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Abstract
Thermal expansion measurements have been carried out for the Zn-substituted
compounds $Y_1Ba_2(Cu_{1-x}Zn_x)_3O_y$ $(0 \leqslant x \leqslant 4\%)$ with a high-resolution
dilatometer using the three terminal capacitance technique. The present setup
is sensitive enough to detect changes in α of about 10^{-8} K^{-1}. Results indicate
that the jump $\Delta\alpha$ in the coefficient of linear thermal expansion decreases with
an increase in Zn content. For $x = 1\%$, $\Delta\alpha$ decreases by a factor of about
five whereas the oxygen content and transition temperature do not change
appreciably. There is strong evidence that the temperature dependences of α
for compounds with high Zn concentration depend on the conditions of sample
growth.

1. Introduction

There have been many efforts to find new superconducting materials while seeking to explain
the transport mechanism in ceramic high temperature superconductors. Several investigators
have studied the substitution effects in high T_c superconductors. In particular, substituting,
for example, Zn, Fe, Ni, Co or Al for Cu dramatically affects the superconducting and normal
state properties [1–6]. This demonstrates the important role of Cu. The addition of these
impurities results in the breaking up of Cooper pairs and thereby a drastic reduction in the
superconducting transition temperature is obtained.

Different impurities have preferential occupancies because of the presence of two copper
sites, a plane and a chain. It has been observed that for dopants like Fe and Co, which
occupy plane sites, there is an orthorhombic to tetragonal transformation [1–3]. However
no such transformation is observed for Zn and Ni that occupy chain sites [4–6]. Because of
structural changes, doping by Fe, Co, Ni, etc affects not only the properties associated with the
superconducting state of YBaCuO but also properties like the lattice components of specific
heat [7, 8], coefficient of thermal expansion [7, 9–13] and the pressure dependence, dT_c/dP of
T_c [14–17]. Detailed thermal expansion studies have been carried out by many investigators on

the dopants which occupy copper plane sites. These reports indicate that the jump in thermal expansion increases with an increase in dopant concentration [7, 10, 11].

Little work on thermal expansion [7, 12, 13] seems to have been done on the dopants that occupy copper chain sites. The only detailed studies seems to have been done on the Ni doped YBaCuO compounds [12]. These results indicate that the jump in thermal expansion decreases with increase in Ni concentration. Non-magnetic impurities like Zn, on the other hand, are of great interest. This is because Zn doping causes significant changes to the local electronic structure without much change in hole concentration. It is also observed that the electronic density of states and the Debye temperature increase with increasing Zn concentration [8]. In fact the effects of non-magnetic impurity on superconductivity were theoretically predicted for a d-wave superconductor [18, 19]. These predictions were examined by many experimental investigations such as NMR [20, 21], electronic specific heat [22] and muon spin rotation [23]. No systematic work seems to have been done on the thermal expansion of Zn doped YBaCuO compounds. There are perhaps only two reports on this system. Meingast *et al* [7] have observed a decrease in $\Delta\alpha$ with increasing dopant concentration. In addition to this Li *et al* [13] have observed abrupt changes in lattice parameters at several temperatures, which has been attributed to the occurrence of some kind of local structural adjustment, like the tilting of the CuO_5 pyramid. It was therefore interesting to carry out a systematic study of the measurement of thermal expansion for Zn doped compounds. These measurements have been carried out on the substituted compounds $Y_1Ba_2(Cu_{1-x}Zn_x)_3O_y$ for $0 \leqslant x \leqslant 0.04$, in the temperature range 70–300 K.

2. Experimental techniques

All the samples were prepared using the well-known solid-state reaction technique. Appropriate amounts of Y_2O_3, $BaCO_3$, CuO and ZnO were thoroughly mixed in an agate mortar and then calcined at 930 °C in air for 12 h. The mixing and calcination was repeated three times to improve the homogeneity. The power was cold pressed into pellets and sintering was done in flowing oxygen for 72 h, this was followed by slow cooling to 450 °C and then slowly cooled to room temperature. The oxygen content per unit formula for each sample was determined iodometrically. Titration for each sample was performed twice to check the reproducibility. High purity argon gas was used to create an inert atmosphere. The accuracy of the oxygen content determination was ±0.03. The oxygen content of the samples is comparable to that in the literature [17]. The transition temperature determination was done using the standard four-probe technique. The x-ray diffraction technique was used to determine the atomic spacing of superconducting compounds and to see if any impurity phases are present. These parameters, along with the density, ρ, for each specimen, are given in table 1.

Measurements of the linear thermal expansion coefficient were carried out using a three terminal capacitance dilatometer developed by Prakash *et al* [24]. The dilatometer design was such that there are no significant contributions to δl (the change in length of the sample) from the sample mounting system. The dilatometer was evacuated and filled with helium gas at low pressure. Then the sample was cooled to a temperature of about 70 K by pumping liquid nitrogen. After the sample attained the bath temperature, the dilatometer was evacuated to a pressure of about 10^{-6} Torr. The sample was heated to successively higher temperatures in steps of 0.3 K. At each temperature, it was ensured that the sample was in thermal equilibrium. Heating the sample changes the capacitance from which the change δl in the length of the sample was determined as a function of temperature. In the present configuration δl consists of two parts namely one due to the expansion of the sample and the other due to the mounting plate. The contribution of the expansion of the plate was determined as a function of T by removing

Table 1. Various parameters of the $Y_1Ba_2(Cu_{1-x}Zn_x)_3O_y$ compounds.

x (%)	a (Å)	b (Å)	c (Å)	T_c (K)	y ±0.03	ρ (g cm^{-3})
0	3.817	3.886	11.682	92	6.93	5.34
0.25	3.819	3.884	11.680	88	6.92	5.32
0.5	3.817	3.885	11.678	86	6.95	5.28
0.75	3.821	3.884	11.673	83	6.93	5.30
1.00	3.820	3.884	11.670	80	6.98	5.35
2.00	3.822	3.886	11.672	71	6.96	5.36
4.00	3.824	3.887	11.677	64	6.95	5.32

the sample and directly measuring the capacitance between the capacitance plates. The thermal expansion coefficient was determined using the following procedure. Two polynomials in T, one for $T < T_c$ and the other for $T > T_c$ were fitted to the experimental data of change in length per unit length of the sample. For both these polynomials, data in the temperature range of about 3–4 K around T_c was excluded. The differentiation of the polynomials thus obtained gives α as a function of the temperature. The sample length varied from 30–35 mm. In the present setup we could control temperature within ±5 mK. At each temperature the capacitance of the parallel plate capacitor was measured using a GR-1620 capacitance bridge in the three terminal configurations. The dilatometer is sensitive enough to detect changes of the order of about 10^{-8} K^{-1} in α.

3. Results and discussion

All the superconducting samples show a metallic behaviour in the normal state. The transition widths in these compounds lie in the range 1–3 K. The electrical resistivities of the samples in the present investigations are in good agreement with that in the literature. To compare the results, the resistivity of the sample with $x = 0.5\%$ at 100 K is 0.9×10^{-4} Ω cm, whereas that observed by Yoshida *et al* [17] is about 0.5×10^{-4} Ω cm. The temperature variation in the thermal expansion coefficient α in the temperature range 77–300 K for various Zn-doped compounds are shown in figure 1. The value of α obtained for a 0.5% doped sample of Zn in the present work at 80 K is 5.25×10^{-6} K^{-1}, whereas that obtained by Li *et al* [13] is about 5.06×10^{-6} K^{-1}. The present results of α do not show a sharp discontinuity in α around the transition temperature; instead α increases gradually as the sample undergoes the transition from the normal to the superconducting state.

By contrast, in conventional superconductors, a sharp discontinuity is observed in the thermal expansion coefficient at the transition temperature. This difference in behaviour is due to the broad transition widths (about 2–3 K) in high T_c superconductors compared with the sharp widths (about 1 mK) in conventional superconductors. The jump in thermal expansion coefficient at T_c, was determined by extrapolating the two branches of α/T versus T curves at T_c. α/T is plotted instead of α because the jumps in thermal expansion are best seen in this plot. Figure 2 shows the variation of α/T versus T in the vicinity of the transition temperatures. In order to ascertain that the values of jump in α thus obtained are not due to the extrapolation procedure itself, this procedure was applied to α/T versus T data obtained in a non-superconducting sample of undoped compound. It is satisfying to note that in this sample the difference in the two extrapolation values was less than 1.5×10^{-8} K^{-1}. To ascertain that the jump in thermal expansion is not due to any anisotropy or associated strain, we prepared two samples each with $x = 0\%$ and 0.5%. The values of jump for two samples of the same
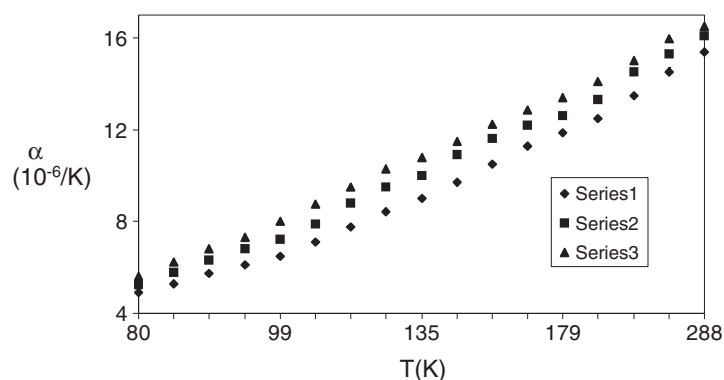
Figure 1. Thermal expansion versus temperature. Series 1, 2 and 3 denote $x = 0\%$, 0.5% and 1%, respectively.
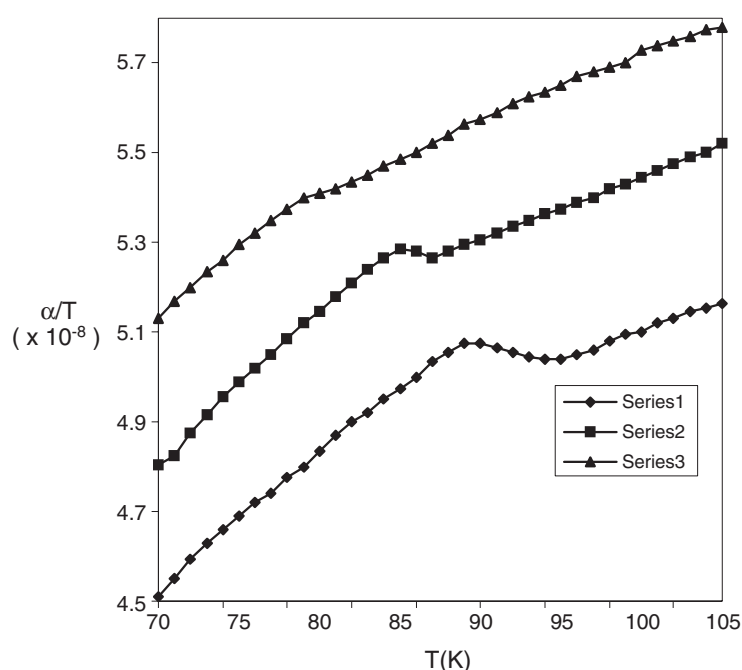

Figure 2. Temperature variation of α/T in the vicinity of the transition temperature. Series 1, 2 and 3 denote $x = 0\%$, 0.5% and 1%, respectively.

doping level is identical within experimental errors. For example, for $x = 0.5\%$, the values of jump varied from 3.2×10^{-8} to 2.6×10^{-8} K^{-1}. This suggests that the jump is indeed due to the second order phase transition and not due to the anisotropy or the associated strains.

Figure 3 shows the temperature variation of $\Delta\alpha$ for Zn doped compounds. It is observed that $\Delta\alpha$ decreases linearly as the impurity concentration is increased. The jump $\Delta\alpha$ decreases from 6.7×10^{-8} to 1.2×10^{-8} K^{-1} as x increases from 0 to 1%. The results obtained in the present investigations are not in good agreement quantitatively with those of Meingast *et al* [7]. The latter reports that with an increase in Zn concentration first there is a decrease in $\Delta\alpha$ (for $x = 1\%$) and then there is an increase in $\Delta\alpha$. Table 2 gives a comparison of α and $\Delta\alpha$ values obtained in the present investigation with that in [7]. The disagreement is perhaps because of
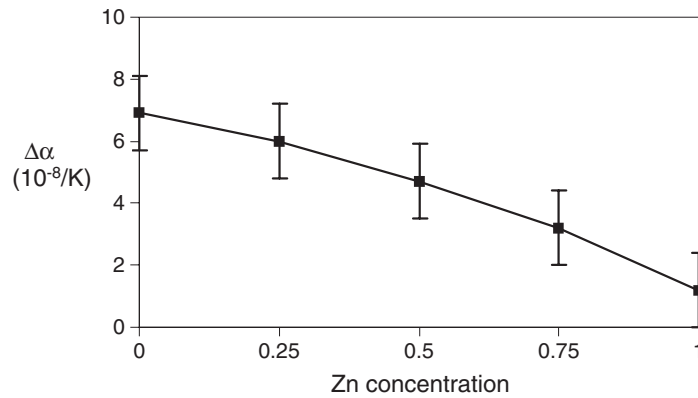
Figure 3. Dependence of $\Delta\alpha$ on Zn concentration.

Table 2. Comparison of α and $\Delta\alpha$ values.

x (%)	α $(\times 10^{-6})$		$\Delta\alpha$ $(\times 10^{-8})$	
	Present data	[7]	Present data	[7]
0	15.6	11.62	6.7 ± 1.5	4.5 ± 0.5
1	16.8	11.57	1.2 ± 1.0	-4 ± 1
2	17.0	a	a	a
2.5	a	11.08	a	0 ± 1

a Denotes data not available.

differences in oxygen content or strains in the samples. As a matter of fact, Meingast *et al* [7] have not reported the oxygen content of the samples.

It is important to mention that replacing 1% Cu by Zn has little effect on the transition temperature; however, the decrease in $\Delta\alpha$ is about a factor of 5. This clearly demonstrates that these substituents are being incorporated into the superconductors as a whole and not in the form of a local cluster. If Zn were substituted in the form of local cluster, then it would not have any effect on $\Delta\alpha$ because thermal expansion is a bulk property.

Apart from the discontinuity in the thermal expansion coefficient α around T_c, there are several reports of observations of additional anomalies [7, 25–30]. For example, it has been observed that a broad minimum in α around 160 and 240 K occurs. Meingast *et al* [7] have also reported some anomalies, like a jump in α at $T = 250$ K, hysteresis in the temperature region $50 \leqslant T < 250$ K and non-reversible length changes at low temperature ($T < 45$ K), for specimens with higher concentration. Anomalies of this type have been observed by Rao *et al* [10–12]. In fact they have also observed that two specimens cut out of the same sample behave differently. It is quite likely that these anomalies are due to internal strain or inhomogeneities in the sample. In the present work, for very carefully prepared samples of higher Zn concentration (2 and 4%), no such anomalies were observed. These samples were prepared by sintering in air at $930\,°C$ for 48 h. This process was repeated five times in order to ensure homogeneous distribution of the substituted oxide. Finally the powder was reground and pressed into rectangular bars and annealed in flowing oxygen at $950\,°C$ for 48 h. This was followed by slow cooling to $450\,°C$ at the rate of about $1\,°C\,min^{-1}$.

To study the effect of strain on the thermal expansion coefficient, these well annealed samples were given strain by keeping them at $200\,°C$ for 8 h and followed by quenching to
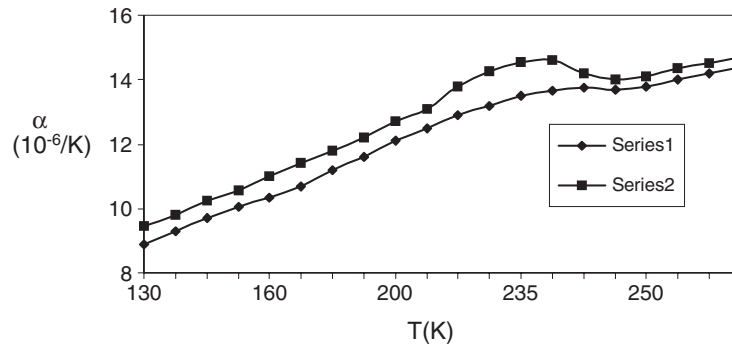
Figure 4. Thermal expansion coefficient versus temperature for the quenched (series 1) and unquenched (series 2) specimens with $x = 2\%$.

room temperature. The reason for choosing the temperature of 200 °C is that the temperature is low enough to prevent loss of oxygen and moreover the aim was to give a small strain to the samples. Figure 4 shows the variation of α as a function of temperature for quenched and unquenched samples of Zn with $x = 2\%$. It was observed that quenched sample shows anomaly around 250 K. In addition to this, the quenched sample exhibits larger α values as compared to the unquenched specimen in the range $77 < T < 260$ K. Beyond this, however, the behaviour is almost identical for both the specimens. Similar results are obtained for the quenched and unquenched samples of Zn with $x = 4\%$. We finally conclude that these anomalies are possibly due to the presence of unstable phases or due to strain in the specimens.

4. Conclusions

The dependence of the jump $\Delta\alpha$ on the Zn concentration shows that $\Delta\alpha$ decreases with an increase in Zn concentration. A similar decrease has also been observed for Ni doped compounds [12]. By contrast, $\Delta\alpha$ is observed to increase with an increase in Fe and Co concentration [7, 10, 11]. This suggests that $\Delta\alpha$ appears to correlate with the substitution site; that is, for dopants such as Fe, Co which occupy copper planes, $\Delta\alpha$ increases. On the other hand, there is a decrease in $\Delta\alpha$ for dopants such as Ni and Zn, which occupy the copper chain sites. These results can be explained using a model suggested by Zernov and Chulkin [31], which is based on the phonon mechanism of superconductivity. It is assumed that for low concentrations, impurities like Fe, Co, Ni, Zn and Al have paramagnetic nature. In the aforesaid model a parameter λ is considered which is related to the electron–phonon interactions, which also depends upon the density of electron states. It is shown in the model that doping by Fe or Co, the density of states $N(E_F)$ increases and consequently the pressure derivative of T_c, dT_c/dP increases and hence an increase in $\Delta\alpha$. By contrast, doping with Zn (or Ni), dT_c/dP decreases hence $\Delta\alpha$ decreases.

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