

## On the crystallochemistry and superconductivity of the $(\text{Bi}_{1\pm x}\text{Cu}_{\pm x})_8\text{Sr}_6\text{Ca}_6\text{Cu}_9\text{O}_{24+z}$

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### Abstract

A series of solid solutions of the  $(\text{Bi}_{1-x}\text{Cu}_x)_8\text{Sr}_6\text{Ca}_6\text{Cu}_9\text{O}_{24+z}$  type with  $0.08 \geq x \geq -0.225$  has been prepared in air at 850°C and identified through X-ray, density, average valency of copper and low temperature resistivity measurements. The Cu-rich side of the series starts from  $x \approx 0.06$ , whereas that of Bi-rich one, comparatively wider, reaches composition very close to  $x = -0.202$ . Within the single phase region, lattice parameter  $a$  of the 2212-structure type unit cell, remains practically constant (around 0.54 nm). At the same time, the parameter  $c$  exhibits a regular decrease vs. growing concentration of bismuth and finally it reaches the value 3.0625 nm at  $x = -0.202$ . The average valency of copper within the series shows a minimum value 2.17 at  $x = 0.00$ . Starting from this value it grows up linearly in both directions, slightly along the Cu-rich side and more efficiently along the Bi-rich one. The atomic content of the elementary unit cell ( $Z$ ), expressed as number of molecules of  $\text{MeO}_{1+v}$ -type (Me = sum of the metallic structure components in their atomic fractions) and calculated from sample densities, indicates that the structure deficiency is characteristic of all the series. However, within its Bi-rich part the deficiency occurs to be much deeper than in the Cu-rich equivalent. Thus, the intermediate composition with  $x = 0$  i.e.  $\text{Bi}_8\text{Sr}_6\text{Ca}_6\text{Cu}_{24+9V(\text{Cu})/2}$ , characteristic of minimum deficiency, minimum valency of copper and minimum  $T_c$ , divides the series into two sub-regions, each of extremely different type of structure deficiency and different critical temperature behaviour.

### 1. Introduction

This work was aimed to find out and to determine domain of existence of the 2212 structure type phase along the  $(\text{Bi}_{1-x}\text{Cu}_x)$  direction. In the quaternary system  $\text{Bi}_2\text{O}_3\text{-SrO-CaO-CuO}$  this direction can be characterized as situated under a certain angle in relation to already well established direction  $(\text{Sr}_{1-x}\text{Ca}_x)$  [1,2]. Mutually, both the directions cross each other at the points of given ratio Sr/Ca and of  $x_{\text{Cu}} = 0$ .

Confirmation of existence of the 2212 structure type solid solution along the  $(\text{Bi}_{1\pm x}\text{Cu}_{\pm x})$  line would give us an important argument for not considering the  $n = 2$  representative of the Bi-based cuprates (to us all of them) as chemical object of fixed stoichiometry 2212 or of  $(\text{Sr}_{1-x}\text{Ca}_x)$  line type compound, but for treating it as real phase of, undefined till now, but unquestionably three-dimensional domain of existence within the system.

Another important question which we hoped to get answered with the work, centered around the problem of cation substitution caused effects such as variation of formal valency of copper ( $V_{\text{Cu}}$ ) and sample transition temperatures ( $T_c$ ) vs. growing concentration of the substituent used, in our case copper on  $\text{Bi}^{+3}$  sites and bismuth on  $\text{Cu}^{+V}$  sites, especially interesting because performed with the use of native components of the phase.

Thanks to some recent results performed mainly in Bellcore Centre [3,4] it has already been well established that  $T_c$ 's of out of  $\text{CuO}_2$  plane substituted cuprates are nearly insensitive to the substituents which do not modify the average structure charge balance (isoelectronic cations). However, they are extremely sensitive to those

that create a charge imbalance (for instance RE's for Sr or Ca in Bi-based cuprates) and thereby modify the formal valency of copper.

Considering substitutions performed within  $\text{CuO}_2$ -planes, sensitivity of sample  $T_c$ 's occurs even higher. The rule is that they, in this case, undergo a drastic reduction even if no change in formal valency of copper is involved.

In our previous paper concerning series of solid solutions of the 2212-structure type and of general formula  $\text{Bi}_8\text{Sr}_{8-x}\text{Ca}_{4+x}\text{Cu}_9\text{O}_y$  [5] we have shown that although isoelectronic cation substitution performed, an evident reduction of sample  $T_c$ 's and of formal valency of copper takes place in these materials. We have proved therein that behavior of this kind is caused by variation of structure unit cell molecular content ( $Z$ ), a factor which in Bi-based cuprates occurs to be dependent on degree of substitution ( $x$ ).

### 2. Experimental

Series of samples of nominal composition reflected by formula:  $(\text{Bi}_{1-x}\text{Cu}_x)_8\text{Ca}_6\text{Sr}_6\text{Cu}_9\text{O}_{24-12x+(9+8x)V/2}$  in which  $-0.225 \leq x \leq +0.08$ , each of 3g, were prepared by solid state reaction of appropriate amounts of  $\text{Bi}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{SrCO}_3$  and  $\text{CaCO}_3$ . Note that for the substitution fraction factor  $x = 0$ , the series reaches its overall composition 8669 and becomes identical (crossing point) with the middle composition of the series  $\text{Bi}_8\text{Sr}_{8-x}\text{Ca}_{4+x}\text{Cu}_9\text{O}$  with  $x = 2$  studied in [5].

The components were presintered at 800°C during one day, pulverized and repelleted twice for 2-, and 3-days long sintering in air at 830°C and 850°C, respectively.

The resulting products were subjected to: 1) 4-point probe ac low temperature measurements, to evaluate sample  $T_c$ 's, 2) X-ray diffraction, to recognize extension of the 2212- structure type domain, 3) iodometric analysis to determine formal valency of copper vs.  $x_{\text{Cu}}$ , 4) density measurements [5], to find out degree of the structure deficiency i.e. deviation of the structure cell molecular content ( $Z$ ) from the ideal value  $Z = 28 \text{ MeO}_{1+y}$  ( $\text{Me} = \text{sum of metallic sample components in their atomic fractions}$ ).

### 3. Results and discussion

X-ray diffraction patterns of some chosen compositions of the series are presented in Fig.1. The series represents solid solution of the 2212 structure type which domain is

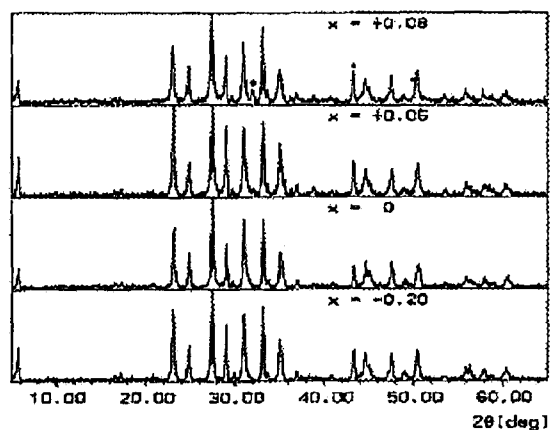


Figure 1. X-ray diffraction patterns of chosen compositions of  $(\text{Bi}_{1-x}\text{Cu}_x)_8\text{Sr}_6\text{Ca}_6\text{Cu}_9\text{O}_y$  series:

- diffraction lines of Cu-sample holder
- ◆ diffraction lines of a secondary phase.

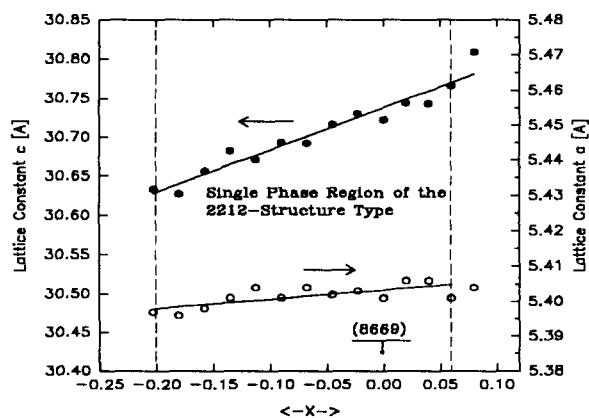


Figure 2. Dependence of lattice parameters  $a$  and  $c$  vs. growing concentration of the substituent ( $x$ ) for the solid solutions of  $(\text{Bi}_{1-x}\text{Cu}_x)_8\text{Sr}_6\text{Ca}_6\text{Cu}_9\text{O}_y$  type.

comprised within  $-0.2025 \leq x_{\text{Cu}} \leq +0.06$ . The latter clearly arises from comparatively strong  $x_{\text{Cu}}$ -dependent character of the  $c$  lattice parameter (Fig.2.).

In relation to the  $x = 0$  (8669) starting composition of the series, the phase domain is evidently shifted towards Bi-rich compositions (negative values of  $x$ ). Surprising is the decrease of both the lattice constants vs. growing concentration of copper substituent i.e. larger in size bismuth. This may indicate on growing deficiency of the structure within the series i.e. on a decrease of the molecular content of each formal elementary unit cell. Indeed, this really happens and is seen through variation of formal valency of copper (Fig.3) and through sample densities (Fig.4). First of all we note that, contrary to our

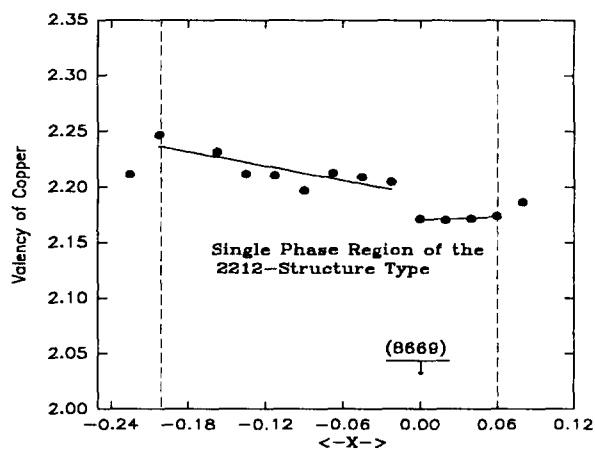


Figure 3. Variation of the average valency of copper ( $V_{\text{Cu}}$ ) within the series of  $(\text{Bi}_{1-x}\text{Cu}_x)_8\text{Sr}_6\text{Ca}_6\text{Cu}_9\text{O}_y$  type.

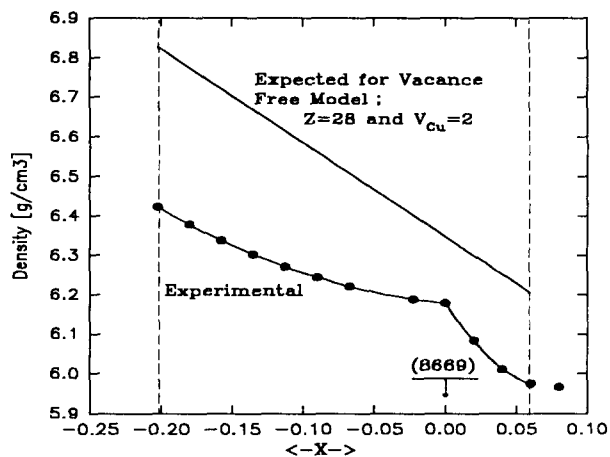


Figure 4. Sample densities of the solid solution of  $(\text{Bi}_{1-x}\text{Cu}_x)_8\text{Sr}_6\text{Ca}_6\text{Cu}_9\text{O}_y$  type as a function of  $x$ .

expectation, replacement of copper ions by +3-valent bismuth within the  $\text{CuO}_2$ -planes, results in further increase (!) of valency of the remaining copper. Considering the Cu-rich interval of the series, the

behavior of the parameter under discussion occurs as expected i.e., vs. growing concentration of copper on  $\text{Bi}^{+3}$  sites, its overall valency slightly increases. Second, we also note an unusual behavior of sample densities (Fig.4). In comparison with the vacancy-free ideal model of the solid solution designed (see solid line on Fig.4.), the experimental values deviate down in both the directions beginning from the starting composition (8669). This univocally indicates on the substitution activated (dependent), growing contribution of vacancies within the structure, higher in the Bi-rich region of the series and somewhat smaller in the Cu-rich one.

In fact, transition of the density values ( $d_{\text{approx}}$ ) to the appropriate  $Z$ 's via eq.  $d=Z(A_{\text{MeO}_{1+y}})/(0.602a^2c)$  reveals (Fig.5) that in the Cu-rich region of the series,

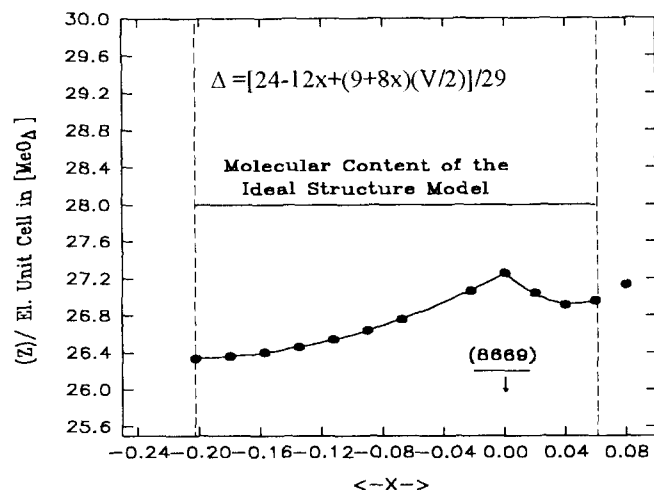


Figure 5. Molecular occupancy of the 2212-type elementary unit cell ( $Z$ ) within the series of  $(\text{Bi}_{1-x}\text{Cu}_x)_8\text{Sr}_6\text{Ca}_6\text{Cu}_9\text{O}_y$  type.

the deficiency ( $28-Z$ ) only slightly exceeds 1Me-site/el. u.cell. In the Bi-rich interval, however, it grows up more efficiently, and at its final composition ( $x = -0.2025$ ) the contribution of vacancies reaches already 1.7Me-site/el.u.cell.

Here we have an explanation of the reason for which introduction of  $\text{Bi}^{+3}$  ions on  $\text{Cu}^{+V}$  sites in 2212-structure type phase results in, quite unexpected, further increase of the  $V_{\text{Cu}}$ -factor. It is the deficiency which occurs to affect not only the structure cationic sublattice but the oxygen sublattice too. In front of this, the response of the structure (defensive in character) is such that some additional oxygen atoms, over those  $(1.5-V^{(0)}/2)8x$  resulting from the substitution, are incorporated to the oxygen sublattice. As the consequence, deficiency of the oxygen sublattice is much smaller and as seen in Fig.6., its atomic occupancy only

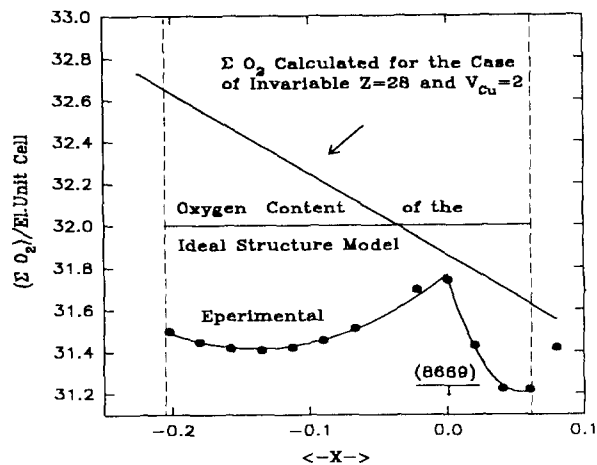


Figure 6.  $x$ -conditioned, total oxygen content of the 2212-type elementary unit cell for  $(\text{Bi}_{1-x}\text{Cu}_x)_8\text{Sr}_6\text{Ca}_6\text{Cu}_9\text{O}_y$  series.

negligibly deviates (maximum 0.8oxygen atom/el.u.cell) from the ideal level of 32 atoms. What emerges from Fig.6. is that self-protecting action of the structure against the deficiency created in its cationic sublattice is evidently more effective within the Bi-rich interval than within the Cu-rich one. The latter is presumably because of opposite sign of the  $(1.5-V^{(0)}/2)8x$  factor, hence much shorter extension of the phase domain therein.

The most striking and controversial results that we got refer, however, to sample transition temperatures  $T_c$  (onset) and to their dependence vs.  $x_{\text{Cu}}$  (Fig.7.). The

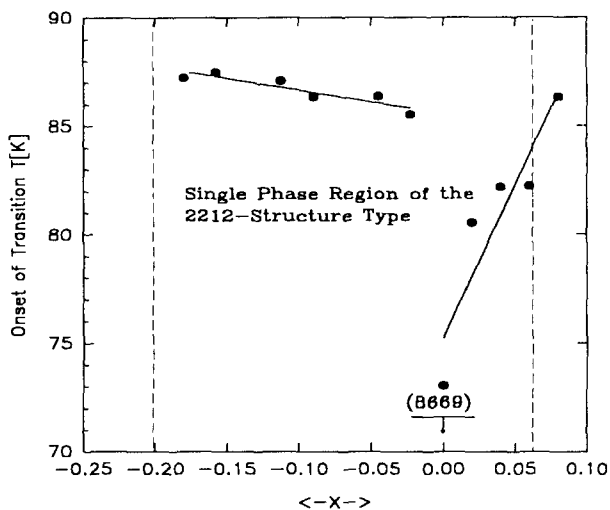


Figure 7. Onset of the superconducting transition temperature ( $T_c$ ) vs. increasing concentration of the substituent  $x$ .

controversy consists in that no matter the type of substitution performed (bismuth on  $\text{Cu}^{+V}$ - sites within  $\text{CuO}_2$  planes or copper on  $\text{Bi}^{+3}$ - sites out of  $\text{CuO}_2$  planes - both expected to create a charge imbalance within the

structure), sample  $T_c$ 's do not undergo a drastic reduction. Contrary, in reference to the series starting composition (8669), they exhibit an evident increase vs. growing structure deficiency. It looks as if there have been a rule according to which higher structure deficiency privileges higher  $T_c$ 's with a minor or secondary role of copper and its valency whose variation expresses a tendency of the structure to preserve mainly its stability.

More details on this subject with an analytical description of structure deficiency found within the series, inclusively, will be published elsewhere in a separate paper.

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