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Superconductivity in Pr- and Ce-doped $Bi_2CaSr_2Cu_2O_y$ systems

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We report here a systematic study of Pr and Ce doping (at the Ca site) in $Bi_2CaSr_2Cu_2O_y$. For both Pr and Ce substitutions T_c decreases with the dopant concentration. Results are interpreted in terms of the hole filling due to aliovalent substitution in the system. At a higher doping level a metal-insulator transition is observed. Near the transition the localization length (α^{-1}) is calculated and the possibility of having local pairs in the insulating phase is invoked. Around the transition region a dimensional changeover from two to three dimensions is observed in the variable-range hopping (VRH) regime and its consequence on superconductivity is discussed. The lattice parameters have been estimated through x-ray diffractometry and the possibility of Pr and Ce existing in more than the 3+ oxidation state in the system is inferred. Results are also compared with the existing data on other rare-earth dopings (at the Ca site) in the same system.

INTRODUCTION

In all high-temperature CuO-based superconductors the phase diagram is such that these materials behave like Mott-Hubbard insulators in the low-carrier-concentration region and superconductors in the intermediate range, while in the heavily doped region they are normal-metal-like.$^{1-4}$ In general, the three types of behavior viz. metallic, superconducting, or semiconducting, can be brought about easily in a high-T_c superconductor. Different aliovalent substitutions or changes in the oxygen stoichiometry can effectively alter the concentration of carriers in the system, resulting in a metal-to-insulator (M-I) behavior for these materials.$^{5-7}$ In the case of both La-based 2:1:4 systems and rare-earth (R)-based 1:2:3 systems, various aliovalent substitutions at both Cu and non-Cu sites and the variation in oxygen stoichiometry in terms of carrier-concentration changes have been studied extensively.[8,9] While in the case of Bi- and Tl-based high-T_c superconductors, only a few aliovalent substitutions have been studied and as a result the occurrence of the M-I transition is reported only scantily.$^{10-12}$ The Ca-R or Sr-R substitutions have been found to be more feasible in both Bi- and Tl-based superconductors as the crystal structure of the parent system remains invariant with these substitutions even though a significant change in the carrier concentration is effected due to 2+ to 3+ cation doping.[10] Hence to bring about the metal-to-insulator transition in Bi- and Tl-based superconductors rare-earth substitutions seem to be the right choice.

Insofar as R-based 1:2:3 compounds are concerned Pr, Ce, and Tb present an interesting situation as they do not show superconductivity, unlike other rare-earth metals,[13,14] with their complete replacement at Y site. The complete Pr-substitution case is still more complex as it is also isostructural with 1:2:3 perovskite structure, unlike Ce and Tb, where only multiphases are seen. These substitutions have been tried in both R-based 1:2:3 and 1:2:4 systems and the depression of T_c has been explained in more than one way, such as either a hole-filling mechanism (based on their existence in the structure as tetravalent[15,16]), or by the localization of the mobile holes (considering Pr to be in a trivalent state[17]), or by the pair-breaking effects due to their magnetic moments.[18,19] There are contradictory reports about their 3+ and 4+ valence states in the compound. Strictly, the valence state of Ce, Pr, and Tb in these materials is still a challenging problem to be understood properly.

In this paper we have studied the M-I transition in the $Bi_2CaSr_2Cu_2O_y$ (Bi 2:1:2:2) system through Pr and Ce substitutions at the Ca site. We could find, to our knowledge, only one report each on Ce (Ref. 20) and Pr (Ref. 21) dopings in the Bi 2:1:2:2 system. Also, because the cause of T_c depression due to Pr and Ce in 1:2:3 and 1:2:4 systems is not yet clear, we present here another system with Pr and Ce doping which is isostructural to the parent system, at least up to 50 at. % doping level, to elucidate the situation. Such a study is expected to provide some understanding on the valence state of Ce and Pr in the Bi 2:1:2:2 system.

There seems to be no consensus on what is the mechanism operating in the layered high-T_c superconductors. Several models emphasize the BCS type of pairing mechanism to be responsible for high T_c in these materials. From our studies of electronic properties in substituted and/or oxygen-deficient materials, we observe clearly the onset of superconductivity at the verge of the insulator-metal transition. This poses difficulty in understanding the mechanism within the BCS framework. In this paper we argue how the degree of localization could possibly influence the appearance of superconductivity as in dirty or bad metals. In the phase of small carrier concentration where disorder has an important role in localizing the electronic states, interelectronic correlation appears to be strong. The semi-conductor-like behavior in this

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phase is in contrast with the Mott-Hubbard or charge-transfer insulating phase. From our studies we wish to raise some basic issues on how to understand pairing for the low-T_c phase in the small carrier region in terms of localization and interaction.

EXPERIMENTAL DETAILS

The samples of $Bi_2Ca_{1-x}M_xSr_2Cu_2O_8$ (M =Pr and Ce) for $0 \leq x \leq 0.5$ were prepared by solid-state reaction of appropriate quantities of metal oxides and carbonates with purity better than 4*N*. The calcination was carried out at 820, 830, and 840 °C each for 12 h followed by furnace cooling to room temperature with intermediate grindings. Reacted materials were pulverized and cold pressed into three sets of rectangular bars suitable for resistivity measurements. In the final reaction samples were brought to partially molten state at temperatures between 930 and 980 °C depending on the x value, and then reacted at 860 °C in air for 12 h and quenched to room temperature. The details of the technique are described elsewhere.[22] The samples were characterized by the powder x-ray diffractometry using Cu $K\alpha$ radiation. Dc resistivity of the rectangular-shaped samples was obtained in the temperature range 4.2–300 K by the conventional four-probe technique. The temperature of the sample was monitored using a standard platinum resistance thermometer of 100 ohms in conjunction with the Keithley 195A digital multimeter with an accuracy of ±0.1 K in the temperature range of 70–300 K. A liquid-He cryostat with a carbon glass resistance temperature sensor was used for the temperature range of 4.2–70 K. The entire measurement system, comprising of nanovoltmeter, constant current source, and temperature controller and indicator, was hooked onto a IBM PC/AT system for automatic data acquisition and control.

RESULTS AND DISCUSSION

The x-ray-diffraction patterns of the Pr- and Ce-doped Bi 2:1:2:2 system are shown in Figs. 1(a), 1(b), and 1(c)

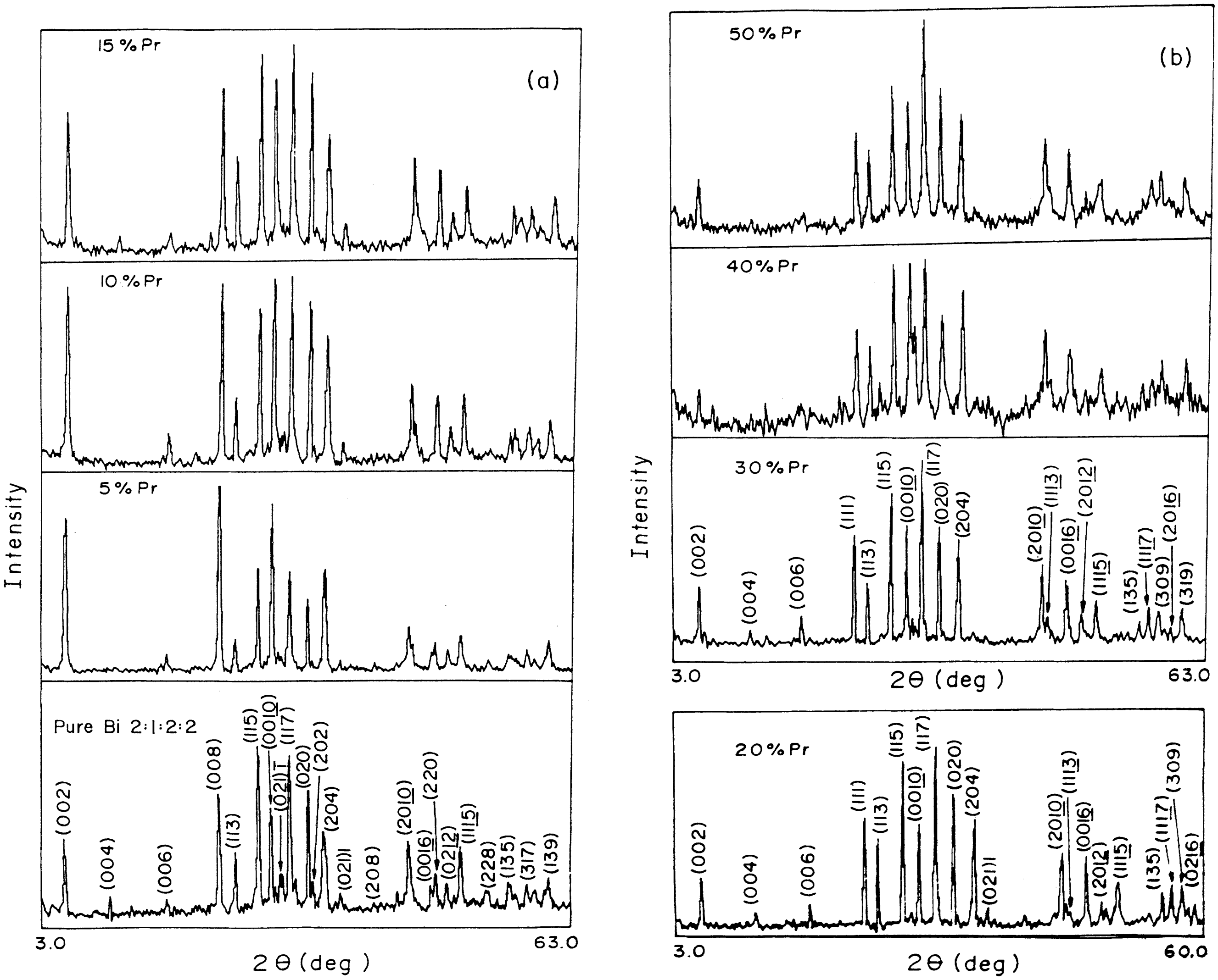

FIG. 1. (a) XRD patterns of $Bi_2Ca_{1-x}Pr_xSr_2Cu_2O_8$ samples with ($0 \leq x \leq 0.15$). (b) XRD patterns of $Bi_2Ca_{1-x}Pr_xSr_2Cu_2O_8$ samples with ($0.20 \leq x \leq 0.50$). (c) XRD patterns of $Bi_2Ca_{1-x}Ce_xSr_2Cu_2O_8$ samples with ($0.10 \leq x \leq 0.40$).

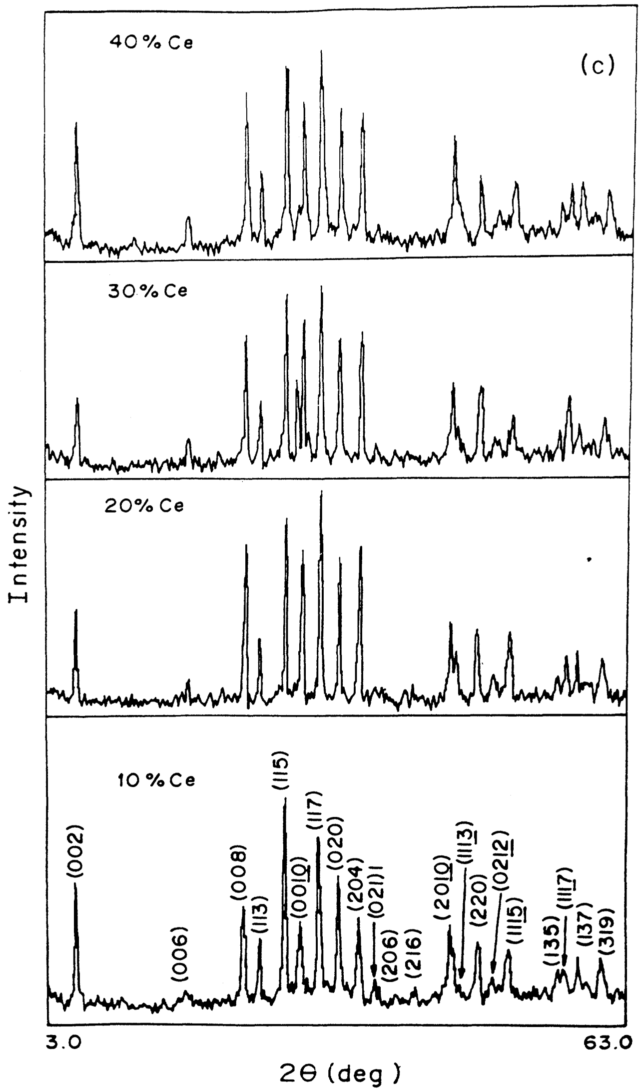

FIG. 1. (*Continued*).

with increasing dopant concentration x. All the samples exhibit a single-phase nature with small orthorhombicity as reported earlier.[23] The lattice parameters obtained for pure sample are also in good agreement with the reported values.[10] The variation of lattice parameters with x (dopant concentration) is depicted in Fig. 2. The c parameter decreases monotonically for both Ce and Pr substitutions at the Ca site in the system. Such a decrease in c parameter may be a consequence of either the increase in the oxygen content due to higher valence cation substitution or due to lower ionic size of the substituent ion than Ca, existing in the same eightfold coordination in the system. Decrease in the c parameter emanating from the increase in the oxygen content as a result of either treating the compound in the reducing atmosphere or by rare-earth ion substitution at the Ca site has been reported by several workers.[24–27] As far as the ionic sizes are concerned, the eightfold coordinated ionic radii of Ce^{3+} and Ce^{4+} are 1.143 Å and 0.97 Å, while for Ca^{2+} it is 1.12 Å, indicating that Ce exists in the system either in trivalent state or at least in between 3+ and 4+ valence states. In the case of Pr also, the decrease in c parameter may be attributed to the incorporation of both eightfold coordinated Pr^{4+} (0.96 Å) and Pr^{3+} (1.126 Å) at Ca site. The a and b parameters exhibit very little change (decrease) with the doping level x. In some reports an increase in the a parameter is indicated,[28] which has been ascribed to the change in the planar Cu-O bond distance due to hole filling in the system. The possibility of increments in a parameter with Ca R substitution in the Bi 2:1:2:2 system has already been discussed and discarded in this system.[29]

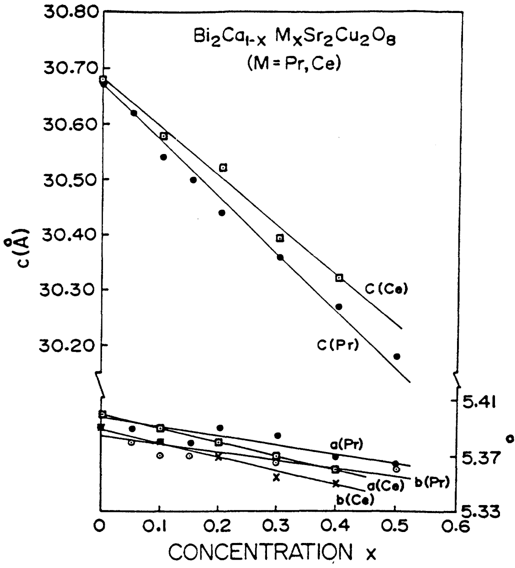

FIG. 2. Variation of lattice parameters a, b, and c vs dopant concentration.

Figures 3 and 4 depict the resistivity-versus-temperature behavior of the Bi 2:1:2:2 system with Pr and Ce doping (at Ca site) up to the 50 at. % level. The normal-state resistivity ρ_n for the samples measured at 300 K increases linearly with the doping concentration for low x values and rises sharply (nearly exponential) for higher doping levels. The increase of ρ_n with doping seems to show that the system enters the variable-range hopping (VRH) regime at higher dopant concentrations, indicating a metal-insulator-like transition in the system.

$T_c(R=0)$ for a pure Bi 2:1:2:2 ($x=0$) sample is found to be around 90 K. Figures 3 and 4 show that $T_c(R=0)$ decreases gradually with the increase of either Pr or Ce doping in the system. In Pr-doped samples, $T_c(R=0)$ state is observed until 30 at. % of doping level, and only T_c onset is observed near 44 K in 40 at. % doped sample. The sample with 50 at. % Pr substitution exhibits nonsuperconducting behavior. Here we examine what is the nature of the insulating phase. Is it like a strongly correlated Mott-Hubbard or charge-transfer insulator or like a doped semiconductor having variable-range hopping of the electronic states with weak or no electronic correlation? For both 40 and 50 at. % doped systems normal-state resistivity behavior could be fitted well with the expression

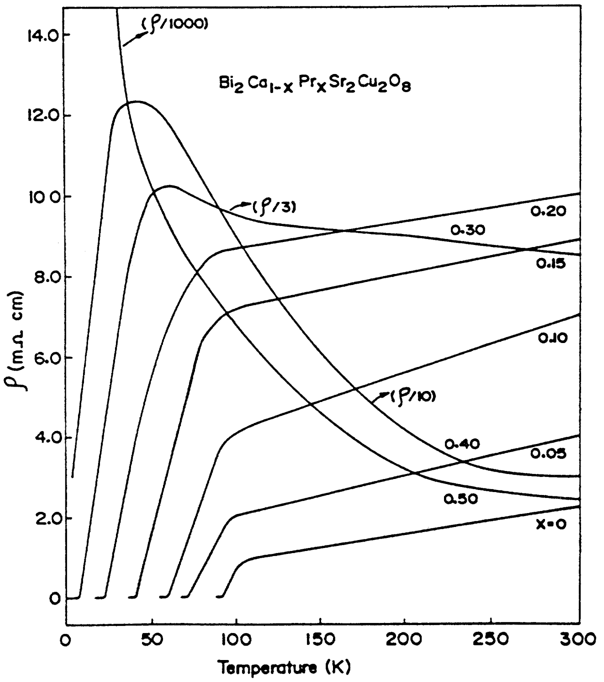

FIG. 3. Resistivity-vs-temperature behavior of $Bi_2Ca_{1-x}Pr_xSr_2Cu_2O_8$ samples with $(0 \leq x \leq 0.50)$.

$$\rho_T = \rho_0 \exp(T_0/T)^m \ . \qquad (1)$$

The value of the exponent m in the above equation determines the nature of the hopping mechanism in the semiconducting region of the resistivity[30] behavior. A value of $m = \frac{1}{3}$ corresponds for two-dimensional (2D) VRH, while it is found to be $\frac{1}{4}$ in the case of a 3D VRH process. For Ce-doped samples both the semiconducting behavior and nonsuperconductivity are observed at relatively low concentration levels of the dopant, as can be seen from Fig. 4. $T_c(R=0)$ depression rate with Ce doping is also relatively more in comparison to the Pr doping in the system. Similar to the Pr case, the normal-state resistivity behavior with temperature in the semiconducting regime of the Ce-doped samples (Ce 30 at. %, Ce 40 at. %) could also be fitted well to Eq. (1). Data of the insulating samples in the temperature range 5–150 K are also analyzed using Eq. (1). The results are presented in Figs. 5 and 6. In Fig. 5 curve fitting for the 40 at. % Pr-doped sample with both $m = \frac{1}{3}$ and $m = \frac{1}{4}$ is given. It is to be emphasized here that the difference between the two fittings is quite subtle.[31] The 2D VRH process ($m = \frac{1}{3}$) seems to be operative over a broader temperature range than the 3D VRH process ($m = \frac{1}{4}$). It is interesting to note here that when the semiconducting region follows 2D VRH behavior, the system exhibits superconductivity (T_c onset).[31] Figure 6 shows the fitting of the highly semiconducting and nonsuperconducting Pr- and Ce-doped samples with $m = \frac{1}{4}$ indicating a 3D VRH process. Fitting with other exponents was seen to be inferior to the one shown in Fig. 5. For Pr 0.50, Ce 0.30, and Ce 0.40 samples we find T_0 values of 400 K, 1.8×10^4 K, and 6×10^4 K, respectively. In the case of both Pr- and Ce- doped Bi 2:1:2:2 systems, T_0 values increase with increasing dopant concentration. The ρ_{min} point which is in general found to be in the vicinity of the metal-insulator transition is seemingly lacking below 300 K. Hence ρ_{min} for these samples must be somewhere above 300 K. The localization length α^{-1} (α is the coefficient of exponential decay of localized states) is calculated for different samples using the following expression:[32,33]

$$\alpha^{-1} = [K_B T_0 N(E_F)/16]^{-1/3} \ , \qquad (2)$$

for 3D VRH process, and

$$\alpha^{-1} = [4\pi K_B T_0 N(E_F)/27]^{-1/2} \ , \qquad (3)$$

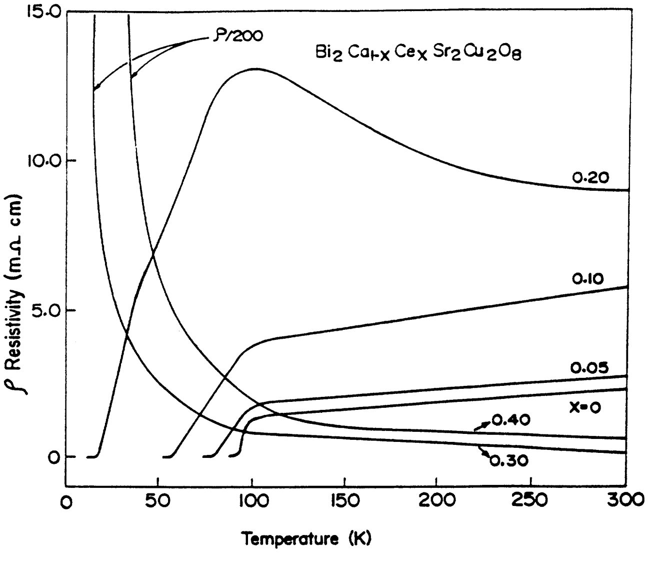

FIG. 4. Resistivity-vs-temperature behavior of $Bi_2Ca_{1-x}Ce_xSr_2Cu_2O_8$ samples with $(0 \leq x \leq 0.40)$.

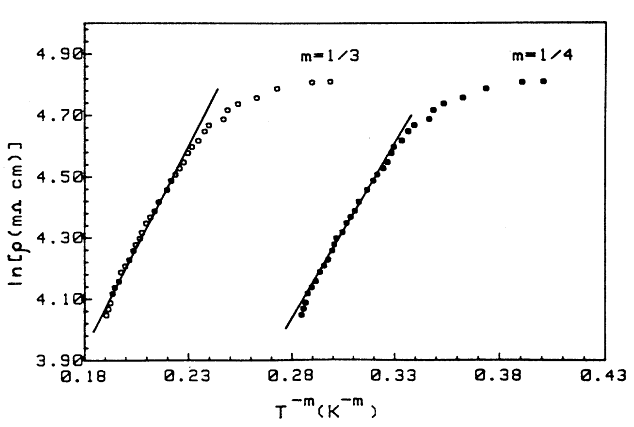

FIG. 5. ln ρ vs T^{-m} plots for Pr 0.40 sample for both $m = \frac{1}{3}$ and $m = \frac{1}{4}$.

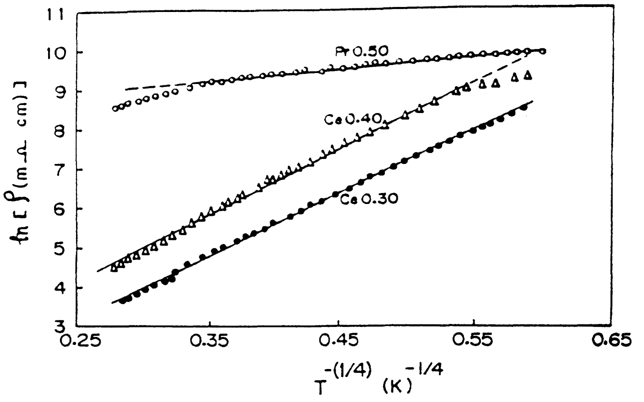

FIG. 6. ln ρ vs $T^{-1/4}$ behavior for Pr 0.50, Ce 0.30, and Ce 0.40 samples.

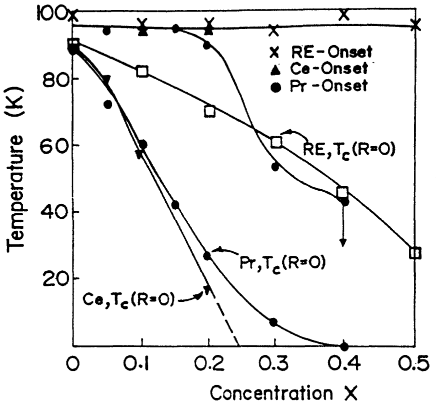

FIG. 7. $T_c(R=0)$ and T_c onset-vs-doping concentration behavior of $Bi_2Sr_2Ca_{1-x}M_xCu_2O_8$ samples ($M=R$,Pr,Ce) and $(0 \leq x \leq 0.50)$.

for 2D VRH process. $N(E_F)$ is the density of states at Fermi level and K_B is the Boltzmann constant. The value of $N(E_F)$ derived from various experiments[34,35] lies in the range of 10–25 states/eV cell. The value of localization length (α^{-1}) estimated from the above equations is seen to be maximum for the Pr 0.40 sample (~24 Å) while for Pr 0.50 it is found to be about 8 Å. In case of Ce 0.30 and Ce 0.40 it is even less than 1.5 Å, taking $N(E_F)$ to be 10 states/eV cell for simplicity's sake. It is interesting to note here that for all the samples showing semiconductor-like behavior superconductivity is seen only in the case of Pr 0.40 doped sample which follows the 2D VRH process, and also having a higher localization length (α^{-1}). In the case of the $La_{2-x}Sr_xCuO_4$ system, as the doping proceeds over an insulating phase the carrier density increases resulting in the hopping motion of the carriers becoming easier. The states of the carriers become less localized which continues until the insulator-metal transition takes place.[31] For the Bi 2:1:2:2 case, however, we have a reverse situation. Here we start from a metallic phase in the undoped case and when Pr or Ce doping increases, carrier density decreases, effecting higher localization and eventually the metal-insulator transition. In the above estimate we have used the variable-range hopping concept as envisaged in the transport of carriers in semiconductors. In the oxide materials the carrier motion is somewhat correlated in view of the antiferromagnetism in the insulating phase and the onset of superconducting at the verge of insulator-metal transition.

However, it is clear that in the regime of the higher Pr or Ce doping before the onset of superconductivity, the quasi-particle states are localized and the extent of localization depends on the doping strength (or concentration). Since the normal phase of the higher doped system (i.e., beyond 30% Pr and 20% Ce content) is not metallic, it is interesting to see the connection between the localization and superconductivity.

The localization is influenced by both the disorder and the correlation effects.[36] If the localization length covers a few neighbors in the lattice, it is possible to have local pairs in the insulating phase[37] that behave like charged bosons. On lowering the temperature one can observe a non-BCS type of superconductivity based on the mechanism of condensation of the charged Bose gas. In the case of the Bi 2:1:2:2 system both T_c and the normal-state metallic behavior are affected by increasing Pr and Ce concentration. It appears that there is a likelihood of a crossover of the non-BCS mechanism in these materials controlled by doping. More analysis of this idea is in progress.[38] This idea also receives credence from recent reports[39,40] for the dependence of oxygen isotope shift on the transition temperature of $Y_{1-x}Pr_xBa_2Cu_3O_7$ and $YBa_{2-x}La_xCu_3O_7$ systems where a strong suppression of the isotope effect is observed as T_c approaches its optimum value.

Figure 7 depicts T_c behavior with x for both Pr- and Ce-doped samples. This also contains the already reported[29] results of the other rare-earth metal (Eu, Dy, Tm)-doped systems. Both $T_c(R=0)$ and T_c onset decrease with the increasing dopant (Pr, Ce) concentration. The T_c depression rate is found to be more for Pr- and Ce-doped samples than for the other R-doped ones. The reason for T_c depression in the case of the R-doped 2:1:2:2 system has been assigned to be the hole-filling mechanism.[28,29,41] For different rare-earth metals doping in the system, T_c depression rates are found to be quite similar.[29,41] Also, with aliovalent substitution, extra oxygen has been seen to be intercalated in the redox Bi-O layers.[42] T_c depression and the transition broadening as observed can, therefore, be assigned to be due to the above two factors. In case of Ce and Pr doping also, the hole filling and excess oxygen intercalation takes place in the system as the valence state of Ca is 2+ and that of Ce and Pr is to be either 3+ or in between 3+ and 4+. The faster $T_c(R=0)$ depression rate of Ce and Pr doping than other R doping suggests the existence of Ce and Pr in the system to be more than 3+. Hence both resistivity and x-ray diffraction (XRD) data show the existence of Ce and Pr towards a tetravalent state in the doped Bi 2:1:2:2 system.

CONCLUSIONS

A systematic study of Pr and Ce substitution at the Ca site in the nominal composition of Bi 2:1:2:2 is reported here. Results of T_c decrease and the superconducting transition broadening with dopant concentration have been interpreted in terms of the hole-filling process as in other rare-earth metals doped systems and the extra oxygen intercalated between Bi-O layers, resulting from the aliovalent cation replacement. Through *c*-parameter variation and ionic radii considerations, it seems that Pr and Ce may exist between the 3+ and 4+ valence states in the compound.

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