Effect of praseodymium substitution on the growth and properties of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($0 < x < 0.4$) single crystals[†]

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Abstract. In the present paper, a modified self-flux technique has been successfully employed for the growth of pure and praseodymium substituted (partially) large single crystals of high temperature superconducting $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($x = 0.0, 0.2, 0.4$). Typical sizes of the platy and bulky crystals of pure YBCO(123) material are $\approx 2 \times 2 \times 0.1 \text{ mm}^3$ and $4 \times 1 \times 1 \text{ mm}^3$, respectively. In case of Pr-substitution, the typical sizes of platy and bulky crystals of $Y_{0.8}Pr_{0.2}Ba_2Cu_3O_{7-\delta}$ and $Y_{0.6}Pr_{0.4}Ba_2Cu_3O_{7-\delta}$ materials are $\approx 2 \times 3 \times 0.1 \text{ mm}^3$ and $5 \times 1 \times 1 \text{ mm}^3$ and $\approx 1 \times 1.5 \times 0.1 \text{ mm}^3$ and $7 \times 0.2 \times 0.1 \text{ mm}^3$, respectively. The morphology and growth habit of the as-grown single crystals and the critical transition temperature (T_c) of the oxygenated crystals were found to depend on the Pr-content.

Keywords. High temperature superconductor; crystal growth; $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.

1. Introduction

Since the discovery of the new high temperature superconductors, extensive work had been carried out to understand the physical properties of these materials. However, the mechanism of superconductivity has continued to remain elusive and the general characteristics of these HTSCs have shown that we are still far from having even a satisfactory model of this exciting phenomenon in the new materials. Most of the work done so far is mainly based on the polycrystalline materials because of the easier way of preparation and synthesis compared to single crystals and epitaxial films. Further, it is evident that some of the physical properties like anisotropic behaviour, and fundamental parameters like energy gap ' Δ ' can not be obtained from randomly oriented polycrystalline materials. Hence, it is of vital importance that high quality large single crystals be available for investigations of their anisotropic properties and other properties leading to the understanding of superconduction in these materials. Also, because of difficulty in getting bigger single crystals by the techniques available so far, the improved methods of crystal growth are needed.

It is well known that substitution of trivalent rare earth elements (Nd, Sm, Eu, Gd, Dy, Ho etc) in place of yttrium does not effect the superconducting properties of the material while the substitution of certain tetravalent elements like Pr, Cs etc suppress the critical transition temperature ' T_c ' (Radousky 1992; Sun *et al* 1994). Although many models have been given so far to understand the cause of ' T_c ' depression with substitution of Pr or Cs elements in place of Y in the YBCO(123) material yet the cause is not fully understood. Particularly, for understanding the properties (T_c -depression) of Pr-substituted YBCO(123) material, many models consisting of the contradictory thoughts (Radousky 1992; Takenaka *et al* 1992; Fehrenbacher and Rice 1993; Khomskii 1993) have been suggested till now. These include — (a) hole filling model where it is assumed that — Pr is in the (+4) state which gives one extra electron per atom

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compared to $Y(3+)$ and fills one hole, (b) in the second model, it is assumed that Pr is in the $+3$ state and hybridizes with that of O_{2p} state of the CuO planes, which will result in a localization effect and for pair breaking, (c) another model is based on the charge redistribution of the 1D CuO chains and CuO_2 planes. In this case, the holes are 'passed away' from the CuO_2 planes to CuO chains by Pr-doping and (d) moreover, it has been stressed (Fehrenbacher *et al* 1993) that it is plausible to have unaffected 1D Cu-O chains by Pr-substitution. Most of the models given so far are based on the data obtained from polycrystalline materials because of the nonavailability of large and good quality single crystals of these Pr-substituted materials. However, there is only one report available (Sun *et al* 1994) on the growth of Pr-substituted (partially) good quality single crystals.

In the present paper, apart from the growth of Pr-substituted large single crystals of (Y,Pr)BCO the substitution effect of stable tetravalent Pr on the morphology and superconducting properties of YBCO single crystals is presented.

2. Experimental

The self-flux technique was successfully employed for the growth of large single crystals of pure $YBa_2Cu_3O_{7-\delta}$ (Singh and Kashyap 1994). The same technique when modified suitably, resulted in the growth of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($x = 0.0, 0.2, 0.4$) HTSC material in the form of bulk, needles and platelets. A mixture of 72 mol% CuO and 28 mol% $BaCO_3$, corresponding to the composition at eutectic point in the phase diagram of CuO and $BaCuO_2$ (Nevriva *et al* 1988) was used as self-flux in the present case. The self-flux was prepared by grinding the pure powder (99.9%) of above constituents for many hours with an agate mortar and pestle. The calcined powder of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($x = 0.0, 0.2, 0.4$) was prepared by the multiple calcination process from pure (99.9%) powders of Y_2O_3 , $BaCO_3$ and CuO in the stoichiometric ratio of Pr:Y:Ba:Cu = $x:1-x:2:3$ by calcining at 910 and 920°C, for 12 h each with intermediate grindings for 4 h each time before the calcination was carried out. The overall composition of the charge, a mixture of calcined powder of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($x = 0.0, 0.2, 0.4$) and flux, was selected in the weight ratio of 1:10 for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$:flux. The high density alumina crucibles were found to be useful for holding the charge as less quantity of molten charge reacted with the walls of the crucible. The growth run was carried out in a box-type programmable furnace (Heraeus, Model-K1522) with a suitably adjusted thermal cycle. After soaking the charge at 1000°C for 20 h it was allowed to cool to 820°C with a cooling rate of 2°C/h so that only a limited quantity of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($x = 0.0, 0.2, 0.4$) was available first for nucleation and then for crystallization. The grown crystals were easily removed from the flux after exposing the charge to humid atmosphere for a few days. The oxygenation of these as-grown single crystals was carried out under oxygen pressure (3 atm.) at a temperature of 475°C for 15 days.

The superconducting behaviour of the oxygenated crystals was studied by using ac-magnetic susceptibility and resistivity vs temperature ($R - T$) measurements in the temperature range of 15–100 K achieved by using the Superconductor Characterization Cryostat (SCC) [APD Cryogenics, Inc., Model: P/N 257171A]. The APD Cryogenics, Inc. SCC, provides a 19 mm diam. $\times$ 180 mm long isothermal refrigerated

sample well for characterizing materials as a function of temperature from 12 K to 350 K. The ac-magnetic susceptibility measurement is made by inserting a pair of secondary coils (sample and reference; inner diam. = 4.2 mm, length = 3.0 mm

Figure 1.

Figure 1. Optical photographs of as-grown crystals of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$: (a) $x = 0.0$, (b) $x = 0.2$ and (c) $x = 0.4$.

Figure 2. SEM micrograph of a platy crystal of $Y_{0.8}Pr_{0.2}Ba_2Cu_3O_{7-\delta}$ showing layer growth.

and total number of turns = 96, for each coil), into the sample area. The secondary coils are designed in our laboratory for detecting the small signal produced by the crystal in an alternating magnetic field. External to secondary coil is a long primary coil. The sample is inserted into the centre of one of the two secondary coils. A low frequency current is passed through the primary coil. This produces an alternating magnetic field inside the primary which in turn produces a large voltage in each

Figure 3.

Figure 3. SEM micrographs showing spiral shapes on the surfaces of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ crystals: (a) octagonal ($x=0.0$), (b) tetragonal ($x=0.0$) and (c) tetragonal ($x=0.2$).

secondary coil. However, the two secondary coils are precisely wound in opposite directions and thus are balanced so that the sum of two induced voltages is zero. Now, when a sample is introduced into the sample secondary, the two secondary coils become unbalanced, and a voltage appears at the lock-in amplifier. This voltage is directly proportional to the magnetization produced by the primary field in the sample.

3. Results and discussion

Typical sizes of the platy and bulky crystals of pure YBCO(123) material are $\approx 2 \times 2 \times 0.1 \text{ mm}^3$ and $4 \times 1 \times 1 \text{ mm}^3$, respectively. In case of Pr-substitution, the typical sizes of platy and bulky crystals of $Y_{0.8}Pr_{0.2}Ba_2Cu_3O_{7-\delta}$ and $Y_{0.6}Pr_{0.4}Ba_2Cu_3O_{7-\delta}$ materials are $\approx 2 \times 3 \times 0.1 \text{ mm}^3$ and $5 \times 1 \times 1 \text{ mm}^3$ and $\approx 1 \times 1.5 \times 0.1 \text{ mm}^3$ and $7 \times 0.2 \times 0.1 \text{ mm}^3$, respectively. The pure and Pr-substituted as-grown single crystals are shown in figure 1. The amount of the platy crystals was found to be converse of Pr-substitution in YBCO, while the reverse was observed for bulky crystals. The morphology of praseodymium substituted single crystals is thus observed to depend upon the Pr-content.

The SEM in figure 2 shows a layer (two-dimensional) growth for $x=0.2$ in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ platy single crystal. The micrograph shows three consecutive layers grown one by one in the ab-plane. The topographic study revealed that in the beginning, when the melt is at a temperature much higher than the solubility limit, supersaturation is quite high and the layer growth mechanism is operative in the growth of these crystals. In addition to morphology, the growth habit also appears to

Figure 4. AC-magnetic susceptibility measurements for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($0 < x < 0.4$) single crystals.

depend upon the Pr-concentration in the starting flux. The spiral shape, observed by scanning electron microscopy (SEM) [Model: Phillips 525], was found to vary from octagonal–tetragonal (figures 3a and b), tetragonal (figure 3c) to no spiral with $x = 0.0, 0.2$ and 0.4 respectively. The observed shapes of the growth spirals in the present case could be the consequence of low kink density/high roughness and high kink density/low roughness of the growth steps for octagonal and square spirals, respectively, in accordance with the periodic bond chain (PCB) theory (Sun *et al* 1989). It is a matter of fact that at lower supersaturation the growth is favoured by the operation of screw-dislocations and results in spiral formation. Also, additional nucleation on the entire surface is hampered because of the presence of spirals on the surface of the crystal.

As expected, the as-grown single crystals were found to be non-superconducting. The oxygenation of these crystals under oxygen pressure (3 atm) at a temperature of 475°C for 15 days made them superconducting. From the ac-magnetic susceptibility measurements (at a.c. field of 100 mOe, 540 Hz), as shown in figure 4, the onset values of the critical transition temperatures ($T_{c,on}$) for pure YBCO, $Y_{0.8}Pr_{0.2}Ba_2Cu_3O_{7-\delta}$ and $Y_{0.6}Pr_{0.4}Ba_2Cu_3O_{7-\delta}$ crystals were found to be 82, 60 and 50 K, with transition widths of nearly 22, 20 and 30 K, respectively. The superconducting transition ($T_{c,max}$) is observed to decrease with increase in the Pr-concentrations in confirmation with the earlier observations (Sun *et al* 1994).

4. Conclusions

We have successfully grown large single crystals of praseodymium substituted 123 ($Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ where $x_{max} = 0.4$) by modified self-flux method. The morphology and growth habit of the as-grown single crystals, and the critical transition temperatures

(T_c) of the oxygenated crystals of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ HTSC-material were found to depend on the Pr-content—higher the concentration of praseodymium, lower is the transition temperature.

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