. Since $\ln(1 - D_o/D) \rightarrow 0$ as $D \rightarrow \infty$, Eq. 5 yields the following expression for T_c:

$$T_c = E_a / [k \ln(1/\phi\sigma\tau)]. \tag{6}$$

Based on the activation energy, E_a, and intercept, $\ln(1/\phi\sigma\tau)$, determined for Stage II annealing, T_c is estimated to be ~360 K under the Ne^+ irradiation conditions and ~710 K under the conditions for the 1.5 MeV Kr^+ irradiations. This increase in T_c with projectile mass (average recoil energy transferred) is similar to behavior previously reported in Si [10] and CuTi [13].

In addition to the irradiations discussed above, irradiation with 1.0 MeV Ar^+ at 300 K and 1.5 MeV Xe^+ ions at 15 and 300 K also induced a crystalline to amorphous transformation. The effects of recoil energy spectra on the dose for complete amorphization at 15 and 300 K are summarized in Fig. 5 by a plot of amorphization dose as a function of the average energy transferred to recoils (calculated at 100 nm). Within experimental uncertainty, the dose for complete amorphization at 15 K (~0.36 dpa) is independent of recoil-energy spectra for the Ne^+, $Kr^+$and Xe^+ irradiations. At 300 K, the dose for complete amorphization increases for all ions, consistent with the effects of temperature. The dose at 300 K (0.57 dpa) is independent of recoil energy spectra for the Ar^+, Kr^+, and Xe^+ irradiations, which suggests that the recoverable (mobile) defect concentrations are similar for these heavy-ion irradiations. On the other hand, the amorphization dose at 300 K for the Ne^+ irradiations at both a factor of 2 and a factor of 7 higher ion flux is 1.39 dpa, which is significantly (2.5 times) higher than for the heavier ions. The Ne^+ results, which indicate no significant dose rate effect, reflect enhanced defect recovery at 300 K, as discussed above, due to a change in the nature of the damage produced (larger fraction of mobile defects and smaller cascades) from the low-energy recoils produced by the Ne^+ ions. The results suggest that the fraction of closely-spaced defects produced under the Ne^+ irradiations is about 2.5 times higher than under the heavy-ion irradiations. Also included in Fig. 5 is the amorphization dose (~0.30 dpa) reported previously for the lower-dose-rate (3 x 10^{-9} dpa/s) 95 keV Pu recoil effects in polycrystalline Cm-doped $Ca_2Nd_8(SiO_4)_6O_2$ [1,2], where amorphization primarily occurs directly within the displacement cascade of the Pu recoil. The results from the present study indicate that the amorphization dose at 300 K under the high-dose-rate (~10^{-4} to 10^{-3} dpa/s) heavy-ion irradiations is about a factor of 2 higher than for the Cm-doped polycrystalline material; this effect may be due to a higher efficiency of the Pu-recoil nucleus for the amorphization process (direct-impact amorphization, with few defects), since this amorphization dose is similar to that observed at 15 K under ion irradiation. Based on the above results, it is not surprising that previous irradiation of $Ca_2Nd_8(SiO_4)_6O_2$ with He^+ ions (<1 eV/nm/ion) to 0.46 dpa [3] does not result in observable amorphization.

Acknowledgements

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Figure Captions

Fig. 1. Calculated displacement damage based on TRIM-90 [8].

Fig. 2. Electron diffraction patterns of $Ca_2La_8(SiO_4)_6O_2$ after irradiation with 1.5 MeV Kr^+ ions at 300 K. (A) Unirradiated, (B) 0.22 dpa, (C) 0.33 dpa, and (D) 0.51 dpa.

Fig. 3. Temperature dependence of amorphization in $Ca_2La_8(SiO_4)_6O_2$.

Fig. 4. Arrhenius plot of $\ln(1 - D_0/D)$ versus 1/kT in $Ca_2La_8(SiO_4)_6O_2$.

Fig. 5. Dependence of amorphization dose in $Ca_2La_8(SiO_4)_6O_2$ on the average energy transferred to recoils.

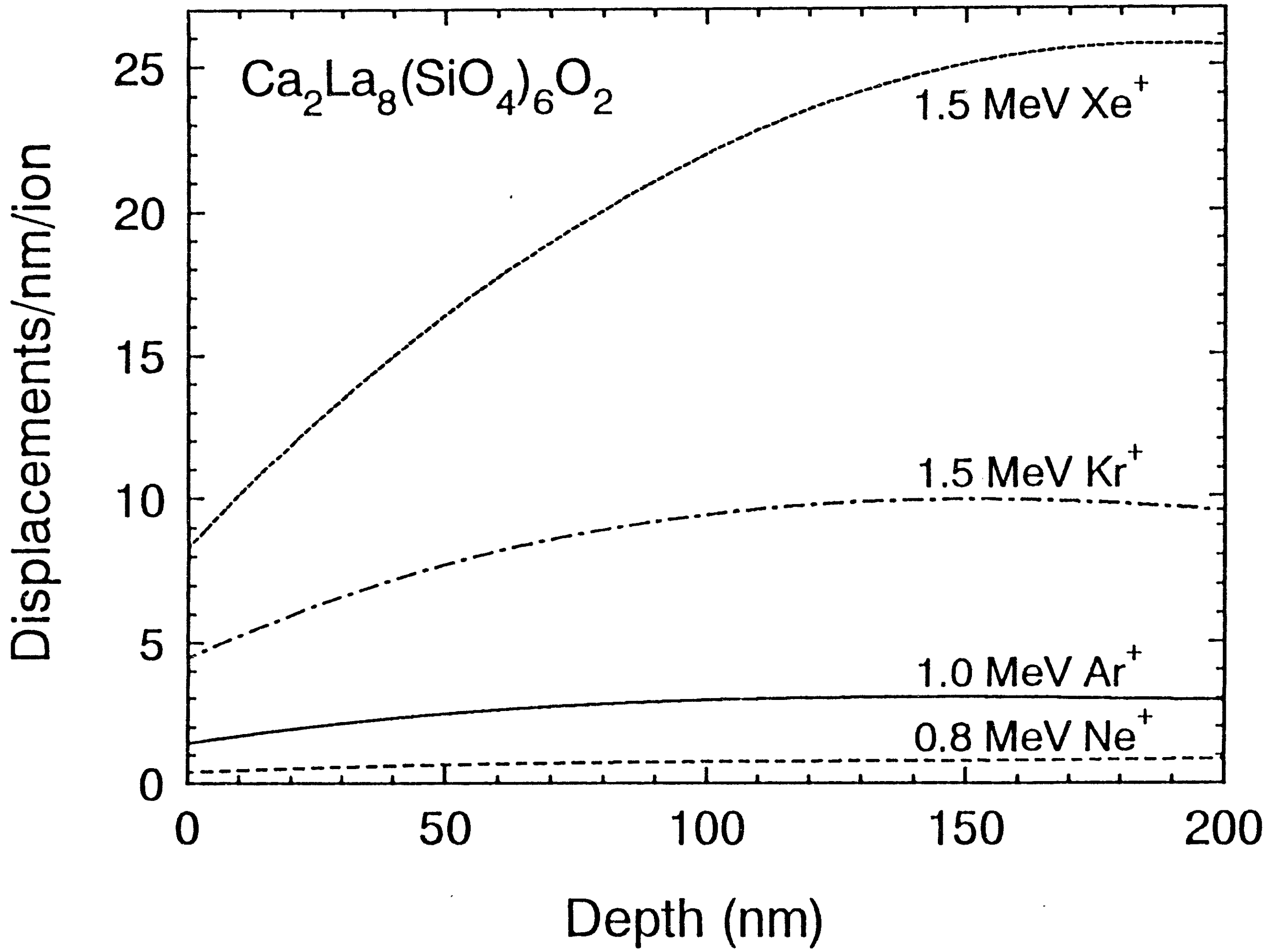

$Ca_2La_8(SiO_4)_6O_2$
1.5 MeV Xe^+
1.5 MeV Kr^+
1.0 MeV Ar^+
0.8 MeV Ne^+
Displacements/nm/ion
0
5
10
15
20
25
0
50
100
150
200
Depth (nm)

Fig. 1

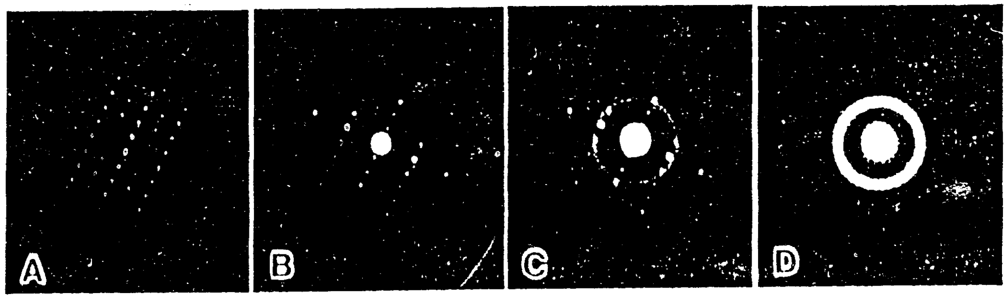
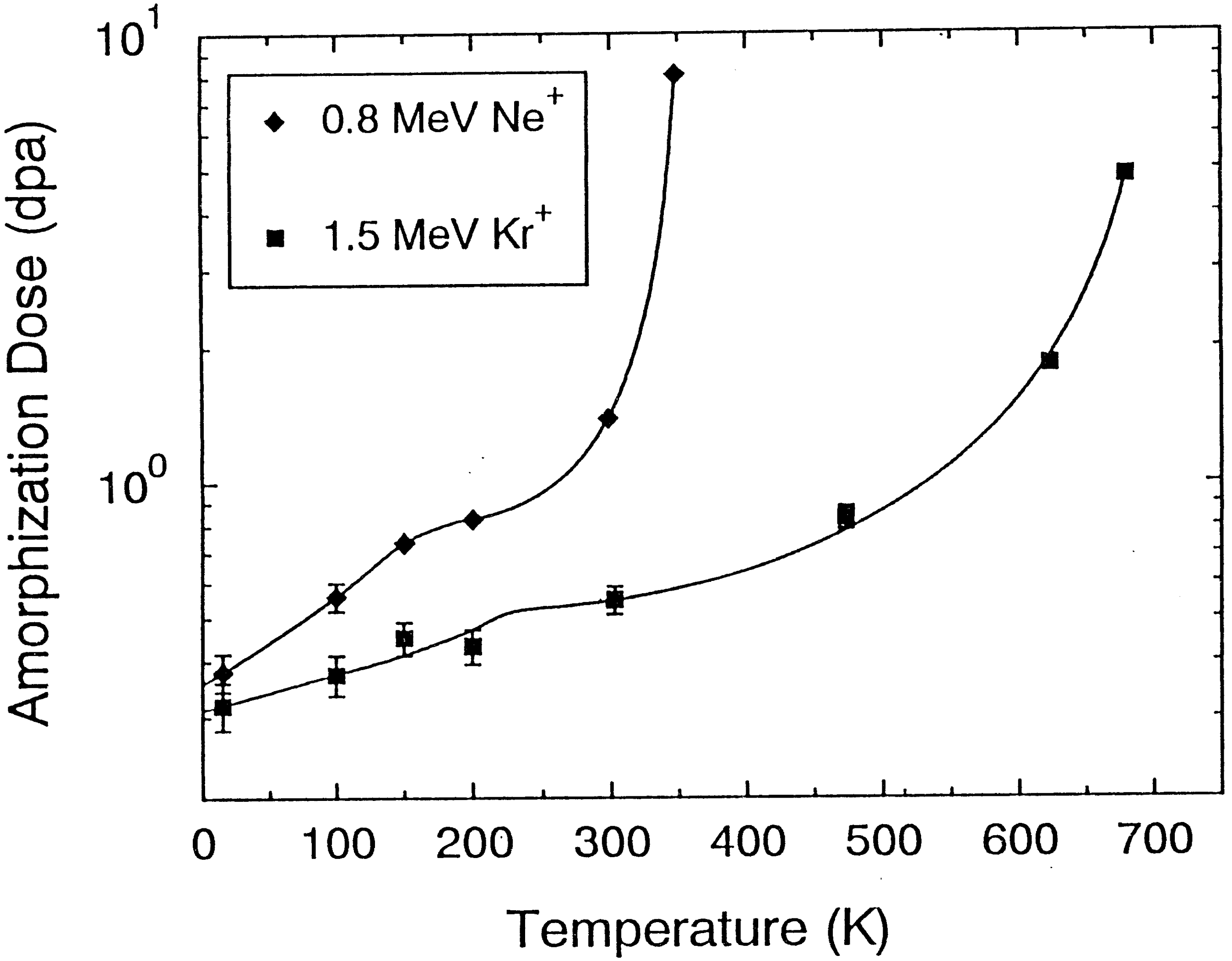
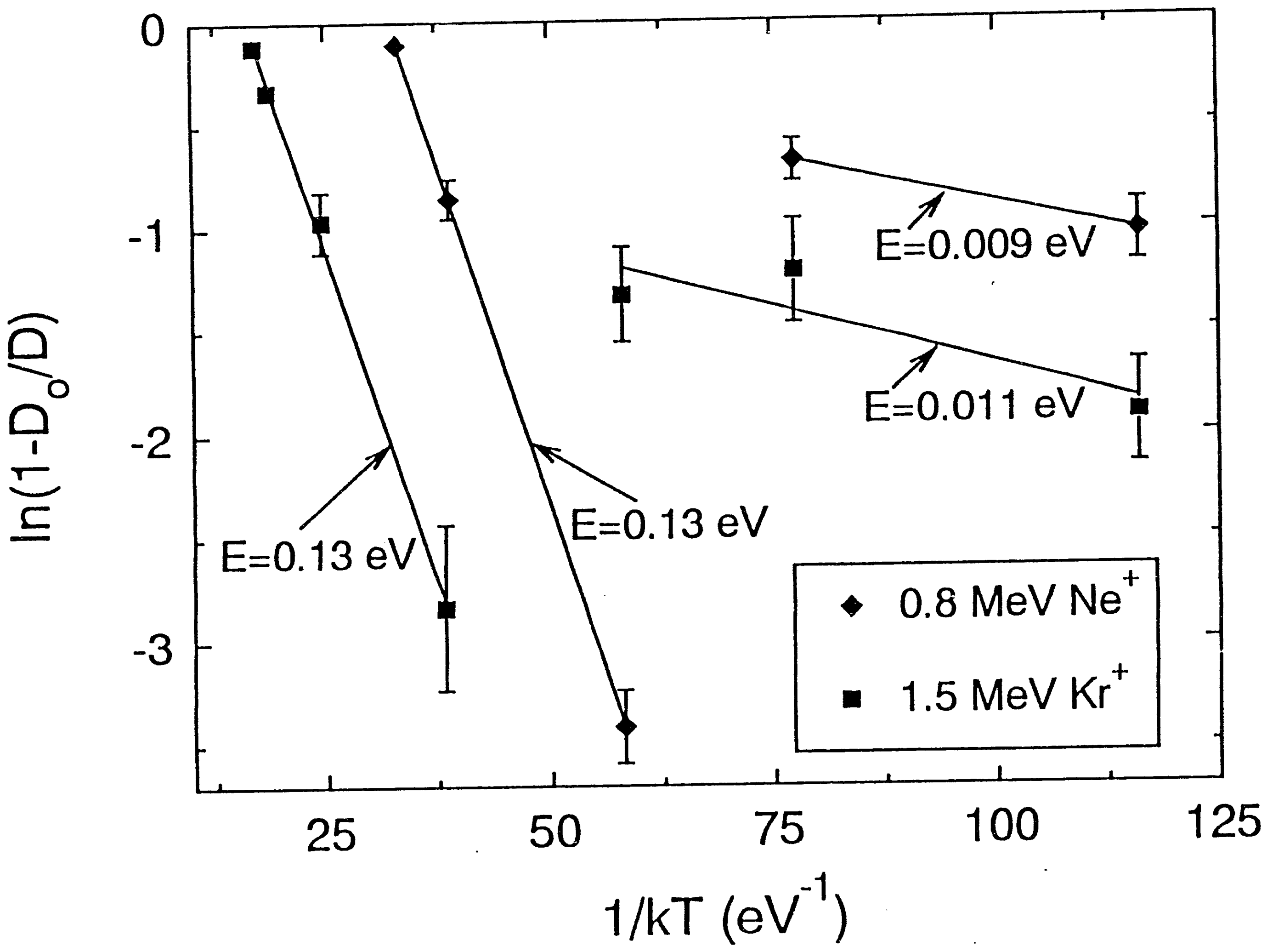


Fig. 2



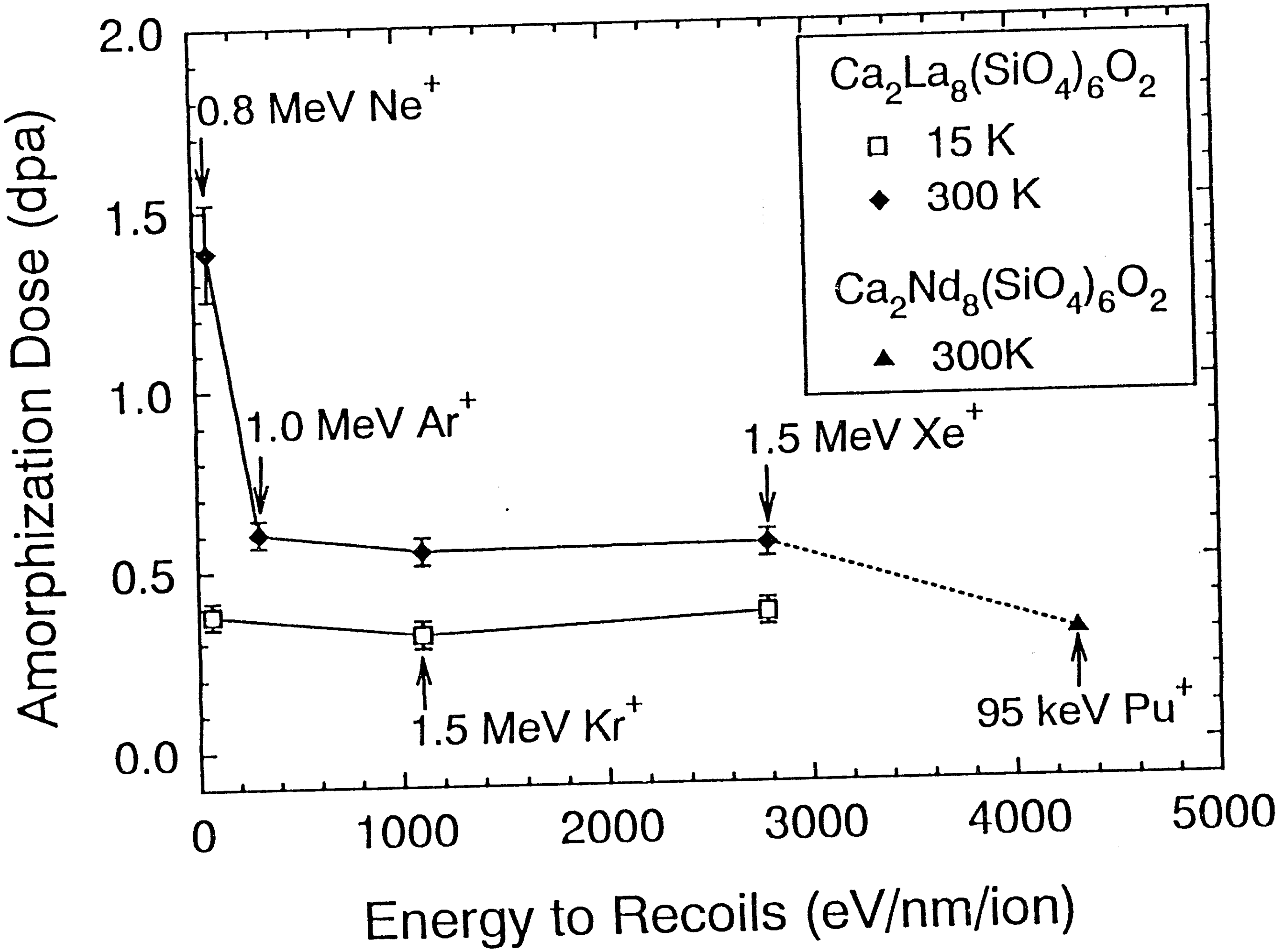
Amorphization Dose (dpa)
10^1
10^0
◆ 0.8 MeV Ne+
■ 1.5 MeV Kr+
0
100
200
300
400
500
600
700
Temperature (K)

Fig. 3



0
-1
-2
-3
ln(1-D_o/D)
25
50
75
100
125
1/kT (eV^-1)
E=0.13 eV
E=0.13 eV
E=0.009 eV
E=0.011 eV
◆ 0.8 MeV Ne+
■ 1.5 MeV Kr+

Fig. 4



Amorphization Dose (dpa)
2.0
1.5
1.0
0.5
0.0
0
1000
2000
3000
4000
5000
Energy to Recoils (eV/nm/ion)
$Ca_2La_8(SiO_4)_6O_2$
□ 15 K
◆ 300 K
$Ca_2Nd_8(SiO_4)_6O_2$
▲ 300K
0.8 MeV Ne^+
1.0 MeV Ar^+
1.5 MeV Xe^+
1.5 MeV Kr^+
95 keV Pu^+

Fig. 5

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