

Letter

Effect of La_2O_3 addition on crystal structure of the 2201-type Bi–Sr–Cu–O phase $\text{Bi}_3\text{Sr}_2\text{La}_n\text{Cu}_{1.25}\text{O}_{7.75+1.5n}$

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The addition of La_2O_3 to a two-phase matrix sample of a fixed nominal composition $\text{Bi}_3\text{Sr}_2\text{Cu}_2\text{O}_{8.5}$ results at 800 °C in a series of solid solutions of the 2201 structure type similar to those reported by Horyń *et al.* [1]. The maximum solubility of lanthanum oxide reaches 0.6 La_2O_3 molecule as referred to $\text{Bi}_3\text{Sr}_2\text{Cu}_2\text{O}_{8.5}$ ($n_{\text{LaO}_{1.5}} = 1.2$). The secondary phase which is CuO, present in the starting sample in a quantity of 5.6 wt.%, does not change significantly through all the series (see Fig. 1) and in the end sample of the series ($n_{\text{LaO}_{1.5}} = 1.2$) it remains equal to 4.73 wt.%. The above was determined on the basis of reflection intensity ratios of the coexisting phases after the intentional enrichment of each particular sample with some known quantities of CuO. This has permitted us to establish that the series is based on, and in fact it originates from, the 2201-structure-type phase of the terminal composition corresponding to $\text{Bi}_3\text{Sr}_2\text{Cu}_{1.25}\text{O}_{7.75}$. Measured densities were corrected for the presence of the additional phase (CuO) according to the formula

$$\frac{100}{d_{\text{average}}} = \frac{\text{wt.}\%(\text{CuO})}{d(\text{CuO})} + \frac{\text{wt.}\%(2201)}{d(2201)}$$

It is interesting to note the atypical variation of the lattice parameters *vs.* $n_{\text{LaO}_{1.5}}$ (Fig. 2), especially of *a* and *b*. As determined from the splitting of 200 and 020 reflections (Fig. 3) the orthorhombic distortion reaches its maximum level not at the end of the series (*i.e.* for $n_{\text{LaO}_{1.5}} = 1.2$) but somewhat earlier ($n_{\text{LaO}_{1.5}} = 0.9$). It should be noted that almost identical results are reported by Sales and Chakoumakos [2] although referred to a different series of solid solutions, namely to $\text{Bi}_2(\text{Sr}_{1-x}\text{La}_x)_2\text{CuO}_x$ type.

A similar anomaly has been found considering sample densities observed within the series. As can be seen in Fig. 4 (crosses), for the La_2O_3 concentration interval $0 \leq n_{\text{LaO}_{1.5}} \leq 0.1$, the densities increase sharply; then, up to $n_{\text{LaO}_{1.5}} = 0.4$, they remain constant. For still higher concentrations of La_2O_3 a parabolic-like decrease of sample densities can be seen. It should be noted that all

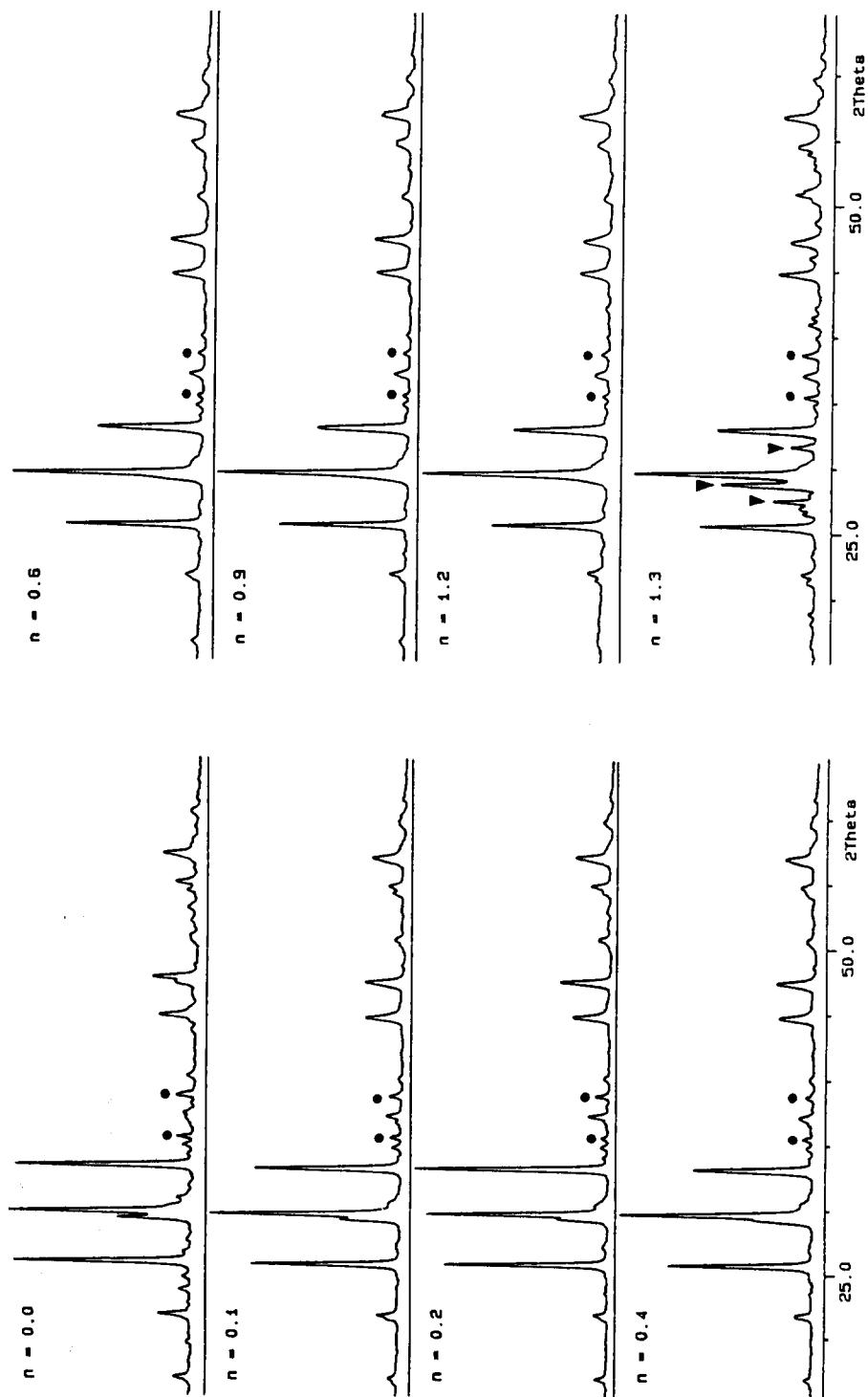


Fig. 1. Chosen X-ray diffraction patterns for the series of solid solutions of $\text{Bi}_3\text{Sr}_2\text{La}_n\text{Cu}_{1.25}\text{O}_{7.75+1.5n}$, type vs. n : ●, CuO ; ▼, unidentified phase.

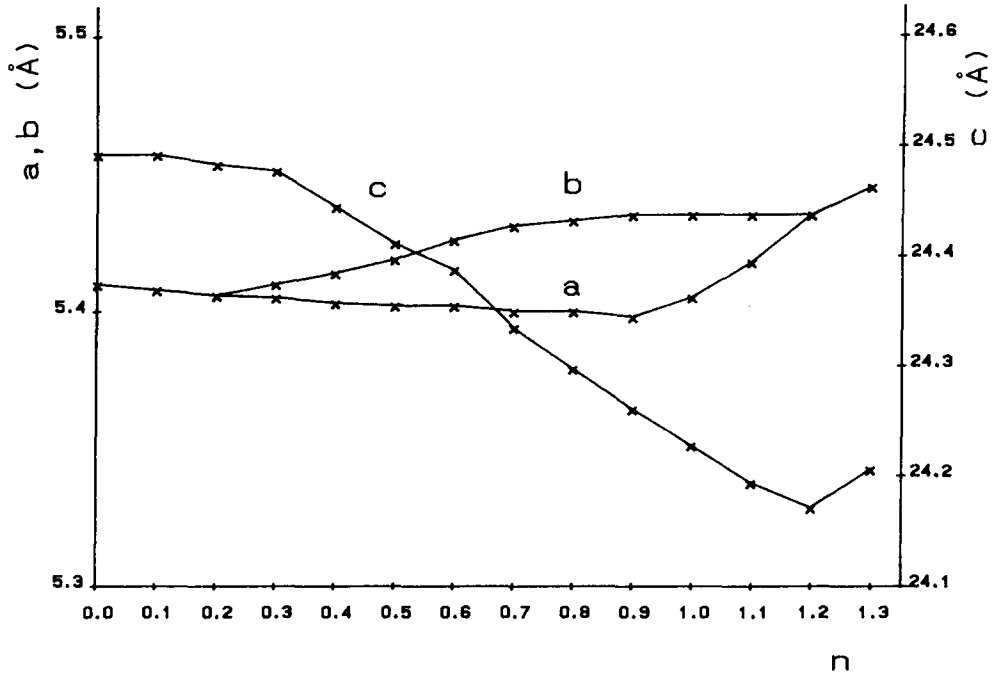
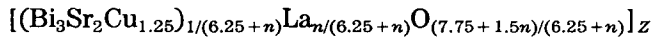


Fig. 2. Variation of lattice parameters a , b and c vs. La_2O_3 content for the series of $\text{Bi}_3\text{Sr}_2\text{La}_n\text{Cu}_{1.25}\text{O}_{7.75+1.5n}$ type.

these variations take place within the single-phase region of the matrix structure. This means that, depending on the concentration of La_2O_3 , a variable number of defects within the 2201-type structure is created.

For an analytical description of the behaviour mentioned above, the series has been expressed with a different formula, so as to be more suitable for further consideration, namely



In this formula the terms in square brackets represent atomic contributions of separate structure components for each particular sample of given $n_{\text{LaO}_{1.5}}$. In this way the formula reflects a hypothetical oxide of MeO_x type with

$$x = \frac{7.75 + 1.5n}{6.25 + n}$$

Z is the number of MeO_x molecules in the unit cell; the atomic per cent of bismuth plus strontium plus copper is equal to $6.25/(6.25 + n)$ and the atomic per cent of lanthanum is $n/(6.25 + n)$.

Using the classical equation for density

$$d = Z \cdot \frac{W_{\text{MeO}_x}}{6.02 \cdot V(\text{\AA}^3)} \cdot 10$$

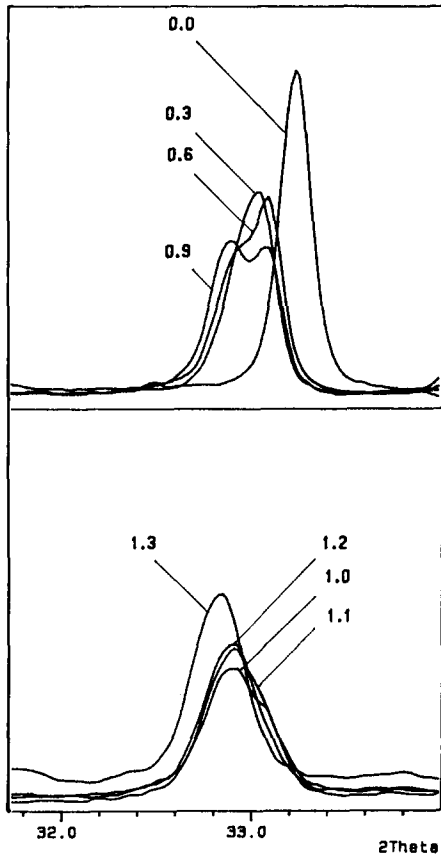


Fig. 3. Orthorhombic distortion within the series: the profiles of split 200 and 020 reflections for $n=0-0.9$ (top) and $n=1.0-1.3$ (bottom).

we have been able to determine Z as a function of $n_{\text{LaO}_{1.5}}$. The results are shown in Fig. 5 as crosses. Our supposition concerning possible variations of the structural unit cell content is now quite evident. Three different regions of specific structure defectiveness are as follows.

(1) For $0 \leq n \leq 0.1$, a deeply deficient ($Z \approx 19$) origin matrix of the 2201 type is observed in which the vacant atomic sites become quickly occupied with increasing $n_{\text{LaO}_{1.5}}$ to the normal level $Z \approx 20$.

(2) For $0.1 \leq n \leq 0.4$, a region of close to normal (free of vacancies) solid solutions of the 2201-type structure is obtained, characteristic of an n -independent content of the unit cell ($Z \approx 20$).

(3) For $0.4 \leq n \leq 1.1$, a region is observed within which the solid solutions are characteristic of an n -dependent level of vacancies. The origin of these solid solutions is the 2201-structure-type matrix phase of a 21-atom unit cell [3].

The analytic fitting to the experimental values (curves 1, 2 and 3 in Figs. 4 and 5) looks satisfactory. The appropriate formulae used for the

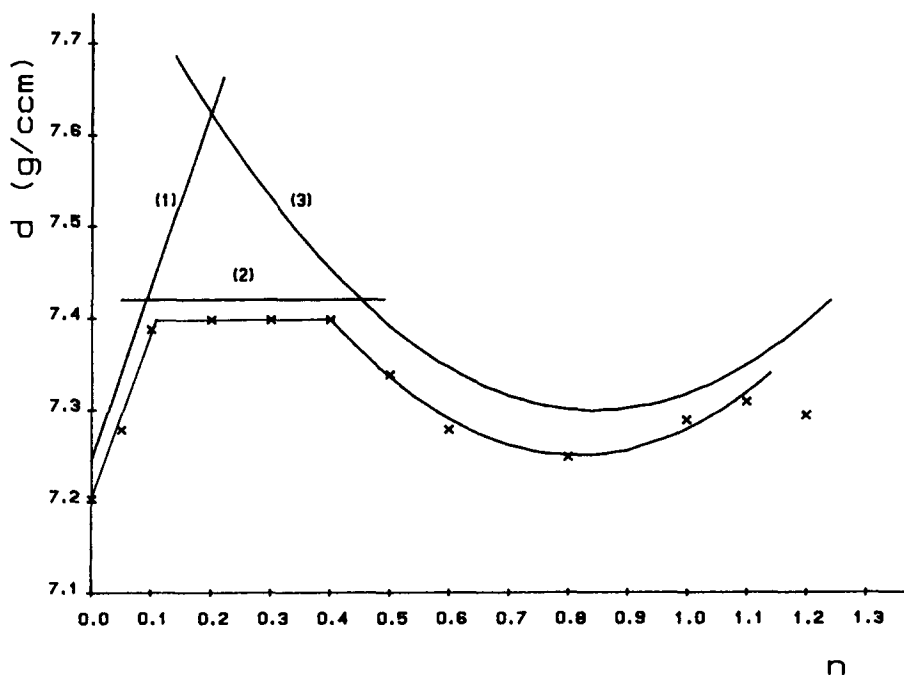


Fig. 4. Experimental and calculated densities for the series of solid solutions of $\text{Bi}_3\text{Sr}_2\text{La}_n\text{Cu}_{1.25}\text{O}_{7.75+1.5n}$ type vs. n : \times , experimental values; curves 1, 2 and 3, calculated densities.

calculations are the following: (1) $0 \leq n \leq 0.1$, $Z = 19.3 + \delta$, and $\delta = 2N_{19}$; (2) $0.1 \leq n \leq 0.4$, and $Z = 20 - 0.1$, where Z is constant and does not depend on $n_{\text{LaO}_{1.5}}$; (3) $0.4 \leq n \leq 1.1$ and $Z = 21 - \Delta$ where

$$\Delta = \frac{N_{21} - (N_{21}^2 - N_{19}^2)}{F}$$

Here $N_{21} = 21n/6.25$ and $N_{19} = 19n/6.25$ are the number of lanthanum atoms recalculated for a 21-atom or 19-atom unit cell respectively; $F = 6.25/(6.25 + n)$ is the atomic fraction of bismuth plus strontium plus copper.

Without detailed structural studies there is no possibility of defining a way in which La atoms build into the crystal lattice of the solid solution prepared here. In this respect, there are several possibilities such as a directed substitution, *i.e.* a substitution referred to a given structure component (for instance strontium), or a proportional one, *i.e.* subjected to each of the structure components. Indeed, apart from classical (free of vacancies) exchange of ions (region 2), both the mechanisms can ensure a charge of the structure unit cell within region 3 with an appropriate amount of vacancies. However, none of them can cause variation of these vacancies to go as a function of $n_{\text{LaO}_{1.5}}$ along the parabolic-like line, as observed. In our opinion the real mechanism responsible for the structure defectiveness in this region is much more complex. From the analytical equation found, we can only

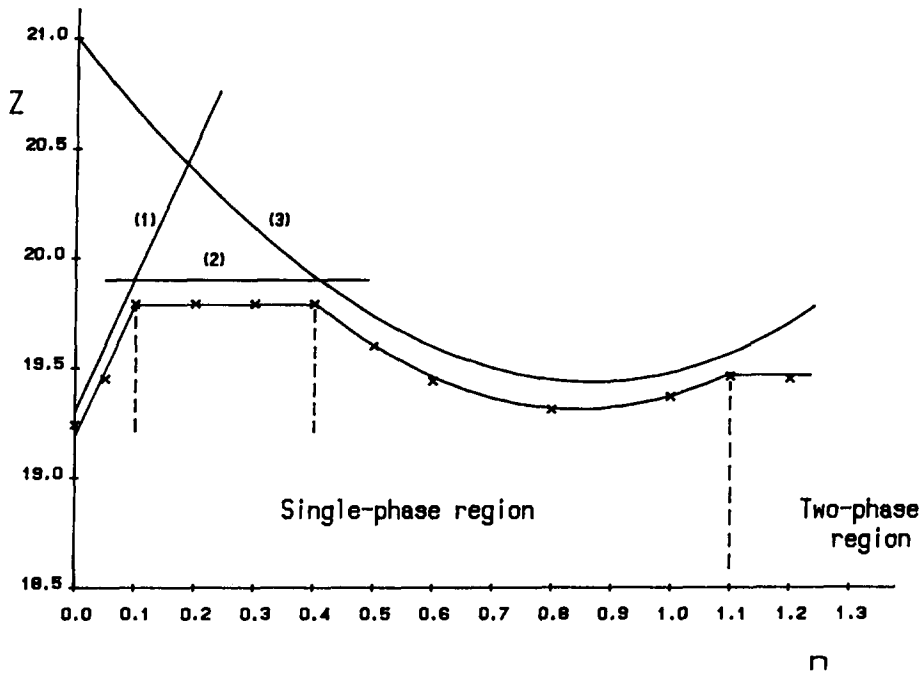


Fig. 5. Experimental and calculated Z values for the series of solid solutions of $\text{Bi}_3\text{Sr}_2\text{La}_n\text{Cu}_{1.25}\text{O}_{7.75+1.5n}$ type vs. n : \times , Z resulting from measured sample densities; curves 1, 2 and 3, calculated values.

guess that linearly increasing the total amount of vacancies N_{21}/F vs. $n_{\text{LaO}_{1.5}}$ (logically proportional to the number of lanthanum atoms and inversely proportional to the atomic contribution of the remaining Me structure components) becomes the subject of modification due to the complexity mentioned above.

The case of region 1 seems to be simple. According to us, it consists of a direct introduction of N_{19} La ions into the most convenient Me–O structure layer of layers (all of them are satisfactorily deficient), accompanied by the stream of extra N_{19} ions of all the structure components in a 3:2: n :1.25 ratio, distributed through the appropriate Me–O layers to ensure a twice as fast densification of the unit cell, as observed in real samples.

References

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- 2 B. C. Sales and B. C. Chakoumakos, *Phys. Rev. B*, 43 (1991) 12994.
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