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Growth and characterization of superconducting $\text{Bi}_2\text{Sr}_2\text{Ca}_{(1-x)}\text{Ce}_x\text{Cu}_2\text{O}_{8+\delta}$ single crystals

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Abstract

Superconducting single crystals of $\text{Bi}_2\text{Sr}_2\text{Ca}_{(1-x)}\text{Ce}_x\text{Cu}_2\text{O}_{8+\delta}$ were grown by spontaneous nucleation technique from stoichiometric melt composition. The effects of Ce on the growth as well as on the superconducting properties were studied. The morphology and the composition of the grown crystals were studied using the Scanning Electron Microscope (SEM) and Inductively Coupled Plasma Technique (ICP) respectively. The powder X-ray diffraction pattern reveals that the lattice parameters a and b increase, while c decreases with the progressive substitution of Ce. The susceptibility measurement delineates that the T_c decreases gradually, with increase in the Ce concentration.

1. Introduction

A lot of substitutional studies have been made on the High Temperature Superconductors (HTS) in both Cu and non-Cu sites [1–3] to assess the various physical properties and to depict the underlying mechanism of superconductivity. It has been found from the literature that the substitution in Cu site in the case of YBCO destroys superconductivity [4], whereas in the Bi-system, the superconductivity increases to a maximum and then decreases [5]. The Bi-2212 with Y substituted in the Ca-site is the most widely studied as it forms a complete solid solution [6,7]. In the case of Y doped Bi-2212 a decrease in the carrier concentration is observed with the progressive substitution of rare earths which in turn

results in the decrease of T_c . However, the understanding of the effect of dopants on various physical properties, is a sensitive problem, with polycrystalline samples and in order to overcome this, studies on single crystals are very much inevitable. Several reports are available in literature for the growth of Y-doped Bi-2212 single crystals by floating zone technique [8] and flux technique [9]. There are only a limited number of reports regarding the Ce substitution in the Bi-2212 system [10–12]. The Ce substitution poses a complicated situation because of its mixed valency. Also it has been reported that the substitution of Ce, Tb and Pr in the RE-123 compounds affects superconductivity to a great extent. A lot of studies has been made on the $\text{Y}_{(1-x)}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{(7-\delta)}$ and the decrease in T_c has been explained by hole filling and pair breaking mechanisms [13]. Though there are only very few reports available on the Ce substituted Bi-2212, there is discrepancy in the T_c values for ceramic and bulk

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single crystals. Recently, Jin et al. [14] have reported on the crystal growth of Ce-doped Bi-2212 from the eutectic melts. They have reported that the T_c decreases gradually with the increase of Ce concentration in the crystal and superconductivity vanishes only when the Ce concentration exceeds 0.4. Whereas Awana et al. [11] and Ramasita et al. [12] have reported that the T_c vanishes drastically even for $x > 0.1$. In view of this, we report a plenitude of investigation on the growth, surface morphology, X-ray and superconductivity properties of $\text{Bi}_2\text{Sr}_2\text{Ca}_{(1-x)}\text{Ce}_x\text{Cu}_2\text{O}_{(8-\delta)}$ for $x = 0.1$ to 0.5. ICP analyses were done to determine the exact crystal composition.

2. Experimental

The crystals were grown by flux technique with slow cooling in a temperature gradient furnace. The starting compositions were high pure mixtures of Bi_2O_3 , SrCO_3 , CaCO_3 , CuO and CeO_2 . Five batches of nominal composition 2:2:1:2 were prepared with various Ce concentrations (0.1, 0.2, 0.3, 0.4 and 0.5). The powders were thoroughly mixed in a mortar and pestle and fused in a high purity alumina crucible. Each of the five batches of the composition was taken in a 25 cc crucible of 25 gm charge. The mixture was heated to 750°C and kept at this temperature for 10 hours. This process was repeated two or three times and after proper calcination, the samples were loaded in a silicon-carbide furnace fitted with a precise temperature controller (Eurotherm). The growth temperature was fixed from the repeated growth runs and also by observing the nature of the samples after calcination. The growth temperature

increases with increase of Ce concentration as reported for Y-doped Bi-2212 by our group [9] and is listed in Table 1. The mixture was heated to the maximum temperature and soaked for 15 hours in order to attain proper homogenization. The melt was then cooled down to the eutectic at the rate of 2°C/hr. The grown crystals were mechanically separated from the solidified matrix by cleavage. The crystals were found almost over the entire volume of the crucible. The morphology and the form of crystals were examined using SEM (Leica Cambridge Stereoscan 440).

3. Results and discussions

3.1. Morphological studies

The as-grown crystal is shown in Fig. 1. From the figure it is clear that the crystals are free of flux and no other inclusions are found. The crystals are shiny and the size of the crystal increases with the increase of Ce concentration. Black shiny layers of crystals were found on the top of the melt surface, however bulk crystals which were randomly oriented were found in the bottom portion of the crucible. The concentration flows due to the horizontal and vertical temperature gradients might have caused the random orientation of the crystals at the bottom of the crucible. These bulk crystals were separated by carefully breaking the crucible, then flake like crystals were cleaved out for the SEM and for superconductivity studies.

Fig. 2a shows the parallel growth steps in the [100] direction are observed on the well developed (001) face. Regular layer growth habit was hindered by inclusions or local heterogeneities which “pinned” the parallel growth steps. Fig. 2b shows the higher magnification of the pinning in the layers. The layer growth pattern observed in one of the crystals is shown in Fig. 3 which clearly indicates that the crystal grows by means of two dimensional nucleation mechanism. Spiral dislocations are not seen in these crystals as in the case of YBCO, this may be due to the fact that the bonding between the Bi-atoms in the Bi–O double layer is very weak and this weak bond combined with the long c spacing

Table 1
Starting Ce concentration and growth temperature for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Ce}_x\text{Cu}_2\text{O}_{8+\delta}$

Sample No.	Starting Ce concentration (mol%)	Growth temperature (°C)
1.	$x = 0.1$	1000–830
2.	$x = 0.2$	1020–830
3.	$x = 0.3$	1020–830
4.	$x = 0.4$	1050–830
5.	$x = 0.5$	1050–830

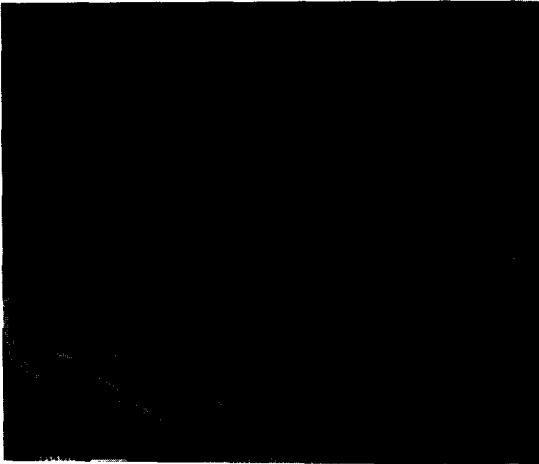


Fig. 1. Scanning electron micrograph of an as-grown crystal $\text{Bi}_{1.86}\text{Sr}_{1.89}\text{Ca}_{0.87}\text{Ce}_{0.086}\text{Cu}_{1.85}\text{O}_{8+\delta}$.

and a superlattice along the b -axis makes the spiral formation difficult [15].

3.2. Compositional analysis

The chemical composition of the as-grown crystals is estimated by the inductively coupled plasma (ICP) analysis. The quantitative measurements have been carried out by normalizing the molar ratio of Cu as 2. Flux free single crystals have been collected from the center of the crucible for the preparation of solution for ICP analysis. It has been found that the starting composition and the crystal composition are almost the same except for Ce. Due to the lower segregation co-efficient of Ce (< 1) as reported by Tarascon et al. [16] for Nd–Ce–Cu–O compound, the concentration of Ce in the crystal is much less than the starting composition. The starting composition and the crystal composition along with the changes in the lattice parameter are listed in the Table 2. No traces of Al content were found in the crystals as the crystals were picked up from the center portion of the crucible. This indicates that the reaction of the charge with the crucible is minimal. The Ce atoms are actively captured by the divalent Ca as a result, the melt is locally depleted and the concentration of Ce/Ca ratio in the crystal varies, which can be overcome by having longer soaking period.

3.3. X-ray and superconductivity studies

Powder X-ray diffraction measurements were carried out using $\text{CuK}\alpha$ radiation on selected single crystals to identify the phases. Within the experimental resolution, it can be ascribed to the orthorhombic symmetry and the crystals are phase pure (2212) with no intergrowth of 2201 phase. The intergrowth of 2201 is not observed in this case because of the high crystallization temperature as reported by Leonyuk et al. [17]. The lattice constants were calculated by a program for unit cell refinement by a least squares fit. It has been observed that the c -parameter decreases with the increase of Ce concentration while

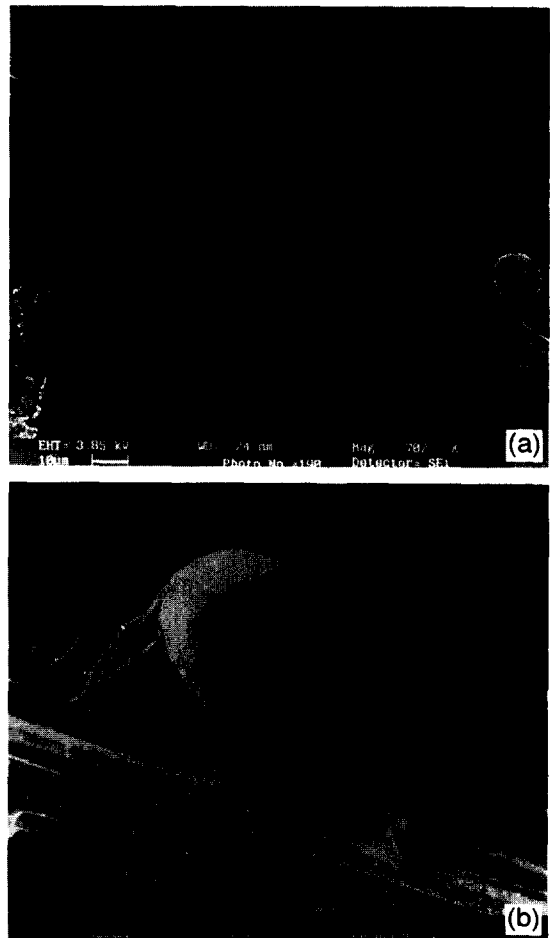


Fig. 2. (a) Parallel growth steps observed in the [100] direction along with the pinning of the layers. (b) The pinning of the layers under higher magnification.



Fig. 3. Layer growth pattern observed in one of the crystals ($x = 0.263$).

a and b increase. An analysis of our data indicates the orthorhombic distortion with b slightly larger than a in all the samples. The decrease in the c -parameter may be attributed to the fact that the substitution of Ca by Ce leads to an increase in the oxygen content and as reported by Tarascon et al. [18] the excess oxygen could be incorporated into the Bi–O layers. This induces a contraction of Bi–O layers and causes an increase in the covalency of Bi–O bonds [19] this effect results in the decrease of the c -parameter. Also the decrease in the c -parameter may be due to the smaller ionic size of Ce^{4+} ion compared to the Ca ion.

The temperature dependence of AC susceptibility (normalized values) measured with an applied field perpendicular to the ab plane is shown in Fig. 4. The T_c onset value for $x = 0.1$ is 90 K and drops for further doping of Ce. The decrease in the T_c is not so rapid as reported by Awana et al. [11] for polycrystalline samples. The T_c decreases gradually as the Ce

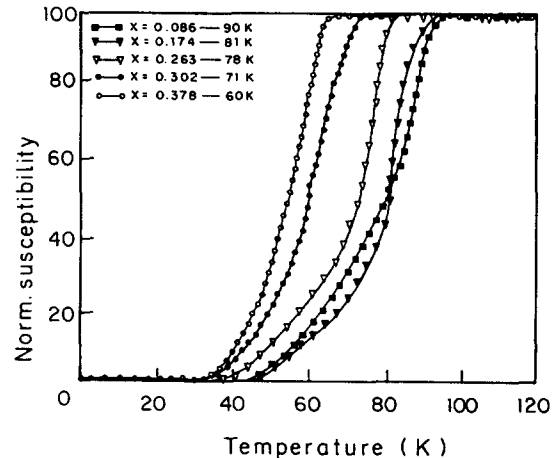


Fig. 4. The temperature dependence of the AC susceptibility for various Ce concentrations ($x = 0.1-0.5$).

concentration increases and this may be attributed to the hole filling mechanism as in the case of other rare-earth doped systems [20].

4. Conclusion

Single crystals of Ce-doped Bi-2212 for various Ce concentrations (0.1 to 0.5) were grown. The lattice parameters a and b increase while the c -parameter decreases with the increase of Ce concentration; from the variation in the lattice parameter and the ionic radii it seems that the Ce may exist in between the 3+ and 4+ valence state. However, detailed XPS study is essential to confirm the exact valence state. The compositions of the grown crystals were measured using the ICP analysis, due to the lower segregation coefficient of Ce, the concentration of the Ce in the crystal is much less than the

Table 2
Starting composition, crystal composition, lattice parameters and T_c values

Sl. No.	Starting composition					Crystal composition					Lattice parameter (Å)			T_c (K)
	Bi	Sr	Ca	Ce	Cu	Bi	Sr	Ca	Ce	Cu	a	b	c	
1.	2	2	0.9	0.1	2	1.86	1.89	0.87	0.086	1.85	5.3926	5.4003	30.9487	90
2.	2	2	0.8	0.2	2	1.92	1.88	0.82	0.174	2.11	5.4166	5.4198	30.8659	81
3.	2	2	0.7	0.3	2	1.87	2.15	0.72	0.263	2.06	5.4204	5.4284	30.8486	78
4.	2	2	0.6	0.4	2	1.94	2.14	0.58	0.302	2.09	5.4271	5.4362	30.7624	71
5.	2	2	0.5	0.5	2	1.88	1.91	0.47	0.378	2.00	5.4356	5.4481	30.6929	60

starting composition. The superconducting transition temperature is found to decrease gradually with the progressive substitution of Ce.

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