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SUBSTITUTIONS OF 3-d TRANSITION METAL IONS FOR COPPER IN $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ [♦]

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Samples of $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ have been prepared in both the n=2 (80 K) phase and the n=3 (105 K) phase. For both phases, 5 mol-% of the copper has been replaced with the transition elements Ti, V, Mn, Fe, Co, Ni, and Zn. X-ray diffraction data show that the n=2 structure still forms with all of these substitutions. The n=3 structure will form with the Ti, V, Mn, and Zn substitutions, but not with the Fe, Co, or Ni. The measured change in lattice parameters correlates with the substituent's ionic radii, indicating incorporation into the structure. Resistivity and magnetization data show marked differences in T_c for the various replacements. Moreover, the resistivity indicates uniform substitution for the n=2 phase samples, but non-uniform substitution for those in the n=3 phase.

1. INTRODUCTION

Transition metal substitutions in $\text{YBa}_2\text{Cu}_3\text{O}_7$ have contributed to an understanding of the dominant role of copper-oxide planes versus the copper-oxide chains in that material. Since the pairing of carriers in the Cu-O_2 planes is responsible for high temperature superconductivity in all copper-oxide ceramics, it is of interest to alter the electronic structure of, as well as to introduce magnetic impurities into, the Cu-O_2 planes. The 3-d transition elements were chosen because their valences and ionic radii suggest that they might substitute for the Cu in these materials.

2. SAMPLE PREPARATION

All samples were prepared from appropriate amounts of Bi_2O_3 , SrCO_3 , CaCO_3 , and CuO . The transition elements were introduced by the addition of TiO_2 , V_2O_3 , MnO_2 , Fe_2O_3 , Co_3O_4 , NiO or ZnO . The powders were then calcined, pressed into pellets and sintered in air. The n=2 (2212) phase samples were calcined at 840°C for 36 hours, and sintered at 848°C for 54 hours.

The n=3 (2223) phase material was prepared in a phase-pure form, free of the n=2 phase, by using a nominal (Bi,Pb)-Sr-Ca-Cu composition of (1.6,0.4)-2-3-4. Preparation procedures and x-ray evidence of the phase purity will be pub-

lished in more detail elsewhere.² The control sample was calcined at 825°C for 36 hours and sintered at 850°C for 108 hours. The substituted samples were sintered at higher temperatures as needed to produce phase-pure 2223 material as evidenced by x-ray diffraction.

3. X-RAY STRUCTURE

The x-ray analysis showed that all 2212 substituted samples produced single-phase n=2 material. The lattice parameters were refined using 18-28 peaks. The effect on the lattice parameters is seen most clearly in the c-axis spacing, which is plotted in Fig. 1(a). Also plotted is the expected change in lattice parameter based on the ionic radii of the substituted ions.³ The agreement is excellent assuming that the valence state of all the transition elements is 2⁺ in this structure, except for Ti with a valence state of 3⁺.

The c-axis distances for the five 2223 samples which by x-ray analysis form the phase-pure n=3 structure are illustrated in Fig. 1(b). Note that the data imply a valence 2⁺ state for the Zn, and valence 3⁺ for the Ti, V, and Mn.

4. TRANSITION TEMPERATURES

For the n=2 phase, the effects of the substitutions on the resistive transition are illustrated in Fig. 2.

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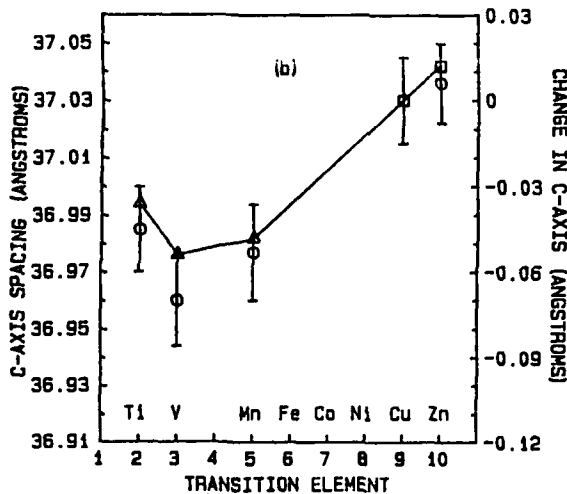
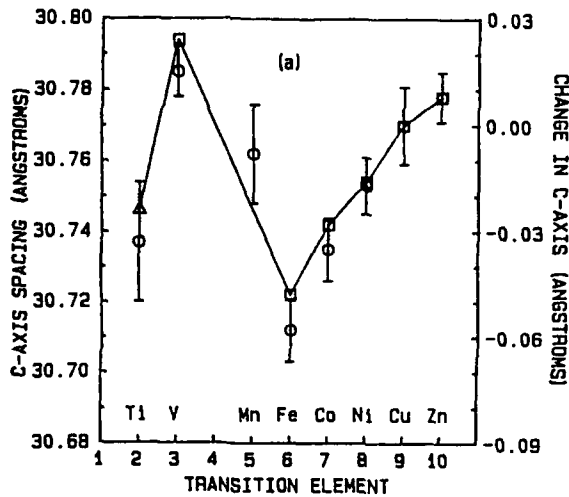


FIGURE 1

The refined c-axis lattice parameter (O, indicated on the left-hand axis) vs. transition element for the (a) 2212 and (b) 2223 samples. The expected change in lattice parameter for the valence 2^+ (□) and 3^+ (Δ) transition elements is indicated on the right-hand axis.

Table 1 summarizes the effects of the substitutions on the transition temperature, listed in increasing order of suppression. The transition temperatures were also measured by magnetic susceptibility and the results agree with the resistance measurements.

The resistance vs. temperature results for two of the five samples which formed the 2223 phase are also illustrated in Fig. 2. All of these substituted samples show a small fraction, less than the percolation threshold, of

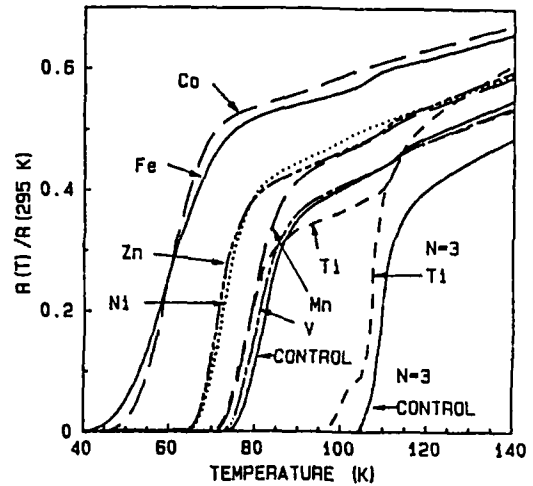


FIGURE 2

Normalized resistance versus temperature for the 2212 samples (left eight curves) and two representative 2223 samples (right two curves).

the non-substituted 2223 phase near 105 K. This is interpreted as due to inhomogeneous substitution. The "foot" going to $R=0$ probably represents the actual suppression of the transition due to the replacement ion, since the x-ray measurements show no $n=2$ phase present. No definitive conclusions can be drawn until sharp transitions are achieved. Further work on processing these 2223 samples is in progress.

TABLE 1

Effect on resistive transition temperature for substituted 2212 phase.

REPLACEMENT ELEMENT	$T_0 \pm \Delta T_0$ (MIDPOINT)	T_0 ($R=0$)
CONTROL	82 ± 5	74
V	81 ± 7	73
Mn	80 ± 6	71
Ti	78 ± 6	71
Ni	73 ± 6	65
Zn	71 ± 5	64
Co	60 ± 7	47
Fe	60 ± 11	43

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