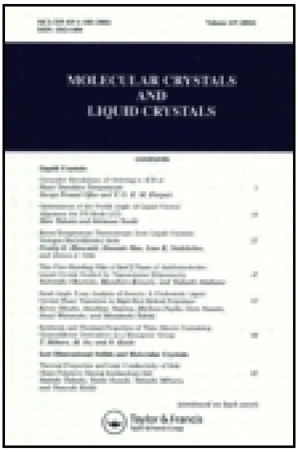

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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Version of record first published: 22 Sep 2006.

To cite this article: Koichi Niwa, Takuya Uzumaki, Atsushi Tanaka, Nobuo Kamehara & Kazunori Yamanaka (1990): Synthesis of Single Phased Bi-Pb-Sr-Ca-Cu-O Superconductor, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 184:1, 325-333

To link to this article: http://dx.doi.org/10.1080/00268949008031782

Mol. Cryst. Liq. Cryst., 1990, vol. 184, pp. 325–333
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Printed in the United States of America

SYNTHESIS OF SINGLE PHASED Bi-Pb-Sr-Ca-Cu-O SUPERCONDUCTOR

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Abstract We studied high-Tc phase formation (Tc ~110 K) of bulk samples and films of the Bi-Pb-Sr-Ca-Cu-O superconducting systems. We investigated the role of Ca_2PbO_4 in high-Tc phase formation. In the Pb-doped Bi-Sr-Ca-Cu-O system, Ca_2PbO_4 is formed at around 750 ℃. During the formation of the high-Tc phase, Ca_2PbO_4 decreases as the firing time increases. The bulk high-Tc phase was synthesized by adding Ca_2PbO_4 to a mixture of the 80 K phase, the 10 K phase and CuO. The synthesized bulk consists mainly of the high-Tc phase, as determined by X-ray diffraction and magnetization measurments. It seems that the synthesis process of the high-Tc phase formation is accelerated by a reaction between the 80 K phase, CuO and Ca^{2+} in the liquid phase which is composed of a Ca-Pb oxide flux.

INTRODUCTION

Since the high-Tc Bi-Sr-Ca-Cu-O superconductor (Tc~110 K) was dicovered by Maeda et al.[1], many researchers have attempted to fabricate a single-phased sample of the 110 K phase in the Bi-Sr-Ca-Cu-O system. The 110 K Tc superconductor is promising for application to electronics. Film and bulk formation have been studied extensively. The $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ system was found to have 3 superconducting phases corresponding to Tc =7 K for n=1 (10 K phase)[2,3], 80 K for n=2 (low-Tc phase)[1], and 110 K for n=3 (high-Tc phase)[1]. Takano et al.[4] reported that the substitution of Pb for Bi increases the volume fraction of high-Tc phase. However, the process responsible for high-Tc phase formation is still not well understood.

We examined the Bi-Pb-Sr-Ca-Cu-O system using X-ray diffraction and Raman scattering. Powder X-ray diffraction of Bi-Pb-Sr-Ca-Cu-O bulk samples fired at 841℃ for 10, 50, and 200 hours mainly showed peaks corresponding to both high- and low-Tc phases. The high-Tc peaks became stronger as the firing time was increased. Unknown materials about 10μm in diameter were observed for these samples[5]. Micro-Raman scattering was used to identify unknown peaks in X-ray diffraction pattern. The measurement revealed that PbO addition in the Bi-Sr-Ca-Cu-O system causes the formation of Ca_2PbO_4. As the firing time for these samples increases, the X-ray peaks of the Ca_2PbO_4 become weak. This indicates that Ca_2PbO_4 is related to the formation of high-Tc phase.

We synthesized the high-Tc phase in bulk and thin films, and invstigated the reaction process for the high-Tc phase as it relates to Ca_2PbO_4. We report on the preparation of high-Tc phase samples with Ca_2PbO_4, the low-Tc phase and the 10 K phase, and on the reaction process of high-Tc phase formation.

SAMPLE PREPARATION

Bi-Pb-Sr-Ca-Cu-O, and addition of Ca_2PbO_x to Bi-Sr-Cu-O

Samples were prepared by thermal reaction with the nominal compositions of 2:x:2:2:3 (x=0, 0.5, 1.0). Bi_2O_3, PbO, $SrCO_3$, CaO, and CuO starting powders were mixed, ground, then shaped under 200 MPa to form pellets. The preparation conditions of the samples are listed in Table I. In sample 3C, 30 wt% Ca_2PbO_4 was added to Bi:Sr:Cu=2:2:3. The sample was then fired at 848℃ for 24 hours, shaped under 200 MPa, and fired again at 848℃ for 50 hours.

Addition of Ca_2PbO_x to Bi-Sr-Ca-Cu-O

We examined[6] the high-Tc-phase formation by firing a mixture of the 10 K phase, low-Tc phase, CuO, and Ca_2PbO_4. Bi_2O_3, PbO, $SrCO_3$, CaO, and CuO starting powders were mixed and ground with a nominal composition of Bi:Sr:Ca:Cu=2:2:1.5:3.5. These ground powders were fired at 820℃ for 6 h in air. This fired powder (sample 4A)was comprised of the low-Tc phase, the 10 K phase, and CuO. 14.5wt% Ca_2PbO_4 was then added to sample 4A. The powders were mixed, ground, and fired at 845℃ for 23 h in air. The fired powder was mixed, ground again, and then shaped under 200 MPa. Sample 4B was fabricated by firing the pellets at 845℃ for 80 h in air.

TABLE I Composition and preparation conditions.

Specimen	Nominal composition (at. ratio)					Firing
	Bi	Pb	Sr	Ca	Cu	
2A	2.0	0.0	2.0	2.0	3.0	841℃, 15 h, air
2B	2.0	0.5	2.0	2.0	3.0	841℃, 15 h, air
2C	2.0	1.0	2.0	2.0	3.0	841℃, 15 h, air
2D	2.0	0.5	2.0	2.0	3.0	750℃, 9 h, air Quenched to room temperature.
3A	2.0	0.0	2.0	0.0	3.0	841℃, 24 h, air
3B	0.0	1.0	0.0	2.0	0.0	817℃, 17 h, air
3C	Addition of sample 3B (30 wt%) to sample 3A					848℃, 74 h, air

Bi-Pb-Sr-Ca-Cu-O thin film

Thin film samples were deposited by rf magnetron sputtering with three targets, as described in other previous reports[8]. The films were deposited on MgO (100) single crystals heated at 400℃. We used a Bi-Sr-Ca-Cu-O (BSCCO) target with a composion of Bi:Sr:Ca:Cu = 3:2:2:3. PbO and CuO targets were also used. PbO and CuO layers were stacked repeatedly on BSCCO layers to precisely control composition. The films were sintered in air using a "two-step" process. They were first heated to around 800℃ at 10° /min, and then further heated to around 850℃ at 1 ° /min. They were sintered for various intervals.

MEASUREMENT

The DC resistivity of the bulk and film samples were measured at temperatures between 77 and 300 K using the four terminal method. X-ray diffraction patterns for the samples were obtained with monochromatic CuKα radiation and a diffractometer. The samples were analyzed by electron microanalysis (EPMA) or inductively coupled plasma analysis (ICP). The magnetization hystersis curve of the sample 4B was measured at 77.3 K, using a vibrating sample magnetometer.

RESULTS AND DISCUSSION

Bulk

Figure 1 shows the X-ray diffraction patterns for samples 2A, 2B, and 2C. For x = 0, the peaks corresponding to the low-Tc phase, and a smaller one corresponding to the 10 K phase were observed, but there was no visible peak corresponding to the (002) high-Tc phase. No high-Tc phase materials were produced with the stoichiometric composition Bi:Sr:Ca:Cu=2:2:2:3 under the firing conditions shown in Table I. For x = 0.5, the 4.8° peak corresponding to the (002) high-Tc phase was observed. At x = 1.0, no peak corresponding to the (002) high-Tc phase was observed. The Ca_2PbO_4 peak increased as PbO content was increased. The high-Tc phase was synthesized with the composition of Bi:Pb:Sr:Ca:Cu = 2:x:2:2:3. The optimum amount of PbO was found to be about x = 0.5

Figure 2 shows the X-ray diffraction pattern of sample 2D which was quenched to room temperature. Ca_2PbO_4 and the 10 K phase were produced at 750℃. In the other phase, unreacted CuO was found.

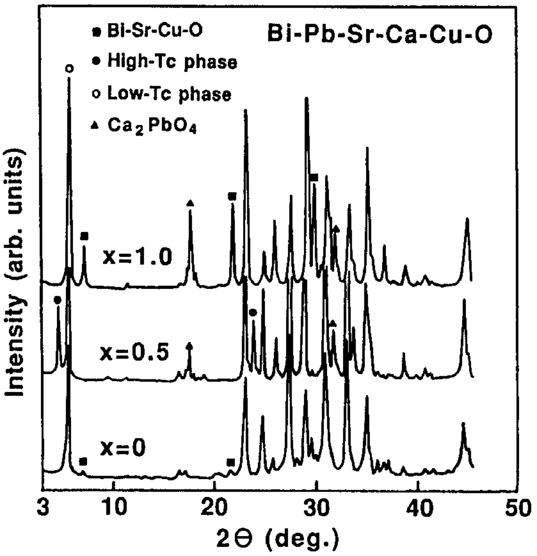

FIGURE 1 Powder X-ray diffraction patterns for Bi-Pb-Sr-Ca-Cu-O = 2:x:2:2:3 (x = 0, 0.5, and 1.0) fired at 841℃ for 15 h.

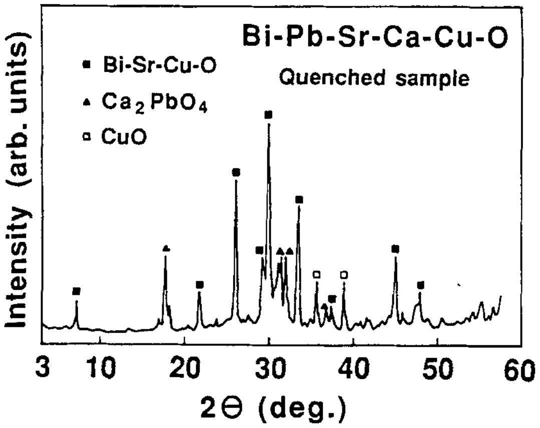

FIGURE 2 Powder x-ray diffraction pattern for Bi:Pb:Sr:Ca:Cu = 2:0.5:2:2:3 fired at 750℃ for 9 h and quenched to room temperature.

Sample 3A is comprised mainly of the 10 K phase but some CuO was also detected. The X-ray diffraction pattern of sample 3C, in which Ca_2PbO_4 was added to sample 3A, is shown in Fig. 3. The high-Tc phase was produced and the ratio of high- to low-Tc phases increased, compared with the corresponding ratio in the Bi-Pb-Sr-Ca-Cu-O sample[5] which was fired at 841℃ for 200 h.

In the Pb-doped Bi-Sr-Ca-Cu-O system, the X-ray diffraction results suggest that the 10 K phase and Ca_2PbO_4 are produced at around 750 ℃. The low-Tc phase can be formed at temperatures higher than about 800℃. The 10 K phase decomposed at 841℃ after 15 hours of firing, and high- and low-Tc phases were formed. The phase diagram of CaO-PbO[8] shows that Ca_2PbO_4 decomposes into CaO and a liquid phase at 822℃. We believe these two phases act as accelerators in the formation of the high-Tc phase. The presence of CaO and a liquid phase is expected to accelerate the chemical reaction between decomposed CaO, which moves in the liquid phase, and double CuO layers, which are superconductive at 80 K.

Ca_2PbO_4 supplies CaO to the system which consisted of the 10 K phase and CuO. The phase produced at 840℃ when Ca_2PbO_4 is added to this system is mainly the high-Tc phase. We suggest the reaction process shown schematically in Eqs. (1), and (2), and consider that Ca atoms in the crystal structure of the high-Tc phase are supplied by Ca_2PbO_4.

$$aBi_2Sr_2CuO_y + bCa_2PbO_4 + cCuO \xrightarrow[air]{} dBi_2Sr_2Ca_1Cu_2O_y + eCa_2PbO_4 + fCuO \quad (1)$$

$$dBi_2Sr_2Ca_1Cu_2O_y + eCa_2PbO_4 + fCuO \xrightarrow[air]{\sim 840℃} Bi_2Sr_2Ca_2Cu_3O_y \quad (2)$$

a, b, c, d, e, f : coeffcient

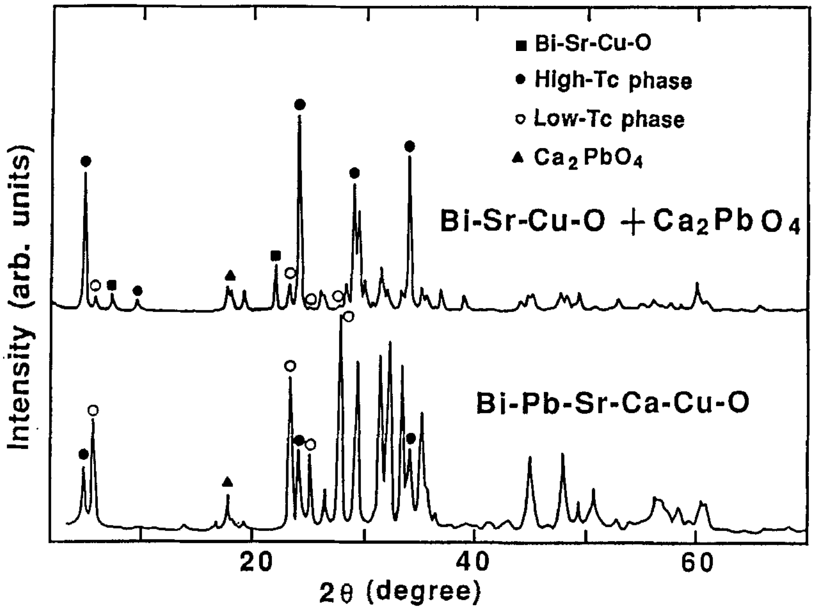

FIGURE 3 Powder X-ray diffraction patterns for the sample with 30wt% Ca_2PbO_4 added to Bi:Sr:Cu = 2:2:3 and for the composition Bi:Pb:Sr:Ca:Cu = 0.7:0.3:1:1:1.8. at 841℃ for 200 h.

We think that Ca_2PbO_4, the 10 K phase, and the low-Tc phase are precusors in the high-Tc phase formation. We attempted synthesis of the high-Tc phase by reaction between the precusors. As a result, Fig. 4 shows the temperature dependence of the resistivity for sample 4B . The resistivity dropped at 110 K and a Tce of 100 K was obtained.

As the result of the magnetization measurement, the volume

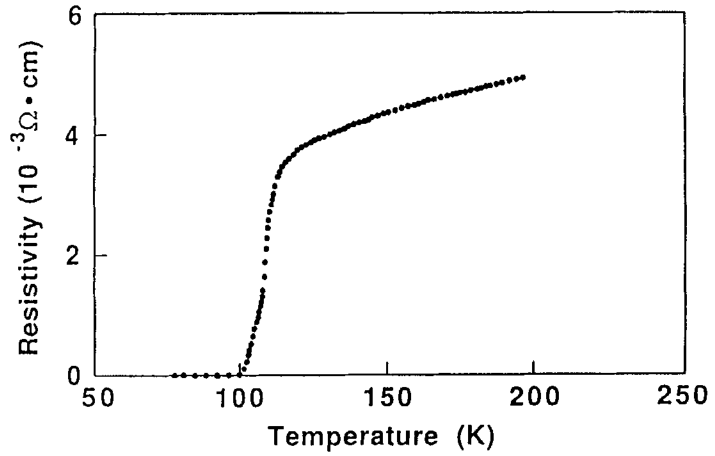

FIGURE 4 Temperature dependence of resistivity for sample 4B.

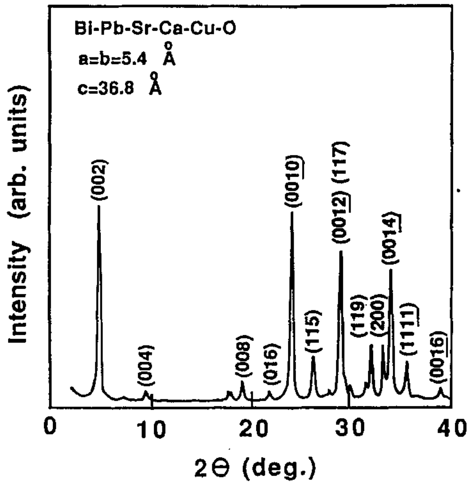

FIGURE 5 X-ray powder diffraction pattern for the sample fired at 845℃ for 103 h.

fraction of the superconducting phase above 77.3 K of sample 4B was calculated. The x-ray powder diffraction pattern showed that there is no low-Tc phase present (Fig. 5). This suggests that the volume fraction of the high-Tc phase is close to 74%.

Film

In the thin film preparation, the sintering temperature greatly affects the amount of the high-Tc phase formed . The low-Tc phase forms below 848℃ and above 853℃. For Bi:Pb:Sr:Ca:Cu = 1.00:0.80:1.00:0.99:1.64, we obtained a nearly single-phase high-Tc thin film after sintering at 851℃ for 1 hour in air. The resistivity showed zero resistance at 106.5 K[7]. the peaks corresponding to the high-Tc phase in the X-ray diffraction pattern of the film are very strong because of strong c-axis orientation.

Figure 6 shows the X-ray diffraction patterns of the thin film samples for which the sintering process was interrupted. The 10 K phase and Ca_2PbO_4 are formed before the 805℃ firing, and the low-Tc phase is formed during the 805℃ firing. And then, the strongly-oriented low-Tc phase and slight high-Tc phase formation is complete before 855℃ sintering. During the 855℃ sintering, the mount of high-Tc phase increases, and the low-Tc phase decreases. Unreacted Cu in these samples was detected by EPMA. Accordingly, the thin film also has basically the same reaction process as the bulk samples.

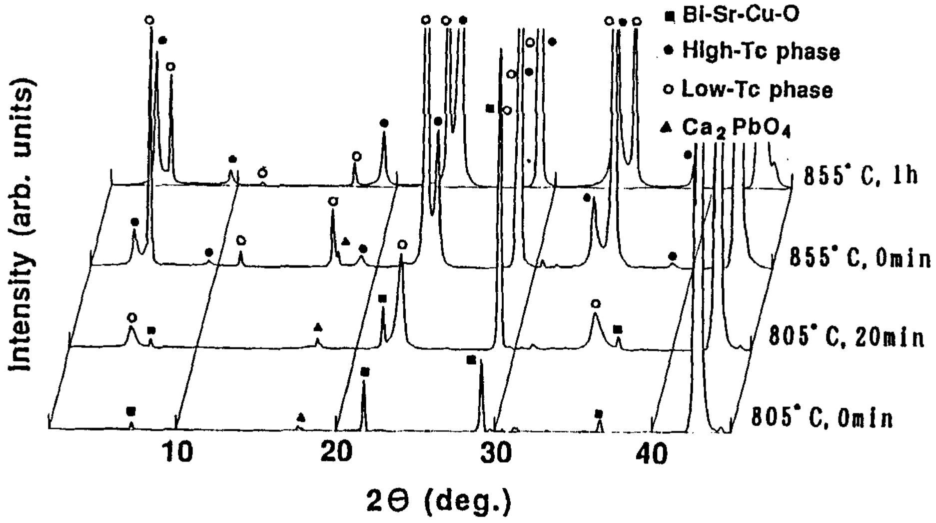

FIGURE 6 X-ray diffraction patterns of the thin film samples which had their sintering process interrupted.

Reaction mechanism

In near-stoichiometric Bi-Sr-Ca-Cu-O system for the high Tc-phase, the high-Tc phase increases by firing at around 865℃ in air[1, 9]. However, according to other reports[4, 8], the high-Tc phase formation is promoted by firing at around 845℃ in Pb doped and near-stoichiometric Bi-Sr-Ca-Cu-O system. Also, our results are in agreement with them. Pb seems to have the function similar to that of a catalyst in the chemical reaction forming the high-Tc phase from the Pb doped Bi-Sr-Ca-Cu-O system. Many reaction paths for the 110 K phase formation are predicted[10, 5]. We assume that the high-Tc phase is formed as the result of the reaction in which Cu, Ca ions are supplied to the low-Tc phase, and it is necessary to have large diffusion of Cu, Ca in the thermal reaction in order to effectively form the high-Tc phase. In Pb-doped Bi-Sr-Ca-Cu-O, it seems that the flux which assists the diffusion of Ca, Cu ions is the Ca-Pb-O liquid phase formed at temeperatures lower than the synthsis temperature, as shown in Eqs. (3), and (4).

$$Bi_2Sr_2CaCu_2O_y + pCa_2PbO_4 + qCuO$$

$$\xrightarrow[\sim 822℃,\ air]{} Bi_2Sr_2CaCu_2O_y + (rCa^{2+} + sCu^{2+}) \text{ in Ca-Pb-O liq.} \qquad (3)$$

$$\xrightarrow[\sim 840℃,\ air]{} Bi_2Sr_2Ca_2Cu_3O_y \qquad (4)$$

p, q, r, s: coefficient

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