ON THE SUBSTITUTION OF Sr IONS AT Y SITES IN YBa$_2$Cu$_3$O$_{7-d}$

S.A. Siddiqi**, K. Sreedhar***, D. Drobac†,
HTS Laboratory,
International Centre for Theoretical Physics, Trieste, Italy,

C. Infante††, F.C. Matacotta and P. Ganguly***
HTS Laboratory,
International Centre for Theoretical Physics, Trieste, Italy.

1. INTRODUCTION

The effect of Sr substitution at the Ba sites in YBa$_2$Cu$_3$O$_{7-d}$ has been studied 1), attempts to substitute Sr exclusively at Y sites have not been successful. We have been able to substitute Sr at Y sites only when the Ba ions are simultaneously substituted by Sr to give solid solutions of the type Y$_{1-x}$Sr$_x$Ba$_{2-2x}$Sr$_{2z}$Cu$_3$O$_{7-\frac{1}{2}d}$. These samples show superconducting transitions higher than 78 K without significant deterioration in the magnitude of the ac susceptibility. The substitutions are best understood in terms of size constraints on the ions occupying the Y and Ba sites.

The compounds were prepared by using better than 99.9% purity Y$_2$O$_3$, CuO, Sr(NO$_3$)$_2$ and BaCO$_3$ as starting materials. In general the starting mixture was ground and prefired in air at 850°C for about twelve hours. The material was reground and fired again in air at temperatures varying between 930 – 970 °C. The final firing temperature increases with increasing value of x. The compounds were then reground, pelleted and heated in oxygen in the usual manner. The value of d was obtained by iodometric titration. The purity of the phase is a sensitive function of the preparation history including the nature of the starting material. We obtain best results when we use Sr(NO$_3$)$_2$ and BaCO$_3$. SrCO$_3$ and BaO$_2$, for example, did not yield single-phase material in the early stages of preparation. Prolonged high-temperature treatment, however, always yielded single-phase material.

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2. **CRYSTAL STRUCTURE**

In Table 1 we present the lattice parameters of some representative compounds. It is to be noted that when \( y = 0.25 \) the effect of increasing \( x \) is mainly changing the \( b \) parameter with the \( a \) parameter being fixed. This is quite different from that observed when \( x = 0 \) and \( y \) is varied. The results of Veal et al. show that in the latter case the \( b \) parameter remains fixed while the \( a \) parameter changes rapidly.

<table>
<thead>
<tr>
<th>( Sr )</th>
<th>( a(\text{Å}) )</th>
<th>( b(\text{Å}) )</th>
<th>( c(\text{Å}) )</th>
<th>( \text{vol.}(\text{Å}^3) )</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.55</td>
<td>3.802</td>
<td>3.866</td>
<td>11.623</td>
<td>170.84</td>
<td>6.75</td>
</tr>
<tr>
<td>0.65</td>
<td>3.806</td>
<td>3.866</td>
<td>11.607</td>
<td>170.82</td>
<td>6.71</td>
</tr>
<tr>
<td>0.75</td>
<td>3.802</td>
<td>3.863</td>
<td>11.549</td>
<td>169.58</td>
<td>6.67</td>
</tr>
</tbody>
</table>

3. **SUPERCONDUCTING PROPERTIES**

In Table II we report the resistivity characteristics of the \( y = 0.25 \) samples for various values of \( x \) with \( d = 0.24 \). In Fig. 1 the \( ac \) magnetic susceptibility results on the same samples are shown. The nature of the magnetic susceptibility curve near the transition shows systematic changes which may be associated with changes due to increasing \( x \). Thus the \( x = 0.05 \) sample shows a sharp transition typical of the onset of bulk superconductivity. On further increase of \( x \) the transition to the bulk superconducting state due to interparticle coupling (where the diamagnetic susceptibility increases sharply) is shifted to progressively lower temperatures while the interparticle contribution persists over a higher range.
Table II

Resistivity vs. temperature characteristics of Sr doped Y-123 superconductors

<table>
<thead>
<tr>
<th>Sr</th>
<th>ρ(300 K) (mΩ cm)</th>
<th>Tc(ρ = 0) (°K)</th>
<th>T onset (°K)</th>
<th>ΔTc</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>1.3</td>
<td>78</td>
<td>84</td>
<td>6.0</td>
</tr>
<tr>
<td>0.65</td>
<td>0.9</td>
<td>81</td>
<td>86.5</td>
<td>5.5</td>
</tr>
<tr>
<td>0.55</td>
<td>0.8</td>
<td>84</td>
<td>89.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Fig. 1 a.c. susceptibility curves for the y = .25 and z = .05; x = .15 and x = .25 samples.
4. IR ABSORPTION SPECTRA

In Fig. 2 we show the infra-red absorption spectra in the range 650–400 cm\(^{-1}\) for the \(y = 0.25\) samples for various values of \(x\). When \(x = 0.05\) or 0.15 the spectra are very similar to that of pure \(YBa_2Cu_3O_y\) \(^{2)}\). When \(x = 0.025\), however, features change considerably with the appearance of a strong band around 590–600 cm\(^{-1}\) along with other features around 550 and 500 cm\(^{-1}\). We shall not attempt to assign these bands in the present paper. We point out that the band around 590 cm\(^{-1}\) is observed prominently in \(d > 0.7\) samples of \(YBa_2Cu_3O_{7-d}\).

Fig. 2 IR absorption spectra: \(a, d : x = .25;\) \(b, e : x = .15;\) \(c, f : x = .25\). Curves \(a, b, c\) are taken from air treated samples; curves \(d, e, f\) are taken from oxygen treated samples.
5. DISCUSSION

Our studies show unequivocally for the first time that single-phase material may be obtained by the substitution of Sr at Y sites. However, the requirement that two Ba ions be replaced simultaneously by Sr, seems to indicate that size constraints are important. The average size \(^3\) of two Ba ions in ten-fold coordination (at A2 site) and one Y ion in eight-fold coordination is 1.35 Å while that for two Sr ions in ten-fold coordination and one in eight-fold coordination is 1.33 Å.

The constraints on the ionic size of the A ions is in agreement with the model of Ganguly and Sreedhar in understanding the structural features of YBa\(_2\)Cu\(_3\)O\(_y\). As discussed by Ganguly and Sreedhar \(^4\), the accommodation of the large Ba\(^{2+}\) ion (radius = 1.52 Å in ten-fold coordination) in an unit-cell with small \(a\) parameters leads to pressure on the 0\(\text{I}_{\text{I}}\),\(\text{I}_{\text{II}}\) oxygens and tends to decrease the distance between the Cu\(_2\) planes. This would be resisted by the ions at the Al sites above a critical value of the ionic radius. The amount of displacement is given in the hard–sphere model by the size of the oxide ion. We assume that the average diameter of the oxide ion is given by the square root of the average of the \(a\) and \(b\) parameters (\(\sim 3.86\) Å). The limiting size of the ion at the Al site should be 1.08 Å for a given \(c\) parameter of 11.67 Å. Y\(^{3+}\) ion has a radius of 1.019Å which is consistent with the above model. The Sr\(^{2+}\) ion has a radius of 1.26 Å which is too large. For such an ion at the A1 site the maximum radius at the A2 site should be 1.40 Å (keeping the \(c\) parameter fixed at 11.67Å) compared to the value of 1.36Å for Sr\(^{2+}\) ions in ten-fold coordination. This would account for the fact that the substitution of Sr at Y sites should be accompanied by a simultaneous substitution of Ba by Sr ions.

An interesting aspect of this system is that the high temperatures of preparation leads to very well sintered samples with densities approaching the theoretical densities. Further studies at higher pressures are under way to increase the oxygen content and to see the influence on the superconducting properties.

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REFERENCES


** On leave from Centre for Solid State Physics, University of Punjab, Lahore, Pakistan.
*** On leave from Indian Institute of Science, Bangalore, India.
† On leave from Institute of Physics, University of Zagreb, Yugoslavia.
†† On leave from Department of Physics, University of Chile, Santiago, Chile.