X-ray Irradiation Effects on the Superconductive Properties of YBa$_2$Cu$_3$O$_y$ and GdBa$_2$Cu$_3$O$_z$

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We observed a metastable change in the superconducting properties of YBa$_2$Cu$_3$O$_y$ (YBCO) and GdBa$_2$Cu$_3$O$_z$ (GdBCO) induced by X-ray irradiation. $T_c$, which is defined as the temperature below which the electric resistance is zero within the measurement accuracy, was increased by up to 1.9 K in YBCO and GdBCO. The irradiation effect was more pronounced for the YBCO sample with lower $T_c$. These observations are consistent with those of light irradiation, and are attributable to hole doping in the CuO$_2$ plane via the generation of electron–hole pairs by the X-ray and subsequent trapping of the electrons at oxygen vacancies. The relaxation of the irradiation effect was observed to be within 100 h from the viewpoint of conductivity and Raman spectra, and is explained as the detrapping of the electrons and recombination with holes, similarly to the case of light irradiation.

1. Introduction

Superconductors are extensively studied because of their unique features, such as zero conductivity and the Meissner effect. Since the discovery of cuprate superconductors$^{(1)}$ with a superconducting transition temperature ($T_c$) above the temperature of liquid nitrogen (77 K)$^{(2)}$, studies of superconductivity have become more widespread.

It has long been known that the properties of cuprate superconductors depend strongly on the carrier concentration. Thus far, the carrier concentration has been controlled in several approaches. The most common approach is chemical doping, in which carriers are doped via chemical composition, similarly to the case of inorganic semiconductors. One of the shortcomings of the chemical doping is that the achievable carrier concentration is limited by stable chemical composition. External doping is an alternative method. An example is doping with light irradiation. In a previous paper, the increase in $T_c$ by up to 7 K has been reported with laser irradiation onto YBa$_2$Cu$_3$O$_y$ (YBCO: $y = 6.4–6.9$) thin films.$^{(3–5)}$ This effect is explained with the hole doping in the CuO$_2$ plane: light irradiation generates electron–hole pairs. The electrons are trapped at the O vacancies in the CuO chain, which is confirmed by Raman spectroscopy,$^{(6)}$ and the holes are doped in the CuO$_2$ plane. It is known that the $T_c$ in YBCO differs with different $y$ values in the chemical formula. The light irradiation effect was more significant for the sample with a smaller $y$, i.e., lower $T_c$.$^{(3–5)}$ The effect of the X-ray irradiation was shown to be more pronounced with higher irradiation temperature.$^{(7–9)}$

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These reports lead to a hypothesis that X-rays, which have high permeability and energy, can enhance the superconductive properties of not only thin films, but also bulk materials. In this paper, the effects of X-ray radiation on the conductivity of YBCO and GdBa$_2$Cu$_3$O$_7$ (GdBCO) pellets are reported. In addition, the relaxation process is analyzed from the viewpoint of conductivity and Raman spectra.

2. Materials and Methods

YBCO and GdBCO ceramic samples were synthesized by the amorphous citrate method. This method is known to have an advantage in preparing samples with uniform composition. For the synthesis of YBCO, Y$_2$(CO$_3$)$_3$ (99.99%), BaCO$_3$ (99.99%), and CuO (99.99%) were mixed in a stoichiometric ratio. The mixed powder was dissolved in water with citric acid. The molar amount of citric acid was 5 times that of Y$_2$(CO$_3$)$_3$. The solution was concentrated at 453 K for 12 h. Subsequently, the concentrated solution was pyrolyzed at 773 K to obtain the precursor. The precursor was calcined at 1217 K for 12 h. Finally, the obtained powder was pressed into pellets and calcined, typically at 1227 K for 15 h and subsequently at 673 K for 12 h in air or vacuum. GdBCO was synthesized using Gd$_2$O$_3$ (99.9%), BaCO$_3$ (99.99%), and CuO (99.99%) as raw materials and by the same procedure as YBCO. To prepare the samples with different superconductive properties, the samples were calcined at different temperatures and atmospheres (in air or vacuum) at the final stage of the sample preparation.

The crystal structure of the samples was characterized by X-ray diffraction (XRD; Ultima IV, Rigaku) using Cu Ka radiation. To analyze the uniformity, energy-dispersive X-ray (EDX) elemental analysis was performed (FE-SEM S-4800, Hitachi High-Technologies). The electric resistance was measured by a four-probe method. A Au electrode was deposited onto the samples via sputtering. The gap between the electrodes was 1 mm. To measure the electric resistance at low temperature, the sample was attached onto a Teflon sheet on a sample holder made of copper. The sample was cooled with a closed-cycle-type liquid He refrigerator (Daikin Cryotec). The temperature of the sample was monitored using a AuFe-chromel thermocouple attached onto the sample holder. The sample was irradiated with X-rays from a Cu X-ray tube operated at 40 kV and 40 mA (XGD 2300-HK, Rigaku). The sample was irradiated inside the cryostat through a Be window. The sample size was 13 mmφ and the beam spot size in the cryostat was significantly larger. Thus the entire part of the sample was irradiated with the X-rays. The details of the irradiation and measurement system are described in a previous paper. The irradiation was performed at room temperature. Subsequently, the electric resistivity as a function of temperature was measured. For the analysis of relaxation, the sample was irradiated with X-rays for 72 h, and the electric resistivity as a function of temperature was measured several times. The sample was kept at room temperature between measurements. For the analysis of the electron trapping after the irradiation, Raman spectroscopy is performed for the sample irradiated with X-rays for 72 h, because the irradiation effects are most clearly observed for this irradiation duration in the conductivity (NRS-5100, Jasco).
3. Results and Discussion

Figure 1 shows the XRD patterns of YBCO and GdBCO samples. The patterns are consistent with those in the PDXL Database. The obtained samples are composed of a single phase. Figure 2 shows the elemental mapping results of GdBCO using EDX. The mapping patterns are consistent for all the elements, which indicates that the elemental composition is uniform in the sample. The modulation in the intensity in the maps is attributable to the uneven surface of the sample.

Figure 3 shows the temperature dependence of the electric resistance of a YBCO sample (#2) before and 18 and 72 h after the X-ray irradiation. Before the irradiation, the electric resistance...
is zero within the measurement accuracy below 66.5 K, which we define as \( T_c^0 \). After the X-ray irradiation, the resistance is decreased. \( T_c^0 \) is increased by 0.5 and 0.8 K by the X-ray irradiation for 18 and 72 h, respectively. The longer-duration irradiation causes a more pronounced enhancement in \( T_c^0 \). In addition, the temperature of the onset of resistance drop is also enhanced by the X-ray irradiation. Figure 4 shows the temperature dependence of the electric resistance of YBCO samples (#3 and #1) before and after the X-ray irradiation for 72 h. The irradiation effects are more pronounced at around \( T_c^0 \) than the onset of the resistance drop. The change in \( T_c^0 \) is discussed below. Figure 5 shows the temperature dependence of the electric resistance of a GdBCO sample before and after the X-ray irradiation. The \( T_c^0 \) is increased by 1.5 K by the X-ray irradiation for 12 h. These observations strongly suggest that holes are doped in the \( \text{CuO}_2 \) plane with the X-ray irradiation, and the doped holes contribute to an enhancement of the superconductive properties through an increase in the number of Cooper pairs, similarly to the case of light irradiation.\(^{(3–5)}\)

Table 1 summarizes the rise in \( T_c^0 \) of YBCO samples after the X-ray irradiation for 72 h. The rise is larger for the sample with lower \( T_c^0 \). This tendency can be explained as follows: the

![Fig. 4](image_url)

**Fig. 4.** (Color online) Electric resistance of YBCO samples (a) #3 and (b) #1 as a function of temperature before and after X-ray irradiation for 72 h.

![Fig. 5](image_url)

**Fig. 5.** (Color online) Electric resistance of a GdBCO sample as a function of temperature before and after X-ray irradiation for 72 h.

| Sample | \( T_c^0 \) before irradiation (K) | \( T_c^0 \) after irradiation (K) | Rise in \( T_c^0 \) (K) |
|--------|----------------------------------|----------------------------------|------------------------|
| #1     | 51.5                             | 53.4                             | 1.9                    |
| #2     | 66.5                             | 67.3                             | 0.8                    |
| #3     | 75.1                             | 67.6                             | 0.5                    |
holes are doped with the X-ray irradiation through the generation of electron–hole pairs and the subsequent trapping of electrons at oxygen vacancies. Since there are more oxygen vacancies in the YBCO sample having lower $T_{c0}$, the excited electrons can easily be trapped by these vacancies. Therefore, more holes are doped in the CuO$_2$ plane and more Cooper pairs are generated, leading to a greater effect of the X-ray irradiation. This tendency is consistent with that in the case of light irradiation.\(^{(3–5)}\)

Figure 6 shows $T_{c0}$ as a function of time after irradiation. The original $T_{c0}$ of this sample is 52.2 K. After the X-ray irradiation for 72 h, $T_{c0}$ was initially increased to 55.6 K. Subsequently, $T_{c0}$ gradually decreased to the original value within 100 h. This relaxation process is attributable to the decrease in the hole concentration in the CuO$_2$ plane because of the recombination of holes with the trapped electrons. In a previous paper, the relaxation after light irradiation was reported to occur within 100 h.\(^{(5)}\) This time scale is consistent with that in the case of X-ray irradiation. This result indicates that the relaxation occurs in the same process in the case of X-ray and light irradiation.

Figure 7 shows the Raman spectra of the YBCO sample at different times after the X-ray irradiation for 72 h. The peak at approximately 592 cm$^{-1}$ is attributed to oxygen vacancies at the edge of a CuO chain.\(^{(6)}\) The peak intensity increases within 24 h and stays constant afterwards. The time evolution of the peak intensity indicates that the number of such oxygen vacancies increases with time after the irradiation. In a previous study of light irradiation,\(^{(6)}\) the peak intensity decreased with the duration of light irradiation, and the decrease is attributed to the trapping of electrons at the vacancies.\(^{(6)}\) On the basis of this consideration, our observation of the increase in the peak intensity with time is attributed to the detrapping of electrons from the oxygen vacancies. The time scale of this detrapping is consistent with the relaxation in $T_{c0}$. These results strongly suggest that the effect of X-ray irradiation is quite similar to that of light irradiation from the viewpoint of the dynamics of electron–hole pairs. X-ray irradiation is advantageous over laser irradiation from the viewpoint of permeability into bulk materials, and X-rays with higher energy would be useful for the permeability.
4. Conclusions

We have presented the X-ray irradiation effects on YBCO and GdBCO. $T_{c0}$, which is defined as the temperature below which the electric resistance is zero within the measurement accuracy, was increased by the irradiation. The increase in $T_{c0}$ was larger for the YBCO sample with the lower original $T_{c0}$. This increase in $T_{c0}$ can be explained by hole doping in the CuO$_2$ plane originated from the generation of electron–hole pairs by the X-ray and the subsequent trapping of electrons at oxygen vacancies. After the X-ray irradiation, $T_{c0}$ gradually returned to the original value within 100 h. On the basis of the change in the Raman spectra with time after the irradiation, this relaxation is attributable to the detrapping of the trapped electrons and recombination with holes, resulting in the reduction in the hole concentration to the original value. These irradiation effects are quite similar to those of light irradiation.

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