Ion Substitution Effects on the Structure Stability of Cuprate Superconductors

M. K. Wu¹, D. H. Chen¹, D. Y. Chen¹, S. R. Sheen¹ and F. Z. Chien²

¹Materials Science Center, National Tsing Hua University, Hsinchu, Taiwan ROC
²Department of Physics, Tamkang University, Tamsui, Taipei, Taiwan ROC

Abstract

We have demonstrated that using a transition metal ion to partially substitute Cu ion of the YSr₂Cu₃O₇ can stabilize its crystal structure and retain superconductivity. The superconducting transition temperature in YSr₂(Cu₁₋ₓMₓ)₃O₇, where M is transition metal ion, ranges from 40K to 80K depending on the specific M ion. Lattice contraction due to Sr substitution makes the Ba/Sr ion to move closer to CuO plane, and consequently leads to a charge transfer between oxygen. Our study shows that the key factor controlling the structural stability in Y-Sr-Cu-O system is the effective ionic radius Sr in lattice. The introduction of transition metal doping is to increase the effective ionic radius of Sr through the increase of oxygen content.

Key Words: superconductivity; lattice parameters; perovskite; tolerance factor

1. Introduction

Ion substitution has been used extensively to elucidate the mechanism of superconductivity in cuprate superconducting systems. For the YBa₂Cu₃O₇ (YBCO) system, substitution of Y by all rare-earth (RE) elements revealed that, except Ce, Pr and Tb, the other (RE)BCO remain superconducting with Tc ~ 90K [3,9]. The substitution of Cu by most metal ions results in degradation of superconductivity, although the magnitude of suppression depends on the particular ionic species. Generally, greater suppression occurs when the substituted ions occupy the Cu-site at the CuO₂-plane, whereas much less if the ions locate in the linear-chain Cu-site [2]. A partial substitution of Ba by small amount of other divalent ions, such as Sr, generally also resulted in a relatively minor effect on the superconducting transition temperature. However, most early attempts to complete substitute Ba by other ions failed to maintain the crystal structure.

Progress was made in complete substitution of Ba by Sr to maintain the correct crystal structure and superconductivity. These results consequently generated enormous activity. The earliest report by Wu et al. [8] indicated the possible existence of an YSr₂Cu₃O₇ (YSCO) phase with Tc about 80K in a multiphase system. Later reports, including one using high-pressure synthesis [6], however, though showed the possibility of stabilizing YSCO phase, provided no samples with a clean superconducting phase. Cava et al. [1] found by adding Pb the existence of new compounds in a series of Pb₂(RE)Sr₂Cu₃O₇ with Tc ~ 40K. The structure has tetragonal crystal symmetry and is similar to that of YBCO but with an exceptional Pb-O cage embedded between Cu-O planes. This discovery led to successful synthesis of a new cuprate series, the so called “1212” system, which includes the Tl-based Tl-Y-Sr-Ca-Cu-O [4] compounds. This system has attracted great attention because of its relatively high Tc and its superconducting characteristics under strong magnetic fields are comparable to those of YBCO. It also subsequently generated many interesting new superconducting cuprates, such as Pb-Hg-Sr-Ca-Cu-O system [5].
The first clean superconducting YSCO with 123-structure was achieved by the addition of MoO₃ [10] in a small proportion to YSr₂Cu₃O₇. Depending on the oxygenation conditions, superconducting transition in the range of 40-80 K was observed. The presence of Mo atom was found to decrease the reaction temperature and is essential for the formation of the pure high-Tc phase. Similar phase stabilization can also be achieved by the introduction of other transition metals such as Fe, Al, Co and etc [7]. Therefore, a detailed systematic study on the YSCO system using ion-substitution provides us an opportunity to unravel the mechanism relevant to the structural stability of these superconducting phases. Furthermore, it also provides us a possible direction for the search into new superconducting oxides. In the following, we summarize the results of the effects of Mo-doping to the Y(Ba-Sr)₂(Cu-Mo)₃Oₓ system. We observed that the addition of Mo-atom changes the effective ionic radius and/or the effective valence of Sr in lattice through the increase of oxygen content. This effect subsequently leads to the structural stability in the Y-Sr-Cu-O system.

2. YSr₂(Cu,Mo)₃Oₓ system

Figure 1 is the measured x-ray powder diffraction pattern of YSr₂(Cu,Mo)₃Oₓ in the range of 20° to 100° in 2θ. A tetragonal structure with lattice parameters \( a = 3.8085 \) Å and \( c = 11.5335 \) Å was determined using the Rietveld program DBWS9600. The corresponding atomic positions of space group P4/mmm and the isotropic Debye-Waller factors listed in Table 1 were determined based on the stoichiometry of YSr₂Cu₂.₈Mo₀.₂O₆.₉₇ with Mo atom assigned at the Cu(1) and Cu(2) site.

The occupancy of oxygen at each site was refined and all sites except O(3) were found to be fully occupied. An occupancy number of 1.18 for the O(3) site was determined which is consistent with that determined from iodometric titration on the sample with Mo-ion assigned with hexa-valency, which was based on the x-ray photoelectron spectra (ESCA). The volume of the unit cell is about 3.5% smaller than that of YBCO.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B (Å²)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>1d</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>1.6</td>
<td>1</td>
</tr>
<tr>
<td>Sr</td>
<td>2h</td>
<td>0.5</td>
<td>0.5</td>
<td>0.1944</td>
<td>2.8</td>
<td>2</td>
</tr>
<tr>
<td>Cu(1)</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.3</td>
<td>0.90</td>
</tr>
<tr>
<td>Mo(1)</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.3</td>
<td>0.10</td>
</tr>
<tr>
<td>Cu(2)</td>
<td>2g</td>
<td>0</td>
<td>0</td>
<td>0.3537</td>
<td>1.7</td>
<td>1.89</td>
</tr>
<tr>
<td>Mo(2)</td>
<td>2g</td>
<td>0</td>
<td>0</td>
<td>0.3537</td>
<td>1.7</td>
<td>0.11</td>
</tr>
<tr>
<td>O(1)</td>
<td>2g</td>
<td>0</td>
<td>0</td>
<td>0.1663</td>
<td>0.6</td>
<td>2</td>
</tr>
<tr>
<td>O(2)</td>
<td>4I</td>
<td>0.5</td>
<td>0</td>
<td>0.3759</td>
<td>0.4</td>
<td>4</td>
</tr>
<tr>
<td>O(3)</td>
<td>2f</td>
<td>0</td>
<td>0.5</td>
<td>0</td>
<td>5.9</td>
<td>1.18</td>
</tr>
</tbody>
</table>

\( a = 3.8085(1) \) Å
\( c = 11.5335(2) \) Å
\( R_p = 4.32\% \)
\( R_{wp} = 6.85\% \)

Without adding MoO₃, the YSCO superconducting phase does not form when samples are prepared at a temperature less than 1300°C. Hence the high-Tc phase in the YSCO compound is thermodynamically stable only at higher temperatures. The role of Mo in the formation of a high Tc phase may be to stabilize it through the dispersion of a fine metallic oxide. Nevertheless, a better understanding the phase formation requires further detailed investigation. Scanning-electron micrographs and EDX analysis show that Mo atoms form a solid solution with Y-Sr-Cu-O. Similar phase stabilization was also observed in Bi- and Tl-containing superconductors with the addition of lead oxide. Based on ESCA results and x-ray diffraction analysis, Mo atom has a +6 valence state and partially occupies the Cu(1) site at low Mo-doping. It then gives rise to a more positive charge at Cu(1) site and introduces more oxygen atoms to the vacancies on \( z = 0 \) plane.

![Figure 1. Observed and calculate powder x-ray diffraction pattern of YSr₂Cu₂.₈Mo₀.₂O₆.₉₇.](image-url)
so bestowing tetragonal symmetry. The superconducting transition of YSCMoO is extremely sensitive to the nature of oxygenation processes. A critical process of oxygen diffusion is required to prepare superconducting samples without altering the crystal structure. This result indicates that the presence of Mo alters oxygen diffusion to affect the formation of superconducting phase.

3. \( Y(Ba_{1-x}Sr_x)(Cu_{1-0.07x}Mo_{0.07x})_3O_y \) System

A systematic variation of \( T_c \) was observed in this series of materials, as shown in Figure 2.

Figure 2. Superconducting transition temperature vs. \( x \) for \( (\bigcirc) Y(Ba_{1-x}Sr_x)(Cu_{1-0.07x}Mo_{0.07x})_3O_y; \) \( (\square) Y(Ba_{1-x}Sr_x)Cu_3O_y; \) \( (\bullet) Y(Ba_{1-x}Sr_x)(Cu_{1-0.07x}Mo_{0.07x})_3O_y \)

\( T_c \) decreases slightly for \( x < 0.4 \), and then drastically decreases from 80 K to 25K for \( x \) between 0.4 and 1. Table 2 displays the lattice parameters and the unit cell volume \( V \) for the compound series \( Y(Ba_{1-x}Sr_x)(Cu_{1-0.07x}Mo_{0.07x})_3O_y \). Clearly, a transition from orthorhombic to tetragonal structure occurs at \( x=0.4 \). A factor of more than 2 times in \( T_c \) reduction is observed for the whole range while the volume reduces only \( \sim 5\% \). The resistivity at 300 K of the samples increases as \( x \) increases but with a less pronounced jump at \( x = 0.4 \). The increase in normal state resistivity above \( T_c \) with increasing Sr concentration may be due to the combined effects of increasing Ba/Sr disorder scattering from the increase of Mo content. Moreover, the normal state resistivities of this series clearly exhibit a gradual change from linear to non-linear temperature dependence as \( x \) increases.

It is well known that altering the oxygen content of \( YBa_2Cu_3O_y \) leads to its orthorhombic to tetragonal transformation. The addition of Sr is found to decrease the oxygen content of \( Y(Ba_{1-x}Sr_x)Cu_3O_y \). The lattice contraction by Sr substitution weakens the stability of oxygens on O(4) and O(5) sites and causes the overall reduction of oxygen content. This is consistent with the ionic potential calculations which indicate that the repulsive force between O(4) and O(5) ions increases when lattice contracts. Based on the observed reduction in b-parameter is almost 4 times larger than that of a-parameter, major oxygen loss comes from the reduction of O(4). On the other hand, the inclusion of Mo-ion which has +6 valence attracts oxygens to occupy the vacant O(5) site. We believe that such a rearrangement in oxygen occupation, without altering much the oxygen content, is the major factor for the orthorhombic to tetragonal transition in \( Y(Ba_{1-x}Sr_x)(Cu_{1-0.07x}Mo_{0.07x})_3O_y \) at the critical concentration \( x \sim 0.4 \).

Table 2. Refined lattice parameters of \( Y(Ba_{1-x}Sr_x)(Cu_{1-0.07x}Mo_{0.07x})_3O_y \)

<table>
<thead>
<tr>
<th>( x )</th>
<th>( a (\text{Å}) )</th>
<th>( b (\text{Å}) )</th>
<th>( c (\text{Å}) )</th>
<th>( V(\text{Å}^3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.8197</td>
<td>3.8854</td>
<td>11.6805</td>
<td>173.35</td>
</tr>
<tr>
<td>0.1</td>
<td>3.8740</td>
<td>3.8411</td>
<td>11.6491</td>
<td>172.42</td>
</tr>
<tr>
<td>0.2</td>
<td>3.8217</td>
<td>3.8672</td>
<td>11.6395</td>
<td>172.02</td>
</tr>
<tr>
<td>0.3</td>
<td>3.8288</td>
<td>3.8505</td>
<td>11.6296</td>
<td>171.45</td>
</tr>
<tr>
<td>0.35</td>
<td>3.8320</td>
<td>3.8395</td>
<td>11.6172</td>
<td>170.92</td>
</tr>
<tr>
<td>0.4</td>
<td>3.8360</td>
<td>3.8360</td>
<td>11.6111</td>
<td>170.86</td>
</tr>
<tr>
<td>0.45</td>
<td>3.8333</td>
<td>3.8333</td>
<td>11.6019</td>
<td>170.48</td>
</tr>
<tr>
<td>0.5</td>
<td>3.8306</td>
<td>3.8306</td>
<td>11.6028</td>
<td>170.25</td>
</tr>
<tr>
<td>0.6</td>
<td>3.8279</td>
<td>3.8279</td>
<td>11.5925</td>
<td>169.86</td>
</tr>
<tr>
<td>0.7</td>
<td>3.8216</td>
<td>3.8216</td>
<td>11.5703</td>
<td>168.98</td>
</tr>
<tr>
<td>1.0</td>
<td>3.8085</td>
<td>3.8085</td>
<td>11.5335</td>
<td>167.29</td>
</tr>
</tbody>
</table>

In order to account for the observed \( T_c \) suppression, we estimated the mobile hole on the Cu-O planes (Psheet) based on the empirical relation developed by Tokura et al. Figure 3 is the relation between \( T_c \) and the mobile holes for \( Y(Ba_{1-x}Sr_x)(Cu_{1-0.07x}Mo_{0.07x})_3O_y \). For those samples with higher \( T_c (T_c > 70 \text{ K}, \text{ or } x < 0.3) \), a linear relation between \( T_c \) and Psheet is observed. While \( T_c \) is almost independent of Psheet for those samples with \( T_c \sim 40 \text{ K} (\text{or } x > 0.3) \). It is found that...
the low $T_c$ value is smaller than the value estimated from the linear extrapolation of the high $T_c$. This result indicates that $T_c$ suppression in these two ranges may have different origins.

![Figure 3](image_url)  
**Figure 3.** Temperature of zero resistance ($T_c$) versus the hole concentration on the CuO$_2$ planes ($P_{\text{sheet}}$) of Y(Ba$_{1-x}$Sr$_x$)$_2$(Cu$_{1-0.07x}$Mo$_{0.07x}$)$_3$O$_y$.

Our detailed refinements show that for $x < 0.3$ the major factor to affect $T_c$ originates from the Sr-sustitution effect. Lattice contraction due to Sr substitution (to Ba) makes the Ba/Sr ion to move closer to CuO$_2$ plane. This effect leads to a charge transfer from O(2) and O(3) which is confirmed from the bond-valence-sum estimated from the bond lengths. Consequently, $T_c$ decreases linearly as the hole concentration of CuO$_2$ planes decreases. On the other hand, for $x > 0.3$ the Mo-substitution effects become dominant. Detailed xray analysis show that Mo atom at low concentration ($x < 0.3$) occupies Cu(1) site. However, Mo occupies both Cu(1) and Cu(2) sites as $x > 0.3$. The Hall coefficient measurements are also consistent with such an observation. This Mo-substitution to Cu(2) site is the major factor to cause the abrupt $T_c$ suppression, observed at $x \sim 0.4$, due to an unknown pair-breaking mechanism as that observed in the case of Zn-substitution to Cu.

**4. Structural stability of YSr$_2$Cu$_3$O$_y$**

From the previous results, it is clear that one can not obtain single phase Y(Ba$_{1-x}$Sr$_x$)$_2$Cu$_3$O$_y$ samples for $x > 0.6$ unless Cu is partially substituted by transition metal elements such as Mo. Another possibility to achieve single phase YSr$_2$Cu$_3$O$_y$ compound is to use high pressure synthesis. It is therefore essential to understand better what are the key factors controlling the structure stability of this system. This result will provide not only the knowledge for processing high quality materials, but also a guideline for the development of new superconducting systems. In order to achieve this goal, we have made a systematic study and comparison of two similar series Y(Ba$_{1-x}$Sr$_x$)$_2$(Cu$_{1-0.07x}$Mo$_{0.07x}$)$_3$O$_y$ with $r = 0.05$ and 0.07.

![Figure 4](image_url)  
**Figure 4.** Crystallographic cell parameters versus $x$ of Y(Ba$_{1-x}$Sr$_x$)$_2$(Cu$_{1-0.07x}$Mo$_{0.07x}$)$_3$O$_y$.

Figure 4 displays the cell parameters of Y(Ba$_{1-x}$Sr$_x$)$_2$(Cu$_{1-0.07x}$Mo$_{0.07x}$)$_3$O$_y$. From these data, the contractions of lattice parameter $a$, $b$, and $c$ and volume $V$ for due to Sr substitution are 0.3%, 2.0%, 0.3% and 3.5%, respectively. These values are much smaller compared with those calculated based on the ionic radii of Ba (1.56 Å) and Sr (1.36 Å) assuming a close pack lattice. This observation strongly suggests that the size of Cu-O-Cu cage dominates the structural stability of Y(Ba$_{1-x}$Sr$_x$)$_2$Cu$_3$O$_y$ system. The crystal becomes unstable when Sr replaces Ba such that the crystal can no longer sustain a close pack lattice. Such a picture can be more quantitatively described by considering the tolerance factor for a perovskite-like structure.

It is well known that the definition of the tolerance factor [11], for an ideal perovskite ABO$_3$, is $t = (r_A+r_O)/\sqrt{2}(r_B+r_O)$, where $r_A = 1.52$ Å, $r_B = 0.73$ Å, are ionic radii for Ba and Cu, respectively, and $r_O = 1.40$ Å. Based on the crystal structure of YBa$_2$Cu$_3$O$_7$, its modified tolerance factor is $t = 0.97$. Similarly, assuming an ideal 123 structure for YSr$_2$Cu$_3$O$_7$, we find its tolerance factor $t = 0.88$.

![Figure 5](image_url)  
**Figure 5.** Critical doping level, $x_{\text{min}}$, of M and its valence.
for a stable YSr$_2$(Cu$_{3-x}$M$_x$)O$_y$ compound, where M stands for various transition metals. $x_{\text{min}}$ is smaller for ion with higher valence. A direct consequence of this observation is that the stability of YSr$_2$Cu$_3$O$_y$ is closely related to the sample oxygen content. Figure 6 is the tolerance factor versus doping level for various transition metals. The data suggest that there exists a critical tolerance factor, $t = 0.92$, below which a stable YSCO phase no longer exists. Although the data also suggest the presence of an upper limit for doping level, we believe it is due to the appearance of impurity phases in high doping cases.

Consequently, the calculated tolerance factor is larger than the critical value, 0.92, for all values of $x$, as shown in figure 7. Thus, stable Y123 phase exists in the whole series Y(Ba$_{1-x}$Sr$_x$)$_2$(Cu$_{1-x}$M$_x$)$_3$O$_y$. On the other hand, the tolerance factor, for the series Y(Ba$_{1-x}$Sr$_x$)$_2$Cu$_3$O$_y$, which is larger than the critical value appears only for $x < 0.6$. This is identical to the critical composition for the solubility of Ba and Sr in Y(Ba$_{1-x}$Sr$_x$)$_2$Cu$_3$O$_y$ system. We can then conclude that the key factor controlling the structural stability in Y-Sr-Cu-O system is the effective ionic radius or the effective valence of Sr in lattice. The introduction of transition metal doping is one route to increase the effective ionic radius of Sr through the increase of oxygen content. Similar stability enhancement can also be achieved using high-pressure synthesis.

In summary, we have demonstrated that using a transition metal ion to partially substitute Cu ion of the YSr$_2$Cu$_3$O$_y$ can stabilize the crystal structure and retain superconductivity. The superconducting transition temperature in the compound YSr$_2$(Cu$_{3-x}$M$_x$)$_3$O$_y$, where M is transition metal ion, range from 40K to 80K depending on the specific M ion. In addition, the transition temperature of the compound series Y(Ba$_{1-x}$Sr$_x$)$_2$(Cu$_{1-x}$M$_x$)$_3$O$_y$ decreases with the M-content. For smaller $x$ ($x < 0.3$), where M atom occupies Cu1 site, major factor to affect $T_c$ originates from the Sr-substitution effect. Lattice contraction due to Sr substitution (to Ba) makes the Ba/Sr ion to move closer to CuO plane, and consequently leads to a charge transfer from O(2) and O(3). $T_c$ then

The coordination number for Ba in an ideal, fully oxygenated YBa$_2$Cu$_3$O$_7$ sample is 10. Our titration data give the oxygen content ~ 7 for all the Y(Ba$_{1-x}$Sr$_x$)$_2$(Cu$_{1-x}$M$_x$)$_3$O$_y$ samples with proper 123 phase. In this case the coordination number of Ba (or Sr) is expected to be 10.
decreases linearly as the hole concentration of CuO planes decreases. On the other hand, for $x > 0.3$, M-substitution effects become dominant such that M occupies both Cu(1) and Cu(2) sites. This Mo-substitution to Cu(2) site is the major factor to the abrupt $T_c$ suppression due to an unknown pair-breaking mechanism. Furthermore, our study shows that the key factor controlling the structural stability in Y-Sr-Cu-O system are the effective ionic radius or the effective valence of Sr in lattice. The introduction of transition metal doping is to increase the effective ionic radius of Sr through the increase of oxygen content. Similar stability enhancement can also be achieved using high-pressure synthesis.

Reference


