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# Electron irradiation induced amorphization in $YBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$ superconductors

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Transmission electron microscope specimens of the oxide superconductors $YBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$ have been irradiated at 35 K with 1 MeV electrons and doses up to $1.5\times10^{23}$ $e/cm^2$. Electron diffraction data show the two different superconductors do not respond similarly with $GdBa_2Cu_3O_7$ being more resistant to amorphization than $YBa_2Cu_3O_7$. Amorphization appears to be dependent on displacements occurring at the Y/Gd lattice site. In addition, it appears that within each material, the electron dose required to initiate amorphization is lower for grain boundary irradiations relative to large single grain irradiations.

Recent studies involving the new class of high-temperature oxide superconductors have shown these materials to be very sensitive to particle irradiation,[1-6] producing alterations to electrical and structural properties. Room-temperature ion irradiation studies have shown that the loss of superconductivity is correlated with the formation of an amorphous phase at grain boundaries.[1,2,6] Studies employing 3 MeV electron irradiation at 20 K have also proven effective at reducing the superconducting transition temperature but resulting structural changes were not examined.[5] In the present letter we examine the amorphization ability of 1 MeV electrons on $YBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$ superconductors cooled to 35 K.

Bulk samples of the high-temperature superconductors $YBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$ were produced using standard powder metallurgy techniques.[7] Transmission electron microscope (TEM) specimens were prepared from the bulk superconductors using a standard ion thinning technique. Milling took place at 126 K using 6 keV Ar and a thinning angle of 15°. TEM examination of the as-milled specimens indicated that the material was fully crystalline and that milling damage was kept to a minimum.

High-energy electron irradiation studies were performed in the Argonne National Laboratory High Voltage Electron Microscope (HVEM). The samples were cooled to $35\pm3$ K and irradiated with 1 MeV electrons at peak electron dose rates between $2.48\times10^{19}$ and $6.97\times10^{19}$ electrons/$cm^2$/s. A catalog of TEM micrographs and diffraction patterns at various electron doses was maintained through the irradiations. Focused electron irradiations were performed at both the centers of large single grains, and at grain boundaries which appeared to be clean and free of any second phases, crystalline or amorphous.

The calculated number of atomic displacements resulting from the electron irradiations (dpa) was estimated using Oen's tables of total cross sections for atomic displacements by fast electrons.[8] A displacement energy of 20 eV for all was assumed. This value was chosen based on the recent electron irradiation work of Mitchell *et al.*[9] and Kirk *et al.*[10] and results reported by Clark *et al.* that prolonged 300 keV electron irradiation amorphized $YBa_2Cu_3O_x$.[6] Assuming a 20 eV displacement energy led to a calculated number of atomic displacements per unit electron dose of $43.3\times10^{-24}$ and $42.0\times10^{-24}$ dpa $cm^2$/electron for $YBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$, respectively.

Electron diffraction patterns and micrographs from a $GdBa_2Cu_3O_7$ grain boundary region as a function of electron dose are presented in Fig. 1. The two zone axes irradiated were $[02\bar{1}]$ and $[2\bar{3}1]$. A twin structure can be observed in the micrograph taken of the unirradiated state, Fig. 1(a). After exposing the grain boundary region to $2.5\times10^{21}$ $e/cm^2$ (0.10 dpa) no change in the diffraction pattern was observed but a loss of contrast from the twin structure was evident, Fig. 1(b). The diffraction pattern after $1.1\times10^{22}$ $e/cm^2$ (0.46 dpa) continued to remain crystalline in nature and did not suggest the presence of an amorphous phase. However, electron micrographs taken at this dose were increasingly devoid of any contrast; twins and bend contours present in the unirradiated specimen were no longer present, Fig. 1(c). A broad diffuse diffracted ring, indicating the formation of an amorphous phase, was not observed following an irradiation of $4.1\times10^{22}$ $e/cm^2$ (1.72 dpa), but could be observed following a dose of $6.6\times10^{22}$ $e/cm^2$ (2.77 dpa). Micrographs taken from the boundary region at this dose were devoid of contrast and did not show preferential contrast change at the boundary interface, Fig. 1(d).

Electron diffraction patterns from a [010] oriented $GdBa_2Cu_3O_7$ grain revealed that a single crystal of $GdBa_2Cu_3O_7$ is reasonably insensitive to 1 MeV electron irradiation. The diffraction pattern taken after the maximum electron dose of $1.5\times10^{23}$ $e/cm^2$ (6.30 dpa) was very similar to the initial unirradiated pattern and did not show any evidence for the formation of an amorphous phase.

Diffraction data from the irradiation of an $YBa_2Cu_3O_7$ grain boundary region are presented in Fig. 2. The zone axes

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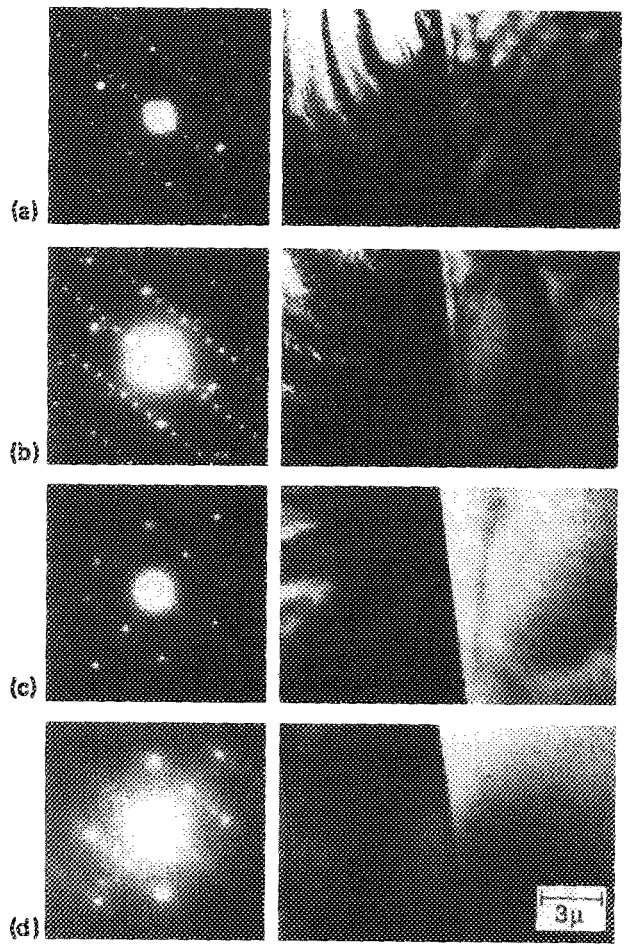


FIG. 1. Electron diffraction patterns and micrographs from a $GdBa_2Cu_3O_7$ grain boundary (g.b.) region (a) before electron irradiation, and (b) after an exposure to $2.5\times10^{21}$ $e/cm^2$, (c) $1.1\times10^{22}$ $e/cm^2$, and (d) $6.6\times10^{22}$ $e/cm^2$.

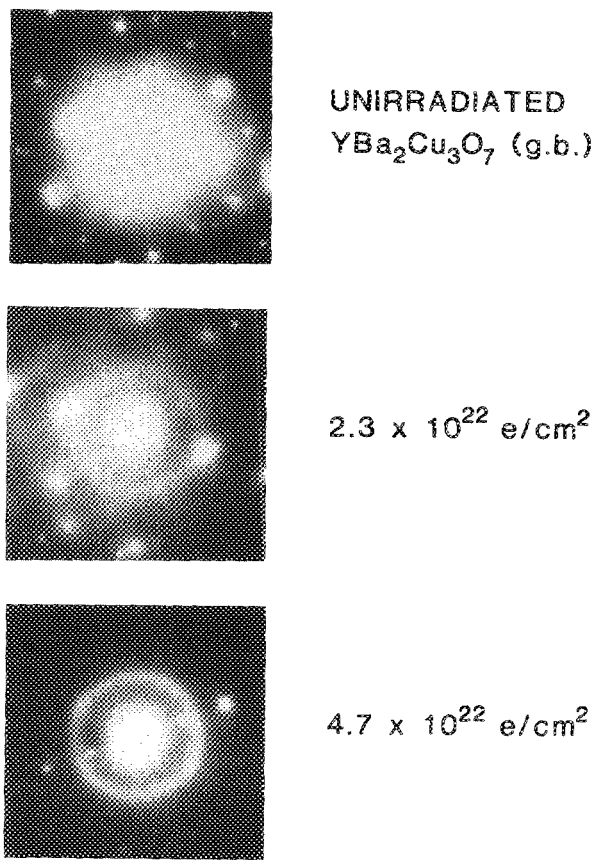


FIG. 2. Electron diffraction patterns from an $YBa_2Cu_3O_7$ grain boundary before and after electron irradiation.

of the two grains irradiated were $[0\bar{2}1]$ and $[\bar{5}72]$. The diffraction patterns remained crystalline for doses up to $1.7\times10^{22}$ $e/cm^2$ (0.74 dpa). A broad diffuse ring, indicating the formation of an amorphous phase, was observed after an irradiation of $2.3\times10^{22}$ $e/cm^2$ (1.00 dpa). Diffraction signals from both a crystalline phase and an amorphous phase were observed after a maximum dose of $4.7\times10^{22}$ $e/cm^2$ (2.04 dpa). Micrographs of the boundary region at this dose did not show any preferential contrast change at the boundary interface.

Electron diffraction patterns taken from a large single grain of $YBa_2Cu_3O_7$, irradiated along the $[0\bar{5}3]$ axis, indicated the existence of only crystalline material for electron doses up to $2.5\times10^{22}$ $e/cm^2$ (1.08 dpa). Following a dose of $3.1\times10^{22}$ $e/cm^2$ (1.34 dpa), the diffraction pattern began to display broad diffuse rings, which were double diffracting from intense crystalline diffraction spots. The relative intensity of the amorphous diffraction signal to the crystalline diffraction signal was observed to increase with electron dose. Both patterns persisted for doses up to $5.5\times10^{22}$ $e/cm^2$ (2.38 dpa).

These electron irradiation data have shown that the superconducting materials, $YBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$, do not behave similarly to 1 MeV electron irradiation at 35 K, with $GdBa_2Cu_3O_7$ being more resistant to amorphization than $YBa_2Cu_3O_7$. In addition, it appears that within each material, the electron dose required to initiate amorphization is lower for grain boundary irradiations relative to large single grain irradiations. The onset of amorphization for grain boundary regions was observed to occur between the doses of $1.7\times10^{22}$ and $2.3\times10^{22}$ $e/cm^2$ (0.74–1.00 dpa) for $YBa_2Cu_3O_7$ and between $4.1\times10^{22}$ and $6.6\times10^{22}$ $e/cm^2$ (1.72–2.77 dpa) for $GdBa_2Cu_3O_7$. The onset of amorphization for large single grains was observed to occur between the doses of $2.5\times10^{22}$ and $3.1\times10^{22}$ $e/cm^2$ (1.08–1.34 dpa) for $YBa_2Cu_3O_7$ and was not observed for $GdBa_2Cu_3O_7$ at the maximum dose of $1.5\times10^{23}$ $e/cm^2$ (6.3 dpa).

The fact that amorphization at grain centers was observed in $YBa_2Cu_3O_7$ but not in $GdBa_2Cu_3O_7$ can be explained in terms of a difference in the displacement cascade between these materials. The maximum energy transferred, $T_m$, from a 1 MeV electron is 271 eV for O, 72 eV for Cu, 49 eV for Y, 32 eV for Ba, and 28 eV for Gd. Assuming a reasonable effective displacement threshold of 20 eV for the metal and oxygen atoms, and using Oen's electron displacement cross section tables,[8] shows that direct displacements of Ba and Gd from electron collisions are small compared to O, Cu, and Y displacements. The principal source of metal atom displacements occurs in the O, Cu, and Y displacement cascades.

TRIM Monte Carlo simulations[11] of O, Cu, and Y displacement cascades were used to determine the number of Y, Ba, Cu and Gd, Ba, Cu displacements in the two materials using a displacement energy of 20 eV, thus obtaining the



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stoichiometry of displaced metal atoms in the cascade. The average stoichiometry $S$ per target atom is defined as

$$S = \sum_i P_i \int_{T_1}^{T_m} \frac{d\sigma}{dT} S(T)\, dT \Big/ \int_{T_1}^{T_m} \frac{d\sigma}{dT}\, dT, \qquad (1)$$

where $i$ represents O, Cu, and Y recoils, $P_i$ is the relative probability of producing an O, Cu, or Y recoil in a $123O_7$ target with a 1 MeV electron, $d\sigma/dT$ is the differential scattering cross section for an O, Cu, or Y atom receiving a recoil energy $T$, and $S(T)$ is the resulting recoil energy dependent stoichiometry.

For these calculations, $S(T)$ was defined as the ratio of displaced Y, Ba, and Gd atoms to Cu atoms, setting the Cu stoichiometry at 3 for comparison with that in the material. To be consistent with this definition of $S(T)$, the integrals in Eq. (1) were performed from values of $T_1$ corresponding to the minimum recoil energy for displacing a metal target atom or a Cu atom in the case of the O cascade, and $T_m = 271$ eV. The relative stoichiometry of metals is only meaningful when at least one type of metal atom is displaced.

The TRIM values for $S(T)$ from an O recoil stimulated cascade are given in Fig. 3 for Y, Gd, and Ba in the two materials. The calculated values of $S$ using Eq. (1) and a Seitz and Koehler approximation to the McKinly–Feshbach displacement cross section[12] are $Y_{0.4}Ba_{0.3}Cu_{3.0}$ and $Gd_{0.1}Ba_{0.3}Cu_{3.0}$. This result shows that the stoichiometry of the cascade is different between the Y-based material and the Gd-based material with the probability of Y displacements being four times that of Gd, in reasonable agreement with our observations. A conclusion that can be reached is that the nucleation of an amorphous phase in either of the two materials is dependent on the cascade displacement stoichiometry and/or the number of displacements that occur at the Y/Gd lattice sites.

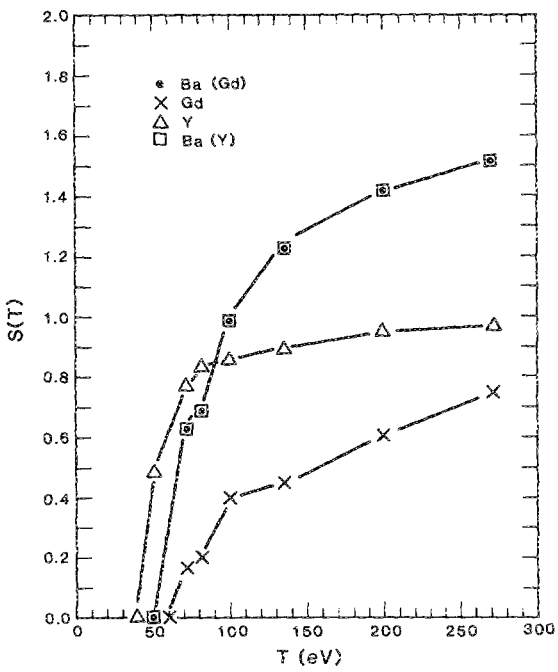


FIG. 3. TRIM calculations of the ratio of displaced Y, Ba, and Gd atoms to Cu atoms, $S(T)$, produced by O recoils of energy $T$, in the materials $GdBa_2Cu_3O_7$ (Gd) and $YBa_2Cu_3O_7$ (Y). Displacement values for Y, Ba, and Gd have been normalized by setting the Cu displacement stoichiometry at 3.

A similar analysis was also carried out assuming an electron energy of 300 keV to examine the experiments of Clark *et al.*[6] Calculated values for $S$ in this case were $Y_{0.3}Ba_{0.1}Cu_{3.0}$ and $Gd_{0.01}Ba_{0.1}Cu_{3.0}$. This result shows an even greater difference in the stoichiometry of the cascade relative to the 1 MeV case, and suggests that the amorphization dose at 300 keV will be 30 times larger for $GdBa_2Cu_3O_7$ relative to $YBa_2Cu_3O_7$. However, the Y stoichiometry is little affected between 300 keV and 1 MeV.

We have also observed that amorphization occurred more easily at grain boundaries relative to grain centers with electron doses being reduced by approximately 28% for $YBa_2Cu_3O_7$ and more than 64% for $GdBa_2Cu_3O_7$. These observations are consistent with the work of Clark *et al.* which showed the appearance of a grain boundary amorphous layer in $YBa_2Cu_3O_7$ following low-dose room-temperature ion irradiations.[2] Ion-induced grain boundary amorphization was attributed to grain boundary defect accumulation resulting from irradiation-enhanced diffusion and segregation. In the present experiments the samples were maintained at 35 K during the irradiations in an attempt to eliminate or minimize diffusional effects. Thus, our observations suggest that either irradiation generated defects in these materials are mobile at 35 K and are producing an amorphous phase by accumulating at grain boundaries or that the increased free energy of the nominally disordered grain boundary reduces the number of additional displacement needed to nucleate the amorphous phase.[13]

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