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Amorphization of ZnAl₂O₄ spinel under heavy ion irradiation

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Abstract

ZnAl₂O₄ spinels have been irradiated with several ions (Ne, S, Kr and Xe) at the IRRSUD beam-line of the GANIL facility, in order to determine irradiation conditions (stopping power, fluence) for amorphisation. We observed by Transmission Electron Microscopy (TEM) that with Xe ions at 92 MeV, individual ion tracks are still crystalline, whereas an amorphisation starts below a fluence of $5 \cdot 10^{12} \text{ cm}^{-2}$ up to a total amorphisation between 1×10^{13} and $1 \times 10^{14} \text{ cm}^{-2}$. The coexistence of amorphous and crystalline domains in the same pristine grain is clearly visible in the TEM images. All the crystalline domains remain close to the same orientation as the original grain. According to TEM and X-Ray Diffraction (XRD) results, the stopping power threshold for amorphisation is between 9 and $12 \text{ keV} \cdot \text{nm}^{-1}$.

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Introduction

Spinel is a ternary compound that belongs to the space group $Fd-3m$ with stoichiometry AB_2O_4 , where the anion sublattice is arranged in a cubic close-packed network and cations are distributed in one-eighth of the tetrahedral sites (A ions) and half of the octahedral sites (B ions). This structure is known for exhibiting cation exchange, this cation disorder is quantified by the inversion parameter that specifies the fraction of trivalent B ions that occupy tetrahedral sites. At least one of them, $MgAl_2O_4$, is known to have relatively good resistance to irradiation and is considered as a possible candidate for transmutation matrices in nuclear reactors [1, 2]. Other spinels, such as $ZnAl_2O_4$, $MgFe_2O_4$ or $MgGa_2O_4$ were submitted

to irradiation with low-energy ions (nuclear regime) [3-6] or swift heavy ions [7-11] in order to study the structural stability of this material family under irradiation. For all of them irradiation induces cationic disorder and some cases amorphisation. Those irradiations are summarized in the table 1. In particular, previous results indicate that the minimal electronic stopping power (Se) for amorphisation of MgAl_2O_4 is $7.5 \text{ keV}\cdot\text{nm}^{-1}$ [12], whereas ZnAl_2O_4 seems to be more resistant to amorphisation (no amorphisation up to $9 \text{ keV}\cdot\text{nm}^{-1}$) [10]. The aim of this work is to determine the electronics stopping power threshold for amorphisation in ZnAl_2O_4 .

Experimental

High-purity ZnO (99.99%) and Al_2O_3 (99%) powders were blended and calcinated for one hour at 1473 K to obtain a ZnAl_2O_4 powder. This powder was compacted and sintered eight hours at 1673K under atmospheric pressure. Samples were polished (specular) to collect accurate X-ray diffraction diagrams. For the TEM analyses, powder deposited on carbon foils was used. The grain sizes, determined by TEM analysis, are 100 nm to 200 nm range. Irradiations were performed at the IRRSUD beamline with 92 MeV ^{129}Xe ($\text{Se} = 20 \text{ keV}\cdot\text{nm}^{-1}$) ions delivered by the GANIL facility, at fluences ranging from $10^{11} \text{ ions}\cdot\text{cm}^{-2}$ to $4.5\cdot 10^{14} \text{ ions}\cdot\text{cm}^{-2}$ with a flux of $2\cdot 10^9 \text{ cm}^{-2}\cdot\text{s}^{-1}$. Irradiations with a 6 μm Al foil was already performed. The Xe ion has an energy of $30 \pm 2 \text{ MeV}$ ($\text{Se} = 11.7 \pm 0.3 \text{ keV}\cdot\text{nm}^{-1}$) after the foil. Other irradiations were performed with ^{36}S ion at 30 MeV ($\text{Se} = 8 \text{ keV}\cdot\text{nm}^{-1}$) and ^{86}Kr at 74 MeV ($\text{Se} = 16 \text{ keV}\cdot\text{nm}^{-1}$). All irradiations were performed at room temperature.

Results and discussion

Three bulk samples were irradiated with 92 MeV Xe ions, at fluences of 10^{11} , 10^{12} , and 10^{14} ions.cm⁻². X-Ray diffraction patterns collected with an incidence of 1° indicates that the material is totally amorphous at a fluence of 10^{14} cm⁻² and is partially crystalline at 10^{12} cm⁻². Therefore, the complete amorphisation of the material occurs between 10^{12} cm⁻² and 10^{14} cm⁻². TEM analyses have been made on powder samples irradiated with Xe 92 MeV at fluences ranging from 10^{11} cm⁻² to 10^{14} cm⁻², in order to define more precisely this transition. In the single impact regime (low fluence, no tracks overlapping), no amorphous phase can be detected in the samples, and the material remains crystalline in the ion tracks, as shown in figure 1. Nevertheless it is worth noting that a recrystallisation in the tracks during TEM observations assisted by the electron beam of the microscope cannot be formally excluded. At a fluence of 4.10^{12} cm⁻², some amorphous zones are visible, imbedded inside the crystalline phase, as shown in the figure 2. The number of amorphous zones increases with the fluence. All the crystalline domains of a given pristine grain have the same orientation after irradiation. There is no recrystallisation of amorphous domains during TEM observations, so the individual tracks are probably not recrystallised.

On the sample irradiated with 10^{14} cm⁻² 92 MeV Xe ions, X-Ray diffraction diagrams were collected with different X beam incidence angles, in order to probe the irradiated region up to different depths of the sample, as shown in figure 3. When collected at 1° incidence, the diagram appears completely amorphous, but not at 2°. At 1°, the analysed depth (in which 90% of X-rays are diffracted) is 2.4 µm, whereas at 2° this depth is 4.6 µm. Simulation made using SRIM 2006 [13], gave stopping power of 15 keV.nm⁻¹ at a depth of 2.4 µm and 9 keV.nm⁻¹ at 4.6 µm. We can then conclude that a stopping power threshold for amorphisation should be between those two values.

This is confirmed by TEM analyses on powder irradiated at different stopping powers. Table 1 summarises the stopping power for several ions in ZnAl_2O_4 and the behaviour of ZnAl_2O_4 (amorphous or not). We deduce that amorphisation threshold is between 9 and 12 $\text{keV}\cdot\text{nm}^{-1}$.

Different spinel materials have been irradiated with swift heavy ions, mainly MgAl_2O_4 for nuclear applications and magnetic spinels (MFe_2O_4 with $\text{M}=\text{Mg}, \text{Ni}, \text{Fe}$ and Zn) [7, 8, 10, 11]. These studies deal with the order-disorder transition of the cationic sublattices, determined by XRD or indirectly by Mössbauer spectroscopy, but amorphisation was also studied. For MgAl_2O_4 , the electronic stopping power threshold for amorphisation is 7.5 $\text{keV}\cdot\text{nm}^{-1}$ [12]. For ZnFe_2O_4 irradiated with Kr ions ($\text{Se}=12.5 \text{ keV}\cdot\text{nm}^{-1}$), high resolution electron microscope (HREM) shows the presence of microdomains with various lattice spacings in the tracks. This is attributed to spatially localized atomic motions in the initial spinel structure followed by a rapid quench and recrystallisation in the same structure, but with some random orientation. No amorphous phase was detected. At higher stopping power ($\text{Se}=23.2 \text{ keV}\cdot\text{nm}^{-1}$), the core of the latent tracks appear to be composed of small amorphous domains around the main trajectory of the ions, but there are no continuous amorphous tracks. As observed in ZnAl_2O_4 , individual ions tracks are not amorphous, whereas some amorphous domains coexist with crystalline domains for high stopping power ($23.2 \text{ keV}\cdot\text{nm}^{-1}$). The threshold for amorphisation is above $12.5 \text{ keV}\cdot\text{nm}^{-1}$. For ZnAl_2O_4 , irradiations with 820 MeV Kr ions induce no amorphisation, but only an increase of the inversion parameter. The authors indicate that the electronic stopping power is $9 \text{ keV}\cdot\text{nm}^{-1}$. This result seems to be consistent with ours (amorphisation threshold between 9 and $12 \text{ keV}\cdot\text{nm}^{-1}$). Nevertheless, the stopping power was calculated with SRIM code, taking the actual density of the samples (67% of the theoretical density), whereas in one grain the local density is the theoretical one. Therefore,

the stopping power of 820 MeV Kr inside a grain is 14.5 keV.nm^{-1} . This difference in amorphisation stopping power could be attributed to velocity effect. But this irradiation with 820 MeV Kr ions was done with a flux of $10^{10} \text{ ions.cm}^{-2}$, so we could not avoid a temperature effect. Irradiation with 820 MeV Kr ions at lower flux are planned in order to check this point. The electronic stopping power threshold for amorphisation in ZnAl_2O_4 is then between those of two others spinels MgAl_2O_4 (7.5 keV.nm^{-1}) and ZnFe_2O_4 ($>12.5 \text{ keV.nm}^{-1}$).

Conclusion

Zinc aluminate spinels irradiated with Xe have been studied by X-Ray diffraction and Transmission Electron Microscopy. From the TEM analyses, we can say that the process of amorphisation starts at least for a fluence of $4.10^{12} \text{ cm}^{-2}$. Amorphous zones appear in the material at this fluence, and then grow with the fluence, up to a completely amorphous material at a fluence between 10^{13} cm^{-2} and 10^{14} cm^{-2} . The samples remain crystalline in the single impact regime, so amorphisation occurs by defect accumulation. Concerning the stopping power threshold for amorphisation, we can conclude that, for ions with energy less than 1 MeV/u, it is between 9 keV.nm^{-1} and 12 keV.nm^{-1} . Irradiations between 10^{13} cm^{-2} and 10^{14} cm^{-2} are planned in order to define the threshold fluence for total amorphisation with 92 MeV Xe ions more precisely.

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Figure Captions

Figure 1: TEM picture of a ZnAl_2O_4 sample irradiated with 10^{11} cm^{-2} Xe ion

Figure 2: TEM picture of a ZnAl_2O_4 sample irradiated with a) $4 \cdot 10^{12} \text{ Xe.cm}^{-2}$ b) $8 \cdot 10^{12} \text{ cm}^{-2}$ Xe
c) $10^{13} \text{ Xe.cm}^{-2}$ and d) $10^{14} \text{ Xe.cm}^{-2}$

Figure 3: X-Ray diffraction patterns of samples irradiated with 10^{14} cm^{-2} ions. Incidences angles are ranging from 1° for the bottom line to 4° for the top line.

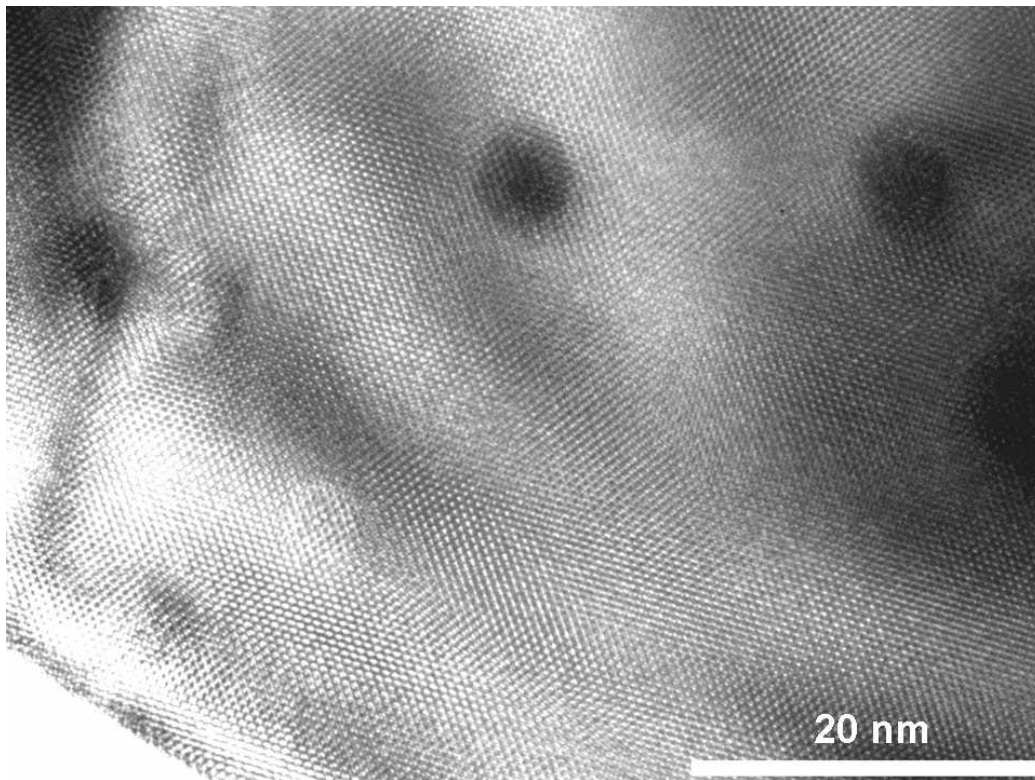


Figure 1

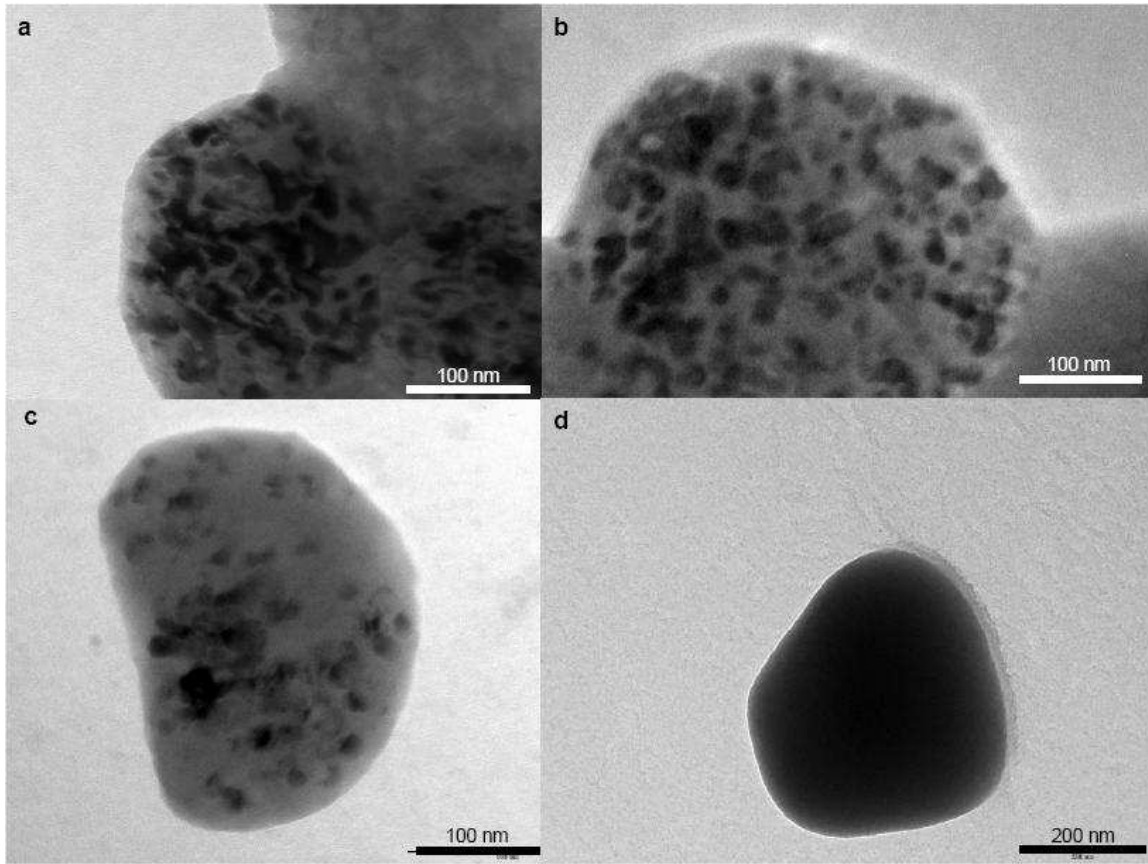


Figure 2

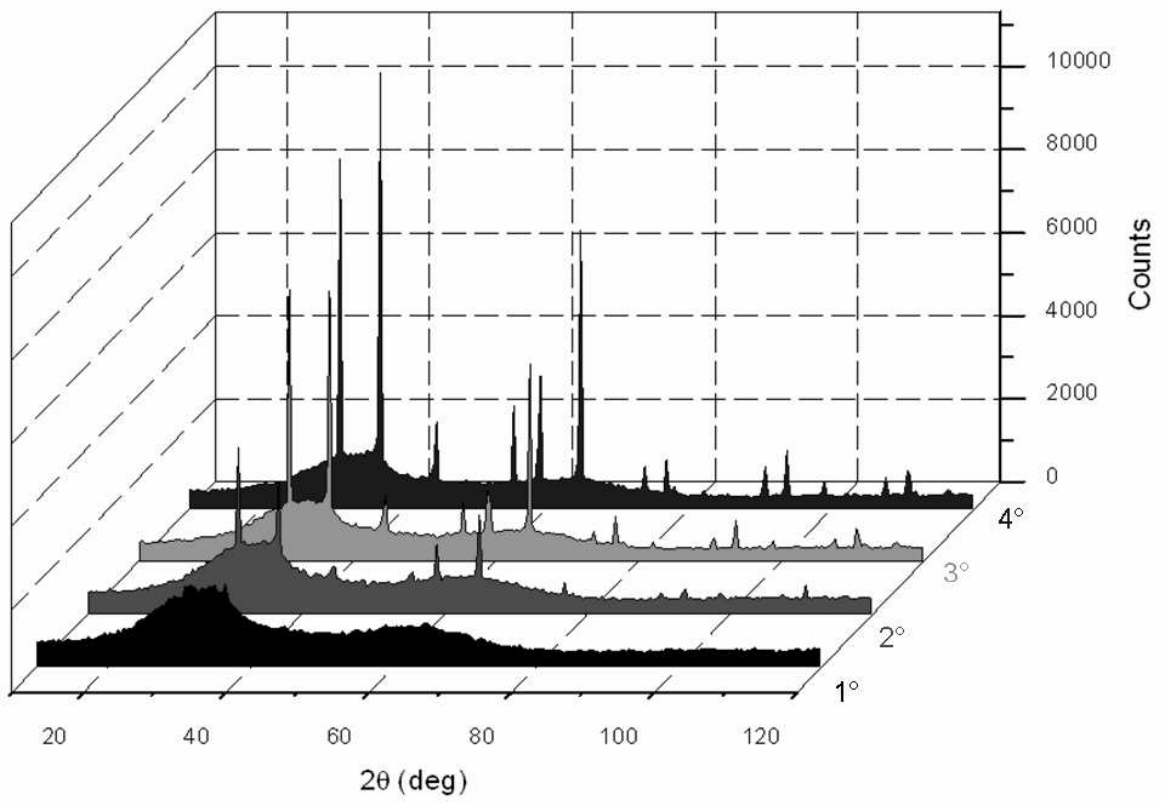


Figure 3

Table

Type of spinel	Temperature of irradiation	Nature of the ion	Energy (MeV)	Electronic Stopping power (keV.nm ⁻¹)	Fluence (cm ⁻²)	State	Reference
ZnAl ₂ O ₄	Room temperature	¹²⁹ Xe + 6μm Al	30±2	11.7±0.3	10 ¹⁴	amorphous	This work
ZnAl ₂ O ₄	Room temperature	¹²⁹ Xe	92	20	10 ¹⁴	amorphous	This work
ZnAl ₂ O ₄	Room temperature	⁸⁶ Kr	74	16	10 ¹⁴	amorphous	This work
ZnAl ₂ O ₄	Room temperature	³⁶ S	30	7.3	10 ¹⁴	crystalline	This work
ZnAl ₂ O ₄	Room temperature	¹⁹⁷ Au	4	7	10 ¹⁶	crystalline	[3]
MgGa ₂ O ₄	100K	Kr	0.3	0.5	4.10 ¹⁶	crystalline	[5]
MgFe ₂ O ₄	Room Temperature	Kr	3100	17	5.10 ¹²	crystalline	[8]
MgAl ₂ O ₄	Room temperature	Xe	200	25	2.10 ¹²	crystalline	[2]

Table 1 : Summary of the stopping power of the ions used for spinels irradiations calculated with SRIM

2006