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Effect of lead substitution in bismuth-based cuprate systems containing both low-T_c and high-T_c phases

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We report the results of resistivity, ac-susceptibility, and specific-heat measurements carried out on samples of $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_{10+x}$ $(0 \le x \le 0.7)$ that were characterized by x-ray diffraction and high-resolution scanning tunneling microscopy. The zero resistance temperature, T_c $(R=0)$, shows a peak at $x=0.3$ and the susceptibility data indicate that although a high-T_c 2:2:2:3 phase is present at 110 K, there is a second transition at 90 K that seems to indicate the existence of an additional low-T_c 2:1:2:2 phase. The specific-heat data unambiguously indicate a clear and distinct anomaly around T_c for samples with $x=0.3$–0.4 and smearing of the anomaly for $x>0.5$. Based on the results obtained from these combinations of experiments, the role of lead substitution in Bi samples, particularly in the stabilization of the 2:2:2:3 phase has been discussed.

I. INTRODUCTION

Since the discovery of high-temperature superconductivity in the Bi-Sr-Ca-Cu-O system, a wide variety of methods for the synthesis has been explored to stabilize the 2:2:2:3 phase.[1,2] Considering the difficulty in the formation of a 2:2:2:3 phase from the stoichiometric composition, the substitution of lead (Pb) in place of bismuth (Bi) has been suggested.[3,4] Although it is known that the mismatch of the valence state (Bi^{3+}/Pb^{2+}) produces a change in the electron density and thereby the superconducting properties, the role of Pb in the formation and stability of the high-T_c phase is not clearly understood. The chemical measurements show that Pb substitution is connected with the oxygen partial pressure,[5] while the high-resolution STM-STS studies have revealed that Pb substitution at the Bi site produces depletion of the excess oxygen, thereby improving the metalicity of the Bi-O layer.[6]

The specific-heat measurements, however, report either a distinct anomaly or a broad hump in the vicinity of T_c.[7] This anomaly has been observed in both pure and also Pb substituted samples and although this anomaly is comparatively weak, it is essentially analogous to what has been observed in Y 1:2:3.[7–14] The broad hump that is depicted by a gradual change in the slope of the specific-heat curve, has been attributed to intrinsic fluctuations, which are assumed to be inherently present in the system.[15,16] The Ginzburg-Landau coherence length in these high-temperature superconductors being extremely low (10 Å),[17] the unusual shape of the specific-heat anomaly may be due to inhomogeneous broadening by sample imperfections or inherent fluctuation.[18] As discussed, sample inhomogeneities may arise due to the intermixing of 2:2:2:3 and 2:1:2:2 phases in the multiphase Bi system. Thus a systematic study of formation of 2:2:2:3 phase in $(Bi)_{2-x}Pb_xSr_2Ca_2Cu_3O_{10+y}$ is considered to be important. Interestingly, the distinct anomaly in specific heat ($\Delta C/T_c = 49.5$ mJ/mol K^2) or sharp transitions in magnetic susceptibility have been observed in those samples where x always lies around 0.4.[8,19] Rhee *et al.*,[4] Zhu *et al.*,[20] and Liu *et al.*[21] have reported that the superconducting transition becomes pronounced and reproducible [maximum $T_c(R=0)$] for the samples again for which x is within 0.3–0.4. Yu *et al.*[14] have shown that when these phases are properly formed, multiple but clear specific-heat jumps at each transition temperature of the corresponding phases can be observed.

It is in this context that we report a systematic study of the specific heat and the magnetic susceptibility of the Pb substituted multiphase high-quality polycrystalline samples of Bi-Sr-Ca-Cu-O systems to understand the mechanism of formation of the high-T_c phase.

II. EXPERIMENTAL DETAILS

The bulk polycrystalline samples of nominal composition $(Bi)_{2-x}Pb_xSr_2Ca_2Cu_3O_{10+x}$ $(0 \le x \le 0.7)$ were prepared using the starting ingredients of purity 99.99% and following the usual procedure.[6,4] The different samples prepared are designated as BSCCO-*P* (Pure) and BSCCO-*X* [where $X=1$–7] corresponding to the Pb contents of $x=0$–0.7, respectively. The characterization of the samples for phase purities was carried out by x-ray diffraction (XRD), using a Siemens D-500 diffractometer with Cu-K_α radiation. The conventional four-probe technique was used for studying the resistive transitions of the samples. The ac magnetic susceptibility was measured by a Lakeshore 7000 susceptometer. The sample was cooled in a low field of 2.513 Oe [rms], frequency 166.7 Hz superimposed with a dc field of 1 Oe through its transition temperature (T_c) and X' and X'' were measured while warming up slowly. A suitable demagnetization factor for each sample taken from the instrument manual was used to calculate the absolute value of susceptibility. The specific heat was measured by a fully automated quasiadiabatic calorimeter, where the instrument controlling and data acquisition were carried out

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through a Hewlett-Packard HP 9332 model computer. The sample holder was a sapphire block (diameter is 8 mm), PTR100 was used as thermometer, and the heating element was made from NiCr film deposited on a thin sapphire plate.[22] Silicon diodes were used to monitor and control the temperature of the thermal shield through a temperature controller (Lakeshore 91C). The specific heat of the sample was obtained by subtracting the heat capacity of the addenda consisting of a sapphire block, a heating element, and apiezon *N* grease, etc.; oxygen free high conductivity copper was used for calibration, and it turns out that the absolute error in the specific-heat measurement is estimated to be less than 1%. The details of the measuring set up and the calibration procedure of the instrument will be published elsewhere.[23]

III. RESULTS

A. XRD results

Figure 1 shows the XRD patterns for three samples BSCCO-*P*, BSCCO-3, and BSCCO-4 (the rest are not shown). Lines corresponding to the 2:2:2:3 phase are represented by *H*, while those of 2:1:2:2 phase are denoted by *L*. The characteristic peaks of *H* at (002) ($2\theta=4.9$) and (00$\underline{10}$) at ($2\theta=24$), etc., are observed in all the samples. The representative "*L*" line at (00$\underline{20}$) is found to be present apart from (200) in all the samples. Therefore, except in BSCCO-*P*, both the phases are present in these samples, and the predominant phase is "*H*." It may be pointed out that the peaks corresponding to the unreacted lead have not been observed. A few higher-angle peaks (other than Pb) in the samples BSCCO-6 and BSCCO-7 have appeared, which cannot be indexed. The lattice parameters are calculated by taking all the important peaks for 2:2:2:3 and 2:1:2:2 phases taking the tetragonal *Fnnn* structure. Figure 2 shows the lattice parameter *c* of the 2:2:2:3 phase as a function of *x*, the BSCCO-*P* data have not been included as they are mostly dominated by the 2:1:2:2 phase (Fig. 1). Figure 2 also shows the *c* of the 2:1:2:2 phase, and comparison of both these *c*'s with that of Rhee *et al.*[4] It is clear that *c* of 2:2:2:3 phase increases with *x* up to 0.4 and then almost

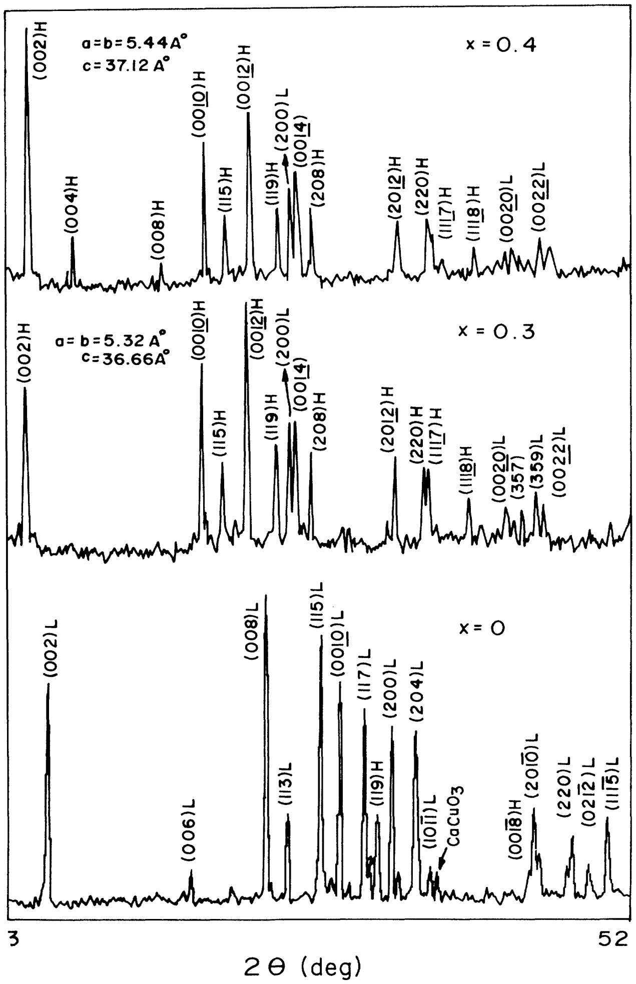

FIG. 1. XRD patterns for the samples BSCCO-*P*, BSCCO-3, and BSCCO-4.

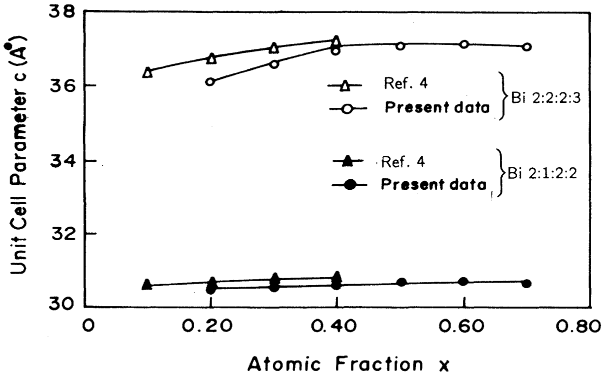

FIG. 2. *c* as a function of atomic fraction (*x*).

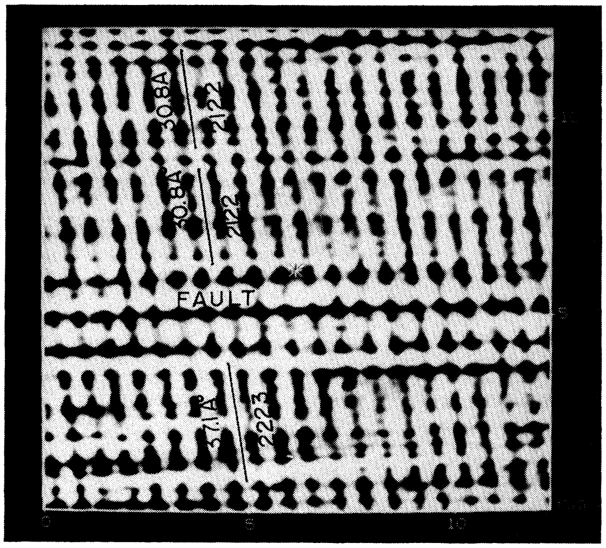

FIG. 3. Intergrowth in Bi 2:2:2:3 showing a single unit cell of Bi 2:2:2:3, a faulted region at the Bi-O interface, and two unit cells of Bi 2:1:2:2; a top view scan 12 nm × 12 nm.

saturates with x, which is in agreement with Rhee *et al.*[4] As far as the c of the 2:1:2:2 phase is concerned, Rhee *et al.*,[4] Boekholt *et al.*,[24] and our observation indicate that c of the 2:1:2:2 phase is also increasing with the Pb substitution; however, the decrease of c of 2:1:2:2 phase is also reported.[21]

B. STM description

The simultaneous existence of both well-formed phases in BSCCO-4 sample can be seen in the high-resolution STM image, obtained perpendicular to the c direction of the unit cell, shown in Fig. 3. The clear molecular stacks of the 2:2:2:3 and 2:1:2:2 phases with c parameters 37.1 Å and 30.8 Å, respectively, are seen in the figure. The micrograph also shows the unit cells of these phases and their separation by a faulted region of Bi-O interface.

C. Resistivity

Figure 4 shows the normalized resistance as a function of temperature in the samples $0 \le x \le 0.7$, T_c (onset) and T_c $(R = 0)$ are also shown. Interestingly, a systematic increase in both the T_c (onset) and T_c $(R = 0)$ has been observed with the increase in x up to $x = 0.3$, and then, although T_c (onset) remains in the vicinity of 115 K, T_c $(R = 0)$ starts decreasing with a further increase in Pb. The highest T_c $(R = 0)$ at 110 K is obtained for the BSCCO-3 sample with minimum width of resistive transition (within 5 K). Thereafter, this width is slowly increasing with the increase and/or decrease in x. Figure 5 shows the obtained T_c $(R = 0)$ for all the samples with a comparison of the reported T_c values of Ref. 20. A peak in T_c $(R = 0)$ at $x = 0.3$ has been observed in both the reports with a decrease in T_c $(R = 0)$ for the further increase and/or decrease in x.

D. ac susceptibility

Figure 6 shows the results of susceptibility $(X = X - iX'')$ measurements in the temperature range 77–130 K for the four samples BSCCO-3, BSCCO-4, BSCCO-6, and BSCCO-7. From X' versus T curves in Fig. 6, it is seen that the flux expulsion starts at 108.5 K in all the samples. However, for BSCCO-3 and BSCCO-4 (even in BSCCO-5), there is a second transition in X' at lower temperature of about 90 K, and also for these samples X'' exhibits a peak just below this second transition temperature, while in BSCCO-6 and BSCCO-7, X' shows only one transition at 108.5 K, the second transition in X' and the corresponding peak in X'' are not observed down to 77 K. It is possible that the X'' peak of these samples get shifted to temperatures below 77 K. This may imply that transition in X' may occur at temperature much below 77 K in these samples (BSCCO-6 and BSCCO-7). The transition in X' at 108.5 K in all the samples BSCCO-3, BSCCO-4, BSCCO-6, and BSCCO-7 confirms the presence of a high-T_c phase (2:2:2:3), which is evident from the XRD patterns also. In the samples BSCCO-3 and BSCCO-4, the second transition in X' curves at about 90 K and the peaks in the X'' curve just below 90 K indicate the presence of a low-T_c phase in these samples and also the occurrence of the intergranular coupling in this phase. In the samples BSCCO-6 and BSCCO-7

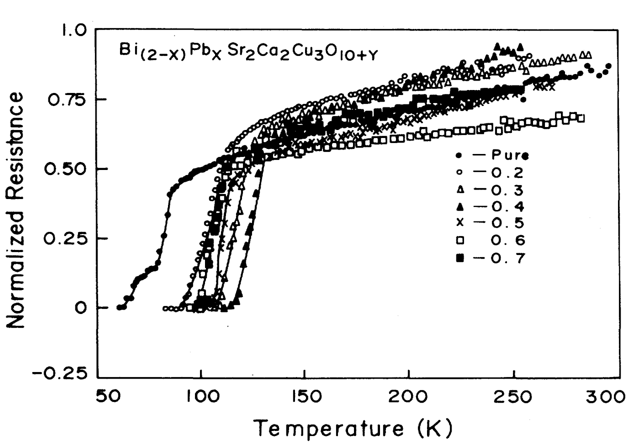

FIG. 4. Normalized resistance vs temperature curves for BSCCO-*P*, BSCCO-2, BSCCO-3, BSCCO-4, BSCCO-5, BSCCO-6, and BSCCO-7.

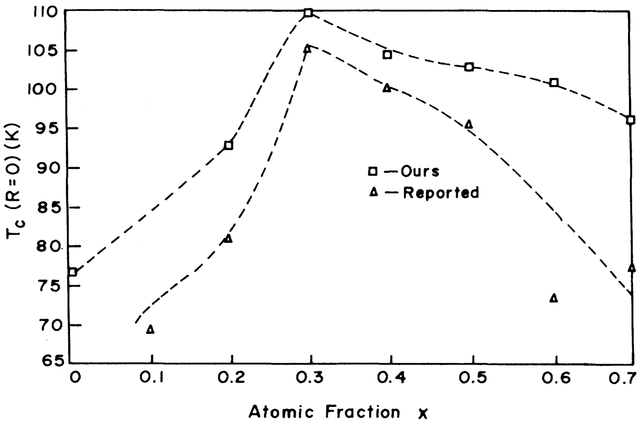

FIG. 5. $T_c(R = 0)$ as a function of the atomic fraction (x) of Pb in Bi 2:2:2:3 and compared with the reported data of Zhu *et al.* (Ref. 20).

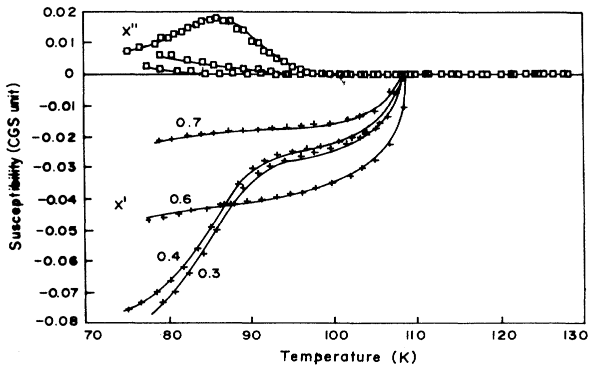

FIG. 6. ac susceptibility vs temperature curves for BSCCO-3, BSCCO-4, BSCCO-6, and BSCCO-7.

there is no transition in X' at 90 K, and, as pointed out earlier, this transition probably gets shifted to below 77 K. This suggests that an increase in Pb content of the samples beyond $x=0.4$ drastically affects the superconducting properties of the 2:1:2:2 phase, whereas the 2:2:2:3 phase seems to be relatively less affected.

As reported,[25–30] the susceptibility and magnetization data are difficult to interpret as the percentage of full diamagnetism observed in field-cooled experiments (Meissner fraction) is dependent on other factors such as external field, sample size, and perfection, bearing little relation to the proportion of the superconductor present in the sample. Moreover, it may also be possible that the relative change in the diamagnetic signal could also reflect an improvement in the superconductivity at the grain boundaries or a better connection of superconducting paths in the sample. However, as mentioned, the measurements were carried out under field-cooled and identical conditions on different samples; the diamagnetic amplitudes at a particular temperature, in the first approximation, can be considered as a qualitative measure of the amount of the superconducting phase at that temperature.

The approximate estimation of the relative volume fractions of the superconducting phase in the samples can be carried out following the method in Ref. 31. The susceptibility data of the samples in Fig. 6 have been expressed in terms of relative susceptibilities and shown in Figs. 7 and 8. In each case the values of X' and X'' have been normalized with respect to the sample weight and with reference to X' and X'' of BSCCO-3. From Figs. 7 and 8 it is seen that the diamagnetic amplitude of the sample above 90 K, that is, above the transition temperature of the 2:1:2:2 phase, decreases as the Pb content of the sample is increased from $x=0.3$, thereby implying that the volume fraction above 90 K of the high-T_c (2:2:2:3) phase decreases in the samples containing higher Pb concentration. It is also observed from the values of X' (relative) in Fig. 7 at 77 K, the relative volume fractions (compared to that in sample BSCCO-3) of the total superconducting phase (2:1:2:2 + 2:2:2:3) are 75%, 50%, and 30% for the samples BSCCO-4, BSCCO-6, and BSCCO-7, respectively. This implies if (2:1:2:2 + 2:2:2:3) of BSCCO-3 is 80%, in BSCCO-4 it is 60%, and so on. It is therefore evident that with an increase in Pb content ($x>0.3$) the total volume of the superconducting phase in the sample decreases. It may be mentioned here that in the case of BSCCO-6 ($x=0.6$), the diamagnetic signal above 90 K is more than in the sample $x=0.3$ and 0.4. This is because we were not able to estimate the sample volume and demagnetization correction factor for this sample. However, as evident from Figs. 6 and 7 even for this sample the total superconducting volume at 77 K is less than for the samples with Pb concentration $x=0.3$ and 0.4.

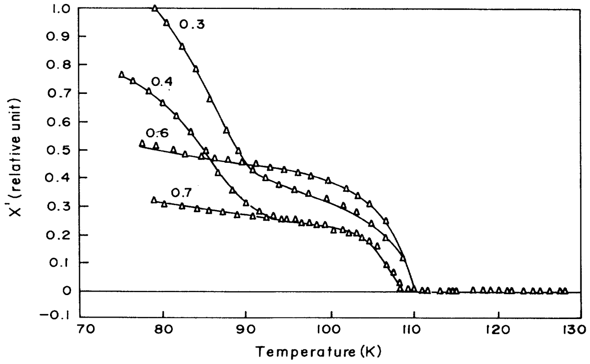

FIG. 7. Estimated X' (relative) vs temperature for BSCCO-3, BSCCO-4, BSCCO-6, and BSCCO-7.

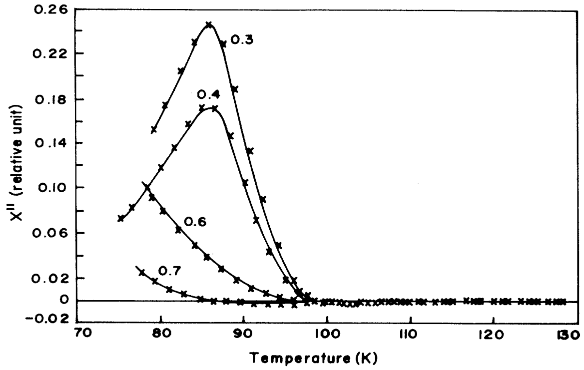

FIG. 8. Estimated X'' (relative) vs temperature for BSCCO-3, BSCCO-4, BSCCO-6, and BSCCO-7.

E. Specific heat

It is to be mentioned here although we have studied in the temperature range 300–77 K, we concentrate here on the data at temperature closer to T_c. Figure 9 shows the calculated molar specific heat of the samples BSCCO-3 and BSCCO-4. A distinct and clear specific-heat anomaly can be seen at 92 K for these samples. Figure 10 shows the molar specific heat data of the samples BSCCO-6 and BSCCO-7. It can be seen that the specific anomaly, which is observed for the samples BSCCO-3 and BSCCO-4, is not observed in BSCCO-6 and BSCC0-7. A little fluctuation in data was observed for these samples

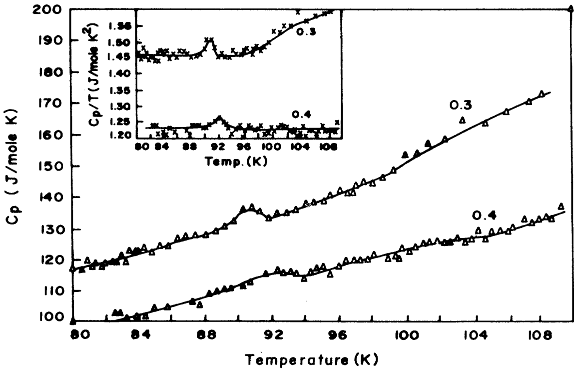

FIG. 9. Molar specific heat (Cp) vs temperature (T) curves for BSCCO-3 and BSCCO-4; the inset shows Cp/T with T for these samples.

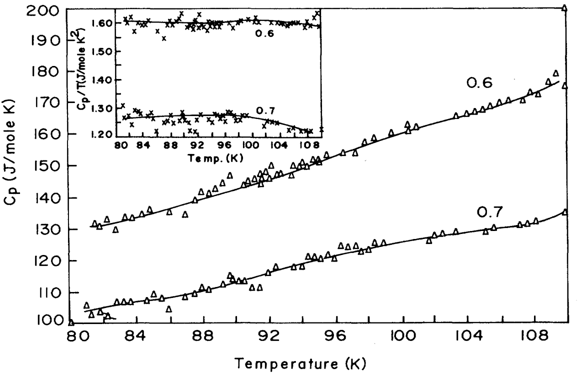

FIG. 10. Molar specific heat (Cp) vs temperature (T) curves for BSCCO-6 and BSCCO-7; the inset shows Cp/T with T for these samples.

[BSCCO-6 and BSCCO-7] in the vicinity of the transition temperature although all these experiments were carried out in an identical condition. This can be further cleared by plotting Cp/T versus T for these samples, which are shown in the inset of Figs. 9 and 10 and the observed transition at 89 and 92 K for the samples BSCCO-3 and BSCCO-4 is in agreement with others.[7] The specific-heat jump, which is associated with bulk superconducting properties, turns out to be for the samples BSCCO-3 and BSCCO-4, 4.8 and 3.2 J/mol K, respectively. The estimated $\Delta Cp/T_c$ for these samples is 54 and 35 mJ/mol K^{-2}, respectively, and these agree well with the published data.[7,9-11] The characteristic parameters, like the Sommerfeld constant (γ) or Debye temperature (Θ_D), are difficult to estimate in these oxide superconductors because the electronic contribution of specific heat in the specific-heat anomaly is strongly affected by the phononic contribution.[22] The basic difficulty is that at this high-temperature phononic contribution cannot be measured independently through suppression of superconductivity by using a high magnetic field or creating enormous disorder by irradiation. Moreover, the coexistence of multiple phases complicates phonon density of states and the application of the mean-field approximation is difficult. However, in order to indicate the possible trend in the nature of coupling, Sommerfeld constant (γ) was estimated in a first-order approximation from the susceptibility experiment.[32,9] The molar susceptibility as a function of temperature for BSCCO-3 and BSCCO-4 shows that the temperature-dependent susceptibility does not vary with the temperature and can be fitted to $X(T)=X_0+[C/(T+\theta)]$. The obtained value for this sample is $X_0=1.75\times10^{-4}$ emu/mol, $C=0.124$ and $\theta=210$ K. In the nearly-free-electron model, γ is proportional to the Pauli susceptibility (X_p), and the ratio of γ is given by Wilson's ratio, $\gamma/X_p=[\pi k_b/\mu_B]^2/3$. After correcting the temperature-independent susceptibility X_0 for the diamagnetic core and Landau contributions in the usual way, we obtain γ for BSCCO-3 48 mJ/mol K. The reported values of γ in these systems are lying in the range 10–50 mJ/mol K (Refs. 32 and 33), and our rough value falls within this region. Similarly, the Debye temperature is calculated from the specific-heat data at all temperatures using the theoretical Debye function on the assumption that the three-dimensional Debye model is valid in this system. An iterative method has been developed to obtain the best-fitted value. The obtained Debye temperatures are found to be temperature dependent, and the average value of the Debye temperature around the transition temperature is found to be 400 K and 350 K for BSCCO-3 and BSCCO-4, respectively. These values seem to agree well with the earlier reported data.[9]

III. DISCUSSION

The results from these combinations of experiments indicate two distinct types of behavior, (i) in the region of Pb content $x \leq 0.4$ and (ii) for $x>0.4$. $T_c(R=0)$ from the resistivity measurement, the flux exclusion onset temperature from susceptibility and the anomaly observed in the specific-heat indicate that a Pb substitution of $x \leq 0.4$ stabilizes the superconducting phase consisting of both high-T_c and low-T_c fractions. However, when x is beyond 0.4, the absence of the second transition in X' and also the specific-heat anomaly at 90 K suggests that the overall proportion of the superconducting phase in the sample diminishes as a result of the decrease of both 2:2:2:3 and 2:1:2:2 phases in the system.

As mentioned, trivalent Bi^{3+} is having an ionic radius 1.03 Å, while the divalent Pb^{2+} is 1.19 Å. Hence, the substitution of Bi^{3+} with larger ionic radius Pb^{2+} results in the increase in c parameter as is substantiated through XRD measurements. Therefore the saturation of c for the samples with Pb content >0.4 suggests two possibilities (i) without being substituted as Pb^{2+} at Bi^{3+} sites, Pb remains unreacted in the system and (ii) Pb may substitute in tetravalent state Pb^{4+} [where the ionic radius is 0.84 Å at Ca^{2+} site (the ionic radius 0.99 Å)]. As we have not observed any line corresponding to the unreacted Pb in the XRD patterns, the first possibility of unreacted lead in the system may be ruled out. The second possibility seems to suggest that c should decrease with x when Pb content of the sample is more than $x=0.4$, which is also not observed in the present case. Therefore, from the crystallographic point of view, it is conjectured that beyond the concentration of $x=0.4$ Pb partially substitutes at the Bi^{3+} site in the Pb^{2+} state and partially at the Ca^{2+} site in Pb^{4+} state. Since the Pb substitution at these two different sites have opposite effects on c, there is no overall significant change in the value of c of the samples when Pb content increases above $x=0.4$. A similar possibility of Pb getting substituted as Pb^{4+} in Ca^{2+} sites in Bi 2:2:2:3 has been discussed from neutron-diffraction experiments by Sastry *et al.*[34] and Miehe *et al.*[35] As far as the change in c of 2:1:2:2 phase is concerned ($x=0.4$), it seems that it increases with substitution of Pb, which agrees well with the findings of Boekholt *et al.*[24] Thus at the initial level of substitution Pb^{2+}/Bi^{3+} site, the number of hole carriers increases resulting in an increase in conductivity in the Bi-O layer, which is evident from Fig. 5 (an increase in T_c of the sample up to $x=0.4$). However, for $x>0.4$; (i) the first process yields an increase in the number of hole carriers and (ii) the second process results a decrease in carrier concentration. This decrease is very rapid compared to the increase in the first process, and as a result there is a decrease in $T_c(R=0)$, an increase in transition width, and also a reduction in the superconducting volume fractions, which may smear off specific-heat anomaly.

From the specific-heat measurement one can obtain the BCS weak-coupling limit from the expression $\Delta C/\gamma f T_c$, where f is the volume fraction of the superconducting phases. We assume the Sommerfeld constant, which is shown to be 48 mJ/mol K^2 and does not change appreciably for these two samples, BSCCO-3 and BSCCO-4. In the susceptibility measurement the volume fraction of the superconducting phases is shown to be roughly 80% and 60% at 77 K for the samples BSCCO-3 and BSCCO-4, respectively. The calculated value of $\Delta C/\gamma f T_c$ is obtained as 1.40 and 1.21 for BSCCO-3 and BSCCO-4, respectively, which are within the limit of the weak-coupling BCS value of 1.43. On the other hand, tunneling experiments have shown that most of the high-T_c superconductors are strongly coupled,[36] and consequently the present findings are in variance with such a contention. It needs to be pointed out that the point-contact tunneling experiment, especially when carried out on the cuprate superconductors, suffers from the general disadvantage due to the local presence of nonstoichiometric composition or the presence of oxide layer. The present results corroborate weak-coupling nature of this material, which is also substantiated by various other methods, mainly specific-heat measurements.[15]

Therefore, the specific-heat and magnetic-susceptibility measurements seem to indicate that distinct properties like specific-heat anomaly or the flux expulsion due to the Meissner effect are observable only when the sample contains a substantial amount of the volume fraction of the desired phase. However, as has been observed by others,[11,12] we find also that a 2:2:2:3 phase does not form a dense interpenetrating network; as a result it does not expel all the flux present in the sample and would allow the detection of the 2:1:2:2 phase, while 2:1:2:2 phase forms a network easily, and this may result in the screening of the minority phase. Although the exact contribution of fluctuations of the order parameter has not been evaluated, the clear specific-heat anomaly clearly shows that the nature of superconducting transition in BSCCO-3 and/or BSCCO-4 is similar to that of other observed systems.[14]

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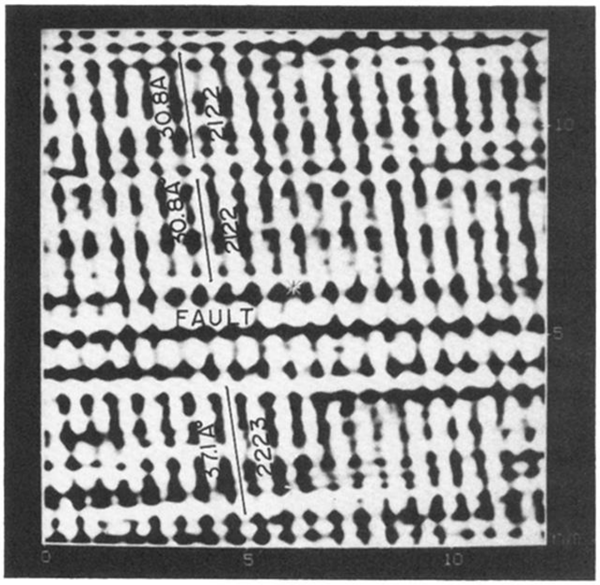

FIG. 3. Intergrowth in Bi 2:2:2:3 showing a single unit cell of Bi 2:2:2:3, a faulted region at the Bi-O interface, and two unit cells of Bi 2:1:2:2; a top view scan 12 nm × 12 nm.