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SEEBECK EFFECT IN SUPERCONDUCTING $BaPb_{1-x}Bi_xO_3$ SYSTEM

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Seebeck effect was observed on superconducting $BaPb_{1-x}Bi_xO_3$ system in $x = 0 \sim 0.4$ from 4.2K or T_c to 300K. Seebeck coefficient seems to consist of two contributions; one from the dominant metallic electrons and the other from additional unidentified carriers with fairly low mobility. The calculated ε_F, $N(\varepsilon_F)$ and m* from the metallic contribution tend to increase with x to maxima around $x = 0.2$, where T_c also becomes maximum.

I. Introduction

The development of high temperature superconductors has been the recent object of active interest and many new materials have been investigated till now. One of these is $BaPb_{1-x}Bi_xO_3$ system in which Sleight et al.[1] found superconductivity in $x = 0.05 \sim 0.3$ in 1975. The critical temperature T_c is 9K at $x = 0.05$ and increases to a maximum of 13K at $x = 0.3$, which is exceptionally high in the oxides and/or compounds containing no transition elements. This system has a perovskite-like structure and the superconducting region is characterized with tetragonal system[2] similar to that of the low temperature form of $SrTiO_3$. It is unusual for this crystal structure since according to Cohen[3] T_c for perovskites is not expected to exceed 1K [4]. These suggest that detailed investigation on the electrical properties are desired to elucidate the superconducting mechanism.

In our previous observation on resistivity ρ and Hall coefficient R_H in this system[5], following results are obtained. (i) The system shows n-type conduction in R_H while ρ is metallic for $x \lesssim 0.2$ and nonmetallic for $x \gtrsim 0.2$. (ii) Superconductivity is observed in $0.05 \lesssim x \lesssim 0.35$ and maximum T_c is 11.7K at $x = 0.25$. (iii) The x-dependence of carrier concentration n* is deduced from R_H at 77K or 300K and shows almost same x-dependence as T_c. The maximum n* is $4 \times 10^{21} cm^{-3}$ at $x = \sim 0.25$ which is one order of magnitude smaller than those of usual superconductors.

In this paper we will report the observation of Seebeck effect in normal state to get further information on the electronic states in this peculiar system. It should be noted that since it is a non-current observation the measurement of thermopower is useful for the investigation of transport properties in the system with macroscopic disorder such as grain boundaries.

II. Experiments and Results

All the samples measured were prepared by hot-press technique under oxygen atmosphere. The SEM observation shows that the sample is polycrystal with no void, though the observed density is 0.91(x = 0) or 0.81(x = 0.3) of the expected one. Detailed procedures for sample preparation are described in [5]. For the measurement of Seebeck effect we used differential copper/constantan thermocouple to detect the temperature difference of ∿0.2K and thermoelectric force was detected through gold lead wires.

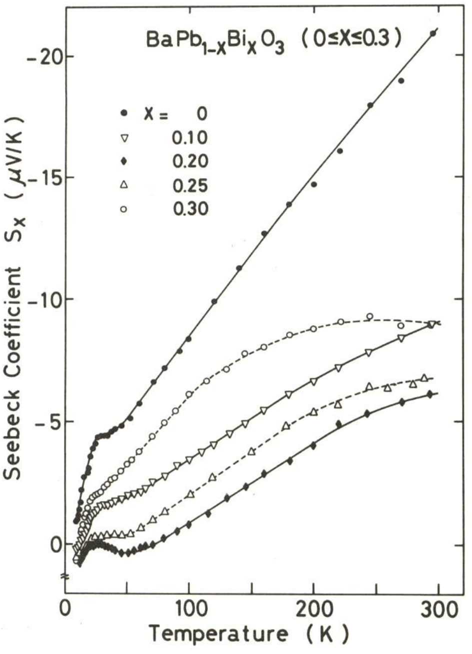


Fig.(1) Absolute Seebeck coefficient of $BaPb_{1-x}Bi_xO_3$ system

The temperature dependences of absolute Seebeck coefficient S_x in $0 \leq x \leq 0.3$ are shown in Fig.(1), where the contribution from that of gold is corrected[6]. These results show the typical metallic behaviors which are characterized by the linear temperature dependence, though the extended line from the linear part to 0K does not cross the origin. The behaviors are apparently different from that of x = 0.4 shown in Fig.(2), which resembles the typical behaviors of semiconductors and will be described elsewhere. In any Bi content, the sign of dominant contribution in S_x is negative, which is consistent with that of R_H[5] and shows n-type conduction in the system.

The temperature dependences of ρ are also measured simultaneously and it is confirmed that the electric and transition properties are the same as those in Fig.(3) in [5].

III. Discussions

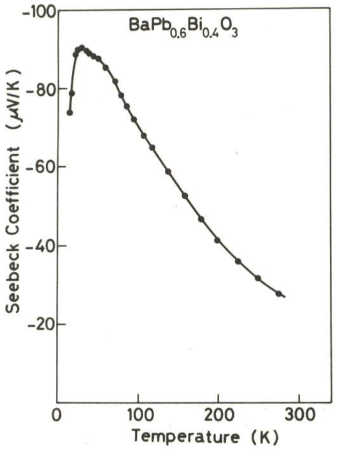


Fig.(2) Seebeck coefficient of non-metallic and non-superconducting $BaPb_{0.6}Bi_{0.4}O_3$

We consider here the results on the superconducting composition range shown in Fig.(1). The characteristic features are itemized as follows. (a) There are strongly temperature dependent contributions below 50K which depend on the Bi content. (b) The temperature region exists in any sample above 50K where S_x increases linearly with temperature. (c) Saturation of S_x appears at higher temperature region with increasing x. This is more pronounced above x = 0.2.

The deviation from T-linear dependence in (c) may be attributed to the resultant increase in the Fermi energy with temperature. This is consistent with the appearance of the temperature dependence(at 77K & 300K) in n* at $x \gtrsim 0.2$ deduced from R_H[5]. Thus the observed S_x can be considered to consist of two parts: the low temperature contribution S_g and the higher temperature electronic contribution S_e

as $S_x = S_g + S_e$. Further, S_e can be expressed as $S_e = AT + S_0$ as is seen from Fig.(1); the first term corresponds to T-linear contribution and the second to T-independent one. A and S_0 are determined experimentally as shown in Fig.(3-a). Both show the systematic change with x and in particular S_0 changes its sign in $0.1 < x < 0.3$. Usually the temperature independent Seebeck coefficient suggests the existence of rather immobile carriers[7]. Therefore, it seems natural to analyze the data by assuming the existence of two kinds of carriers; one is immobile which contributes to S_0 and the other metallic to AT. Brief consideration reveals that AT represents the feature of metallic carriers directly while S_0 may be fairly reduced from its original value.

In the degenerate electron system, Seebeck coefficient is proportional to T and expressed as follows[6];

$$S = \frac{\pi^2}{3}\frac{k^2T}{e}\left\{\frac{\partial \ln\sigma(\varepsilon)}{\partial\varepsilon}\right\}_{\varepsilon=\varepsilon_F}, \quad (1)$$

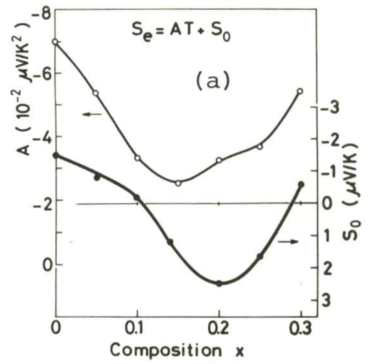
$$= \frac{\pi^2}{3}\frac{k^2T}{e}\left\{\frac{N(\varepsilon)}{n} + \frac{\partial \ln\mu(\varepsilon)}{\partial\varepsilon}\right\}_{\varepsilon=\varepsilon_F}, \quad (2)$$

$$= \frac{\pi^2 k^2 T}{3e\varepsilon_F}\left(\frac{3}{2} + \gamma\right). \quad (3)$$

Symbols are in usual meaning i.e. $\sigma = ne\mu$, relaxation time $\tau \propto \varepsilon^\gamma$ and simple band is assumed. Assuming impurity scattering ($\gamma = -1/2$), ε_F, $N(\varepsilon_F)$ and m* are derived from A and eqs.(1)-(3) as shown in Fig.(3-b), where $n = n^*$ was quoted from [5]. ε_F increases with x and becomes maximum at $x = 0.15$. $N(\varepsilon_F)$ and m* also increase with x and most steeply between $x = 0.15$ and 0.2. These results are in good agreement with the behavior of T_c qualitatively and also provide the first quantitative information on the electronic states in $BaPb_{1-x}Bi_xO_3$ system, though the model might be simple. However, it seems insufficient to explain the high T_c solely by BCS mechanism since each parameter is rather small in comparison with ordinary superconductors (e.g. $N(\varepsilon_F) \simeq 2\times10^{22}\,cm^{-3}eV^{-1}$ for In).

As for the mechanism of superconductivity, the possibility of s-p superconductor is proposed[4], while the participation of d-electrons is suggested from high pressure experiment[8]. In relation to the structural phase transitions observed by the X-ray study[2], the appearance of soft phonon mode and its coupling with the conduction electrons may give rise to high T_c superconductivity.

The present result indicates the existence of rather immobile carriers which scarcely contribute to conduction. The origin is not clear at present[9]; however, it must be added that in this system the



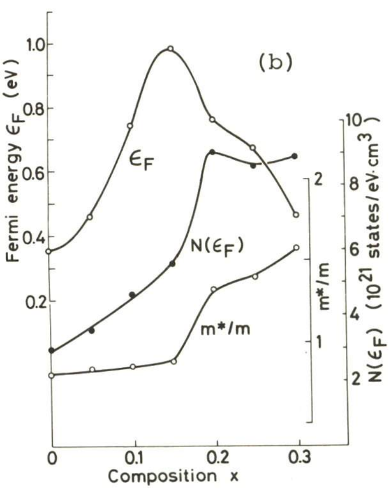


Fig.(3) (a) Slope A and constant term S_0 obtained from the linear regions of the S_x-T curves in Fig.(1), and (b) Fermi energy ε_F, electron density of states at Fermi level $N(\varepsilon_F)$ and effective mass m* of $BaPb_{1-x}Bi_xO_3$ system oxidation states seem to be important and actually in case of $BaBiO_3$ the valence situation is found to be $Ba_2Bi^{+3}Bi^{+5}O_6$ rather than $BaBi^{+4}O_3$ and Bi^{+3} and Bi^{+5} cations take on an ordered arrangement. Pb 6s band in the schematic band model[1] would be deformed significantly in case of mixed compound.

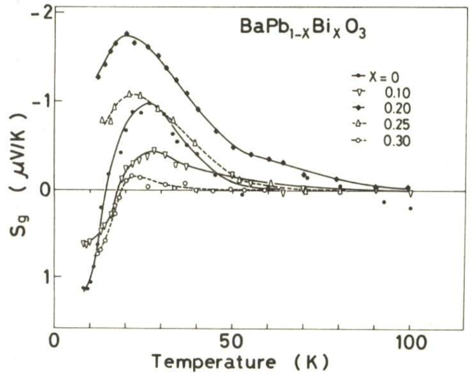


Fig.(4) Low temperature contribution S_g to S_x as obtained by subtructing the linear contribution from the curves in Fig.(1)

The effect of the possible existence of immobile carriers seems to be interesting though speculative at present. In the degenerate semiconductors or semimetals which possess two or more carrier groups, "plasmon" mechanism was proposed[11]. Recently, electron-hole mechanism[12] has been proposed to interpret 'high T_c superconductivity' in CuCl under high pressure. The theory predicts it would be possible if the masses of electron and hole be extremely different each other. In this respect, the appearance of positive S_0 in $0.1 < x < 0.3$ seems to be noteworthy.

Finally, the change in the temperature dependence of S_g with x should be mentioned briefly. The result is shown in Fig.(4). The origin of this term may be lattice imperfection, impurity or phonon drag. If the last is the case as in Bi[13], this might suggest the existence of hole and strong interaction between phonons and carriers.

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