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PROCESSING PARAMETERS AND KINETICS OF BROMINATION AND CHLORINATION IN THE $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ SYSTEM

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Abstract

The introduction of halogens such as Cl_2 , Br_2 can restore 90 K superconductivity to oxygen deficient $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$. This is potentially important for applications to thin film devices due to the low processing temperatures required relative to reprocessing with oxygen. Low temperature 260°C and short time (>5 minute) bromination has been shown¹ to convert initially insulating $\text{YBa}_2\text{Cu}_3\text{O}_{6.2}$ powder to a high temperature superconductor with properties similar to the standard O_7 material. This process has now been extended to single crystals as well, but with somewhat different processing parameters. Thermal gravimetric analysis (TGA) coupled with mass spectrometry indicates that the Br becomes strongly bonded, with no release of Br observed in taking powder samples to 1000°C in flowing forming gas ($2\%\text{H}_2/98\%\text{N}_2$). The reaction has also been found to be highly exothermic for both Br and Cl treatments, which is consistent with the strong bonding of the bromine discussed above.

Introduction

It has been shown by several groups¹⁻⁴ that exposing initially insulating $\text{YBa}_2\text{Cu}_3\text{O}_{6.2}$ ($\text{YBCO}_{6.2}$) to either chlorine or bromine can restore high T_c superconductivity. Radousky et al.,³ have shown that the kinetics of the bromination process is extremely fast, relative to oxygenation. At 260°C the bromination process requires approximately five minutes to restore 90K superconductivity with essentially a full 100% volume fraction to the YBCO_6 powder. It was also reported³ that the bromine is strongly bonded in the material, and was not released even when heated in hydrogen to 1000°C . Outstanding questions still remain as to the location of the Br atoms in the material, the mechanisms of diffusion and reaction, and the mechanism by which the superconductivity is restored in the halogenated materials. In this paper we report a study of the kinetics of bromination of single crystals, and both bromination and chlorination of polycrystalline material.

Experimental Details

The experimental methods used to prepare and characterize the sample has been described in detail previously.³ Briefly, powders of the YBCO materials were prepared with oxygen content near 7.0 and 90 K transition temperatures. These powders were then annealed in flowing nitrogen at 600°C to remove oxygen, which made the powders insulating and non-superconducting. Finally, these powders were exposed to either bromine or chlorine in a sealed vacuum line. The flasks containing the powders were heated to the appropriate temperatures, 160°C for Cl and 260°C for Br and held there overnight to assure that any moisture would be removed from the powders. The temperature was measured using thermocouples which were in close proximity to the powders, but separated by a thin wall of pyrex. For the single crystals, the procedure was similar. The crystals of YBCO were prepared using a flux growth technique described previously.⁵

The crystals were equilibrated at temperature overnight to ensure that the temperature of the crystal was the same as the that of the flask. The temperatures quoted are from the thermocouple reading and are uncorrected. The single crystals which lie on the bottom of the flask are approximately 20°C higher in temperature than the thermocouple reading. The actual temperature of the powders, which surrounded the thermocouple, are close to the uncorrected reading.

Fig. 1. Temperature vs time histories for YBCO_{6+x} powders exposed to bromine or chlorine at 260°C or 160°C respectively. Note the similarity for the Cl and Br time dependences. The sharp fall off in temperature at 60 minutes corresponds to turning off the heater.

Results

Figure 1 shows the temperature vs time curves for one hour halogenations using both Cl starting at 160°C and Br at 260°C . In both cases, a very strong temperature rise was observed starting from when the halogen was introduced into the processing vessel, which shows that this reaction is exothermic in nature. For bromine the temperature rose from 260 to 410°C in three minutes, while the chlorinated sample rose from 160 to 280°C over a three minute time period.

For both halogens, the steep rise was followed by a temperature fall off to a steady state, intermediate between the starting and maximum temperature. This plateau remained until the heater was shut off, causing the sharp downturn in temperature shown in Fig. 1.

Fig.2 Magnetization (emu/g) vs temperature for YBCO powders processed for 60 minutes in chlorine or bromine.

The zero field magnetization curves vs temperature are shown in Fig. 2 for the chlorinated and brominated samples. For both samples, a transition starting near 90 K was observed. The magnetization is plotted as emu/g to allow comparison between samples of different weights.

Fig. 3 and 4 show expanded versions of the early time behavior of the brominated and chlorinated materials respectively. Both curves are well fit with a logarithmic time dependence. The chlorinated sample showed a time delay of nearly 0.3 minutes before the temperature rise began.

Fig. 3. Expanded version of Fig. 2 showing the early time behavior for the brominated sample. The line through the data is a logarithmic fit.

Fig. 4. Expanded version of Fig. 2 showing the early time behavior for the chlorinated sample. The line through the data is a logarithmic fit. Note that for the Cl sample has a small time delay of 0.3 minutes was observed before the sharp temperature rise started.

Figure 5 shows the magnetization results in emu/g for brominations of single crystals for various times at essentially the same temperature 260°C. As the bromination times increase, the curves become much sharper, with the crystal treated for 24 hours being the best obtained so far. Figure 6 shows the estimated crystal superconducting volume fraction as a function of processing time. The error bars in Fig. 6 arise from several sources. These include the uncertainties in the mass of these small samples (typically 100-300 micrograms), the uncertainties in the theoretical density of the halogenated materials, as well as the the uncertainties in the demagnetization factors for these crystals. Within these estimated errors, the volume fraction vs time curve fits fairly well to a logarithmic dependence.

Fig. 5. Magnetization(emu/g) vs temperature for a series of YBCO_{6+x} single crystals brominated for times ranging from 0.5 to 24 hours. The crystals were mounted so that the c axis was perpendicular to the applied field.

Fig. 6. Estimated superconducting volume fraction vs bromination time for the crystals shown in Fig. 5. The line through the data is a logarithmic fit.

Discussion

The kinetics of halogenation in the YBCO system are intriguing and involve many unresolved questions. First, the rate limiting step is not clear, and the process may involve catalysis as well. The de-oxygenated materials are quite reactive and readily take up the bromine, while the fully oxygenated material is observed not to take up any bromine. Understanding these processes are hampered severely by not knowing the exact location of the halogen ions in the lattice.

Related to this is the nature of the exothermic reaction. From the data of Fig. 1 it appears that there are two reactions occurring, a fast reaction which for powders is complete within about 5 minutes, and a slower reaction which proceeds on a long time scale. This is consistent with our previous observation that additional processing time above the optimum of 5 minutes (at 260°C starting temperature) results in the formation of secondary phases. We also know from previous work³ that the Br is strongly bound and does not come back out even if exposed to 950°C in a reducing atmosphere of hydrogen/nitrogen. The similarity in temperature time profiles for the bromine and chlorine experiments indicates that the kinetics for the these two halogens is the same. There is no clear indication, however, as to what is governing the difference in starting temperatures needed to make the reaction begin (260°C for bromine and 160°C for chlorine).

One intriguing aspect of the halogenated materials is the strong binding of the bromine. This binding is consistent with the exothermic nature of the reaction. While bromine is not removed at high temperature, it is still possible to remove oxygen by exposing the sample to a nitrogen atmosphere at 600°C. Preliminary experiments show that after removal of oxygen from the brominated powders, the material becomes insulating again. Exposure of these powders to bromine now for a second time again causes a return to 90 K superconductivity.

The kinetics for the bromination of single crystals appears to be quite different from that of the powders. As Fig. 6 shows, even after 24 hours of exposure, only an estimated volume fraction of 65% is reached in the single crystal samples. This is dramatically different than the results for a similar study done for the powders.³ This drastic difference from the powder behavior may be related to the mechanisms of diffusion in the YBCO system. It has been found for oxygen that diffusion occurs preferentially along the a-b planes,⁶ which implies many fewer paths for thin single crystals than for the powders. This same effect may be operating for the bromine diffusion as well.

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