Journal of Alloys and Compounds, 185 (1992) L9–L11
JALCOM 194

Letter

On the existence of the 2212-structure type of phase in the Bi–Sr–Nd–Cu–O system

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(Received November 25, 1991)

There is a considerable interest for various reasons in studying the properties of bismuth cuprates, in which the divalent cations are partially replaced by a trivalent rare earth or yttrium [1–6]. Of refs. 1–6, the most interesting seem to be those in which successful replacement of the total calcium content in the $Bi_2Sr_2CaCuO_{8+x}$ phase has been achieved [4–6]. These results prove that, to achieve stability of the structure type under discussion, calcium seems to be one of several acceptable components. However, considering the ability of the structure to exhibit superconducting properties, this element seems to be unique. All the rare earth derivatives of $Bi_2Sr_2LnCu_2O_{8+x}$ type (Ln ≡ Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Y) obtained so far have proved to be insulators.

TABLE 1

X-ray powder diffraction data (Cu Kα) for the 2212-structure type phase in the Bi–Sr–Nd–Cu–O system

$h\ k\ l$	$\sin^2 \theta_{obs}$	$\sin^2 \theta_{calc}$
0 0 6	0.0234839	0.0234865
0 0 8	0.0416441	0.0417558
1 1 3	0.0455274	0.0455419
1 1 5	0.0558917	0.0559799
0 0 10	0.0653388	0.0652439
1 1 7	0.0716412	0.0716367
2 0 0	0.0793861	0.0793389
0 0 12	0.0939582	0.0939531
1 1 11	0.1186658	0.1186150
0 0 14	0.1279608	0.1278792
2 0 10	0.1444162	0.1445818
2 2 0	0.1583631	0.1586754
0 0 16	0.1667338	0.1670201
2 0 12	0.1732897	0.1732897

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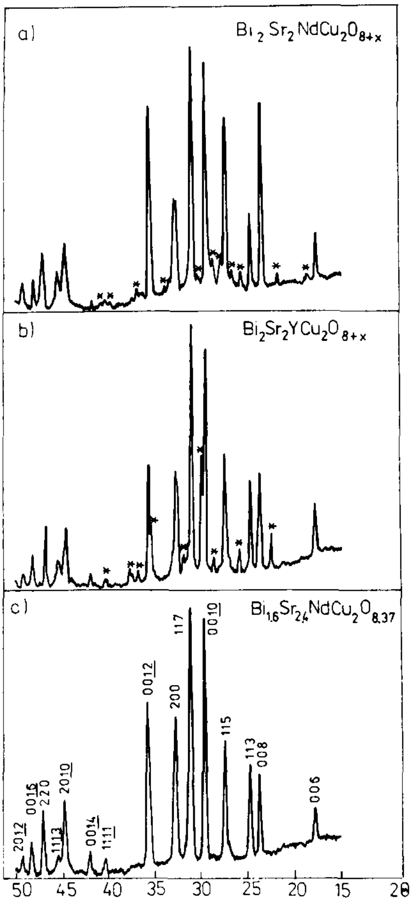

Fig. 1. X-ray diffraction patterns of the Bi–Sr–RE–Cu–O samples (a) $Bi_2Sr_2NdCu_2O_{8+x}$, (b) $Bi_2Sr_2YCu_2O_{8+x}$ and (c) $Bi_{1.6}Sr_{2.4}NdCu_2O_{8.37}$ used in this work: *, reflections of some secondary phases, mainly of the 2201-structure type.

The aim of this work was to verify whether total substitution of calcium in bismuth cuprates of the 2:2:1:2 stoichiometry proceeds as stated above and really produces single-phase samples. For this purpose, neodymium and yttrium have been taken as calcium substituents. As seen in Fig. 1(a) and Fig. 1(b), the resulting products (prepared by heating appropriate stoichiometric quantities of the oxides and/or carbonates at 900 °C for extended periods in air) are evidently of a multiphase nature.

An attempt to determine, by microprobe (JEOL instrument) analysis, the exact composition of the 2212-structure type phases present in our samples, failed. This was because of a comparatively large discrepancy in the resulting values. Finally, classical exploration of the systems was undertaken to find at least one composition within the domains of homogeneity of the phases under discussion.

TABLE 2

Results of chemical analysis for the 2212-structure type phase in the Bi–Sr–Nd–Cu–O system

Chemical composition	$Bi_{1.6}Sr_{2.4}NdCu_2O_{8.37}$
Lattice parameters	$a=b=5.469$ Å; $c=30.156$ Å
Cell volume	$V=902.1$ Å^3
Experimental average valence of copper	$v_{Cu}=2.07$
Experimental density	$d_{obs}=6.989$ g cm^{-3}
Number of MO_x-type molecules in the elementary unit cell (M ≡ sum of at.% (Bi, Sr, Nd, Cu))	$Z=28$
Calculated density	$d_{calc}=6.996$ g cm^{-3}
Electrical properties	Semiconductor

We present some preliminary results obtained in relation to the 2212-structure type phase which is free of calcium and contains neodymium. These results are summarized in Tables 1 and 2 and Fig. 1(c). It is interesting to note the lack of an orthorhombic distortion, which was reported in refs. 4 and 6 as characteristic for the $Bi_2Sr_2RECu_2O_{8+x}$ phases, and also clearly seen in our multiphase samples (Figs. 1(a) and 1(b)). Another difference noted refers to the average valence of copper, which according to the references cited above should result in the overall phase oxygen index close to 8.5. The appropriate value found herein (8.37) is evidently smaller. These factors indicate that the 2212-structure type phase existing in the Bi–Sr–Nd–Cu–O system must exhibit a certain domain of homogeneity, more or less developed, in comparison with its original matrix in the Bi–Sr–Ca–Cu–O system and that the single-phase sample analysed in this work represents only one possible composition of the phase domain.

Work on calcium-free 2212-structure type phases with yttrium is in progress.

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