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Microstructural Variations with Uranium Compound Doping of Bi-Sr-Ca-Cu-O/Ag Superconducting Tapes

Damion A. Milliken, Jung H. Ahn, and Shi X. Dou

Abstract—Doping of Bi-Sr-Ca-Cu-O based silver sheathed superconducting tapes (BSCCO/Ag) with various uranium compounds was carried out. This work aimed at minimising the detrimental effects of doping to allow for later irradiation and fission to create columnar defects for strong flux pinning. The effects on the transport current density of BSCCO/Ag of doping with a variety of uranium compounds up to 2 at% was determined. Microstructural changes due to the doping were investigated. Removal of elements from the BSCCO matrix by uranium compound dopants was studied by energy dispersive spectroscopy. It was found that $\text{UCa}_{1.5}\text{Sr}_{1.5}\text{O}_6$ least degraded electrical performance and microstructure, as it removed the least elements from the matrix. It would appear that $\text{UCa}_{1.5}\text{Sr}_{1.5}\text{O}_6$ most closely approximates an ideal BSCCO compatible uranium compound, but it still removes some amount of copper.

Index Terms—Bi-2223, BSCCO, High-Temperature Superconductors, Uranium Doping

INTRODUCTION

GREAT potential has been shown by (Bi,Pb)-Sr-Ca-Cu-O/Ag superconducting composite (BSCCO/Ag) tapes for commercial realization [1]. However, commercialization has proven elusive because of several inherent problems with BSCCO. One of the more significant detrimental performance and application concerns is the material's low flux pinning strength. A large body of work exists which has attempted, with varying degrees of success and cost efficiency, to address this hindrance [2]–[5]. A method pioneered by Weinstein et al for $\text{YB}_2\text{Cu}_3\text{O}_{7-8}$, known as the uranium/neutron (U/n) method, is highly effective, cost efficient, and directly applicable to BSCCO [6], [7]. This method involves doping the superconductor matrix with ^{235}U , and exposing the doped superconductor to a thermal neutron fluence, hence fissioning the uranium. Passage of the daughter atoms through the matrix creates columnar defects with diameter approximately equal to the coherence length. These coherence length sized defects are excellent pinning sites for magnetic flux. Recent work has shown that the U/n method is able to significantly improve flux pinning and reduce anisotropy in BSCCO/Ag tapes [8].

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Although successful, the U/n method applied to BSCCO has problems with chemical interaction between the dopants and BSCCO [9]. Additionally, during thermal neutron irradiation, the silver sheath of the tapes captures neutrons, forming a γ emitting isotope, and creating a radiation hazard. In order to reduce this danger for practical use, it is necessary to reduce the thermal neutron fluence. However, doing so reduces the number of fission incidents within the BSCCO, and thus also the overall gain in flux pinning capacity. Adding greater amounts of uranium counters this, but carries with it problems of greater phase disruption and microstructural damage. Work was previously carried out to identify and synthesize uranium compounds that are compatible with the BSCCO system [10]. Results were extremely positive, with a six fold increase in uranium additions with the same low 15% reduction in critical current (J_c). Investigation of the effects of doping with different uranium compounds on the phase composition of BSCCO showed a significant increase in the fraction of $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ (2212) phase, at the expense of the $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (2223) phase [11].

Following the success of high doping levels of compatible uranium compounds, the current work extended doping levels of the most favourable compound to higher levels. Additionally, another uranium compound similar to the optimum compound previously determined, but with higher uranium proportion was investigated. Sintering conditions were optimised and the newly doped tapes were characterised electrically. Additionally, scanning electron microscopy (SEM) was performed on all previously doped tapes, to investigate the structural changes occurring within the BSCCO. Energy dispersive spectroscopy (EDS) investigations accompanied the SEM observations, with the intent of determining both the distribution of uranium containing phases, and their actual chemical composition.

EXPERIMENTAL METHODS

All heat treatment work, unless otherwise noted, used cooling rates of $3\text{--}4^\circ\text{C}/\text{min}$. All grinding and sintering were carried out in air. Grinding was carried out in an agate mortar and pestle. Sintering was carried out on Alumina (Al_2O_3) plates, unless otherwise noted.

A. Uranium Compound Synthesis

U_3O_7 , UCa_2O_5 , $\text{UCa}_{1.5}\text{Sr}_{1.5}\text{O}_6$, and the new compound UCaSrO_5 were synthesised using $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and $\text{Sr}(\text{NO}_3)_2$ [11]. Appropriate

stoichiometric mixtures of the precursor compounds were ground for 5 minutes. The mixtures were then calcined on pyrex glass at 400°C for 1 hour with a 0.83°C/min heating rate. The calcined materials were pressed into pellets at 13.8 GPa, and sintered at 1250°C for 24 hours with a 3.4°C/min heating rate. The sintered compounds were crushed and ground for 5 minutes.

B. Uranium Compound Doping of BSCCO/Ag

3 new tapes were produced, using the same method as used previously [10]. One tape with 2at% $\text{UCa}_{1.5}\text{Sr}_{1.5}\text{O}_6$, and two tapes with UCaSrO_5 (0.57at% and 1.1at%) were produced. The BSCCO precursor powders used were doped with the appropriate masses of compounds, ground for 20 minutes, pressed into pellets at 13.8 GPa, and calcined at 810°C for 5 hours with a 3°C/min heating rate. The calcined powders were crushed and ground for 20 minutes.

C. Tape Preparation and Thermal Processing

The doped powders were packed into fine silver tubes of 8 cm length, 6.5 mm outer diameter, and 1mm wall thickness. The packed tubes were degassed at 820°C for 3 hours with a 3°C/min heating rate. The degassed packed tubes were then drawn into 2 mm diameter wires in a 19 step drawing process, with an intermediate anneal at 500°C for 15 minutes. These wires were rolled to a thickness of 200 μm in 20 passes. 4 cm samples of the tapes were cut and subjected to the two step processing treatment reported by Zeimet et al [12]. The tapes underwent an initial sintering operation, with the temperature parameter varying between batches from 828°C to 844°C, in increments of 4°C. Between the 1st and 2nd sintering operations, a pressing at 3.3 GPa for 10 seconds was carried out. The 2nd sintering step was carried out at a temperature of 815°C, 820°C, or 825°C.

D. Characterisation of BSCCO/Ag Composite Tapes

After thermal treatment, critical current (I_c) measurements were made at 77K under self-field using the standard 4-point method with a 1 $\mu\text{V}/\text{cm}$ criterion. 1 cm portions of the tapes were mounted in epoxy, polished to 1 μm , colloidal silica polished for 30 seconds, etched in a mixture of 99.8% 2-Butoxy-Ethanol and 0.2% HClO_4 for 20 seconds, and gold sputter coated for 15 seconds. SEM observation was performed on the mounted samples using a Leica StereoScan 440, and EDS with an Oxford Link ISIS.

RESULTS

Fig. 1 shows the maximum relative I_c values obtained for each level of doping of each compound. Values for the U_3O_7 , UCa_2O_5 , control, and $\text{UCa}_{1.5}\text{Sr}_{1.5}\text{O}_6$ (other than 2at%) tapes are taken from [11]. The values shown for the 2at% $\text{UCa}_{1.5}\text{Sr}_{1.5}\text{O}_6$ and both UCaSrO_5 tapes are the maximum I_c values determined from the 16 sintering optimisation operations.

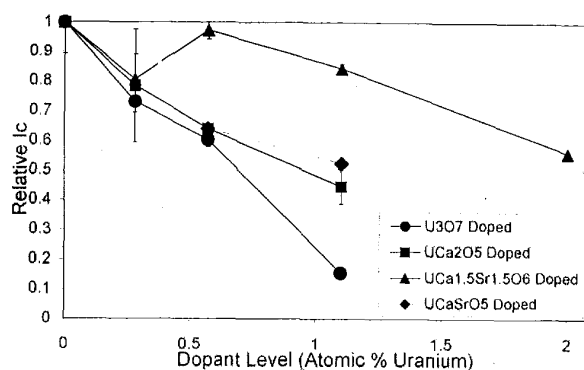


Fig. 1. Normalised comparison of I_c with doping level after optimised sintering. Error bars represent one Standard Deviation.

Figs. 2, 3, 4, and 5 show backscattered electron images of the undoped, 1.1 at% U_3O_7 doped, 1.1 at% UCa_2O_5 doped, and 1.1 at% $\text{UCa}_{1.5}\text{Sr}_{1.5}\text{O}_6$ doped tapes, respectively.



Fig. 2. SEM image of microstructure of undoped BSCCO core.



Fig. 3. SEM image of microstructure of 1.1 at% U_3O_7 doped BSCCO core.



Fig. 4. SEM image of microstructure of 1.1 at% UCa_2O_5 doped BSCCO core.

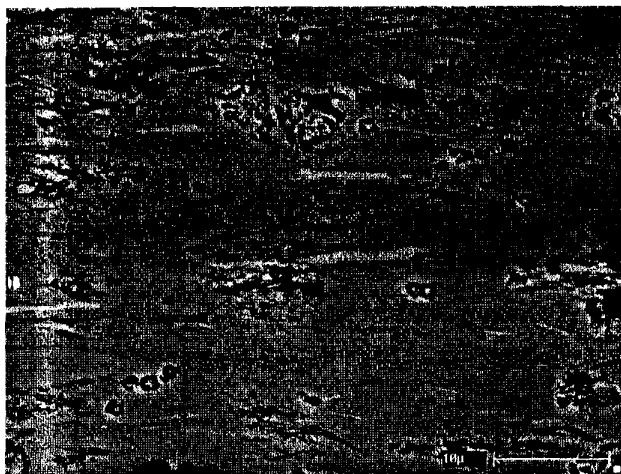


Fig. 5. SEM image of microstructure of 1.1 at% $\text{UCa}_{1.5}\text{Sr}_{1.5}\text{O}_6$ doped BSCCO core.

Table I contains details of the average atomic ratios of calcium, strontium, and copper, normalised to that of uranium, in uranium deposits within the original tapes. The values are averages across the 3 doping levels employed (0.29 at%, 0.57 at%, and 1.1 at%).

TABLE I
ATOMIC RATIOS OF CONSTITUENT ELEMENTS OF URANIUM CONTAINING PHASES WITHIN DIFFERENTLY DOPED TAPES

Dopant	U	Ca	Sr	Cu
U_3O_7	1.00	1.45	1.71	0.32
UCa_2O_5	1.00	2.42	1.31	0.86
$\text{UCa}_{1.5}\text{Sr}_{1.5}\text{O}_6$	1.00	1.77	1.82	0.93

DISCUSSION

At a high doping level of 2 at% uranium (4.5 wt% U) in the form of $\text{UCa}_{1.5}\text{Sr}_{1.5}\text{O}_6$ (10 wt% $\text{UCa}_{1.5}\text{Sr}_{1.5}\text{O}_6$), the transport critical current of the BSCCO/Ag tape was reduced by 45% (Fig. 1). Comparatively, this is a small reduction, considering that as seen in Fig. 1, the best reduction at 1.1 at% for the other dopants is 55% (UCa_2O_5). Although likely too large a reduction in I_c for use at this high doping level, the result

attests to the high compatibility of $\text{UCa}_{1.5}\text{Sr}_{1.5}\text{O}_6$ with the BSCCO matrix. UCaSrO_5 has the same Ca:Sr ratio as the highly compatible $\text{UCa}_{1.5}\text{Sr}_{1.5}\text{O}_6$, but a higher uranium content. It was hypothesised that Ca:Sr ratio may be an important consideration in BSCCO-dopant compatibility. This might seem particularly likely considering that the Ca:Sr ratio in BSCCO is almost the same as that in $\text{UCa}_{1.5}\text{Sr}_{1.5}\text{O}_6$ and UCaSrO_5 . However, upon testing, the UCaSrO_5 compound performed almost identically to the UCa_2O_5 compound. UCaSrO_5 did perform marginally better than UCa_2O_5 at 1.1 at% doping level (50% reduction in I_c rather than 55%, Fig. 1), indicating that Ca:Sr atomic ratio was a consideration in compatibility, but not the most important factor.

Examination of the microstructural differences between undoped BSCCO (Fig. 2), and the various doped tapes provides evidence of phase disruption with increasing dopant additions. The disruption is minimised by doping with more compatible uranium compounds. Doping with 0.29 at% U_3O_7 initially disrupts the microstructure of the BSCCO by engendering formation of copper oxides. At higher doping levels of 1.1 at% (Fig. 3), a significant volume fraction of 2212 phase becomes visible. This latter observation is consistent with XRD analysis carried out previously [11]. Low (0.29 at%) UCa_2O_5 doping initially does little to the microstructure, although slightly higher copper oxide volume fractions would appear to be present. At higher doping levels (0.57 at% and 1.1 at%, Fig. 4), significant amounts of copper oxide begin to form. Serious transformation of 2223 phase to 2212 phase is not apparent at the doping levels used. However, large amounts of calcium oxides form at 1.1 at% doping (Fig. 4). These results are consistent with previous XRD work, and attest to the greater chemical compatibility with BSCCO of UCa_2O_5 compared to U_3O_7 [11].

$\text{UCa}_{1.5}\text{Sr}_{1.5}\text{O}_6$ doping appears to have unusual effects upon the BSCCO matrix. Initially, at small doping levels (0.29 at%), significant amounts of calcium and strontium oxides are formed. With greater doping additions (0.57 at%), the microstructure appears to be similar to undoped BSCCO, and contains much less secondary oxides than low (0.29 at%) $\text{UCa}_{1.5}\text{Sr}_{1.5}\text{O}_6$ doped material. This observation assists in explaining the initial drop then rise in I_c (see Fig. 1) with increasing doping levels of $\text{UCa}_{1.5}\text{Sr}_{1.5}\text{O}_6$. Interestingly, at high doping levels of 1.1 at%, the microstructure of the BSCCO, shown in Fig. 5, appears largely undamaged. There are large secondary phases near the uranium deposits, but little other secondary phases or 2212 apparent. This is consistent with previous X-ray diffraction (XRD) data, which showed that $\text{UCa}_{1.5}\text{Sr}_{1.5}\text{O}_6$ doping had little detrimental effect upon the 2223/2212 phase ratio [11]. Similarly here, it appears that high doping levels of $\text{UCa}_{1.5}\text{Sr}_{1.5}\text{O}_6$ (Fig. 5) promote better microstructural formation of BSCCO than no doping at all (Fig. 2). Perhaps the uranium containing phases form at the grain boundaries; alternatively, the distribution of the uranium containing phases may not be homogenous.

EDS analysis of detectable uranium containing deposits sheds some light upon the reasons for the above observed microstructural changes. As was noted with bulk BSCCO

doped with U_3O_7 , and in Table I, U_3O_7 leached calcium and strontium from the BSCCO matrix [10]. The equilibrium U-Ca-Sr oxide formed in BSCCO/Ag tapes here (U:Ca:Sr=1:1.45:1.71) appears to be very close to the highly compatible $UCa_{1.5}Sr_{1.5}O_6$ (U:Ca:Sr=1:1.5:1.5). This also explains the high presence of copper oxides within the BSCCO microstructure (Fig. 3). With calcium and strontium being taken from the BSCCO matrix by the uranium, the BSCCO matrix would become copper rich, promoting expulsion of excess copper as copper oxide deposits. Doping with UCa_2O_5 results in uranium containing phases with U:Ca:Sr=1:2.42:1.31 (Table I), indicating that some leaching still takes place, although less than in the case of U_3O_7 . Interestingly, strontium was still leached to approximately the same extent as with U_3O_7 doping. The large amounts of calcium oxides present at 1.1 at% doping level, shown in Fig. 4, probably occur because of the calcium excess present in the BSCCO after strontium and copper leaching by UCa_2O_5 .

Leaching of calcium and strontium from the BSCCO matrix was minimal with $UCa_{1.5}Sr_{1.5}O_6$. The final composition of the uranium phases, in Table I, was U:Ca:Sr=1:1.77:1.82, which is very close to the original U:Ca:Sr=1:1.5:1.5. As mentioned in previous work, copper was also leached from the BSCCO matrix by uranium compound dopants [10]. Considering the relative amounts of the different elements leached, it would appear that uranium will preferentially react with strontium, then calcium, and lastly copper. When increasingly strontium and calcium rich dopants were employed, copper was leached to an increasingly large degree (see Table I). With U_3O_7 , 0.32 atomic ratio of copper was taken from the BSCCO. Using UCa_2O_5 resulted in 0.86 atomic ratio, and $UCa_{1.5}Sr_{1.5}O_6$ caused 0.93 atomic ratio of copper to be taken. It would appear that $UCa_{1.5}Sr_{1.5}O_6$ is not an optimal dopant. Copper removal from the BSCCO may explain the microstructural changes discussed above, and the contradiction between apparently high quality microstructure, yet low I_c .

CONCLUSION

High dopant levels of 2 at% $UCa_{1.5}Sr_{1.5}O_6$, while still significantly more compatible with BSCCO than alternative uranium compounds (U_3O_7 , UCa_2O_5 , $UCaSrO_5$), cause a 45% drop in superconducting current carrying capacity of BSCCO/Ag. The most significant consideration for uranium compound compatibility with BSCCO would seem to be the amount of calcium and strontium already present in the compound. $UCaSrO_5$ performed approximately the same as UCa_2O_5 , even though its Ca:Sr ratio was very similar to that of BSCCO and the same as that of the most compatible compound, $UCa_{1.5}Sr_{1.5}O_6$. All dopant compounds tested leached copper from the BSCCO, and results indicated that a compound of the form $UCa_{1.5}Sr_{1.5}CuO_x$ might be more compatible.

Doping with incompatible compounds (U_3O_7 and UCa_2O_5) resulted in microstructural changes due to calcium and strontium extraction from the BSCCO. First, copper oxide deposits began to form, and with greater extraction, 2212

phase began to replace 2223 phase. Doping with $UCa_{1.5}Sr_{1.5}O_6$ caused minor calcium and strontium extraction, and more significant copper extraction. At high doping levels of 1.1 at%, I_c was reduced by 15% but the BSCCO microstructure was largely intact. This increase in doping will allow for further reduction in neutron fluence and hence less radiation hazard. Additional investigation into the location of uranium containing phases in high $UCa_{1.5}Sr_{1.5}O_6$ doped (1.1 at% and greater, such as the newly made 2 at% $UCa_{1.5}Sr_{1.5}O_6$ doped tape) is required. Further work aimed at obtaining a more homogenous distribution of uranium would likely yield beneficial results.

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