decrease in the switching time can provide valuable information about the electric field dependence of the pitch.[5] The measured value of τ is about 100 μs which agrees well with the predicted value of 10–100 μs, based on a reasonable guess for γ_1 to be in the range of 0.1–1.0 P,[9] together with the values for K_1 and t_0 above.

In conclusion, we have demonstrated that the flexoelectric coupling in cholesteric liquid crystals leads to a fast linear electro-optic modulation of light. The speed of this electro-optic response is of the order of 100 μs, and is almost independent of the magnitude of the applied electric field. This effect should be useful in electro-optic devices, particularly for signal processing and optical computing.

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Preparation and properties of Pb-doped Bi-Sr-Ca-Cu-O superconductors

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Electrical and magnetic properties of the superconducting oxides with nominal composition $(Bi_{0.7} Pb_{0.3})_2 Sr_2 Ca_2 Cu_3 O_x$ prepared from polymeric precursors have been investigated. Superconducting transition with zero-resistance temperature at $T = 108$ K was achieved for a sample sintered at 840 °C under a low oxygen pressure. The critical current density at 77 K in a zero magnetic field is ~ 400 A/cm^2, which is much higher than that of the Pb-free sample. Variations of the superconducting transition temperature, the critical current density, and magnetic properties with heat treatment time are discussed in connection with the structural properties.

Since the discovery of high-T_c superconductivity in the La-Ba-Cu-O[1] and Y-Ba-Cu-O systems,[2] intensive studies have been made on cuprate oxides to seek new types of high-T_c superconductors. Recently, Maeda et al.[3] observed two new superconducting phases with $T_c = 80$ and 110 K in the Bi-Sr-Ca-Cu-O system. The low-T_c (80 K) phase could be synthesized over wide starting compositions and identified by several groups[4,5] as $Bi_2(Sr,Ca)_3 Cu_3 O_x$ with the c axis being about 24 Å. Although the ideal composition responsible for the high-T_c (110 K) phase[6] is known to be $Bi_2(Sr,Ca)_4 Cu_3 O_x$ with $c \approx 37$ Å, the formation of the single high-T_c phase in the Bi-Sr-Ca-Cu-O system from the stoichiometric composition is difficult. Very recently, it has been reported that the substitution of small quantities of Pb for Bi in the Bi-Sr-Ca-Cu-O system aids in the achievement of zero-resistance temperatures exceeding 100 K.[7–9] Takano et al.[8] observed that the partial substitution of Pb for Bi in the Bi-Sr-Ca-Cu-O system, together with longtime sintering, results in an increase of the volume fraction of the high-T_c phase. They found zero-resistance temperature at 107 K in the sample with the nominal composition $Bi_{0.7} Pb_{0.3} SrCaCu_{1.8} O_x$ by using powders prepared by the coprecipitation method. The increased formation of the high T_c phase in the Pb-doped Bi-Sr-Ca-Cu-O system was also confirmed for samples prepared by conventional solid-state reaction[10,11] in the same nominal composition. We report here the observation of superconductivity with zero-resistance temperature at ~ 108 K and critical current density higher than 400 A/cm^2 at 77 K in the nominal composition $(Bi_{0.7} Pb_{0.3})_2 Sr_2 Ca_2 Cu_3 O_x$ prepared by using the polymeric precursor synthesis technique.[12,13] Dependence of the superconducting transition temperature, the critical current density, and the structural and magnetic properties on heat treatment time are systematically investigated.

Our Bi-Pb-Sr-Ca-Cu oxide samples were prepared from starting materials of $Bi_2 O_3$, $SrCO_3$, $CaCO_3$, CuO, and $Pb(NO_3)_2$ by procedures similar to those used previously in the preparation of bulk $YBa_2 Cu_3 O_{7-x}$ samples.[13] Briefly, after weighing out the high-purity starting materials to make a stoichiometric composition of $(Bi_{0.7} Pb_{0.3})_2 Sr_2 Ca_2 Cu_3 O_x$, $Bi_2 O_3$ and CuO were dissolved in dilute nitric acid solution at elevated temperature. $SrCO_3$, $CaCO_3$, $Pb(NO_3)_2$, and

citrate acid were then added into the solution. The water was evaporated from the solution in a rotary evaporator at 70–80 °C until a viscous liquid was obtained. This liquid was mixed with ethylene glycol and esterificated at about 130 °C until a glassy polymer formed. The fine powder was obtained by pyrolysis at 450 °C for 2 h and 700 °C for 10 h. The resulting powder was calcined at 800 °C for 10 h in an air flow. The calcined products were pulverized, cold pressed into pellets, and then sintered at 840 °C in a 10% O_2-90% Ar atmosphere. After sintering, the specimen was air quenched.

Electrical resistivity and critical current density were measured by the four-probe technique.[13,14] The x-ray powder diffraction measurements were performed by a Rigaku RAD-B diffractometer with Cu $K\alpha$ radiation. The magnetic properties of the pellets were characterized using a vibrating sample magnetometer. Rectangular blocks of approximate dimension $10 \times 1 \times 0.6$ mm^3 were suspended in the magnetometer. The external magnetic field was applied along the long axis of the samples.

Figure 1 shows the variation of ac resistivity with temperature for samples with different heat treatments. The measuring current was 1 mA. Samples (a), (b), (c), and (d) were sintered at 840 °C for 15, 30, 120, and 180 h, respectively. Each sample shows an approximately linear dependence on temperature from $T = 300$ K down to $T = 115$ K. A noticeable change in the slopes is observed in the vicinity of 110–115 K. This onset temperature of the superconducting transition is comparable to that of a Pb-free sample.[3–5] Around 110 K, the resistance begins to drop off more rapidly. Samples (a) and (b) show clearly a two-step transition shape and indicate the coexistence of the low- and the high-T_c phases. As the sintering time is increased, the two-step transition behavior is gradually removed and the zero-resistance temperature is increased. The resistivity of sample (d) falls below 0.5 $\mu\Omega$ cm at $T = 108$ K.

Figure 2 shows the characteristic curves of voltage versus current density at 77 K for the samples taken from the same pellets used for the resistivity measurements. The zero-field current density (J_c) increases as the sintering time in-
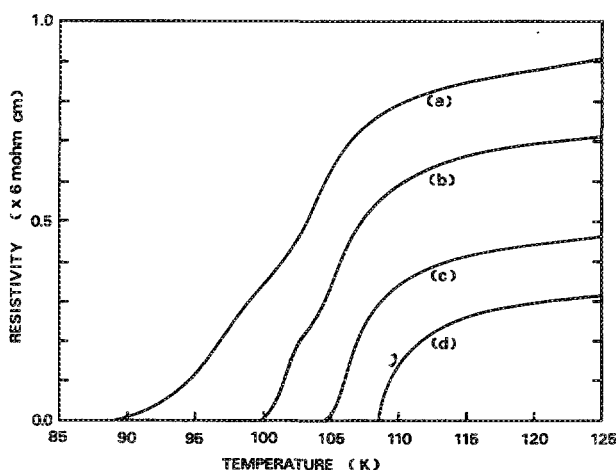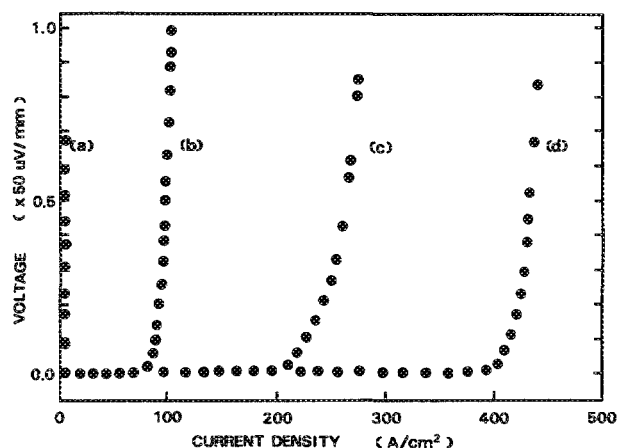

FIG. 2. Characteristic curves of voltage vs current density at 77 K. The samples were taken from the same specimen used for the resistivity measurements.

creases. The J_c value of sample (d) (403 A/cm^2) is much higher than that of a Pb-free sample[15] (~ 1 A/cm^2) and that of Pb-doped samples prepared by the conventional ceramic method.[10,11] It should be noted that the density of this sample is 3.8 g/cm^3, which is much lower than the value of ideal composition. Thus further improvement of critical current density is expected by densification.

Figure 3 shows powder x-ray diffraction (XRD) data for samples (a), (b), and (d). The open circles and the crosses indicate the peaks due to the high-T_c phase[8] and the low-T_c phase,[5] respectively. The majority of the superconducting phase in sample (a) is the low-T_c phase. But opposite structral features could be seen in samples (b), (c), and (d). It would be notable that our technique, compared to the

FIG. 1. Temperature dependence of the resistivity for $(Bi_{0.7}Pb_{0.3})_2Sr_2Ca_2Cu_3O_x$ samples sintered at 840 °C for (a) 15 h, (b) 30 h, (c) 120 h, and (d) 180 h.
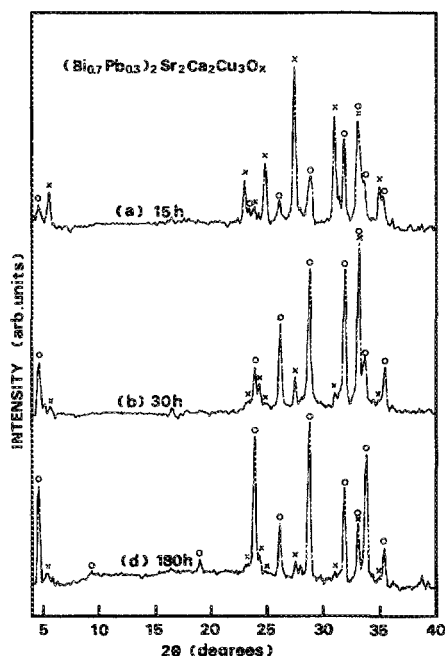

FIG. 3. X-ray diffraction data for samples sintered at 840 °C for various sintering times. Circles and crosses denote the peaks from the high- and low-T_c phases, respectively.
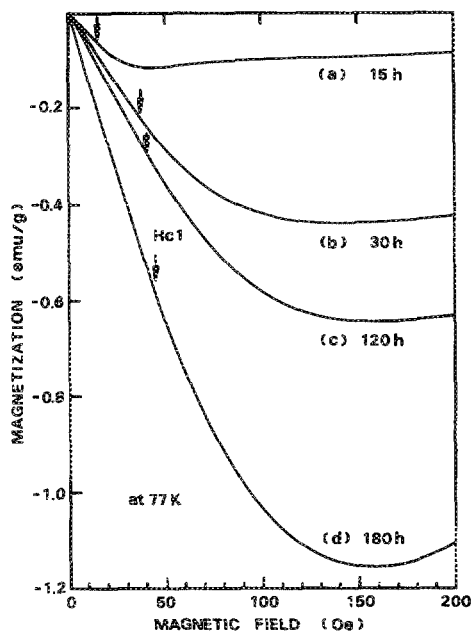
FIG. 4. Initial magnetization curves at 77 K for $(Bi_{0.7}Pb_{0.3})_2Sr_2Ca_2Cu_3O_x$ samples sintered for various sintering times.

conventional solid-state reaction technique, requires shorter heat treatment time to obtain a large amount of high-T_c phase in the Bi-Pb-Sr-Ca-Cu-O system as is seen in sample (b). As the sintering time is increased, the (002) peak intensity of the high-T_c phase at $2\theta = 4.7°$ increases, while the peak intensity at $2\theta = 5.8°$ corresponding to the (002) peak of the low-T_c phase decreases. This implies that the low-T_c phase is transformed into the high-T_c phase with increasing heat treatment time.

Sample (b) was sintered 2 times longer than sample (a). However, the critical current density of sample (b) is higher by two orders of magnitude than that $(0.6 A/cm^2)$ of sample (a). This result seems to be closely related with the structural difference between the two samples as is seen in Fig. 3. This can be understood by assuming that the critical critical current density of the high-T_c phase is much higher than that of the low-T_c phase at 77 K in the bulk specimen.

Figure 4 shows the initial magnetization curves of samples (a), (b), (c), and (d) at 77 K. The linearity between the diamagnetism and the magnetic field is maintained up to about 15 Oe for sample (a) and up to about 40 Oe for samples (b), (c), and (d). If the lower critical field H_{c1} is defined as the field where a deviation of the linear behavior in the initial magnetization curve is observed,[15,16] it would be inferred from Figs. 4 and 3 that H_{c1} of the high-T_c phase bulk specimen is higher than that of the low-T_c phase bulk specimen. However, further study on accurate measurement of H_{c1} seems to be needed because present specimens are not

single-phase materials. From the initial slope of the magnetization curve $(-4\pi M/H)$ below H_{c1}, the volume fraction of the superconducting phase of a sample can be estimated. When this technique is applied to the curves shown in Fig. 4, the volume fraction of the superconducting phase is increased with increasing heat treatment time, which is consistent with the XRD data.

In summary, we have observed the high-T_c superconductivity at 108 K and the critical current density higher than 400 A/cm^2 at 77 K in the bulk oxides with nominal composition $(Bi_{0.7}Pb_{0.3})_2Sr_2Ca_2Cu_3O_x$ prepared by using the polymeric precursor synthesis technique. The variations of the zero-resistance temperature, the critical current density, and magnetic properties are found to be closely related with the enhanced formation of the high-T_c phase with increasing the reaction time. The structural and magnetic properties of the Pb-doped specimens indicate that the low-T_c phase is transformed into the high-T_c phase, but further study on the reaction mechanism of forming the high-T_c phase is required to understand the role of Pb in the Bi-Pb-Sr-Ca-Cu-O system.

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