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AUTHOR(S) Don M. Parkin, CMS
Michael Nastasi

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RADIATION INDUCED AMORPHIZATION IN $\text{YBa}_2\text{Cu}_3\text{O}_7$ AND $\text{GdBa}_2\text{Cu}_3\text{O}_7$ SUPERCONDUCTORS

DON M. PARKIN* AND MICHAEL NASTASI**

*Center for Materials Science, Los Alamos National Laboratory, Los Alamos, NM 87545.

**Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545

ABSTRACT

The response of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{GdBa}_2\text{Cu}_3\text{O}_7$ high temperature superconductors to particle irradiation is examined. Both ion and electron irradiations have been shown to first produce an orthorhombic-to-tetragonal transformation at relatively low doses followed by a tetragonal-to-amorphous transformation at doses roughly a factor of 10 higher. Analysis of the displacement stoichiometry that results from 120, 300, and 1000 keV electron irradiations, 400, and 500 keV O⁺ irradiations, and 300 keV helium irradiations indicate that the orthorhombic-to-tetragonal transformation is driven by O atom displacements either alone or in the presence of metal atom displacements and that the transformation to the amorphous phase is driven by displacements on the Y, Cd or other rare earth atom site.

INTRODUCTION

Investigations of the response of the ceramic high temperature superconductors have shown them to have a very rich, diverse and complicated interaction with various radiation fields.¹ One specific effect is that after sufficient dose of 300 keV electrons,² 1 MeV electrons,³ 300 keV He ions,⁴ 400 keV O ions,⁵ and 500 keV O ions,⁶ an insulating amorphous phase is formed in $\text{YBa}_2\text{Cu}_3\text{O}_7$ and after 1 MeV electron irradiation in $\text{GdBa}_2\text{Cu}_3\text{O}_7$. This observation has technological importance in electronic device applications where it can be used to form devices such as a SQUID.⁶ In a more fundamental context, however, amorphization can be used to study both the crystal stability of these materials as well as how they interact with radiation.

In this paper we present a model of irradiation induced amorphization in $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{GdBa}_2\text{Cu}_3\text{O}_7$. It is shown that the amorphization process consists of two transformations. First, displacement produced disorder on the O sublattice transforms the orthorhombic structure to tetragonal. After further irradiation when sufficient numbers of Y or Gd atoms have been displaced, the defected tetragonal phase transforms to the amorphous phase.

CASCADE STOICHIOMETRY

The large mass difference among the O, Cu, Ba, Y, and Gd atoms in the $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{GdBa}_2\text{Cu}_3\text{O}_7$ superconductors has a strong effect on how particle irradiation couples to the material and starts the damage process. Mitchell et al.⁷ who irradiated $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{GdBa}_2\text{Cu}_3\text{O}_7$ with 120 keV electrons and Kirk et al.⁸ who irradiated $\text{YBa}_2\text{Cu}_3\text{O}_7$ with 131- and 152- keV electrons, both concluded that the displacement energy E_d was near 20 eV for O atoms. The maximum recoil energies of the metal atoms from direct electron collisions are 6 eV or less. Further, the observation of twin boundary motion⁹ is a direct indication of O displacement.

Under low energy electron irradiation, the cascade starts with only O displacements with the reasonable assumption that the metal atom displacement energies are equal to or greater than that for O. This is a situation

in which only one sublattice is involved in the displacement process. As we increase the electron energy, the cascade will start to evolve and include more of the atoms (sublattices). A convenient way to describe this process is to calculate the cascade stoichiometry defined as the relative number of displaced atoms of each atom type. The cascade stoichiometry can be written as $A_w B_x C_y D_z$ in the same manner as that for the material.

The average stoichiometry S per target atom is written as

$$S = \sum_i P_i \int_{T_1}^{T_m} \frac{d\sigma_i}{dT} S_i(T) dT \bigg/ \int_{T_1}^{T_m} \frac{d\sigma_i}{dT} dT, \quad (1)$$

where i is summed over the recoil atoms, in this case O, Cu, Ba, Y or Gd. P_i is the relative probability of producing a recoil of type i , $d\sigma_i/dT$ the differential scattering cross section, and $S_i(T)$ is the recoil energy dependent stoichiometry. Results for O recoils in $YBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$ from TRIM Monte Carlo simulations^{3,9} for recoil energies appropriate for 1 MeV electron irradiations are shown in Fig. 1. The data are presented for $E_d = 20$ eV and $E_d = 40$ eV for all atoms, respectively. The values of $S(T)$ are given by setting the value for Cu equal to 3. It can be clearly seen that in O cascades, the Cu and Ba displacements evolve in the same way in $YBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$, where as, Y and Gd displacements are quite different. This is principally a kinematic effect due to their different masses. Calculated cascade stoichiometries for several irradiation conditions with $E_d = 20$ eV are given in Table I.

Fig. 1 Cascade stoichiometry for O recoils in $YBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$ based on TRIM calculations for energies appropriate for 1 MeV electrons. The data are for (a) $E_d = 20$ eV and (b) $E_d = 40$ eV for all atoms with $S(1)$ being determined by setting the value for Cu equal to 3.

Table I. Calculated Cascade Stoichiometry*

Particle	Energy	$\text{YBa}_2\text{Cu}_3\text{O}_7$	$\text{GdBa}_2\text{Cu}_3\text{O}_7$
electron	120 keV	$\text{Y}_0\text{Ba}_0\text{Cu}_0\text{O}$	$\text{Y}_0\text{Ba}_0\text{Cu}_0\text{O}$
electron	300 keV	$\text{Y}_{0.3}\text{Ba}_{0.1}\text{Cu}_3\text{O}_7$	$\text{Gd}_{0.01}\text{Ba}_{0.1}\text{Cu}_3\text{O}_7$
electron	1 MeV	$\text{Y}_{0.4}\text{Ba}_{0.3}\text{Cu}_3\text{O}_7$	$\text{Gd}_{0.1}\text{Ba}_{0.3}\text{Cu}_3\text{O}_7$
helium	300 keV	$\text{YBa}_2\text{Cu}_3\text{O}_5$	-
oxygen	400 keV	$\text{YBa}_2\text{Cu}_3\text{O}_6$	-
oxygen	500 keV	$\text{YBa}_2\text{Cu}_3\text{O}_6$	-

* $E_d = 20$ eV for all atoms

AMORPHIZATION MODEL

Mitchell et al.⁷ have shown that the loss of the twin structure under 120 keV electron irradiation at 90 K in $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{GdBa}_2\text{Cu}_3\text{O}_7$ is due to irradiation disordering of the O anions. This disordering produces an orthorhombic-to-tetragonal transformation. The "untwinning" process occurs extremely rapidly indicating that the transformation takes place when a critical amount of disorder is reached. The tetragonal structure forms displacively without long-range diffusion. Electron micrographs of 1 MeV electron irradiation of a grain boundary region in $\text{GdBa}_2\text{Cu}_3\text{O}_7$ after Nastasi et al.³ are shown in Fig. 2. In Fig. 2(a) the unirradiated grain boundary and twin structure are shown. In Fig. 2(b) the same region is shown after a dose of 2.5×10^{21} e/cm² (0.10 dpa) where the twins have faded, indicating the orthorhombic-to-tetragonal transformation. A similar transformation was observed by Egner et al.⁴ in $\text{YBa}_2\text{Cu}_3\text{O}_7$ after 300 keV He irradiation at a dose of 0.01 dpa.

Fig. 2 Electron diffraction patterns and micrographs from a $\text{GdBa}_2\text{Cu}_3\text{O}_7$ grain boundary region (a) before electron irradiation, and (b) after an exposure to 2.5×10^{21} e/cm², (c) 1.1×10^{22} e/cm², and (d) 6.6×10^{22} e/cm².

Fig. 3 Crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$. In (a) is the perfect structure, (b) illustrates O vacancies, (c) O vacancies and a Y vacancy, and in (d) is shown the legend identifying each atom or vacancy type.

The orthorhombic-to-tetragonal transformation is seen under 120 keV electron irradiation where only O atoms are displaced. It is also observed under 1 MeV electron irradiation where all atoms are displaced. The very heavy Y, Ba, and Cu atoms have cascade stoichiometry values of 0.4, 0.3, and 0.1 respectively (see Table 1). These values are lower than the compositional ones which are 1.2, and 1. The transformation is also seen under 300 keV He ion irradiation where the cascade stoichiometry is quite close to that of the material. These data show that O displacements alone are sufficient to drive the orthorhombic-to-tetragonal transformation. Under conditions where O and other atoms as well are displaced, the transformation also occurs and is likely driven primarily by the O displacements. This conclusion is illustrated in Fig. 3. In Fig. 3(a), we see the crystal structure of unirradiated $\text{YBa}_2\text{Cu}_3\text{O}_7$ with ordered O atoms and O vacancies. The sufficient condition for the orthorhombic-to-tetragonal transformation by producing O vacancies at normally occupied O sites is shown in Fig. 3(b) where O vacancies are indicated by the boxes.

Upon further irradiation the tetragonal phase transforms to an amorphous phase. This is illustrated in Figs. 2(c) and (d) for $\text{GdBa}_2\text{Cu}_3\text{O}_7$. At a dose of $1.1 \times 10^{22} \text{ e/cm}^2$ (0.46 dpa) the material remains crystalline but is increasingly losing contrast. At a dose of $6.6 \times 10^{22} \text{ e/cm}^2$ (2.77 dpa) the material becomes amorphous as indicated by the loss of contrast and the broad diffuse diffracted ring in Fig. 2(c). Observed amorphization doses for $\text{YBa}_2\text{Cu}_3\text{O}_7$ are ~ 0.1 dpa for 300 keV He ions,⁴ 500 keV O ions,⁵ and

2 MeV He ions,¹⁰ and near 1 dpa for 1 MeV electrons.³ Amorphization occurs at a dose roughly 10 times that for the orthorhombic-to-tetragonal transformation.

Nastasi et al.³ compared in detail the amorphization of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{GdBa}_2\text{Cu}_3\text{O}_7$ with 1 MeV electrons. In grain boundary regions they found the amorphization dose in $\text{YBa}_2\text{Cu}_3\text{O}_7$ to be between $1.7\text{--}2.3 \times 10^{22}$ e/cm² and in $\text{GdBa}_2\text{Cu}_3\text{O}_7$ to be between $4.1\text{--}6.6 \times 10^{22}$ e/cm². For large single grains the amorphization dose for $\text{YBa}_2\text{Cu}_3\text{O}_7$ was between $2.5\text{--}3.1 \times 10^{22}$ e/cm² and at a dose of 1.5×10^{23} e/cm² amorphization was not yet observed in $\text{GdBa}_2\text{Cu}_3\text{O}_7$. The amorphization doses for $\text{GdBa}_2\text{Cu}_3\text{O}_7$ are roughly between 3 and 5 times higher than those for $\text{YBa}_2\text{Cu}_3\text{O}_7$. As is shown in Table I, this factor of 3 to 5 is in good agreement with the difference between the cascade stoichiometry values for Y and Gd. All other values for Ba, Cu, and O are the same. They concluded that amorphous phase formation is dependent on displacement cascade stoichiometry and/or the number of displacements that occur at Y and Gd lattice sites.

We propose that displacements of the Y, Gd or other rare earth atom are a necessary condition for amorphization. This condition is illustrated in Fig. 3(c) where O vacancies (displacements) are shown along with a vacant (displaced) Y site. Displacements of the other metal atoms, Ba and Cu, also occur but they are not sufficient for amorphization. Amorphization then proceeds by a sequence of two sublattice specific displacement processes. First an orthorhombic-to-tetragonal transformation is driven by O atom displacements either alone or in the presence of metal atom displacements. At some higher dose, roughly an order of magnitude after the first transformation, the tetragonal phase transforms to an amorphous phase driven by the presence of displacements on the Y, Gd or other rare earth atom site.

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