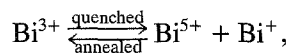


Doping of the Bi-Sr-Ca-Cu-O system with V_B elements and the effect on $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ phase formation

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A series of samples of nominal composition $\text{Bi}_{2-x}\text{M}_x\text{Sr}_2\text{Ca}_2\text{Cu}_{3-y}\text{M}_y\text{O}_z$ ($M = \text{V}, \text{Nb}$ or Ta , $x = 0.0-1.0$, $y = 0.0-0.5$) were prepared. By X-ray diffraction (XRD), $R-T$ and a.c. magnetic susceptibility (χ) measurements it was found that 2223 phase was significantly enhanced by the doping of these elements, and their role was quite similar to that of Pb for stabilizing the 2223 phase. It was also observed that the optimum substitution level is at $x = 0.4$ for all three elements. The highest T_0 obtained is around 100 K which is several degrees lower than that of the Pb-doped sample, though the XRD pattern shows that 2223 phase is the main phase. A reversible reaction:



was also observed in the sample doped with Nb^{5+} . The authors suggest that the beneficial effect of promoting the formation of 2223 phase might be a general property of doping with high-valency cations.

Since the advent of the BiSrCaCuO superconductor [1] for stabilizing and promoting the formation of high T_0 2223 phase, partial substitution of Bi with Pb has been found to be most effective [2]. Recently, it has been reported that doping with Sb also promotes the formation of 2223 phase [2]. In the present work the authors have systematically studied the effect of the high-valency cations V^{5+} , Nb^{5+} and Ta^{5+} on the formation of high T_0 2223 phase and found that doping any one of them can significantly enhance the formation of 2223 phase. Their role is quite similar to that of Pb for stabilizing the 2223 phase.

The samples of nominal composition $\text{Bi}_{2-x}\text{M}_x\text{Sr}_2\text{Ca}_2\text{Cu}_{3-y}\text{M}_y\text{O}_z$ ($M = \text{V}, \text{Nb}$ or Ta , $x = 0-1.0$, $y = 0-0.5$) were preheated at 800 °C for 20 h in air, pelletized, and again heated at 800 °C for 10 min, allowing the low melting point compound to react and to form an intermediate compound. The temperature was then increased slowly ($\sim 2^\circ\text{C min}^{-1}$) to $\sim 880^\circ\text{C}$ and kept there for ~ 140 h. Finally the samples were quenched in air.

XRD was performed on D/max-II_B; the resistance dependence of temperature ($R-T$) by the standard four-probe method with I_n contacts; and the a.c. χ measurements with mutual induction method precision -5×10^{-8} V and ± 0.15 K. The X-ray photoemission spectrum (XPS) data of the core level for each element were collected in the VG ESCALAB MK spectrometer. The pressure during measurement was 1×10^{-9} mbar.

Fig. 1 shows XRD patterns with different amounts of doping with Nb. It can be seen that with increasing Nb substitution ($y = 0.0$, $x = 0.1-1.0$) the amount of 2223 phase at first increases, then decreases; the optimum amount is at $x = 0.4$. Though the peak positions of 2223 and 2212 phases do not shift perceptibly, the width of the diffraction peaks broadens and diffuses with doped Nb. This effect may be due to doping with the high-valency cation leading to serious lattice distortion, and, at the same time, with increasing doping the peaks of CuO and peaks located at $2\theta \sim 31^\circ$ of $\text{Sr}_{0.82}\text{NbO}_3$ phase increase. Besides, it is worth pointing out that 2223 phase was also enhanced with increasing Nb substituted Cu of nominal composition $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_{3-y}\text{Nb}_y\text{O}_z$ ($y \leq 0.3$).

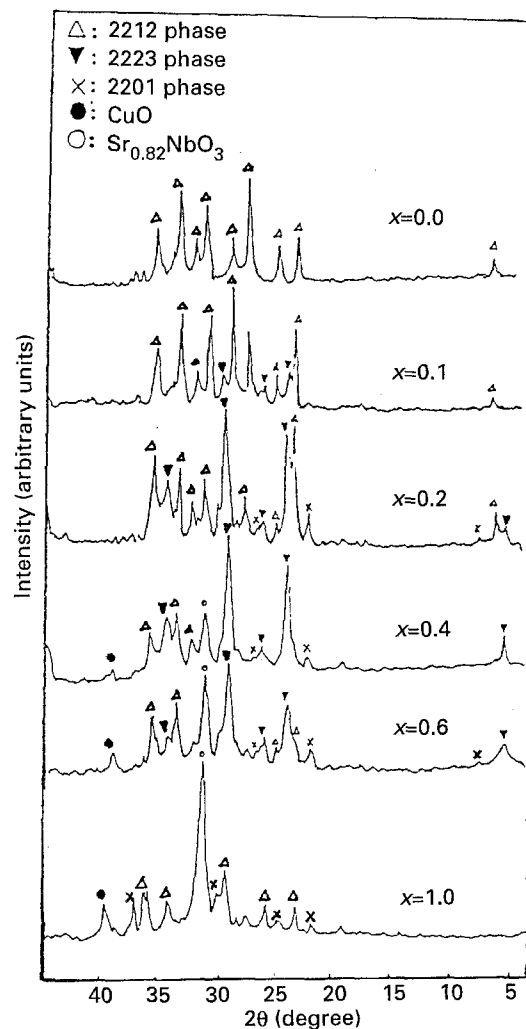


Figure 1 X-ray diffraction patterns of $\text{Bi}_{2-x}\text{Nb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$.

By analysing Bi_{4f} XPS spectra as shown in Fig. 2, that the samples doped with Nb undergo a reversible reaction of $\text{Bi}^{5+} + \text{Bi}^{3+} \rightarrow \text{Bi}^{3+}$ from the quenching process to the annealing process, implying big changes in the Bi-O layer after doping with a high-valency cation. In connection with the changes in the O_{1s} spectra in Fig. 3, we consider that the new peak at the lower binding energy (~ 527 eV) in curve a is due to O_{1s} of oxygen bonding with Bi^{3+} in the form of $\text{Bi}^{3+}-\text{O}^-$. Thus, these effects show that high-valency cations may be substituted not only for Bi but also for Cu.

In connection with the probable instability of the 2223 phase, we suggest that the interlayer linkage is weaker in the Ca-CuO₂-Ca layers as shown in the highlighted part of Fig. 4a. The bonding between the Ca layer and the CuO₂ layer becomes weaker when another Ca layer lies on the other side of CuO₂ and the O of the planar CuO₂ layer is not so favourable for coordination as that from a square pyramidal one where four basal O are somewhat tilted toward the Ca atom. Thus, this leads to a certain degree of instability in the 2223 structure. With substitution of a high-valency cation to the 4-coordinated Cu, more O would be incorporated into the lattice and will enter the \otimes site as shown in Fig. 4b [4, 5]. With additional M-O bond interlayer binding is enforced, and thus the 2223 phase is stabilized.

The XRD patterns of samples doped with V or Ta show the same trend as those doped with Nb, only the impurity phases located at $2\theta = 29^\circ \sim 31^\circ$ are attributed to $\text{Sr}_4\text{V}_2\text{O}_9$ and $\text{Sr}_3\text{Ta}_2\text{CuO}_9$, respectively.

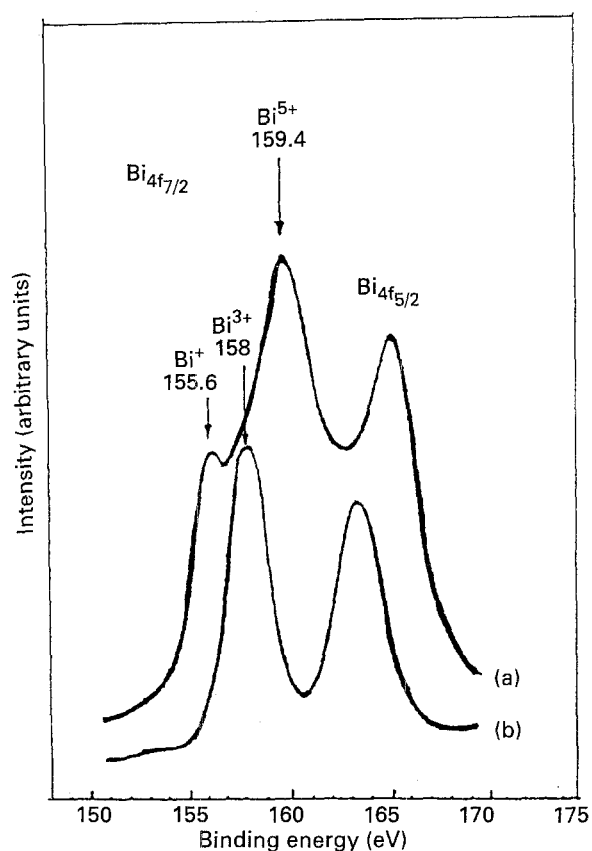


Figure 2 The core spectra of Bi_{4f} in $\text{Bi}_{1.6}\text{Nb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$: (a) for air-quenched sample at 880°C ; (b) for air-annealed sample at 600°C for 10 h.

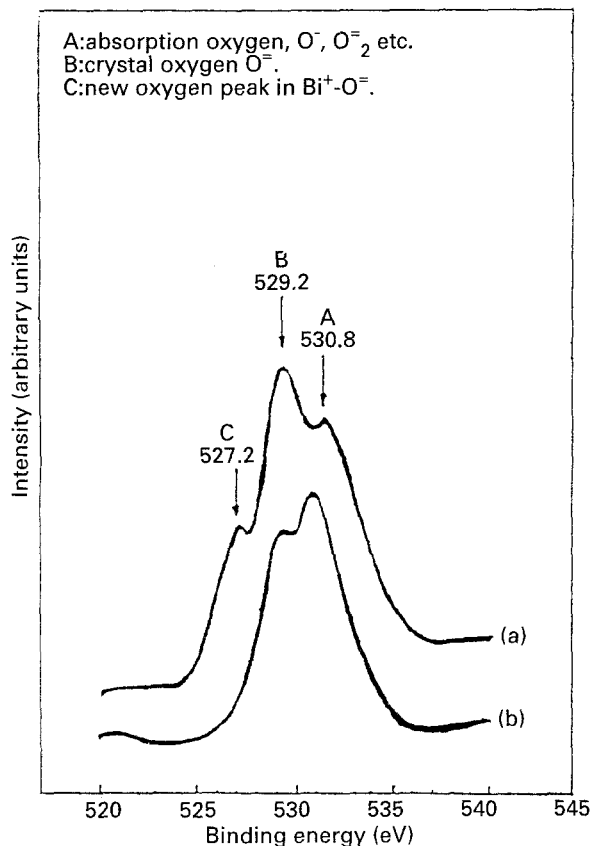


Figure 3 XPS of O_{1s} in $\text{Bi}_{1.6}\text{Nb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$: (a) for air-quenched sample at 880°C ; (b) for air-annealed sample at 600°C for 10 h.

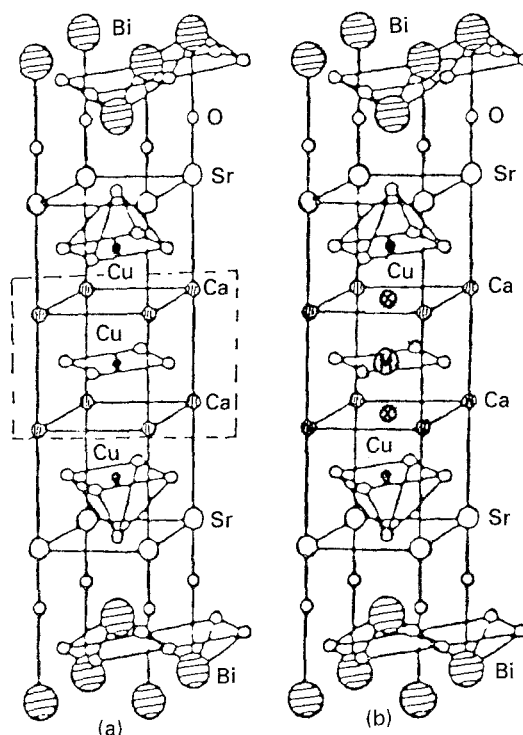


Figure 4 Stabilization of 2223 phase by partial substitution of Cu with a high-valency cation M. (a) Unsubstituted 2223 phase. The highlighted area the supposed weaker interlayer linkage part. (b) Substituted 2223 phase. M , high-valency M; \otimes , extra O added.

Fig. 5 shows the effect of doping levels on the formation of 2223 phase. Obviously, $x = 0.4$ is the optimum doping amount for all three elements. Hence, the speed of formation of 2223 phase is the

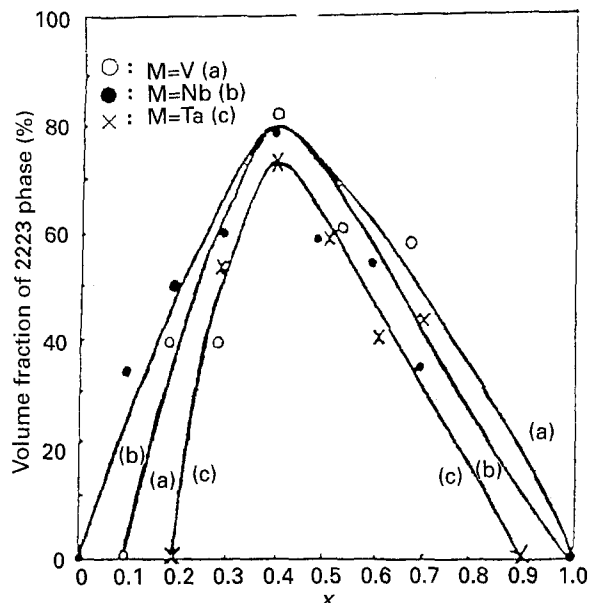


Figure 5 Volume fraction of 2223 phase dependence of doping level in $\text{Bi}_{2-x}\text{M}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$. (The volume fraction of the 2223 phase was evaluated from the relative intensity of the X-ray diffraction peaks, using the equation $I_{h(0010)}/I_{h(0010)} + I_{1(008)}$, where I_h and I_l denote the diffraction intensities of the high- and low- T_c phase, respectively.)

highest, and the 2223 phase content is much more in the sample. Deviation from these compositions leads to a clearly harmful effect. The optimum doping level is so narrow that this may be one reason why these three higher-valency cations are not so easily found to be as beneficial as Pb.

Generally, doping with these high-valency cations may lead to the lowering of the melting point of samples, but they are still $\sim 10^\circ\text{C}$ higher than the corresponding Pb-doped samples. The optimum firing temperature range (less than 10°C) is also narrower than that in Pb doping, which may be another reason why Pb is more easily found to be beneficial.

Fig. 6 shows the $R-T$ curves for samples doped with V, Nb or Ta at $x = 0.4$. Together with a.c. χ measurements it was found that doping with high-valency cations lowers T_0 by several degrees around 100 K. There is no amelioration through low-temperature annealing even for a long time; only for high doping level samples ($x > 0.4$), with annealing at 600°C is diamagnetism of samples significantly stronger than that of the quenched samples, as can be seen from Fig. 7. This may be due to the incorporation of high-valency cations resulting in more random defects in the lattice, especially the change of oxygen voids and the number of carriers [6].

The effect of promoting 2223 phase was also observed in the samples doped with other high-valency cations of nominal composition $\text{Bi}_{1.5}\text{Sb}_{0.1}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$, $\text{Bi}_{1.6}\text{Mo}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ and $\text{Bi}_{1.6}\text{Si}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$.

In summary, doping with V^{5+} , Nb^{5+} or Ta^{5+} high-valency cations greatly enhances the formation of 2223 phase; the optimum nominal composition is $\text{Bi}_{1.6}\text{M}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ ($\text{M} = \text{V}, \text{Nb}$ or Ta). The

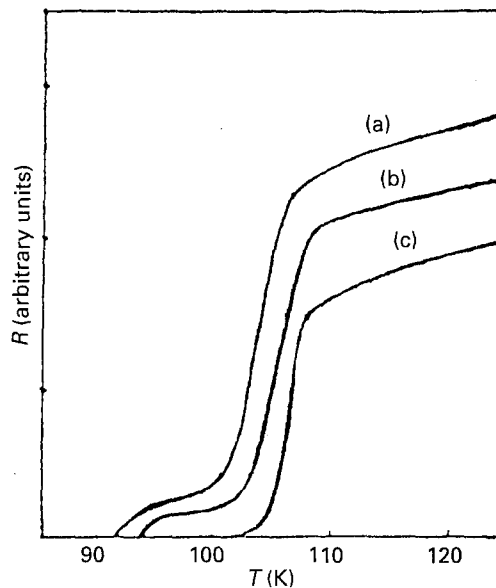


Figure 6 Temperature dependence of the resistivity for $\text{Bi}_{1.6}\text{M}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$: (a) $\text{M} = \text{V}$, (b) $\text{M} = \text{Nb}$, (c) $\text{M} = \text{Ta}$.

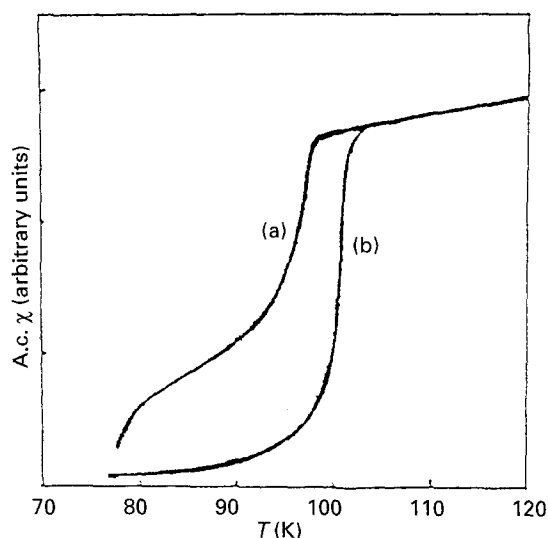


Figure 7 Temperature dependence of a.c. magnetic susceptibilities of $\text{Bi}_{1.4}\text{Nb}_{0.6}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$: (a) quenched in air, (b) post-annealed at 600°C for 12 h.

authors suggest that the beneficial effect of promoting the formation of 2223 phase might be a general property of doping with high-valency cations. The beneficial origin of doping with high-valency cations in Bi-based material was also discussed.

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