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Abstract
The superconducting properties of YBa$_2$(Cu$_{1-x}$Al$_x$)$_3$O$_{7-\delta}$/Y$_2$BaCuO$_5$ bulk superconductors with Al concentrations $x = 0.0025, 0.005, 0.02$ and $0.05$ were studied. The influence of annealing in flowing oxygen (SO) and argon at 800 $^\circ$C with subsequent oxygenation at 400 $^\circ$C on the superconducting and microstructural properties was investigated. The clearest peak effect at 77 K was observed at the lowest Al concentration ($x = 0.0025$) for SO and at the highest Al concentration ($x = 0.05$) for annealing in argon. No decrease of the transition temperature, $T_c$, with increasing Al concentration was observed for Al doped samples annealed in argon up to $x = 0.02$ in contrast to Al doped samples after standard oxygenation, where $T_c$ decreases continuously with Al concentration. The twin structures and the unit-cell lattice parameters of the crystals were investigated by optical microscopy and by X-ray diffraction. The results indicate the possibility of clustering of the Al atoms during annealing in flowing argon at 800 $^\circ$C.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In the early period of high-$T_c$ superconductivity (HTSC) as well as after the discovery of YBa$_2$Cu$_3$O$_7$ (YBCO, Y123) [1], major efforts were made to understand the influence of chemical additions on their main superconducting properties, e.g. microstructure, critical current density, transition temperature, pinning force density, trapped field, etc.

One of the best ways to improve the superconducting properties of YBCO is the formation of nanosized non-superconducting regions by substitution of the YBCO atoms, e.g. Y, Ba or Cu. These regions act as effective pinning centres for flux lines. It is well known that substitutions of the Cu sites can be done by univalent, bivalent or trivalent chemical elements [2]. X-ray and neutron diffraction studies have shown that certain univalent and trivalent chemical elements prefer the Cu(1) sites and substitute the Cu atoms in the CuO chains, such as Al [3–5], Fe [6, 7], Co [8, 9], Ag [10] etc. Other elements that substitute the Cu atoms in the CuO$_2$ planes, such as Zn [5, 11] and Ni [7, 9], are bivalent and prefer the pyramidal coordinated Cu(2) sites.

The twin structure with (110) and (1\overline{1}0) twinning planes is formed at the phase transformation from the tetragonal to the orthorhombic state [12]. The twins form when oxygen ordering in the basal copper plane leads to the elongation of the $b$-axis and the contraction of the $a$-axis of the crystal lattice [2]. If the Cu atoms in YBa$_2$(Cu$_{1-x}$M$_x$)$_3$O$_{7-\delta}$ (where M is a substituent atom) are substituted by trivalent atoms, the spacing between the twin boundaries decreases [4, 5]. Substitution in the CuO chains can cause an orthorhombic to tetragonal (pseudotetragonal) structural phase transition as the doping content increases, which is typical for the trivalent Fe, Co and Al atoms, whereas Ni or Zn doped YBCO remains orthorhombic [7, 9]. The variation in critical temperature, $T_c$, that occurs upon substitution is not influenced by the orthorhombic to tetragonal (O–T) phase transition [2].

Recently the successful Al substitution in single-grain YBCO bulk superconductors (Y$_1$Ba$_2$Cu$_3$O$_7$/Y$_2$BaCuO$_5$...
composites) fabricated by the top-seeded melt–growth (TSMG) process and the influence of annealing in flowing argon on the critical current density and the transition temperature were reported [13]. In this paper we report on a further investigation of Al doped YBCO bulk superconductors with different amounts of Al and two annealing processes (standard oxygenation and annealing in argon). We present results on critical current densities, transition temperatures and microstructures examined by polarized light microscopy as well as additional investigations by x-ray powder diffraction.

2. Experimental details

Al doped YBCO bulk single-grain superconductors were fabricated by the top-seeded melt–growth process (TSMG) in a chamber furnace using SmBa2Cu3O7 seeds. Oxide powders \( \text{YBa}_2\text{Cu}_3\text{O}_7, \text{Y}_2\text{O}_3, \text{Al}_2\text{O}_3 \) and \( \text{CeO}_2 \) (0.5 wt%) [14] for processing reactions were milled for 20 min in a friction mill and pressed into cylindrical pellets of 20 mm in diameter with a thickness of 12 mm. \( \text{Al}_2\text{O}_3 \) was added in amounts suitable to reach a certain Al concentration in \( \text{YBa}_2(\text{Cu}_{1-x}\text{Al}_x)_3\text{O}_{7-\delta} \) after reaction:

\[
12\text{YBa}_2\text{Cu}_3\text{O}_7 + 3\text{Y}_2\text{O}_3 = 10\text{YBa}_2\text{Cu}_3\text{O}_7 + 4\text{Y}_2\text{BaCuO}_4 + 2\text{CuO}.
\]

Four different Al concentrations \( x \) were used for substitution: \( x = 0.0025, 0.005, 0.02 \) and 0.05. Undoped YBCO was made as a reference for comparison with the Al doped samples.

Small samples for oxygenation and magnetization measurements were cut from the \( a \)-growth sector of the top surface of the bulks [15] at a distance of 1 mm from the seed. The samples had the shape of a slab with dimensions \( 2 \times 2 \times 0.5 \text{ mm}^3 \); the smallest dimension was parallel to the \( c \)-axis of the crystal. These samples were oxygenated in a tubular furnace by the standard oxygenation (SO) method and after annealing in flowing argon.

During standard oxygenation, the samples were slowly heated to 800 °C in flowing oxygen atmosphere and kept there for 2 h, then slowly cooled to 400 °C and oxygenated there for 240 h. After the oxygenation process, they were furnace cooled to room temperature. Other samples with the same Al concentrations were first slowly heated in flowing argon atmosphere to 800 °C and kept there for 2 h. Then they were furnace cooled to room temperature. After annealing in argon the oxygenation process in flowing argon atmosphere to 800 °C and kept there for 2 h on the surface of the bulks [15] at a distance of 1 mm from the seed. The samples had the shape of a slab with dimensions \( 2 \times 2 \times 0.5 \text{ mm}^3 \); the smallest dimension was parallel to the \( c \)-axis of the crystal. These samples were oxygenated in a tubular furnace by the standard oxygenation (SO) method and after annealing in flowing argon.

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After oxygenation, all samples were checked for homogeneity by Hall probe scanning [16]. The field dependence of the magnetic moment was obtained using a commercial vibrating-sample magnetometer (VSM) with magnetic fields up to 5 T at a constant sweep rate of 0.25 T min\(^{-1}\). During the magnetization measurements the applied magnetic field was always parallel to the \( c \)-axis of the crystal. The critical current densities, \( J_c \), were calculated from magnetization hysteresis loops (MHL) using the extended Bean model [17] for rectangular samples, 

\[
J_c(B) = \frac{\Delta m(B)/V}{2/[b(1-b/3a)]}, \quad \text{where } \Delta m \text{ is the difference of the magnetic moments between the increasing and decreasing field branches of the MHL and } V \text{ is the sample volume } a \times b \times c. \text{ The critical current densities were determined including self-field corrections. The magnetization measurements were done at 77 K. The transition temperatures, } T_c, \text{ were determined from the magnetic transition curves taken after zero-field cooling as the mid-point of these curves in an applied external magnetic field of 2 mT. The transition widths were defined as } \Delta T_c = T_{c0.9} - T_{c0.1}, \text{ where } T_{c0.1} \text{ and } T_{c0.9} \text{ were determined as 10% and 90% of the transition curve, respectively [18]. X-ray powder diffraction scans were taken with a conventional setup using Cu Kα radiation and an XPERT PRO diffractometer to determine the lattice parameters of the crystals. The twin structures, which appear as a result of the phase transition from tetragonal to orthorhombic structure, were examined by polarized light microscopy.}

3. Results and discussion

3.1. Critical current density and superconducting transition temperature

The field dependence of the critical current densities, \( J_c \), measured at 77 K for Al doped YBCO bulk superconductors is shown in figures 1(a) and (b) for SO (a) and annealing in argon (b).
respectively. The clearest peak effect (PE) is observed at the lowest concentration of Al ($x = 0.0025$) for SO (figure 1(a)) and at the highest concentration of Al ($x = 0.05$) for annealing in argon (figure 1(b)). The critical current density at the highest Al concentration ($x = 0.05$) is not presented for SO, because $J_c$ is negligibly small. Figure 1(a) clearly shows that $J_c$ improves upon Al doping at the lowest Al concentration ($x = 0.0025$) in comparison to the undoped reference sample at low and intermediate magnetic fields.

The transition temperatures, $T_c$, and transition widths, $\Delta T_c$, for both SO and annealing in argon are presented in figures 2(a) and (b), respectively. $T_c$ monotonously decreases with Al content in the Al doped YBCO samples after SO. An additional heat treatment of the samples in flowing argon at 800 $^\circ$C for 2 h led to significant changes in both $T_c$ and the pinning behaviour. The transition temperature is above 90 K and remains high with increasing Al concentration up to $x = 0.02$ (figure 2(a)), similar to the undoped reference sample, but the PE disappears. The transition widths, $\Delta T_c$, are more or less similar for the samples annealed in argon and not strongly influenced by the Al atoms in the whole concentration range, whereas $\Delta T_c$ rapidly rises with Al concentration for the SO samples (figure 2(b)). The rise of the transition width, $\Delta T_c$, with increasing Al content after SO may reflect microscopic inhomogeneities within the samples [3].

In the case of annealing in argon, a decrease of $T_c$, the presence of the PE up to $x = 0.02$ and an increase of $\Delta T_c$ for all Al concentrations are not observed because of the possibility of creating Al clusters during the heat treatment at 800 $^\circ$C. The distance between the disturbed regions, where $T_c$ might be locally suppressed, increases by clustering of the Al atoms and $T_c$ retains its original value in between. Thus, the Al doped samples behave as the undoped reference samples. The tendency to cluster can be explained by the need of trivalent atoms, such as Al, Fe or Co, substituted in the CuO chains to share oxygen atoms in order to increase their coordination number [8, 19].

The decrease of $T_c$ in the argon annealed sample and the appearance of the PE at the highest Al concentration ($x = 0.05$) may be caused by the impossibility to cluster all Al atoms due to the high Al concentration and some rare chances to substitute Cu atoms. It is known that a successful improvement of $J_c$ requires the mean distance between randomly distributed dopant atoms (in our case Al clusters for annealing in argon) or the size of the smallest particles [20] acting as pinning centres to be approximately two coherence lengths, $2\xi_{ab}$, or more, i.e. about 6 nm at 77 K [21, 22]. In the case of SO, when the concentration of Al increases, the mean distance between the dopant atoms becomes shorter than $2\xi_{ab}$ and the locally disordered regions overlap, which could lead to a decrease in $J_c$ [22].

3.2. Microstructure analysis of the twin structure

A typical twin structure of the undoped YBCO bulk sample after standard oxygenation is shown in figure 3. As mentioned above, these twins are formed as a result of the structural transition from the tetragonal to the orthorhombic phase. Figure 4(a) shows that the twin structure of Al doped YBCO bulks at a concentration of Al $x = 0.005$ has a slightly reduced twin spacing between the twin boundaries in comparison to the undoped sample (figure 3). However, a considerable reduction of the twin spacing is observed at the highest Al concentration after SO.
Figure 4. Micrographs of YBa$_2$(Cu$_{1-x}$Al$_x$)$_3$O$_{7-\delta}$ in polarized light showing the twinning structure for $x = 0.005$ (a) and $x = 0.05$ (b) both after standard oxygenation conditions.

Figure 5. Micrographs of YBa$_2$(Cu$_{1-x}$Al$_x$)$_3$O$_{7-\delta}$ in polarized light showing the twin structure for $x = 0.005$ (a) and $x = 0.05$ (b) for samples annealed in flowing argon.

Table 1. The lattice parameters, unit-cell volume, $V_{123}$, and orthorhombicity, $\Phi$, for SO and argon annealed YBa$_2$(Cu$_{1-x}$Al$_x$)$_3$O$_{7-\delta}$ samples measured by x-ray diffraction measurements.

<table>
<thead>
<tr>
<th></th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V_{123}$ (Å$^3$)</th>
<th>$\Phi$</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td>3.8851</td>
<td>11.6699</td>
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<td>3.8845</td>
<td>11.6720</td>
<td>173.3026</td>
</tr>
<tr>
<td></td>
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<td>3.8814</td>
<td>11.6810</td>
<td>173.5654</td>
</tr>
<tr>
<td></td>
<td>$x = 0.02$</td>
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</tr>
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The microstructures of YBa$_2$(Cu$_{1-x}$Al$_x$)$_3$O$_{7-\delta}$ bulk superconductors annealed in flowing argon at 800°C with $x = 0.005$ and 0.05 are presented in figures 5(a) and (b), respectively. No significant change in the twin structures is observed compared with the undoped sample, which has the same twin structure as the SO sample (figure 3), especially at the highest Al concentration ($x = 0.05$) (figure 5(b)). This demonstrates that the Al atoms after annealing in flowing argon do not have a strong influence on twinning as in the case of SO.

In undoped YBCO superconductors in the orthorhombic phase, the Cu atoms in the CuO chains have fourfold oxygen coordination. When the trivalent Al atoms substitute the Cu atoms in the chains they prefer fivefold oxygen coordination, which can cause an increase in the total oxygen content. An oxygen increase can be obtained only if the so-called extra oxygen atoms are added to adjacent $(\frac{1}{2}, 0, 0)$ sites at the $a$-axis of the crystal lattice between the chains [24], as in the case of Co and Fe doped samples [25, 26]. The extra oxygen atoms are adopted by the Al atoms, which now acquire a...
coordination number equal to five, $CN = 5$. The increase in the oxygen content is in agreement with the increase of the unit-cell volume, $V_{123}$ (table 1).

During annealing in flowing oxygen at 800 °C the CuO chains could be partially formed. The Al atoms get enough oxygen for creating the favourable fivefold oxygen coordination during annealing in flowing oxygen at 800 °C and do not need to form clusters in order to share oxygen atoms, as is necessary in the case of annealing in argon. In clusters, two Al atoms place one extra oxygen atom between them at the $a$-axis of the crystal lattice. Extra oxygen atoms are associated with the formation of an early stage tweed like structure. In other words, they are the initial nucleation centres for new twin boundaries. The number of extra oxygen atoms rises with increasing Al concentration and they are randomly distributed within the sample. The initial nucleation of the twin boundaries takes place in the temperature range from 600 to 500 °C during cooling down to room temperature after the melting process or different annealing processes at higher temperatures. With increasing oxygen content during standard oxygenation the twin boundaries are spreading within the sample from the initial nucleation centres. The Al atoms are not mobile during oxygenation at 400 °C.

From this point of view it is clear that the Al atoms can influence the twinning process by introducing extra oxygen atoms. If the extra oxygen atoms are the sources of twins, it follows that the Al atoms can be located at or near the twin boundaries and can pin down the twin walls. Correspondingly, there are more small twins in the standard oxygenated sample at the highest Al concentration ($x = 0.05$) and the spacing between the twin boundaries is reduced (figure 4(b)). But not all Al atoms are at or near the twin boundaries; they are also in between. Schematic illustrations of the possible distributions of Al atoms in Al doped samples are shown in figures 6(a) and (b) for SO and for annealing in flowing argon, respectively. Figure 6(a) shows how the Al atoms can pin down twin walls through the presence of extra oxygen atoms. However, if the Al atoms are clustered (figure 6(b)), extra oxygen atoms are localized in these clusters. Clustered extra oxygen atoms do not have such a strong influence on the twin structure. An argument for Al clustering during annealing in flowing argon is the wider spacing between the twin boundaries (figure 5(b)) for YBa$_2$(Cu$_{0.95}$Al$_{0.05}$)$_3$O$_{7-\delta}$ in contrast to the SO sample without clusters (figure 4(b)). In Al clusters, sixfold coordinated Al atoms possibly exist as well.

The $a/c$ and $a/b$-oxygenation macrocracks visible in all micrographs are formed under the tensile stresses induced around each Y$_2$BaCuO$_5$ (Y211) particle as well as the stress caused by shortening the $c$-lattice parameter of the crystal into the oxygenated surface layer during the oxygenation process [27]. They directly reduce the effective cross-section and consequently the measured critical current density [28]. Also, the Y211 particles are rather large (their mean size is about 1.4 μm), which is reflected by the quite low $J_c$ at low magnetic fields (figures 1(a) and (b)) [29]. Note also that not only the Al or the other trivalent atoms have an influence on the twin structure, but also the Y211 particles and subgrains. The twin structure is significantly influenced by the stress field around the Y211 particles. They can lead to a high inhomogeneity of twins due to the formation of detwinned areas around them or areas with a predominance of one twin domain by twin boundary motion as well as by changing the twin spacing [30, 31].

3.3. Variation of lattice parameters of the samples after SO and annealing in argon

The dependence of the lattice parameters of the Y123 phase and the orthorhombicity as a function of Al concentration are presented in figures 7(a) and (b), respectively. The lattice parameters of the Al doped YBCO samples were determined from x-ray powder diffraction scans by Rietveld’s method. The same results are summarized in table 1, where the unit-cell volumes for both annealing methods are also included. As expected, the $a$ and $b$-axis lattice parameters move together with increasing Al concentration (figure 7(a)). Note that
Figure 7. The unit-cell parameters $a$, $b$ and $c$ are shown for YBa$_2$(Cu$_{1-x}$Al$_x$)$_3$O$_{7-\delta}$ (a) and variation of the orthorhombicity after SO and annealing in argon (b) as a function of Al concentration.

4. Conclusions

The influence of annealing in flowing argon at 800°C for 2 h on the superconducting and microstructural properties of Al doped TSMG YBCO bulk superconductors was investigated and compared with the standard oxygenation (SO) process. A clear peak effect in the $J_c(B)$ curve is induced at the lowest Al concentration ($x = 0.0025$) after SO and at the highest Al concentration ($x = 0.05$) after annealing in argon. It indicates that the mean effective distance between randomly distributed nanosized pinning centres for flux pinning is close to two coherence lengths, $2\xi_{ab}$, in both the argon annealed and the SO sample. In the argon annealed sample with the highest Al concentration ($x = 0.05$), the effective distance between pinning centres could be reached, when the Al atoms are clustered. Another indication for cluster formation is derived from the investigation of the transition temperatures, $T_c$.

The investigations of the twin structures showed a reduction of the spacing between the twin boundaries with increasing Al concentration in the case of standard oxygenation. The increasing amount of twin boundaries by Al substitution is associated with increasing extra oxygen atoms at the $a$-axis of the crystal lattice. After standard oxygenation, the Al atoms are arranged along the twin boundaries and they can pin down twin walls, but Al atoms are also randomly distributed within the sample. No essential influence on the twin structure is observed after annealing in argon, which confirms that the Al atoms do not pin twin walls due to possible clustering.

The x-ray measurements confirm that increasing the Al content in YBCO bulk superconductors leads to an orthorhombic–tetragonal phase transition.

The results of this study confirm the possibility of improving the superconducting properties of Al doped YBCO bulk superconductors by high temperature treatments at different oxygen partial pressures.

Acknowledgments

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References


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