

Depression of superconductivity and the phonon-drag effect in glass-ceramic superconductors obtained by annealing the Fe-doped $(\text{Bi, Pb})_4\text{Sr}_3\text{Ca}_3\text{Cu}_{4-m}\text{Fe}_m\text{O}_x$ glassy precursor

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Electrical conductivities and Seebeck coefficients of Fe-doped Bi-2212 type superconductors have been reported in the temperature range 300–10 K. These superconductors are obtained by annealing the Fe-doped amorphous $\text{Bi}_3\text{PbSr}_3\text{Ca}_3\text{Cu}_{4-m}\text{Fe}_m\text{O}_x$ ($m=0.0, 0.02, 0.04, 0.05, \text{ and } 0.06$) system around 840 °C for 40 h in air. The superconducting transition temperature T_c decreases continuously with a gradual increase of Fe content and finally diminishes for $m \geq 0.06$ supporting the Abrikosov-Gor'kov-type pair-breaking mechanism. Unlike undoped glass ceramics, semiconducting behavior exhibited by all the Fe-doped glass ceramics in their normal states can be explained by Mott's variable range hopping model. The Seebeck coefficients (S) of the glass-ceramic superconductors showed interesting nonlinear variation with temperature. Such nonlinear variation of thermopower is considered to be associated with phonon-drag effect which is, however, not the case in undoped (Fe free) glass-ceramic superconductors. Formation of impurity bonds such as Cu-O-Fe, Fe-O-Fe, etc., is considered to be more important than the magnetic effect for the depression of T_c and nonlinear thermal variation of Seebeck coefficient (S) in these superconductors. [S0163-1829(98)03041-0]

I. INTRODUCTION

Substitution of Cu ions by other magnetic and nonmagnetic ions in the well investigated parent superconducting systems such as Y-Ba-Cu-O, Bi-Sr-Ca-Cu-O, etc., cause interesting changes in the transport properties of these superconducting oxides.^{1–15} One of the most interesting properties of the substituted system is the disappearance of superconductivity with increase of 3d-metal impurity substituting Cu ions. In many Bi-based superconducting compounds,^{1–4} prepared by the standard ceramic heating route, suppression of T_c by substitution of Ni and Zn for Cu has been observed. However, these results so far do not agree from study to study.^{1,13} The pair-breaking mechanism of Abrikosov and Gor'kov¹⁶ was used to explain the decrease of T_c with impurity concentration. This mechanism is, however, found to be inapplicable for the $(R_{1-x}\text{Pr}_x\text{Ce}_{0.5})\text{Sr}_2\text{Cu}_2\text{NbO}_x$ (Ref. 7), $R\text{Ba}_2\text{Cu}_{3-x}M_x\text{O}_7$ ($R=\text{Sm, Dy}; M=\text{Fe, Ni, and Zn}$) (Ref. 5), etc., systems.

In conventional low- T_c superconductors, it is well known that paramagnetic impurities are much more effective T_c suppressors. Such paramagnetic scattering gives rise to a strong pair-breaking effect for the spin singlet s -wave Cooper pairs.⁶ This does not seem to be the case in high- T_c cuprates. For example, the whole family of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ -type compounds with magnetic rare-earth ions has essentially the same T_c values.^{5,17} Furthermore, there seems to be no significant differences in the strengths of T_c suppression between magnetic (Fe) and nonmagnetic (Zn) impurities^{2,14} in systems such as $\text{Bi}(\text{SrCa})(\text{Cu}_{1-x}M_x)\text{O}_z$ (where $M=\text{Ni, Zn}$) indicating a dramatic effect of such substitutions on T_c .

It is to be noted that most of the above-mentioned superconductors have been prepared by the usual ceramic heating route. The superconductors prepared by this route are, in general, porous and not very homogeneous. However, the

superconductors prepared by the glass-ceramic route are homogeneous and are also highly dense.^{18,19} In this method the superconductors (mostly Bi-based), called glass-ceramic (GC) superconductors, are prepared from homogeneous glassy precursors by annealing the glass samples at higher temperatures (above the glass transition temperatures T_g). For studying the effect of doping, the GC route appears to be very suitable because of well mixing during glass formation. However, to the best of our knowledge, very few superconducting samples have so far been prepared by the GC route to study the effect of doping with Fe, Cr, Co, or other magnetic or nonmagnetic ions on the electrical conductivity and thermoelectric power. These studies provide interesting information about the nature of the carriers and phonon-drag effect in oxide superconductors. It is also important to clarify whether the suppression of T_c , as mentioned above, could be associated with Abrikosov-Gor'kov pair breaking or some other mechanism. In a recent paper Goldschmidt *et al.*²⁰ also pointed out that the departure from the TEP curve (plotted against T_c , T_c^{max}) will occur whenever there exists pair-breaking or interaction weakening. This contention also needs further verification.

Our aim in the present paper is to report the temperature-dependent electrical conductivities and thermoelectric powers of the bismuth based GC superconductors obtained from the $\text{Bi}_3\text{PbSr}_3\text{Ca}_3\text{Cu}_{4-m}\text{Fe}_m\text{O}_x$ ($m=0–0.06$) type glassy precursors. These GC superconductors thus obtained are referred to as BiFe-2212-type superconductors. Unlike the conventional ceramic route, these glass-ceramic superconductors with different concentrations of iron are obtained from the corresponding homogeneous glassy phases, for better mixing of the doping atoms and homogeneity of the corresponding GC superconducting samples. The base glass, viz., $\text{Bi}_3\text{PbSr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ (hereafter referred to as [4334] glass) has been chosen as it is well known^{18,19} that this glassy phase is easily converted to the corresponding superconduct-

ing Bi-2212 phase with superconducting transition temperature $T_c \sim 80$ K.

The superconducting transition temperatures of the GC superconductors (BiFe-2212) obtained from the Fe-doped glassy precursors ($[4334]$) or $\text{Bi}_3\text{PbSr}_3\text{Ca}_3\text{Cu}_{4-m}\text{Fe}_m\text{O}_x$ with $m=0-0.06$ are found to decrease linearly with the increase of Fe content which strongly supports the pair-breaking mechanism. An interesting nonlinear variation of Seebeck coefficients exhibited by the corresponding GC superconductor has been correlated with the phonon-drag effect.

II. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

The thick plates (1–2 mm thickness) of $\text{Bi}_3\text{PbSr}_3\text{Ca}_3\text{Cu}_{4-m}\text{Fe}_m\text{O}_x$ (with $m=0.0, 0.02, 0.04, 0.05, 0.06$) glasses are prepared by the rapid quenching technique discussed earlier.²¹ The purity of Fe_2O_3 used for these glasses was 99.99%. All the above glasses (except $m=0.0$ glass) were heat treated at an optimum temperature 840°C for 40 h in air. For the glass with $m=0.0$ the corresponding temperature is also 840°C but the annealing time is only 24 h. The glass transition (T_g) and crystallization (T_x) temperatures were determined by differential thermal analysis (with a heating rate of $10^\circ\text{C}/\text{min}$). Both the as-quenched and the high-temperature ($\sim 840^\circ\text{C}$) annealed glass-ceramic (BiFe-2212) systems are characterized by x-ray powder diffraction (model: Seifert XRD 3000P) and scanning electron microscopic (model 425A, Hitachi, Japan) studies. The dc conductivity (σ_{dc}) and thermoelectric power (TEP) measurements between 300 and 10 K were performed on all the samples using an APD cryocooler (Model HC-2D) with a helium refrigerating system and temperature controller as discussed earlier.²² For the TEP measurement a standard procedure²² was used and a temperature difference of $2^\circ-4^\circ$ was maintained between the two parallel surfaces of the samples under investigation.

III. RESULTS AND DISCUSSION

The XRD ($\text{Cu } K\alpha$) patterns of some of the iron-doped as-quenched $\text{Bi}_3\text{PbSr}_3\text{Ca}_3\text{Cu}_{4-m}\text{Fe}_m\text{O}_x$ glasses (with $m=0.02-0.06$) are shown in Fig. 1 indicating glassy behavior. Some important parameters of the glassy precursors and their room-temperature conductivities are shown in Table I for comparison. It is seen that both T_x and T_g of the glasses increase appreciably even with only a small increase of Fe concentration and the appreciable difference between T_g and T_x also indicates that these Fe-doped glasses are quite stable and could be used for drawing fibers.

Figure 2 shows the XRD patterns of the corresponding $\text{Bi}_3\text{PbSr}_3\text{Ca}_3\text{Cu}_{4-m}\text{Fe}_m\text{O}_x$ glass-ceramic superconductors (BiFe-2212). The appearance of sharp peaks in Fig. 2 is due to the formation of crystalline phases. Most of the peaks belong to the 2212 phase and a few peaks belong to the 2223 phase. The peaks corresponding to the superconducting 2223 phase decrease with increase of dopant Fe concentration. Thus the doping of Fe causes a degradation of the superconducting 2223 phase in the glass ceramics. For glass ceramics with $m=0.02$ and 0.04 no impurity reflections belonging to Fe_2O_3 or FeO are observed, indicating that the dopants are

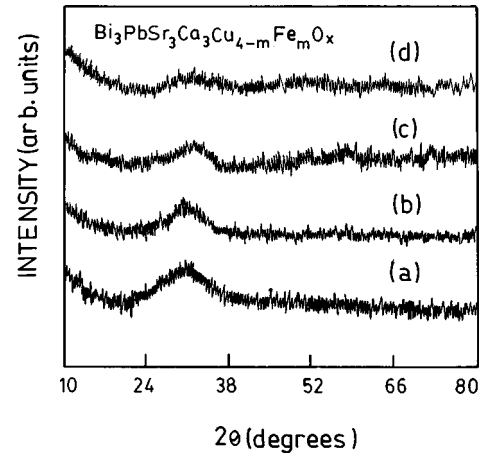


FIG. 1. X-ray diffraction pattern (with $\text{Cu } K\alpha$) of $\text{Bi}_3\text{PbSr}_3\text{Ca}_3\text{Cu}_{4-m}\text{Fe}_m\text{O}_x$ as-quenched glasses: (a) $m=0.02$, (b) $m=0.04$, (c) $m=0.05$, and (d) $m=0.06$, showing amorphous character with a broad hump around $2\theta=30^\circ$.

incorporated into the crystalline structure but for the GC samples with $m=0.05$ and 0.06 very few peaks belonging to FeO are formed (Fig. 2). Since all the above glass-ceramic BiFe-2212 samples are obtained from their respective homogeneous glassy phases, the small impurity phases are homogeneously distributed in the superconducting 2212 phase.

The electrical conductivities of all the glasses shown in Fig. 3 (between 80–450 K) represent semiconducting behavior which can be well fitted with the theory of the “small polaron” hopping conducting mechanism²³ (not shown in this paper). Figure 4 shows the temperature dependence of the resistivity for the Fe-doped and undoped ($m=0$) glass-ceramic samples obtained by annealing the corresponding glassy phases at higher temperatures as mentioned above. All these samples (except the Fe-free sample) show semiconductorlike behavior above superconducting T_c (onset) temperature [Fig. 4(a)]. This is in contrast to the behavior of the corresponding Fe-free glass ceramics which showed metallic behavior in their normal state above their superconducting transitions²² also shown in Fig. 4(a) for comparison. Both T_c and T_{c0} of the Fe-doped GC (BiFe-2212) samples decrease with the increase of Fe content and finally they become completely semiconducting for $m \geq 0.06$ as shown in Fig. 4(b). Variations of superconducting transition temperature T_c and T_{c0} (zero resistance temperature) with Fe concentrations are shown in Table II.

The above-mentioned semiconducting behavior of the normal-state resistivity of the GC phase is found to be well fitted with the Mott variable range [three-dimensional (3D)] hopping (VRH) model.^{23,24} It is well documented in the literature²⁵ that the increase of resistivity with decreasing temperature can be well described by the VRH model.²⁴ In this model it is assumed that the charge carriers move along a path determined by the optimal pair hopping rate from one localized state to another. Band conduction is absent because the extended states are too far away from the Fermi level. The applicability of this model in high- T_c superconducting materials is not unusual. Almost all the insulating phases of high- T_c materials^{9-12,26} exhibit the phenomenon. However, the temperature range over which VRH occurs differs for different materials. For example, in the $\text{PrBa}_2\text{Cu}_{3-x}\text{Ga}_x\text{O}_{7-\delta}$

TABLE I. Some important parameters (T_g and T_x are, respectively, the glass transition temperature and crystallization temperature, ρ is the density, Θ_D is the Debye temperature, and V_0^* is the molar oxygen volume) of the precursor glass $\text{Bi}_3\text{PbSr}_3\text{Ca}_3\text{Cu}_{4-m}\text{Fe}_m\text{O}_x$ ($m=0-0.06$). Θ_D =Debye temperature obtained from resistivity data, $C=(\text{Cu}^{1+}+\text{Fe}^{2+})/(\text{Cu}_t+\text{Fe}_t)$, where Cu_t and Fe_t are, respectively, the total Cu and Fe ion concentrations and density ρ (maximum error in the density measurement is $\pm 2\%$).

Glass with:	$m=0$	$m=0.02$	$m=0.04$	$m=0.05$	$m=0.06$
T_g ($^\circ\text{C}$)	385 ± 5	420 ± 5	430 ± 5	450 ± 5	465 ± 5
T_x ($^\circ\text{C}$)	407.5	480.5	502.5	518.5	525.5
ρ (gm/c.c)	6.76	6.59	6.08	5.94	5.80
V_0 (c.c.)	21.07	21.71	23.37	23.89	23.96
Θ_D (K)	408 ± 5	416 ± 5	470 ± 5	476 ± 5	523 ± 5
C^a	0.78	0.96	0.95	0.94	0.94

^aEstimated from chemical analysis and atomic absorption spectroscopic studies.

(Ref. 27) system, 3D hopping behavior is observed in the temperature range 14–150 K. In the $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (Ref. 28) system 3D VRH behavior is observed from room-temperature (RT) down to 20 K. Fournier, Gagnon, and Aubin¹⁰ reported that Fe-doped Y-123 showed hopping conduction. Sugita *et al.*²⁹ observed 3D behavior in the Y-Ba₂Cu_{3-x}Fe_xO₇ system at higher temperatures but a deviation at low temperatures. There are many other high- T_c systems where the VRH mechanism of conduction was attributed, viz., $\text{La}_{2-x}\text{Sr}_x\text{CuO}$ (Refs. 30 and 31), $\text{PrBa}_2\text{Cu}_3\text{O}_7$ (Ref. 25), $\text{YBa}_2\text{Cu}_{3-x}(\text{Fe}, \text{Zn})_x\text{O}_7$ (Ref. 5), $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_{8-\delta}$ ($R=\text{Nd}, \text{Sm}, \text{Gd}, \text{Dy}, \text{Y}$) (Ref. 32), etc. We fitted the data with the standard (2D) Mott equation² with $\gamma=\frac{1}{4}$:

$$\rho = \rho_0 [T/T_0]^{1/2} \exp(T_0/T)^\gamma, \quad (1)$$

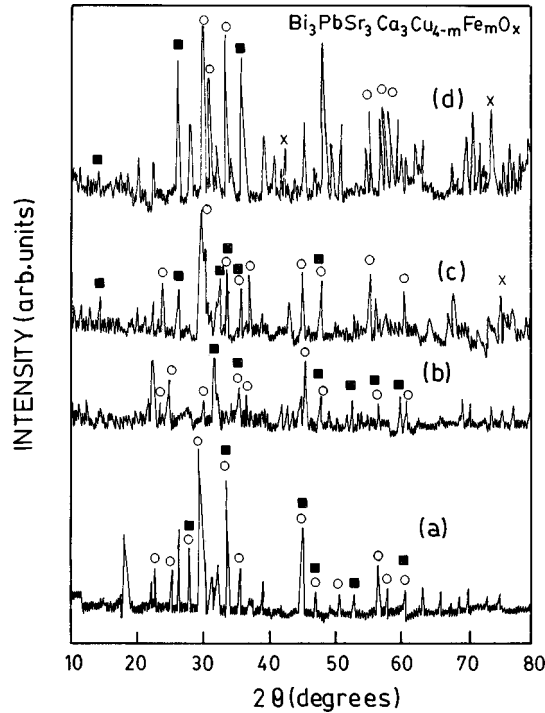


FIG. 2. X-ray diffraction pattern of the glass-ceramic superconductors (obtained by annealing the corresponding glassy $\text{Bi}_3\text{PbSr}_3\text{Ca}_3\text{Cu}_{4-m}\text{Fe}_m\text{O}_x$ phase at an optimum temperature 840 $^\circ\text{C}$ and time 40 h in air): (a) $m=0.02$, (b) $m=0.04$, (c) $m=0.05$, and (d) $m=0.06$. (○) 2212, (■) 2223, and (×) FeO phases.

where ρ is the resistivity and the parameter T_0 is related to density of states $N(E_F)$ at the Fermi level, and the localization length a is $T_0=21/[kN(E_F)a^3]$. Table II shows the parameters used to fit the experimental data. The values of T_0 obtained is quite reasonable.³³

It can be seen from Fig. 5 and Table II that the dopants cause both T_c and T_{c0} to decrease monotonically with the increase of Fe concentration (m). This suppression of T_{c0} occurs even at very low Fe concentration in the present system. In the Y-Ba-Cu-O oxide,³⁴ however, superconductivity diminishes for a large (0.35 wt. %) Fe concentration. This suppression of T_c with very low Fe concentration in the superconducting (GC) BiFe-2212 system is interesting. It appears that due to the addition of Fe some new bridge bonds such as Cu-O-Fe, Fe-O-Fe, etc., are formed in the corresponding glassy phase (increasing both T_g and T_x) as in the case of mixed glassy systems such as $\text{V}_2\text{O}_5\text{-Fe}_2\text{O}_3$ (Ref. 35).

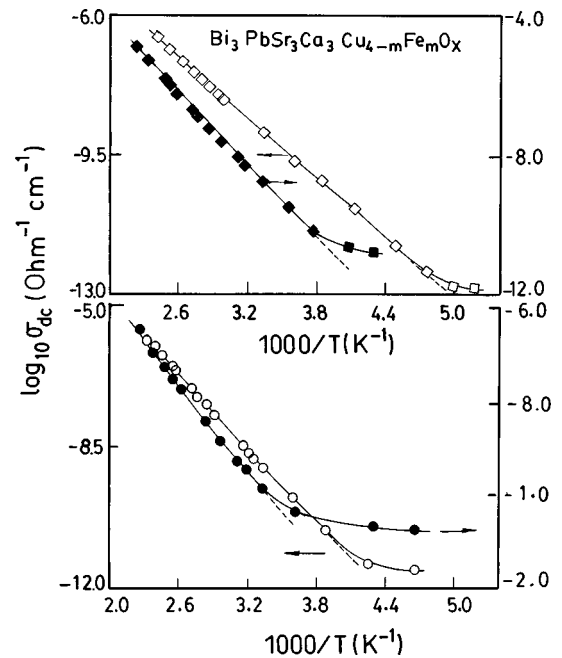


FIG. 3. The logarithm of dc conductivity of the as-quenched $\text{Bi}_3\text{Pb}_1\text{Sr}_3\text{Ca}_3\text{Cu}_{4-m}\text{Fe}_m\text{O}_x$ glasses as a function of T^{-1} : (□) $m=0.02$, (■) $m=0.04$, (○) $m=0.05$, and (●) $m=0.06$. Solid lines are guides for the eyes. The dotted lines met the solid lines at $T = \theta_D/2$.

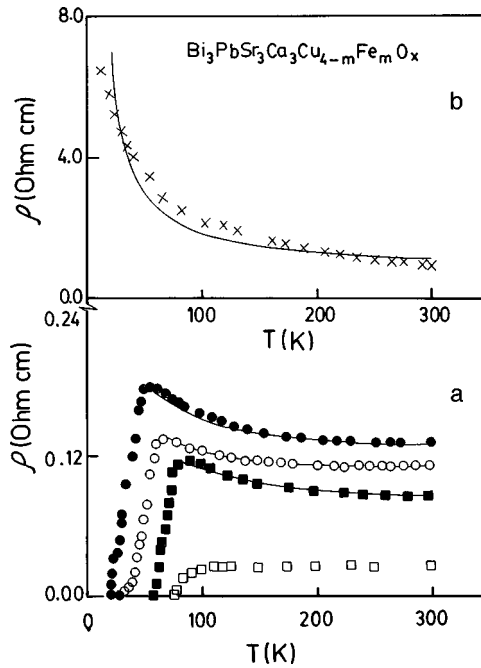


FIG. 4. Thermal variation of resistivity of the superconducting glass ceramics obtained by annealing the $\text{Bi}_3\text{Pb}_1\text{Sr}_3\text{Ca}_3\text{Cu}_{4-m}\text{Fe}_m\text{O}_x$ glasses at 849°C for 40 h in air with $m=0$ (\square), 0.02 (\blacksquare), 0.04 (\circ), 0.05 (\bullet), and 0.06 (\times). Solid lines are least squares fitting with Eq. (1).

These new bonds are also present in the GC phases which behave as impurities and are not equivalent to the Cu-O-Cu bonds already present in the undoped (Bi-Pb-Sr-Ca-Cu-O) system. With the increase of Fe concentration, more and more such new bonds are formed which finally destroy superconductivity. Similar arguments are also applied for the Ni- and Zn-doped Bi-Sr-Ca-Cu-O system^{7,14} where linear depressions of T_c with the increase of Ni and Zn impurities are observed. Therefore, it is not actually the magnetism of the doping transition metal ions which effects the suppression of T_c . Rather, it is the effect of impurity bonds formed with the Cu ions which actually causes the suppression of T_c .

The critical concentration x_{cr} required to suppress T_c to zero is estimated to be around 0.06. According to the Abrikosov-Gor'kov (AG) pair-breaking mechanism,¹⁶ the reduced transition temperature $T_c(x)/T_c(0)$ is a universal function of reduced concentration (x/x_{cr}) given by the relation

TABLE II. T_{c0} and T_c of the BiFe-2212 glass ceramics obtained from the $\text{Bi}_3\text{Pb}_1\text{Sr}_3\text{Ca}_3\text{Cu}_{4-m}\text{Fe}_m\text{O}_x$ ($m=0.02, 0.04, 0.05,$ and 0.06) glass heat treated at 840°C for 40 h [all these glass ceramics show feeble (except $m=0.06$ which shows large) semiconducting behavior in their normal states as shown in Fig. 4.

	ρ_0 (Ohm-cm)	T_0 (K)	T_c (K)	T_{c0} (K)
$m=0.02$	0.0445	11500	80	58
$m=0.04$	0.0600	6200	65	28
$m=0.05$	0.0700	7000	55	20
$m=0.06^a$	0.4750	32000		

^aSemiconductor with no T_c or T_{c0} .

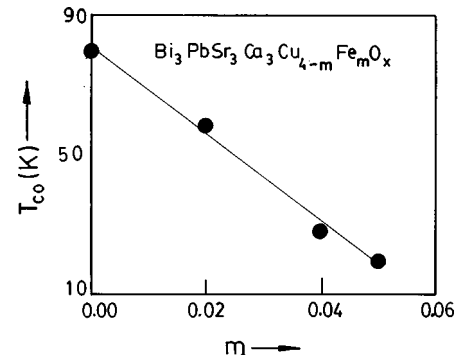


FIG. 5. Linear variation of zero resistance temperature (T_{c0}) with the iron concentration (m) of the superconducting glass ceramics (obtained by annealing the $\text{Bi}_3\text{PbSr}_3\text{Ca}_3\text{Cu}_{4-m}\text{Fe}_m\text{O}_x$ glasses at 840°C for 40 h with $m=0, 0.02, 0.04,$ and 0.05) supporting the pair-breaking mechanism.

$$\ln[T_{c0}(x)/T_{c0}(0)] = \Psi\left[\frac{1}{2} + 0.14 \times T_{c0}/x_{cr}T_c x\right], \quad (2)$$

where Ψ is the digamma function. Figure 5 shows the AG fit of $T_{c0}(x)$ versus m for the present (BiFe-2221) GC superconductors. Therefore, the decrease of T_{c0} with Fe content in the present system can be explained by the AG pair-breaking mechanism. In conventional low- T_c (BCS-type) superconductors, the presence of magnetic impurities depresses T_c more strongly than the nonmagnetic impurities.¹⁶ In the superconducting $\text{Bi}_{1.2}\text{Pb}_{0.8}\text{La}_{0.5}\text{Sr}_{1.5}\text{Cu}_{1-x}\text{M}_x\text{O}_y$ system ($M=\text{Ni}, \text{Zn}$), both Zn and Ni were found to depress T_c at approximately the same rate.³⁶ Also in the $(\text{Bi}, \text{Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_{3-x}\text{M}_x\text{O}_y$ ($M=\text{Zn}, \text{Fe}$) superconductors, both Zn (without magnetic moment) and Fe (with magnetic moment) depress T_c/T_{c0} in a similar manner.^{14,17} This also supports the idea that the effect of impurity bonds with copper, as discussed above, is responsible for the depression of T_c .

Experimental results for samples with low dopant concentration (as in our present system), therefore, indicate that local disorder rather than magnetism is the important factor for the suppression of superconductivity in cuprate superconductors. Disorder also affects the superconductivity according to the theory proposed by Coffey *et al.*³⁷ This theory predicts an increase in normal-state resistivity due to impurity scattering introduced by disorder, accompanied by the depression of superconductivity. It is obvious from Fig. 4 that the normal-state resistivity of all the samples increases with the increase of dopant impurity (Fe). This is due to the formation of new impurity bonds such as Fe-O-Cu, Zn-O-Cu, Ni-O-Cu, Fe-O-Fe, Zn-O-Zn, etc., causing the decrease of T_c .

The temperature variation of thermoelectric power (TEP) of Fe-doped BiFe-2212 GC superconductors are shown in Fig. 6. It is observed from this figure that both type of carriers (holes and electrons) are present in this system. It is also found (Fig. 6) that as the temperature decreases from room temperature, the TEP increases up to a maximum value of temperature T_s (say) followed by a minimum value around the temperature 80 K. The temperature T_s is slightly Fe concentration dependent which shifts to the low-temperature region with increase of concentration. This shift is considered

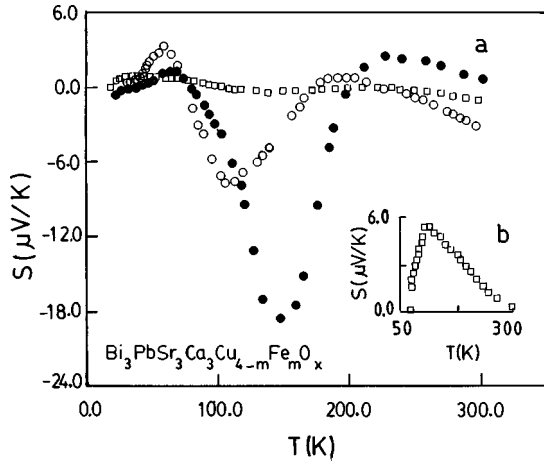


FIG. 6. (a) Nonlinear thermal variation of the thermoelectric power (S) of the superconducting glass ceramics (obtained by annealing the $\text{Bi}_3\text{PbSr}_3\text{Ca}_3\text{Cu}_{4-m}\text{Fe}_m\text{O}_x$ glasses at 840°C for 40 h in air with $m=0.02$ (\bullet), $m=0.04$ (\circ), $m=0.05$ (\square) showing negative peak which decreases with increase of Fe concentration indicating a phonon-drag effect (Ref. 37). (b) The inset curve is for the Fe-free superconducting glass ceramics (obtained by annealing $\text{Bi}_3\text{PbSr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ glass at 840°C for 24 h in air) showing no negative peak unlike the corresponding Fe-doped glass ceramics [in Fig. 6(a)].

to be due to the presence of magnetic impurity in the superconducting glass ceramics. With further decrease of temperature, the TEP increases rapidly up to a maximum value around 60 K followed by a decrease to zero value in the temperature range 20–58 K ($=T_{c_0}$), depending on concentration. This type of thermal variation of Seebeck coefficient (S) indicates unusual thermal behavior of the carriers in these superconductors.

The negative peak that appeared in the temperature variation of S (Fig. 6) becomes gradually suppressed with the increase of Fe content. This behavior is, however, very similar to the $\text{Cu}_{1.8}\text{Mo}_6\text{S}_{8-y}\text{Se}_y$ -type Chevrel compounds³⁸ in which the negative peak is suppressed with increase of Se content. Kaiser³⁹ analyzed the TEP data of these Chevrel compounds by considering that the negative peak is due to phonon drag. In these compounds as the residual resistivity ratio ρ_0/ρ_{RT} (ρ_0 is the residual resistivity, the value just above T_c , and ρ_{RT} is the room-temperature resistivity) increases, the negative peak is suppressed. The increase of ρ_0/ρ_{RT} means the reduction in phonon heat current and also there is a reduction in momentum transferred to the electrons, i.e., phonon drag effect. Therefore, the negative peak in the present Fe-doped samples is ascribed to be due to the phonon-drag effect. An enhancement of thermoelectric power just above T_c is a precursor effect, a feature related to the existence of superconducting fluctuations. Such a feature is not peculiar to those oxide superconductors. It is found in induced intermediate state low- T_c superconductors.⁴⁰

IV. CONCLUSION

From the above discussion it is concluded that the superconducting transition temperature of the Fe-doped $(\text{Bi, Pb})_4\text{Sr}_3\text{Ca}_3\text{Cu}_{4-m}\text{Fe}_m\text{O}_x$ -type GC superconductor (or BiFe-2212) decreases proportionally with the increase of Fe

content, which also supports the pair-breaking mechanism. Samples with higher Fe content ($m \geq 0.06$) are no longer superconductors. Similar behavior has also been recently observed in the Ni and Zn substituted single crystals of $\text{Bi}_2(\text{SrCa})_{2+n}(\text{Cu}_{1-x}\text{M}_x)_{1+x}$ ($M=\text{Ni}$ and Zn).¹⁴ The pair-breaking mechanism was also suggested (Ref. 20) for the substitution of M by Zn or Ni impurities in a 1:2:3 system such as $(\text{Ca}_{0.4}\text{La}_{0.6})(\text{Ba}_{1.35}\text{La}_{0.65})(\text{Cu}_{1-z}\text{M}_z)_3\text{O}_y$.

It has been shown in the literature⁴¹ that there exists a universal TEP curve that describes $S_{290\text{K}}$ as a function of T_c/T_c^{max} and makes the determination of the state of doping of a given material quite easy.⁴¹ Some cuprates including Ca-La-Ba-Cu-O follow this universal curve.⁴² However, when Ni and Zn are introduced, one observes a strong departure from the universal TEP curve and the pair-breaking mechanism was also suggested for this system.²⁰ It was, however, pointed out by Goldschmidt *et al.*,²⁰ that this departure from the universal TEP curve will occur whenever there exists pair breaking or interaction weakening which is supported by the results of the present Fe-doped BiFe-2212 system where a departure from the universal TEP curve is observed and the validity of the pair-breaking mechanism is suggested.

From the thermoelectric power measurements, we observed both positive and negative values of Seebeck coefficient S as in the case of other Bi-based glass-ceramic superconductors.²² The nonlinear thermal variation of TEP in the Fe-doped glass-ceramic superconductors (Fig. 6) can be explained by considering the phonon-drag effect. Exactly the same behavior of TEP data was observed in the Cr- and Ti-doped GC superconductor obtained from the $\text{Bi}_3\text{PbSr}_3\text{Ca}_3\text{Cu}_{4-m}\text{M}_m\text{O}_x$ ($M=\text{Cr, Ti}$, $m=0-0.008$) glass systems (unpublished). This behavior is in contrast to that of the corresponding GC superconductor (Bi-2212) obtained from the undoped $\text{Bi}_3\text{PbSr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ glass. For this undoped Bi-2212 superconductor, however, a two band model⁴¹ was used²⁰ and the phonon-drag effect could not be invoked. It seems that the negative peak in the present Fe-doped samples is associated with phonon-drag effect. However, from the resistivity data it is found that the VRH mechanism takes part in the normal (semiconducting in nature) conduction which apparently contradicts the phonon-drag effect (occurring in the low-temperature metallic or semimetallic part). In a recent paper Isawa *et al.*⁴³ have shown that phonon drag and VRH may exist in TEP. The one bit of supporting evidence of the phonon drag is that the peak falls as the resistance ratio rises, a correlation which is based on metallic resistance (a strongly degenerate gas of delocalized electrons). Other evidence comes from the fact that the peak does not disappear in the presence of magnetic field ($\sim 0.8T$). Therefore, the peak is not of magnetic origin. As far as VRH is concerned, it appears at the semiconducting (not metallic) regime where the electrons are slightly localized (due to the presence of some disorder and granular nature of the materials). VRH has also been reported in many YBCO-type high- T_c materials as referred to above.^{5,10,29} Thus the presence of a very small amount of magnetic impurity (Fe, Cr, or Ti partially substituting Cu) plays a great role in modifying the behavior of the carriers in BiFe-2212 superconductors where the phonon-drag effect could be attributed. Since magnetic or nonmagnetic impurity suppresses T_c with equal

strength, the dominant scattering mechanism responsible for the suppression of T_c arises due to the formation of impurity bonds such as Cu-O-Fe, Fe-O-Fe, Ni-O-Cu, etc. (doped with magnetic ions); and Zn-O-Cu, etc. (doped with nonmagnetic ions), in the superconductors. These bonds also effects the thermal behavior of Seebeck coefficients. Finally we would like to mention that these multicomponent oxides also show complicated behavior. Not many studies have been done on such interesting superconducting oxides. Further study in this direction would be interesting.

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