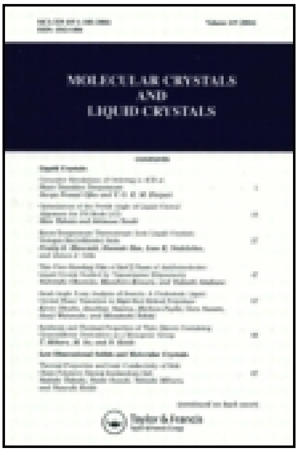

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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To cite this article: Akihiro Moto , Akiharu Morimoto & Tatsuo Shimizu (1990): Chemical and Structural Investigations on the Bi-Based Oxide Superconductors, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 184:1, 285-289

To link to this article: http://dx.doi.org/10.1080/00268949008031776

Mol. Cryst. Liq. Cryst., 1990, vol. 184, pp. 285–289
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Printed in the United States of America

CHEMICAL AND STRUCTURAL INVESTIGATIONS ON THE BI-BASED OXIDE SUPERCONDUCTORS

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Abstract X-ray diffraction, ESR, and Raman scattering measurements were performed on Bi(Pb)-Sr-Ca-Cu-O superconductors. Variations in the oxygen content and the number of CuO_2 planes in the unit are responsible for a change in the phonon mode for oxygen in BiO layers. In contrast with the result of the band calculation for the low-Tc phase, our result suggests that the transition temperature is not affected by the BiO configuration.

Introduction

The electronic and magnetic properties of high-Tc oxide superconductors are found to be very sensitive to the carrier concentration, both hole and electron types. For Bi-system, although calculations suggest that the oxygen distribution in BiO layers causes a change in superconductivity due to the peculiarity of BiO band at the Fermi energy E_F,[1] some spectroscopic studies show zero density of states at E_F implying that the surface BiO layer is nonmetallic.[2]

For clarifying the correlation between the superconductivity and the structure of BiO layers in the Bi-based superconductors, we carried out Raman scattering measurement on the oxygen phonon mode of BiO layers.

Experimental

Samples were prepared by a solid-state reaction of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, and CuO powders. Starting compositions for the low-Tc(2212) and the high-Tc(2223) phases are $Bi_2Sr_{1.2}Ca_{1.8}Cu_2O_8$ and $Bi_{1.84}Pb_{0.34}Sr_{1.9}Ca_2Cu_3O_{10}$, respectively. Both samples were sintered at 850°C for 90-100h with intermediate grindings. Pb-doped 2223 was sintered at the lower oxygen pressure.[3] Raman scattering measurement was carried out at room temperature using the 488 nm line of an Ar ion laser.

Results and Discussion

Figure 1 shows X-ray diffraction (XRD) patterns of O_2 annealed (a)2212 and (b)Pb-doped 2223 samples, indicating that each phase is singled out. Formation of the single phase was also confirmed by ESR measurement, which is a sensitive method to detect impurity phases in Y-Ba-Cu-O compounds.[4] Both samples of 2212 and Pb-doped 2223 shown in Fig.1 show a broad ESR signal. Though Hayashi et al. reported that the ESR signal originates from CuO_2 planes in the Pb-doped 2223 phase,[5] we interpret that ESR signal is also absent for the CuO_2 planes in this system as follows. First, a similar signal is obtained from impurity Sr-Ca-Cu-O compounds in our experiment. Second, the sample of Pb-doped 2223 shows approximately 10^{-3} spins per single copper atom, which is one order of magnitude smaller than that of 2212. The absence of the ESR signal implies a strong magnetic interaction involving Cu spins. When compared with the Y-Ba-Cu-O compounds, inhomogeneous impurity phases seem to be embedded in superconductors, taking account the broad width of the ESR signals.

Figure 2 shows a result of dc-resistivity measurement by a four probe method. Samples A(2212) and C(2223) were annealed in the flow of oxygen gas at 500° C for 12h. Samples B (2212) and D (2223) were annealed in the flow of nitrogen gas at 780° C for 1h and subsequently 700° C for 37h, followed by a slow cooling to room temperature in the same atmosphere. Both phases deterioate in Tc by the oxygen removal from

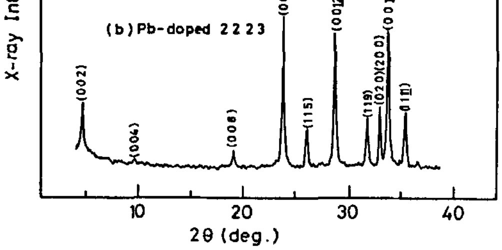

FIGURE 1. X-ray diffraction patterns of O_2 annealed samples.

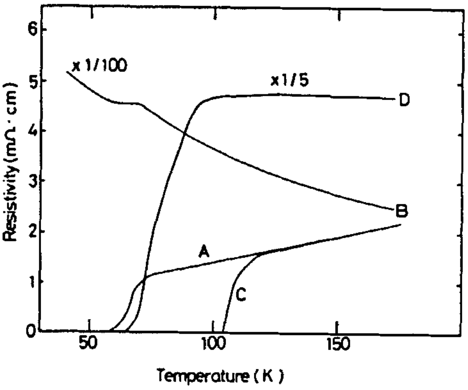

FIGURE 2. Resistivity vs. temperature.

superconducting units, especially semiconducting behavior is apparent for the 2212 phase. Previously we reported the heat treatment effect on Tc for the 2212 phase.[6] If the sample is rich in Sr(Sr/Ca>1), the enhancement of Tc by oxygen removal is clearly observed, which is interpreted as a reduction of the excess hole concentration. Here Sr/Ca=1.2/1.8 was selected for comparison with the 2223 phase in terms of the heat treatment effect. Lattice constants along c-axis for both samples are 30.51A(2212) and 37.11A(2223). The N_2 annealing enlarges these values up to 30.64A(2212) and 37.16A(2223), respectively, owing to the oxygen removal. We can not see any extra peaks in XRD through the N_2 annealing, so that the oxygen breathing works in the same way, irrespective of the number of the CuO_2 planes in the unit cell.

Raman spectra are shown in Figs.3 and 4. The inset in Fig.3 shows the 2212 sample with the composition of Sr/Ca=1.75/1.25. In this case, the sample was rapidly quenched at 870°C instead of the N_2 annealing. The mode of 620-650cm^{-1} is assigned to the vibration of oxygen atoms in the BiO layers.[7] With respect to this band, the shoulder at 650cm^{-1} seen in 2212 disappears in Pb-doped 2223. In order to explain this phenomenon, the idea pointed out by Matsui et al.[8] was adopted. They ascribe the variation of the modulated structure to the different packing modes of the "constituent unit blocks", each of which consists of the wavy perovskite-like layers and the associated wavy phases. They have schematically shown the wavy unit blocks packing in-phase for Pb-doped 2223, and out-of-phase for Pb-free 2223 and 2212(see Fig.5 in Ref.7). For $Bi_2Sr_2CuO_y$(2201) structure, the mode is realized as an intermediate form of two phases. We conjectured that the oxygen vibration in the BiO layer is strongly dependent on the packing of "blocks", that is, the periodicity of the supercell, or the displacement of each blocks.

From this model, it is expected that 2201 shows a different type of shape from the above mentioned Raman mode in Figs.3 and 4. According to Denisov et al.,[9] the Ca-contained 2201 phase has rather single-like band compared with the 2212 phase and its peak position at higher energy. The absence of the 650cm^{-1} mode in the Pb-doped 2223 phase (Fig.4) may be related to the in-phase waving of the "unit blocks".

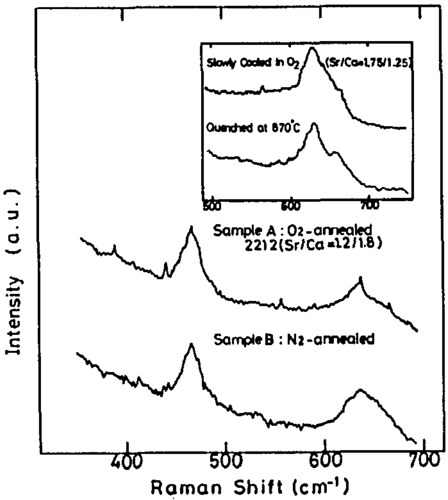

FIGURE 3. Raman spectra of 2212 samples. The inset shows a sample with the composition of Sr/Ca=1.75/1.25.

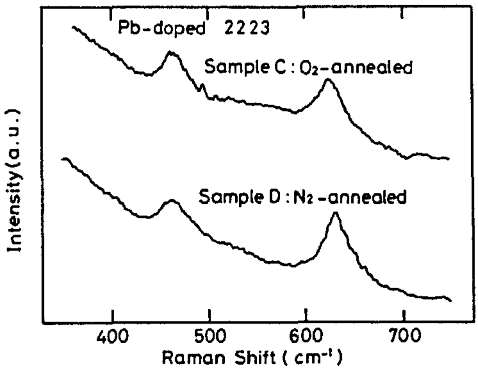

FIGURE 4. Raman spectra of Pb-doped 2223 samples.

As other features for 2212, the weakness of the signal intensity at 650cm^{-1} to one at 630cm^{-1} and the appearance of a new broad scattering at 550-600cm^{-1} are perceptible when oxygen is added. The latter also seems to be a common feature for the Pb-doped 2223 phase. Since the extra oxygen atom seems to be accommodated in the BiO layer and to result in the local modification of this layer,[10] it is plausible that such a variation of the phonon spectra related to BiO layer reflects the redistribution of oxygen atoms in and/or between BiO planes. One of the significant features is that the sample of Sr/Ca=1.75/1.25 also shows the same trend, though the extra oxygen plays an opposite role in Tc, depending on whether the sample is Ca-rich or not. Thus, Tc does not relate to the oxygen phonon mode in BiO layers. It suggests that the superconductivity affected by the density of states at E_F is mainly determined by the oxygen content, but not by the oxygen configuration in the BiO layers as the band calculation showed. At present, because of the less information about accurate oxygen sites, it is difficult to discuss about a detail assignment of the each peak of 620-650cm^{-1} and the broad scattering.

In conclusion, the phonon mode of oxygen atoms in BiO layers is sensitive to their modulated structures, however, it is hardly connected with Tc values.

Acknowledgments We would like to thank Prof. M. Kumeda of Kanazawa university for helpful discussions. We would also like to thank M. Makida and Y. Sugawara for the technical assistance. This work was partly supported by a Grant-in-Aid for Scientific Research on Chemistry of New Superconductors from the Ministry of Education, Science and Culture of Japan.

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