ION BEAM MODIFICATION OF Tl-Ba-Ca-Cu-O TYPE HIGH TEMPERATURE SUPERCONDUCTORS DURING IRRADIATION

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ABSTRACT

Microstructural modification of high temperature superconductor (HTS) single-crystal plates of Tl-1212 and Tl-2212 (numbers designate the Tl/Ba/Ca/Cu cation ratio) was studied during 1.5 MeV Kr^+ and Xe^+ ion irradiation with in-situ electron diffraction and after ion irradiation with high resolution TEM (HRTEM). Similar in-situ temperature dependence effects are seen for both phases. During irradiations from 22K to 673K, an amorphous halo develops after very low ion dose or fluence ($1.7X10^{12}$ ions/cm^2). During irradiation at 100K and 300K, complete amorphization is obtained, while at 22K and $\geq$533K, the halo fades slightly and a polycrystalline ring pattern develops, indicating ion irradiation induced crystallization occurred. After a low ion dose ($8.5X10^{12}$ions/cm^2) at 100K and 300K, HRTEM reveals amorphous regions 5 -20 nm in size which are not columnar and do not all penetrate the entire sample thickness. At 22K and $\geq$533K, Moire fringes and misoriented crystallites of cascade size are observed. The 4 - 6nm crystallites are thallium-rich.

INTRODUCTION

The Tl-Ba-Ca-Cu-O system has produced high temperature superconductor (HTS) phases with critical temperatures, Tc's, to 125 K. Single crystal x-ray diffraction structure refinements, [1, 2], show these materials are tetragonal, *I4/mmm* or *P4/mmm* (depending on double or single Tl-O layers respectively), consisting of alternating perovskite and rock-salt-like layered structure [3]. Four major HTS phases exit: Tl-1212 and Tl-2212, (which are of concern in this study), and Tl-1223 and Tl-2223 (numbers designate the Tl/Ba/Ca/Cu cation ratio). The Tc varies between as well as within the phases. Variations in lattice parameter and Tc values within a particular phase probably result from cation solid solution effects, consistent with the single crystal structure refinements showing the replacement of some of the Ca^{2+} with the slightly smaller Tl^{3+}[1]. In addition, similarity in the *a*-axes of these structural units allows for complex stacking in the *c*-axis direction, much like strained layer superlattice structures.

A serious handicap of these HTS is the easy motion of the magnetic vortices, which results in limitation to the critical current density, Jc, particularly at elevated temperatures in high magnetic fields [4]. The mobility of the vortices can be hindered or pinned by introducing certain defects into the structure, such as nano-size steps, holes, or radiation damage, creating a physical barrier. High Jc is very important in most practical applications of HTS. Ion irradiation can enhance Jc at modest doses (fluences); however, higher doses can decrease Tc and increase normal state resistivity [4].

Electromagnetic characterization of ion beam effects in Tl-type HTS has been reported for Tl-2223 [4, 5] single crystals and thin films irradiated with protons and neutrons. The pinning potential in one such crystal increased by 25% after irradiation with 4.5 MeV protons; however the Tc decreased [6]. Recovery of radiation damage was shown by in-situ resistance measurements [4] in which a Tl-2223 film was irradiated at room temperature with 20 MeV Au^+ ions. The deviation in linearity of the resulting curve for normal state resistance with respect to temperature may be related to ion beam induced changes in the microstructure, and can be modeled as small regions of insulating material imbedded in a conductive medium [4], which suggests a diffusion controlled damage recovery. An activation energy of 0.36 eV has been

calculated for the recovery of normal state resistance with time at 500 keV He^{2+} for the temperature range 250 to 375K [7].

In this paper we explore the microstructural modification of Tl-1212 and Tl-2212 single crystals by high energy ion irradiation in relation to the temperature at which the irradiation occurs. The thermal conductivity, κ (T), of the material must be taken into account. A common behavior has been found for κ (T) of HTS with decreasing temperature to Tc. There is an initial decrease from room temperature, then a peak at Tc, after which κ (T) drastically reduces as temperature decreases to 0 K [8].

EXPERIMENTAL METHODS

Single crystal plates of Tl-1212 and Tl-2212 were grown from a melt of metal oxides [9]. High quality crystals have sharp x-ray precession maxima with little or no streaking between spots and narrow superconducting Meissner transitions. Further studies such as crystal structure refinements, HRTEM, radiation effect studies, Meissner transitions, and annealing studies have been done. High quality crystals were selected for this ion irradiation study. Samples for in-situ ion irradiation and HRTEM were prepared in plan section view of the plates to observe the [100] direction. Submillimeter crystal plates were mounted in slots of $LaAlO_3$ slabs with MBond 610 epoxy and press/cured. These slabs were finely polished down to the desired section with a tripod polisher, attached to a single hole copper (or nickel for EDS study) grid, and mechanically thinned to 80 μm. Specimens were then placed on a dimple grinder until the final thickness was 10 - 20μm. Specimen thickness was measured using a petrographic microscope with a calibrated fine scale focus. The specimens were ion milled with 5 keV Ar^+ employing an angle below 10 degrees to minimize ion mill damage.

The single crystal Tl-2212 and Tl-1212 samples were irradiated with 1.5 MeV Kr^+ and Xe^+ at various temperatures (22 - 673K) and observed in-situ using the HVEM-Tandem Facility at Argonne National Laboratory [10]. Electron diffraction was monitored and photographed during ion irradiation, which continued until the original phase was amorphized or completely modified. In addition, at temperatures, 22 to 673K, samples were irradiated with low dose ($8.5X10^{12}$ ions/cm^2) and were studied later with HRTEM on the JEOL 2010 equipped with a Gatan 694 slow-scan camera in the Earth and Planetary Sciences Department at University of New Mexico. The data were analyzed quantitatively using the Gatan Digital Micrograph software package and nanobeam EDS. Digital HRTEM images were processed using the methods of Sattler and O'Keefe [11].

RESULTS

In-situ TEM has shown both the Tl-2212 and Tl-1212 materials undergo a crystalline to amorphous transformation during 1.5 MeV Kr^+ and Xe^+ ion beam irradiations at temperatures of 100K (≈Tc) and room temperature (300K). It is believed that amorphization occurs directly in the displacement cascades just as in most other complex ceramic materials [12]. The critical ion dose, Dc is the dose at which the amorphization process is complete or, if amorphization does not occur, the original structure is completely modified. In-situ TEM reveals that all Tl-2212 and Tl-1212 samples, ion irradiated at temperatures of 22K to 673K, underwent initial amorphization at only $\approx 10^{12}$ ions/cm^2, a low dose. Dc behaved quite differently at each temperature; although similarly for both phases. Figure 1 shows that at 300K, Dc for Tl-1212 is $9.69x10^{13}$ ions/cm^2 and for Tl-2212 it is slightly larger. Dc increases with increasing temperature above 300K and below 300K it decreases until Tc. Here the minimum Dc occurs ($7.5X10^{13}$ ions/cm^2), indicating the damage is easily quenched and the structure is quickly amorphized.

Unexpectedly, the Dc increases below 100K (Tc) and amorphization does not occur. The original structure is completely modified at a Dc of $3.21X10^{14}$ ions/cm^2 for Tl-1212 and at $6.46X10^{14}$ ions/cm^2 for Tl-2212 . Electron diffraction shows that polycrystalline rings develop

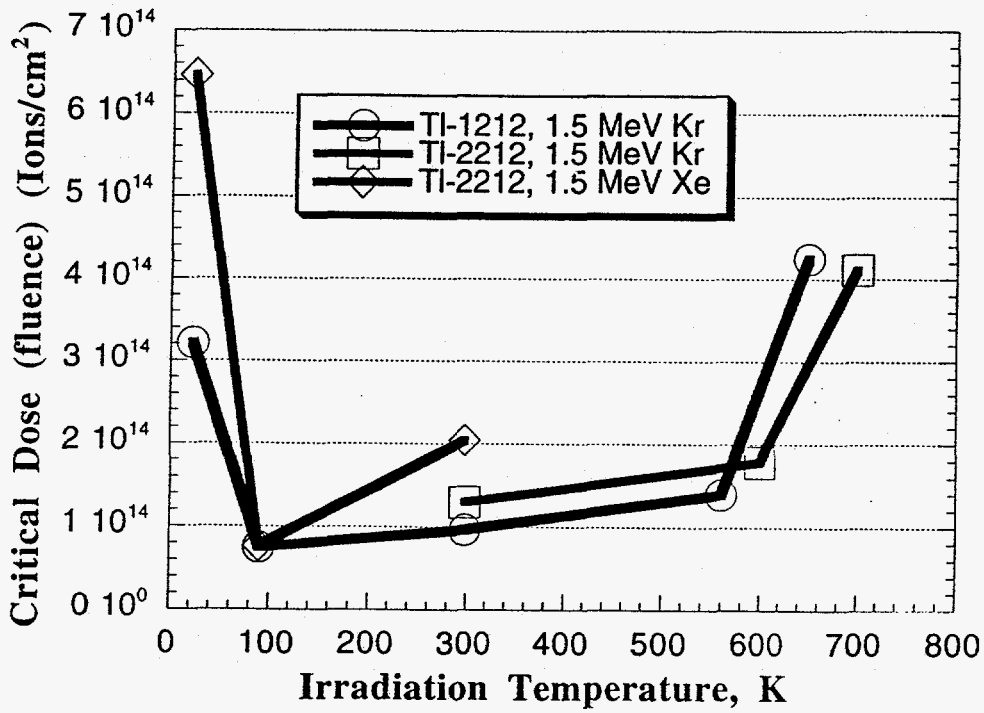

Figure 1. The dose at which the original structure of the HTS single crystal amorphizes or is completely changed in relation to temperature. Below 100K the single crystal transforms to polycrystalline and amorphous domains.

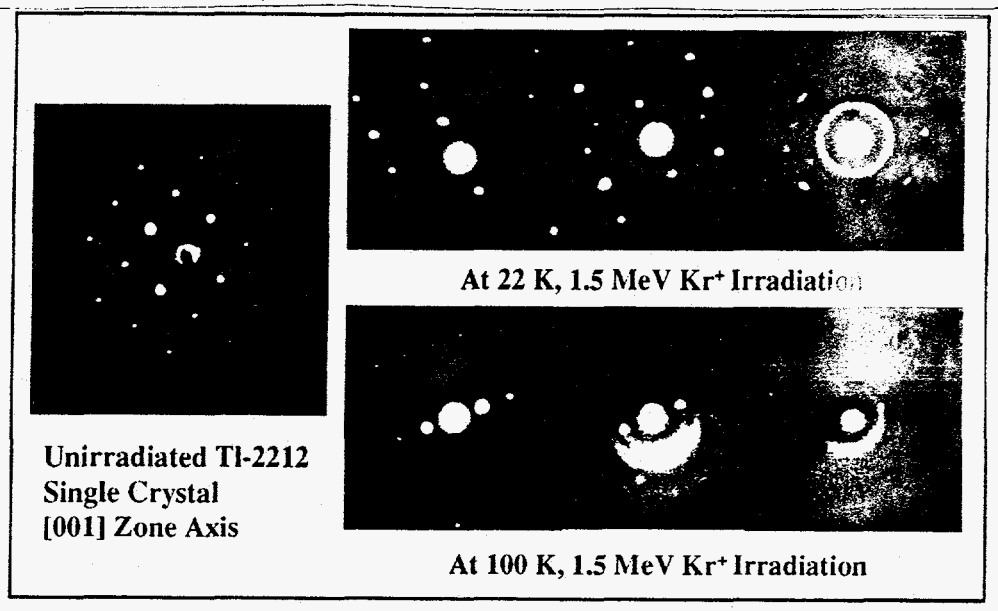

Figure 2. On the left, an electron diffraction pattern for Tl-2212 displays the quality of all the undamaged Tl-2212 and Tl-1212 single crystals before ion irradiation. On top, in-situ electron diffraction from left to right shows the result of continuous ion irradiation until Dc is reached (right) and polycrystalline rings exist. On the bottom, in-situ electron diffraction from left to right shows the result of continued ion irradiation until Dc where complete amorphization occurred.

during the irradiation. This is not consistent with previous studies of temperature dependence of Dc in complex ceramics, $ZrSiO_4$ and (Mg-Fe-Be)SiO_4 non-HTS structures, [13,14] which reveal Dc decreases consistently down to 0 K. One explanation is the unique temperature dependent

behavior of κ (T) in HTS [8]. As temperature decreases below 300K, the temperature dependent behavior for κ (T) in HTS's results in a gradual decrease in κ (T) , an increase at Tc, and a drastic decrease below Tc. One explanation for the temperature dependence of the ion irradiation damage in Tl-2212 and Tl-1212, suggests a relationship to the κ (T) behavior. Below Tc, damage is unable to quench due to the inability to dissipate the heat created by ion induced thermal spike heating and crystallization occurs. At Tc the damage is easily quenched and amorphization occurs. At temperatures $\geq$533K polycrystalline rings developed and thermal annealing effects are probably due mostly to the high temperature environment.

HRTEM was used to observe isolated damage in Tl-2212 and Tl-1212, which were ion irradiated with a low dose of $8.5X10^{12}$ ions/cm^2, between 100 and 533K. Figure 3 shows

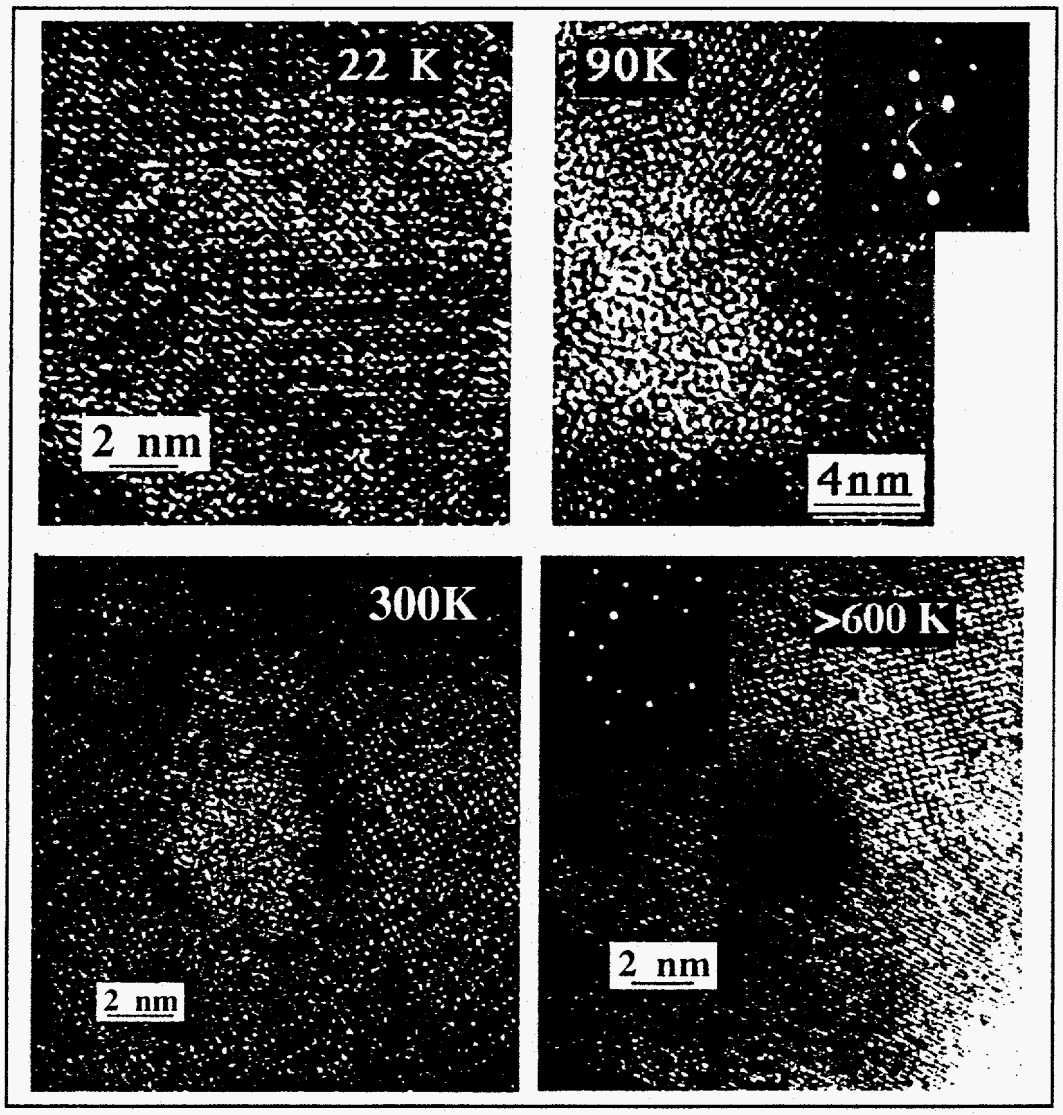

Figure 3. The microstructure of low dose 1.5 MeV Kr^+ ion irradiated samples at temperatures of 22K, 90K, 300K, and $\geq$533K. At 22K, Moire fringes indicate nucleation of misoriented layers. At 90K ($\approx$Tc), an amorphous cascade in a less than coherent matrix indicate an amorphization process occurs quickly in the matrix, notice the strong amorphous halo in the adjoining diffraction pattern. At 300K, an amorphous domain in coherent crystal matrix shows an isolated collision cascade. At >600K, Moire fringes in a coherent region indicate nucleation of misoriented layers.

HRTEM images of amorphous domains (damage cascades) about 5 nm in size, somewhat circular and crescent shapes, in otherwise undamaged coherent crystal matrix; except at 100K, non-coherence was observed around the damage cascades, indicating easy quenching of damage. The damaged regions do not penetrate the entire sample thickness and appear to be planar as opposed to columnar, as indicated by fourier transform of regions which reveal some periodic structure. This is consistent with a model by Miller [15] who has shown 30% of a structure through the observed thickness can be amorphous and yet the HRTEM image looks undamaged.

Below Tc and $\geq$533K, HRTEM of samples which were also ion irradiated with a low dose of $8.5X10^{12}$ ions/cm^2, revealed circular, misoriented, cascade size crystallites and amorphous domains as well as Moire fringes indicating crystallization of mismatched lattice as shown in figure 3. Electron diffraction for these samples show an amorphous halo along with polycrystalline rings. Ion irradiation induced nano-scale polycrystallization has been seen in some intermetallics and other non-HTS ceramics [16]. The ion beam induced crystallites in this study are Tl-rich as identified with nano-beam EDS and the reduced thallium phase, thallous cuprate, has been identified. Although both the Tl-2212 and Tl-1212 single crystal phases exhibited similar ion beam damage effects, more of the thallous oxide crystallites were found in Tl-2212, the more thallium rich phase. This may be an indication the thallium is reducing, from a Tl^{3+} to Tl^{1+} and generating the high temperature phase, Tl_2O. It has been found previously that the formation of oxygen vacancies changes the density of hole carriers and no damage occurs to the cyrstal structure. In particular the Tl-O layers can be deficient in oxygen and small atomic displacements in atom positions, as determined by least squares refinement, are consistent with a model in which small amounts of Tl^{1+} are reversibly oxidized to Tl^{3+} during annealing in the presence of oxygen and Tl^{3+} is reduced to Tl^{1+} during annealing in a reducing environment [5]. This model is used to suggest a mechanism for damage recovery during ion irradiation in high vacuum at various temperatures. The heat induced and/or generated in the sample, because of the inability to dissipate heat from thermal spike annealing, can create oxygen vacancies and the interstitial oxygen could be taken up in the undamaged matrix.

At all temperatures in both Tl-2212 and Tl-1212, crystallization of cascade-size crystallites can also be induced by the electron beam interaction at 200 KeV. These crystallites form only in amorphous regions, as seen by in-situ HRTEM. All samples revealed weak polycrystalline rings after some time in the electron beam; however, this damage can be differentiated from ion beam damage because it occurs slowly enough to observe in HRTEM.

SUMMARY

A better understanding of the relationship between ion-induced damage and chemistry in the Tl-type HTS structure and the control of vortex pinning is necessary for most practical uses of this material. Single crystals of Tl-2212 and Tl-1212, irradiated at temperatures 22K to 670K, behave similarly. The unexpected inability to amorphize the Tl-type single crystals below Tc, may be related to the temperature dependence behavior for $\kappa(T)$ for HTS.

HRTEM of Tl-2212 and Tl-1212 after a low dose of $8.5X10^{12}$ ions/cm^2 revealed isolated damage cascades whose microstructures displayed temperature dependence. At 100K and 300K, ion irradiation produced amorphous domains without much other damage. At temperatures below Tc and above 530K, many defects are created such as crystallized cascades where thallium reduction takes place, lattice mismatched crystallization, and amorphization. More of these ion radiation effects are seen in Tl-2212 than in Tl-1212, suggesting a thallium content dependence, which is consistent with the higher Dc values for Tl-2212. It is believed that thermal annealing takes place at temperatures as low as 22K because the heat created by a thermal spike during irradiation is unable to dissipate due to the lower thermal conductivity.

Image simulation should be done to better interpret the damage regions with respect to the undamaged periodic matrix. Cross-section samples, [001], will be prepared and irradiated by the conditions in this study to determine if a relationship exists between cascade shape and crystallographic anisotropy.

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