

The Influence of Partial Substitution of Copper and/or Barium on the Crystal Structure of YBCO 123 Phase Analogues*

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Received 17 March 1997

Study of structures of YBCO 123 type and its strontium analogues, taken from ICSD database, shows the different modes of oxygen location in the unit cells. For $\text{YBa}_2\text{Cu}_3\text{O}_x$ and $\text{YBa}_2\text{Cu}_{3-y}\text{Me}_y\text{O}_x$ the scatter plots of unit cell parameters/volumes show certain correlations, although they should be treated with caution because of some erroneous data.

ICSD database [1] was searched to study structural changes in YBCO 123 and its strontium analogues. It was found that although the latter ones are similar to the parent phase there are some significant differences which are shown in Figs. 1a—e. It is not possible to obtain pure $\text{YSr}_2\text{Cu}_3\text{O}_x$ unless very high oxygen pressure is applied [2]. However, when copper is partially replaced by other cations, such as Fe, Al, B, Co, Ga, Mo, the phases of $\text{YSr}_2\text{Cu}_{3-y}\text{Me}_y\text{O}_x$ are obtained. ICSD contains data for these phases. Five of them, with Fe, Al, Co, Ga, and Mo, were thought to be most representative and as such are discussed in this paper.

The simplified structure of YBCO 123 is shown in Fig. 1a. The content of oxygen depending on the sample history results in the differences in occupancy factors for oxygens [0, 1/2, 0] and [1/2, 0, 0]. The structure changes from tetragonal to orthorhombic with the increase of the oxygen content, however, the changes of unit cell parameters and atom positions are very small. These changes are accompanied by the increase of occupancy factor of [0, 1/2, 0] oxygen and its decrease for [1/2, 0, 0] oxygen.

The structure of $\text{YSr}_2\text{Cu}_{3-y}\text{Fe}_y\text{O}_x$ [3] is very similar to the parent YBCO 123 phase but it remains tetragonal with the increase of oxygen content.

The structure of $\text{YSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_7$ phase [4], shown in Fig. 1b, is tetragonal (holmium and dysprosium analogues are isostructural). There are three crystallographically independent oxygens in the structure. Oxygen which in parent barium phase is in the [0, 1/2, 0] position, in strontium phase is slightly shifted towards [1/2, 1/2, 0] position. This results in the increase of its multiplicity and in the decrease of its occupancy factor. The other oxygens do not change their positions.

In the phase $\text{YSr}_2\text{Cu}_2\text{AlO}_7$ [5] the [0, 1/2, 0] oxygen is shifted in a similar way as in Mo compound. Also similar shifts are observed for aluminium in [0, 0, 0] position and oxygen in [0, 0, z] position; there is four-fold increase in their multiplicity, and their occupancy decreases four times. Oxygen in the [0, 1/2, z] position is disordered into two equivalent sites. One of them is nearly exactly in the plane of copper atoms, and the other one is shifted upwards by *ca.* 0.3×10^{-10} m along z axis.

In the case of $\text{YSr}_2\text{Cu}_{2.25}\text{Co}_{0.75}\text{O}_x$ [6], atoms of oxygen from position [0, 0, z] are shifted not towards the centre of the unit cell, but parallel to a or b axis. These shifts result in the increase of multiplicity and decrease of occupancy factor by four. Similar shift occurs for [0, 0, 0] copper. Atoms of [0, 1/2, 0] oxygen are splitted and shifted towards the [1/2, 1/2, 0] position.

For $\text{YSr}_2\text{Cu}_2\text{CoO}_x$ [6], or when the copper is substituted by gallium [7], quite a new structure occurs. These compounds crystallize in the *Ima2* space group, which is not observed in the barium 123 type compounds, even in those with partially substituted copper. The unit cell of this new structure is four times bigger than the unit cell of YBCO 123. Its c period doubles the c period of YBCO 123, and a and b periods are diagonals of the base of YBCO cell. Almost all heavy atoms remain in their positions or are very little shifted as compared to parent YBCO 123 phase. Only for copper (or gallium) in the [0, 0, 0] position shifts are slightly bigger. Greater changes are observed for oxygens from the Cu [0, 0, 0] plane. Four oxygen positions with partial occupancy factors transform into two oxygen sites with full occupancy.

Described changes might be probably correlated with changes of ionic radius (*R*) of the atoms substituting copper and with their content, but they can-

*Presented at the *Solid State Chemistry '96* Conference, Bratislava, July 6—12, 1996.

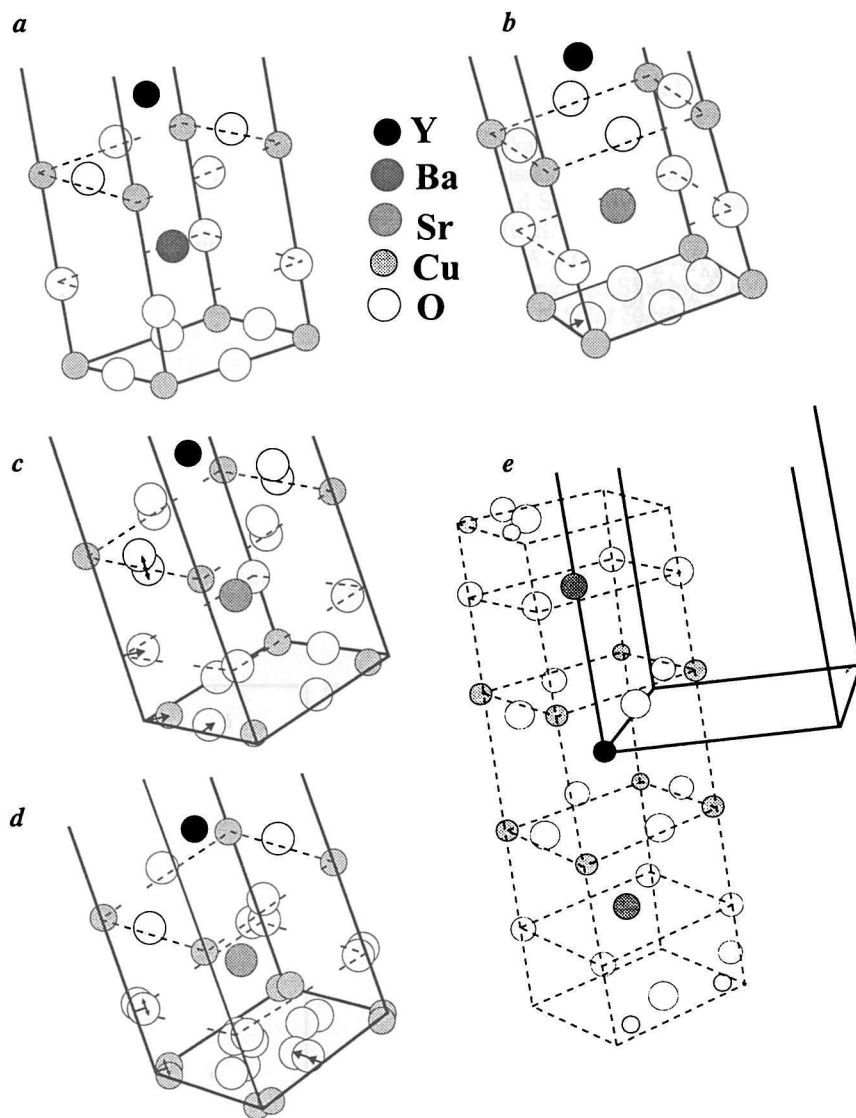


Fig. 1. The crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{6.3}$ (a), $\text{YSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{6.25}$ (b), $\text{YSr}_2\text{Cu}_2\text{AlO}_7$ (c), $\text{YSr}_2\text{Cu}_{2.25}\text{Co}_{0.75}\text{O}_7$ (d), and $\text{YSr}_2\text{Cu}_2\text{GaO}_7$ (e). Solid lines outline unit cell edges and arrows direction in which atoms are shifted as compared to barium compound.

not be assessed quantitatively because there is not enough structural data for $\text{YSr}_2\text{Cu}_{3-y}\text{Me}_y\text{O}_x$ series of compounds in ICSD database. There are however ample data for YBCO 123 structures, and therefore they were used to do the scatter plots of cell parameters, or cell volume as a function of oxygen content, and scatter plots showing correlation between c and two other unit cell parameters. Some of these data are known to be erroneous (*e.g.* data for structures with oxygen content higher than 7 for YBCO 123) but they were nevertheless used to show the differences in the assessment of the structures.

In Figs. 2a and 2b there are plots of the unit cell volume *vs.* the oxygen content for pure Ba 123 phase (Fig. 2a) and for samples with partially substituted copper (Fig. 2b). In Fig. 2a there are two sets of points: the upper one represents the measurements carried

out in high temperature. Clearly for this set of points, and less obviously for the other, one can see a tendency of decreasing the cell volume with the oxygen content increase. It is a good evidence that in the phases of 123 type a steric effect is less important than bounding forces. Higher amount of oxygen causes shrinkage of the unit cells because of strong interactions between copper and oxygen in the copper chains. The scatter observed in the lower set of points, representing the room temperature measurements (Fig. 2a), is rather unusual. It might be caused on one hand by the errors in establishing the oxygen content and in the estimation of cell parameters, and by impurity of samples (*e.g.* due to reaction of a sample with crucibles). On the other hand, this scatter may reflect the differences in the thermal history of the samples. In majority of publications the description of the thermal treatment

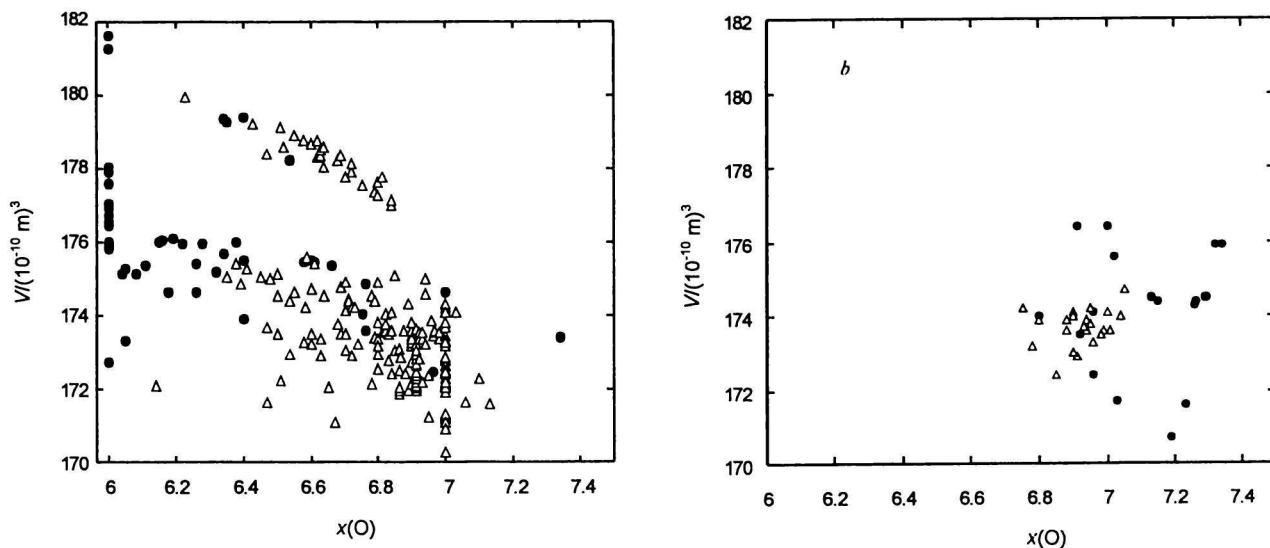


Fig. 2. Scatter plot of cell volumes as a function of oxygen content for pure YBCO 123 (a) and for samples with partially substituted copper (b): ● tetragonal structures, Δ orthorhombic structures.

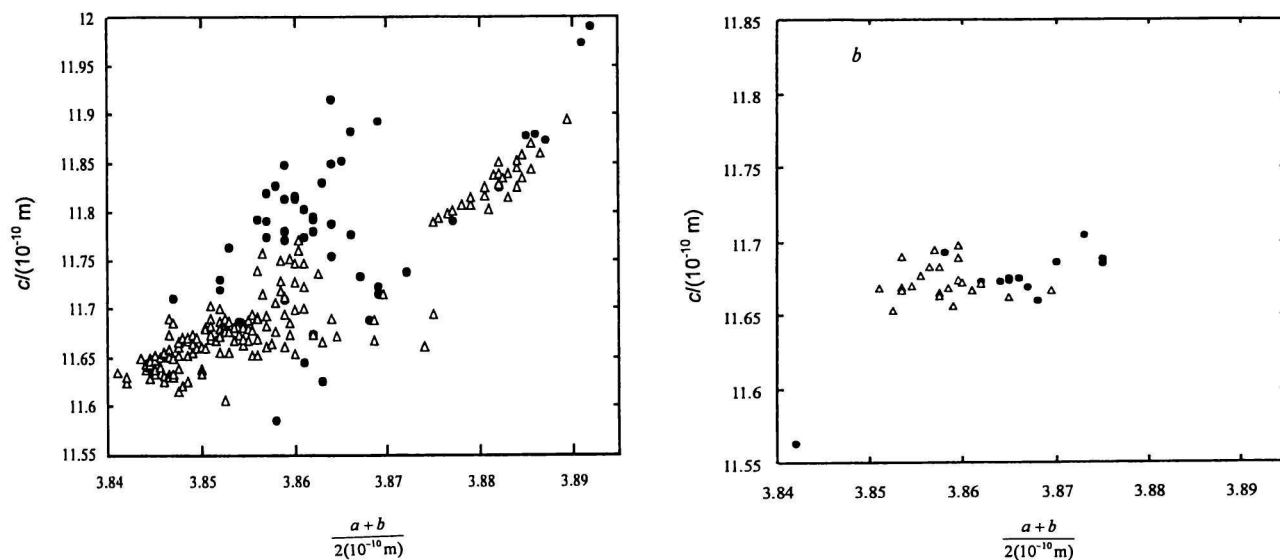


Fig. 3. Scatter plot of c cell periods as a function of average a and b for pure YBCO 123 (a) and for samples with partially substituted copper (b): ● tetragonal structures, Δ orthorhombic structures.

is very brief, e.g. the cooling rate value, which has a strong influence on the crystal size and defects in the sample, is often omitted.

The scatter in Fig. 2b may be additionally caused by the mode of copper substitution. It is not possible to tell which of these is the dominating cause of the observed scatter because even in the pure YBCO 123 structures the scatter was very large.

Fig. 3a shows the changes of c as a function of $(a + b)/2$ for pure YBCO 123 structures and Fig. 3b shows these changes for partially substituted YBCO 123 structures. In the case of pure YBCO with the orthorhombic unit cells we observe nearly linear increase of c . For the structures with tetragonal unit cells there

is no correlation between c and a .

For structures of YBCO 123 with partially substituted copper the pattern of scatter points could be roughly described as reverse: there is no correlation between unit cell parameters for orthorhombic structures and there can be detected linear correlation for tetragonal structures, although poor. One of possible explanations is that in pure YBCO 123 phase small shifts of oxygen and copper positions, causing the transition into orthorhombic phases, stabilize the defects in quite a different way than in the case of tetragonal phases. The Cu substitution occurs mainly in the chains and causes changes in the mechanism of defect stabilization.

CONCLUSION

The results obtained on the basis of data taken from ICSD database show some pitfalls of this study. Poor quantitative correlations can be explained by the different history of samples and by the low accuracy of X-ray powder method in determining the oxygen content in the presence of heavy metals.

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