Fast crystallization of amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ induced by thermally activated electron-beam irradiation

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We investigate the ionization and displacement effects of an electron-beam (e-beam) on amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ synthesized by the co-precipitation and calcination methods. The as-received amorphous specimens were irradiated under electron beams at different energies (80 keV, 120 keV, and 2 MeV) and then characterized by X-ray diffraction and transmission electron microscopy. A metastable fluorite phase was observed in nanocrystalline $\text{Gd}_2\text{Zr}_2\text{O}_7$ and is proposed to arise from the relatively lower surface and interface energy compared with the pyrochlore phase. Fast crystallization could be induced by 120 keV e-beam irradiation (beam current = 0.47 mA/cm²). The crystallization occurred on the nanoscale upon ionization irradiation at 400 °C after a dose of less than 10¹⁷ electrons/cm². Under e-beam irradiation, the activation energy for the grain growth process was approximately 10 kJ/mol, but the activation energy was 135 kJ/mol by calcination in a furnace. The thermally activated ionization process was considered the fast crystallization mechanism. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4936785>]

I. INTRODUCTION

It has been reported that a form of synthetic rock, *SYNROC*, which is composed of mutually compatible minerals and possesses a crystal structure, was proposed as a candidate host phase for the immobilization of actinides and fission products.¹ A chemically durable and radiation-resistant pyrochlore, such as $\text{Gd}_2\text{Zr}_2\text{O}_7$,² is a candidate component phase.^{3–5} Many studies focusing on pyrochlore nuclear waste disposal have been conducted on the various aspects concerning disposal safety, such as theoretical simulations of α -decay damage accumulation,⁶ defect properties on the radiation tolerance^{7,8} and experimental heavy-ion-irradiation-induced disordering and amorphization.^{9–13} A principal concern for the crystalline waste forms is the possibility of ion-irradiation-induced amorphization and the accompanying volume swelling and microfracturing, which would lead to a prominent decrease in the chemical stability of the ceramic waste forms.^{3,4} In the irradiation environment, the nuclear energy loss of incident ions has a larger impact than the electronic energy loss of incident ions or electrons on the ceramic host phases. However, the ionization and excitation effects from electronic energy loss cannot be neglected. For instance, the ionization of the incident ions can induce annealing of pre-existing defects in silicon carbide.¹⁴ E-beam irradiation may inhibit the crystalline-to-amorphous phase transformation owing to the ionization-enhanced defect diffusion and migration.^{15,16} Contrary to

disordering and amorphization induced by displacive incident ions through nuclear energy loss, e-beam irradiation has been reported to enhance the defect recovery, nucleation, and recrystallization through ionization and electronic excitation processes in many amorphous materials, such as strontium titanate, apatites, $\text{CaZrTi}_2\text{O}_7$, $\text{Ca}_2\text{Nd}_8(\text{SiO}_4)_6\text{O}_2$, $\text{Gd}_2\text{Ti}_2\text{O}_7$, LaPO_4 , ScPO_4 , and MgAl_2O_4 .^{17–25} However, the crystallization induced by an e-beam may be attributed to a wide range of mechanisms, and the process is material dependent. The role of electronic deposition and the coupled dynamics of electronic and atomic processes need to be studied over a range of irradiation conditions to elucidate the underlying mechanisms for different classes of materials.²⁶

Lately, the preparation of waste forms on the nanoscale has attracted much attention owing to their enhanced radiation resistance, such as is observed in silicon carbide,²⁷ pyrochlore $\text{Gd}_2(\text{Ti}_{0.65}\text{Zr}_{0.35})_2\text{O}_7$,²⁸ partially inverse spinel MgGa_2O_4 ,²⁹ and YSZ.³⁰ For the nanocrystalline materials, abundant grain boundaries can act as sinks for the irradiation-induced defects and hinder the accumulation of the defects.^{29,31} However, nanocrystalline materials may be more inclined to ion-irradiation-induced amorphization given their very small particle size in which the excess surface energy leads to a more stable amorphous structure. As was demonstrated in MgGa_2O_4 ²⁹ and YSZ,³⁰ the kinetics of defects-recovery may help to counter-balance this thermodynamic instability.¹⁶ The simultaneous effects of thermodynamics and kinetics dominating defect formation and healing in nanomaterials have been discussed by Shen.³² Similar to the ion-irradiation-induced disordering and amorphization process, the electron-irradiation-induced recrystallization

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process may also exhibit a noticeable grain size effect. As shown in CePO_4 ,¹⁶ the critical recrystallization electron fluence was increased with the increase of grain size. From a thermodynamics viewpoint, the total energies are higher in smaller-sized materials owing to the increased interfacial fraction, indicating a lower-energy gap between the crystalline phase and corresponding amorphous state. Therefore, the recrystallization process from the corresponding amorphous state to crystalline phase on the nanoscale may occur more readily. To the best of our knowledge, additional original ionization radiation data regarding the ionization effects of e-beam-irradiation-induced nanoscale crystallization are needed for a better understanding of the behavior of nuclear materials in complex radiation environments. Such data would also be of interest for the study of the recrystallization behavior from the amorphous materials, as in the current study. Herein, amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ was synthesized by the co-precipitation and calcination methods and the thermally activated ionization effects of e-beams on amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ were studied. The phase evolution, crystal growth, and microstructural development were investigated under e-beam irradiations at different energies (80 keV, 120 keV, and 2 MeV) to achieve a greater understanding of e-beam irradiation characteristics and potential mechanisms.

II. EXPERIMENTAL

High-purity $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (>99.99%) and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (>99.99%) were mixed according to the appropriate molar ratios of 1:1 and dissolved in deionized water. Gd^{3+} and Zr^{4+} were co-precipitated by drop-by-drop addition of diluted ammonium hydroxide until pH 11 was obtained. The precipitate was centrifugally separated from the solution and washed several times with distilled water and ethyl alcohol, and then dried at 80 °C for 24 h and calcined at 400 °C for 5 h. Amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ specimens were finally synthesized by cold isostatic pressing of the as-obtained powders into Φ 20 mm $\times$ 2 mm pellets under 200 MPa pressure.

The amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ pellets were irradiated to different temperatures by a 120 keV e-beam (beam current = 0.47 mA/cm² and spot size = 8 mm $\times$ 8 mm) with the Electron-beam Material-test Scenario (EMS60) located at the Southwestern Institute of Physics in China. During the experiments, the surface temperature of the samples was monitored online and controlled by a high-sensitivity infrared pyrometer. For a further understanding of the ionization effect and the atomic displacement effect of the e-beam, two other amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ pellets were irradiated by a 80 keV e-beam (beam current = 0.16 mA/cm² and spot size = 8 mm $\times$ 8 mm) with the EMS60 or by a 2 MeV e-beam (beam current = 0.32 $\mu\text{A}/\text{cm}^2$ and spot size = 2.5 cm $\times$ 40 cm) at the JJ-2 electrostatic accelerator facilities at the Institute of Nuclear Science and Technology of Sichuan University. The phase evolution and crystal growth of the resultant specimens were analyzed by X-ray powder diffraction (XRD, Model DX-2700, Dandong Fangyuan Instrument Co., Ltd., Liaoning, China) with monochromatic Cu K α radiation (λ = 1.5406 Å) in the range of 2θ = 10°–70°. The microstructural developments of the amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ specimens before and after e-beam

irradiation were characterized by transmission electron microscopy (TEM; Tecnai G² F20 S-TWIN, FEI, Hillsboro, OR).

III. RESULTS AND DISCUSSION

Phase evolutions of the obtained amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ pellets calcined in a muffle furnace for 5 h are shown in Fig. 1(a). It is observed that amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ crystallized at a temperature of 600 °C and all of the characteristic diffraction peaks are in agreement with the reflections of the fluorite structure (ICSD No. 16-0799). To understand the differences induced by e-beam irradiation and by calcination in a furnace, amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ pellets were irradiated to different temperatures in the range of 350 °C to 750 °C by a 120 keV e-beam (beam current 0.47 mA/cm² and power = 36 W). The corresponding XRD patterns are plotted in Fig. 1(b). It is clear that amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ crystallized at approximately 400 °C, evidenced by the appearance of the three strong characteristic peaks. From the XRD results, it can be concluded that the e-beam could induce crystallization of amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ at a lower temperature, compared with crystallization in a furnace.

The pyrochlore phase is the derivative superstructure of the fluorite phase. When pyrochlore changes its crystalline phase to fluorite, the cations and anions gradually shift to a state of complete disorder. A previous study has demonstrated that this phase transition occurs at temperatures of approximately 1550 °C.³³ Thus, for $\text{Gd}_2\text{Zr}_2\text{O}_7$, pyrochlore is the low-temperature phase and fluorite is the high-temperature phase. However, it is interesting to observe that the thermodynamically stable fluorite phase is obtained at low temperature while the crystal is on the nanoscale. McHale *et al.* have reported that the difference in the surface energy thermodynamically stabilizes $\gamma\text{-Al}_2\text{O}_3$ over $\alpha\text{-Al}_2\text{O}_3$.³⁴ The same may be true for the nanocrystalline fluorite $\text{Gd}_2\text{Zr}_2\text{O}_7$ owing to its lower surface and interface energies compared with those of pyrochlore. This results in the total energy of fluorite being lower than that of pyrochlore in consideration of the significant surface and interface energies at low temperature. Thus, the synthesis of nanocrystalline $\text{Gd}_2\text{Zr}_2\text{O}_7$ will initially lead to a metastable fluorite phase with increasing temperature, rather than pyrochlore. For $\text{Gd}_2\text{Zr}_2\text{O}_7$, the fluorite structure is far more irradiation-resistant to phase transitions than pyrochlore.⁹ Therefore, the e-beam promotion of fluorite on the nanoscale may aid $\text{Gd}_2\text{Zr}_2\text{O}_7$ to exhibit an enhanced radiation resistance.

The JADE 6.5 software was employed for the whole-pattern profile fitting and subsequent qualitative analysis of the grain growth. Broadening of the diffraction peak was easily observed in the irradiated and calcined samples so that the grain sizes can be calculated using the Scherrer formula.³⁵ Grain sizes versus the irradiated and calcined temperatures of the amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ are plotted in Figs. 1(c) and 1(d). By furnace calcination, the crystal growth was temperature dependent and the grain size growth was almost linear versus temperature, as was expected. The grain growth by e-beam irradiation is known to be more severe than by calcination in a furnace with increasing temperature.²⁴

FIG. 1. XRD patterns of $\text{Gd}_2\text{Zr}_2\text{O}_7$ at different temperatures: (a) calcined in a muffle furnace, (b) irradiated by an e-beam. Temperature dependence of grain size for $\text{Gd}_2\text{Zr}_2\text{O}_7$: (c) calcined in a muffle furnace, (d) irradiated by an e-beam.

Moreover, during e-beam irradiation, the amorphous pellets were fixed on the copper sample holder. Cooling water was flowed beneath the sample holder to lower the heating rate induced by e-beam irradiation, which may also aid in accurately stopping the irradiation when the target temperature is achieved. However, the irradiation heating time was still very short (less than 2 min even irradiated to 750 °C), compared with the calcination period of 5 h required in the furnace. Therefore, one can deduce that crystallization was more rapid by e-beam irradiation. This phenomenon has also been found in other materials, such as LaPO_4 , ScPO_4 , ZrSiO_4 , and CePO_4 .^{16,24} Thus, we observe a fast crystallization of amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ at low temperature induced by an e-beam in this study.

The kinetics of grain growth during furnace calcination and e-beam irradiation were studied by calculating the activation energy.³⁶ Grain growth by calcination in a furnace follows the empirical equation:

$$d^N - d_0^N = k_T(t - t_0), \quad (1)$$

where d is the average grain size at time t , d_0 is the average grain size at t_0 , N is the grain growth exponent, and k_T is a kinetic constant. In a thermally activated growth process, k_T can be determined by

$$k_T = k_0 \exp\left(\frac{-E}{RT}\right), \quad (2)$$

where k_0 is a constant, E is the activation energy for grain growth, R is the gas constant, and T is the annealing temperature. Fig. 2 shows the temperature dependence of grain size as a $\ln\text{--}\ln$ plot. The grain growth exponent was calculated from the slope of the linear regression plots in which the average grain sizes with different annealing times at 800 °C

were used, as shown in the inset of Fig. 2. It was found that N is approximately 3.8 from the near linear law. From the relationship in Fig. 2 and the inset, the resultant activation energy for the isothermal grain growth is approximately 135 kJ/mol, calculated using Eqs. (1) and (2).

Fig. 3 shows the dose dependence of the grain size and temperature under e-beam irradiation. The crystallites were observed at a temperature of 400 °C after a dose of less than 7×10^{16} electrons/cm². V_{irr} at different temperatures (425 °C, 500 °C, and 600 °C) were calculated in the following manner. The grain size difference between adjacent temperatures (400–450 °C, 450–550 °C, and 550–650 °C) was divided by the time interval. When thermal and irradiation-enhanced crystallization are considered as two separate processes, the growth rate, V_g , can be described as^{17,37}

FIG. 2. Linear regression plot of $\ln[(D-D_0)^{3.8}/5]$ versus $1000/T$ used to calculate the activation energy for grain growth during calcination in a furnace. Inset shows a log–log plot of the grain size at 800 °C as a function of calcination time.

FIG. 3. Dose dependence of the grain size and temperature under e-beam irradiation. Inset is the logarithmic plot of grain growth rate as a function of reciprocal temperature.

$$Vg = V_{irr} \exp\left(\frac{-E_{irr}}{RT}\right) + V_{th} \exp\left(\frac{-E_{th}}{RT}\right), \quad (3)$$

where V_{irr} and V_{th} are prefactors, and E_{irr} and E_{th} are the activation energies for the irradiation-enhanced and thermal crystallization processes, respectively. V_{th} is negligible at temperatures below 600 °C. Only the irradiation term is fitted to the data from this study, which yields values of $E_{irr} = 10$ kJ/mol. Hence, one can conclude that the activation energy of e-beam-induced crystallization is significantly lower than the thermal activation energies of amorphous $Gd_2Zr_2O_7$.

Further study was performed using TEM to investigate the phase, morphology, and microstructure changes before and after e-beam irradiation. Fig. 4(a) is a morphology image of the specimen before e-beam irradiation. No obvious grains were observed on the specimens. In the selected area electron diffraction (SAED) pattern of Fig. 4(b), no distinct extra diffraction rings or spots can be resolved. The broad electron diffraction halos result from the scattering induced by the non-periodic atomic arrangement. The HRTEM images are shown in Figs. 4(c) and 4(d). It can be clearly seen that many isolated crystallites (<5 nm in dimension) with random orientations were surrounded by the amorphous matrix. This indicates that nucleation with a negligible growth has occurred at 400 °C by calcination in the furnace. Hence, the specimen exhibits a short-range ordered and long-range disordered structure.

After irradiation to 450 °C by a 120 keV e-beam, nanocrystalline $Gd_2Zr_2O_7$ was obtained. The calculated crystal size obtained from Sherrer's equation was confirmed by the resolved nanocrystals (approximately 17 nm in dimension) in the edge of the TEM images shown in Fig. 5(a2). Microstructures with randomly oriented nanocrystals were also demonstrated in the SAED and HRTEM images. An insignificant amorphous state in the grain boundaries, as shown in the HRTEM images, indicates an almost complete crystallinity of the irradiated specimen. However, the specimen seems to be composed of not-fine crystal grains with many defects or defect clusters in the interior of the grains. Moreover, a relatively large single crystal (about 67 nm in dimension) was observed and shown in the morphology

FIG. 4. (a) TEM image, (b) selected area electron diffraction pattern, and (c, d) high-resolution TEM images of $Gd_2Zr_2O_7$ calcined at 400 °C for 5 h.

image of Fig. 5(a1) and the corresponding HRTEM image of Fig. 5(d). In some positions, the rapid grain growth rate may be attributed to the ionization-enhanced effects of the e-beam.¹⁵

Research on the ionization effect versus displacement cascade events has attracted increasing interest. Based on integrated experimental techniques and computational approaches, researchers have studied the separated and coupled response of some ceramic materials to ion energy loss by electronic energy loss (ionization effects) and nuclear energy loss (displacement events).^{14,26,38,39} Similar to the focused-ion-beam, an incident e-beam also exhibits ionization and displacement effects on the target materials. In this study, some of the possible mechanisms that may be attributed to the high-power e-beam-induced crystallization are the atomic displacement effect,^{40,41} the ionization effect,¹⁹ and the beam-heating effect.^{21,22} Devanathan and Weber used classical molecular dynamics simulations to examine the E_d (the minimum energy required to displace an atom from its ideal lattice site) of $\text{Gd}_2\text{Zr}_2\text{O}_7$, and the results for Gd, Zr, and O atoms were $E_d(\text{Gd}) = 72$ eV, $E_d(\text{Zr}) = 121$ eV, and $E_d(\text{O}) = 41$ eV.⁴² When calculating the transferred energy in the collision between incident electrons and target atoms, the Sonner and Sibley formula⁴³ is commonly used

$$E_t = \frac{2147.7E(E + 1.002)}{A}, \quad (4)$$

where E_t is the maximum energy transferred to the lattice atom by the incident particle in eV, E is the incident electron

energy in MeV, and A is the relative atomic mass of the lattice atom. When the e-beam energy was 120 keV, our calculated E_t values were 1.84 eV, 3.17 eV, and 18.1 eV for Gd, Zr, and O atoms, respectively, as shown in Fig. 4. Since all the E_t values of the collided atoms are much smaller than E_d , the atom displacements may not occur under 120 keV e-beam irradiation in $\text{Gd}_2\text{Zr}_2\text{O}_7$. Accordingly, 120 keV electrons are considered subthreshold electrons, and the atomic displacements effect of the e-beam may be excluded as the fast and low-temperature crystallization mechanism in this study.

For a further understanding of the atomic displacement effect, we carried out another experiment at the JJ-2 electrostatic accelerator. The amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ specimen was irradiated by a 2 MeV e-beam (beam current = $0.32 \mu\text{A}/\text{cm}^2$ and power = 0.4 W) for 3600 s corresponding to a dose of 7.2×10^{15} electrons/ cm^2 , which yielded significant atomic displacements. The temperature increase can be negligible (less than 1 K) calculated by^{19,24}

$$\Delta T = \frac{I}{\pi \kappa e} \left(\frac{\Delta E}{d} \right) \ln \frac{b}{r_0}. \quad (5)$$

From the XRD diffractograms, shown in the inset of Fig. 6, no diffraction peaks of the crystalline phase are observed after irradiation. Hence, this reveals that without a temperature rise, atomic displacement may have an insignificant contribution to the e-beam-induced crystallization in $\text{Gd}_2\text{Zr}_2\text{O}_7$.

FIG. 5. (a) TEM images, (b) selected area electron diffraction pattern, and (c, d) high-resolution TEM images of $\text{Gd}_2\text{Zr}_2\text{O}_7$ after 120 keV e-beam irradiation at a temperature of 450°C. (c) and (d) are the corresponding HRTEM images of (a1) and (a2), respectively.

FIG. 6. The relationship between E_t (maximum energy transferred from an incident electron to Gd, Zr, and O atoms) and e-beam energy calculated using the Sonder and Sibley method. Inset shows the XRD patterns of the amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ pellets before irradiation and after being irradiated by different e-beams.

Previous studies have demonstrated that the mechanism for e-beam-induced crystallization is an ionization process in many nuclear materials.^{15,16,24,25} Therefore, a complementary experiment was conducted for the further study of the ionization effects. An amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ pellet was irradiated by an 80 keV e-beam (beam current = 0.16 mA/cm² and spot size = 8 mm × 8 mm) at EMS60 for 5000 s (corresponding to a dose of 5×10^{18} electrons/cm²) to investigate the ionization effect. Because of the low power of the electron beam (power = 8 W) and the flowing-water cooling effect, the temperature rise of the irradiated sample was not considered. The XRD pattern of the amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ irradiated by an 80 keV e-beam is shown in the inset of Fig. 6. No diffraction peaks of the crystalline phase are observed, indicating that the ionization process cannot be the sole reason for the fast and low-temperature crystallization by e-beams observed in this study. Previous studies have demonstrated that the e-beam-induced crystallization doses of many materials are on a magnitude of more than 10^{20} electrons/cm², such as 1.69×10^{23} (200 keV e-beam) for zircon, 3.65×10^{21} (120 keV e-beam) for ScPO_4 ,²⁴ more than 1.5×10^{20} (200 keV e-beam) for CePO_4 ,¹⁶ and 3.6×10^{21} (200 keV e-beam) for apatite.¹⁹ In this study, the $\text{Gd}_2\text{Zr}_2\text{O}_7$ specimen is still in the amorphous state after a dose of 5×10^{18} electrons/cm² without a temperature rise, but crystallized at a temperature of approximately 400 °C after a dose of less than 10^{17} electrons/cm². Thus, one can conclude that the ionization effects can be thermally activated at relatively low temperatures (a few hundred degrees).

We propose that the co-effect of the ionization and beam-heating results in the fast crystallization of amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ at low temperature by e-beams in the present study. The Spaepen–Turnbull model considered that the crystallization induced by irradiation can be explained by dangling bonds.⁴⁴ Using 80–120 keV (subthreshold electrons) e-beam irradiation, the incident electrons transferred their energy by inelastic interaction with the outer-shell electrons of the target atoms, leading to the ejection of the outer-

shell electrons and generation of electron–hole pairs. Owing to the insulativity of the specimen, recombination of the electrons and holes may be very difficult. Thus, numerous dangling bonds may be produced. For the nucleation and growth processes induced by the e-beam, Meldrum *et al.* considered that the inelastic or ionization processes of subthreshold electrons may cause the breakage of chemically less stable cation–oxygen bonds in the amorphous matrix and rearrangement in the favorable orientation of second-neighbor metal cations, leading to a lower-energy “crystalline” nucleus, upon which subsequent growth may occur.²⁴ For the e-beam inducing much higher solid-phase epitaxial recrystallization rates than thermal rates, the mechanisms may be that the localized electronic excitations affect local atomic bonds and effectively lower the energy barrier for defect recovery and the recrystallization process,^{15,17,19} which may involve local atomic hopping or rotation of the atomic polyhedral.¹⁷ Xiao *et al.* also revealed that a higher excitation concentration may decrease the energy barrier for phase transitions.³⁹ In this study, the enhanced recrystallization kinetics of amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ induced by an e-beam (120 keV) may arise from the ionization-enhanced and thermally activated atomic diffusion and grain boundary migration. The ionized and excited elements were found to be the unusual charge and energy state, promoting their migration by Coulombic repulsion. Thus, ionization irradiation may enhance the mobility of atoms.⁴⁵ The ionization process can be thermally activated, which explains why crystallization upon ionization irradiation was observed at a temperature of approximately 400 °C even with a relatively low electron dose (less than 10^{17} electrons/cm²).

IV. CONCLUSION

Ionization, displacement, and beam-heating effects of amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ were studied by different energy e-beam irradiations. With an insignificant temperature rise, crystallization of amorphous $\text{Gd}_2\text{Zr}_2\text{O}_7$ may not occur by displacive and ionizing e-beam (2 MeV) irradiation and ionizing e-beam (80 keV) irradiation at a relatively low dose, compared with the dose required for crystallization of more than 10^{20} electrons/cm² in other materials. However, fast crystallization occurred at a temperature of approximately 400 °C after a dose of less than 10^{17} subthreshold electrons/cm². Thus, ionization effects can be thermally activated at relatively low temperatures (a few hundred degrees) to enhance the growth of the fluorite phase, which is more effective than the thermal treatment. Under e-beam irradiation, the activation energy for the grain growth process is approximately 10 kJ/mol, and is approximately 135 kJ/mol by calcination in a furnace. The enhanced crystallization kinetics is proposed to arise from the ionizing radiation-enhanced atomic diffusion and grain boundary migration. E-beam irradiation may be a useful way to synthesize fluorite $\text{Gd}_2\text{Zr}_2\text{O}_7$. We also deduce that the generation of nanocrystalline $\text{Gd}_2\text{Zr}_2\text{O}_7$ will result in the metastable fluorite phase owing to the relative lower surface and interface energy compared with the pyrochlore phase. We will use calorimetry to

provide a greater understanding of these results in our future work.

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