APPLIED PHYSICS LETTERS VOLUME 81, NUMBER 13 23 SEPTEMBER 2002

Thermoelectric properties of $Bi_2Sr_2Co_2O_9$ whiskers under hydrostatic pressure

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(Received 21 December 2001; accepted for publication 5 August 2002)

We report the temperature dependence of thermopower (S) in the ab plane of $Bi_2Sr_2Co_2O_9$ (BC-222) single crystalline whiskers under high pressure up to 1.2 GPa. Special modifications were made to our high-pressure transport measurement system to improve the measurement accuracy of S for whiskers with high resistance. Pressure improved the contact resistance dramatically. We observed a slight decrease of S and four-wire electrical conductivity (σ) under high pressure. As a result, the power factor ($S^2\sigma$) was decreased less than 20% by pressure. From the temperature dependence of σ, the band gap of BC-222 whiskers increase very slightly under high pressure. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1510160]

In the past decade there has been a significant amount of research directed toward finding materials with improved thermoelectric performance.[1–5] Both in systems that convert heat into electrical energy (Seebeck effect) and in solid-state cooling systems (Peltier effect), the efficiency of a material is determined by a dimensionless figure of merit

$$ZT=\frac{S^2\sigma}{\kappa}T, \tag{1}$$

where T is the absolute temperature, S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity. It has been demonstrated that low dimensional materials like superlattice structures, quantum wires, and quantum dots can have a significantly higher thermoelectric figure of merit due to an increase of the Seebeck coefficient resulting from the altered electronic density of states (relative to bulk) and the lowering of the lattice contribution to the thermal conductivity due to selective phonon scattering and phonon confinement.[5,6] These discoveries prompt us to study the thermoelectric properties whiskers. Whiskers are quasione-dimensional single crystals of (typically) layer-structured materials with the layer planes oriented parallel to the preferred growth direction. The thermoelectric properties of pentatelluride whiskers have been investigated for cooling (low temperature) applications.[7,8] Recently, it was discovered that oxide materials can have reasonably high values of S (100 μV/K) at high temperatures, making them potentially useful for power generation applications. The thermoelectric properties of polycrystalline samples $Bi_2Sr_2Co_2O_9$ (BC-222) were found to be superior to most other oxides[9] and single-crystal BC-222 whiskers were found to have a power factor ($S^2\sigma$) 5–7 times higher than that of the polycrystalline BC-222 samples. In this letter, we extend the previous studies and investigate the thermoelectric properties BC-222 whiskers under hydrostatic pressure. The use of high pressure in material science can be a powerful tool to simulate hypothetical chemical substitution, to uncover underlying systematics and to provide inputs and insights for band structure theories.[10,11] In fact, the thermoelectric properties of several materials are found to improve upon application of uniaxial pressure[12,13] and hydrostatic pressure.[14] For the BC-222 whiskers, the contact resistance is rather large and may be a serious problem for the thermoelectric applications. We found out that the pressure improves the contact resistance dramatically and has very small side effect for the power factor.

The Seebeck coefficient under high pressure was measured using a very low frequency ac two-heater method.[15] Two surface mount resistors were driven by sinusoid currents that differ in phase by $\pi/2$. The amplitude of the currents can be adjusted to minimize the ac component of the base temperature fluctuation ($\tilde{T}$). The ratio ($\delta T/\tilde{T}$) of ac temperature gradient (δT) versus the base temperature fluctuation was monitored to ensure the correct and precise S from ac measurements.[15] Two pairs of T-type thermocouples (each pair consists of TN and TP wires) were attached to the sample directly using EPO-TEC H20E silver epoxy and three independent signals were measured simultaneously to solve for the base temperature, temperature gradient, and the Seebeck coefficient. The copper leads of the T-type thermocouples were calibrated relative to Pb using data from Roberts.[16] Our Teflon pressure cell is about 3 mm in diameter and 7 mm long, thus the sample size can be much larger than that could be measured in an anvil cell and ensures precise result together with other careful considerations. Even with the surrounding of fairly good thermally conducting pressure medium, the measured Seebeck coefficient is in good agreement with that which is measured outside of the pressure cell. The small pressure effect on thermocouples was also considered and corrected.

$Bi_2Sr_2Co_2O_9$ (BC-222) single crystalline whiskers (Fig. 1) were prepared using the glass-annealing method.[17,18] The samples for the measurement of ab-plane resistivity were

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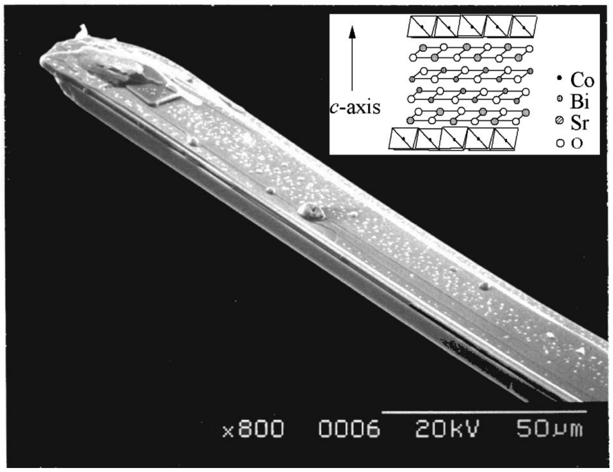

FIG. 1. Scanning electron microscopic image of a BC-222 whisker. The well-grown plane corresponds to the crystallographic *ab* plane. Inset: layered crystal structure of BC-222.

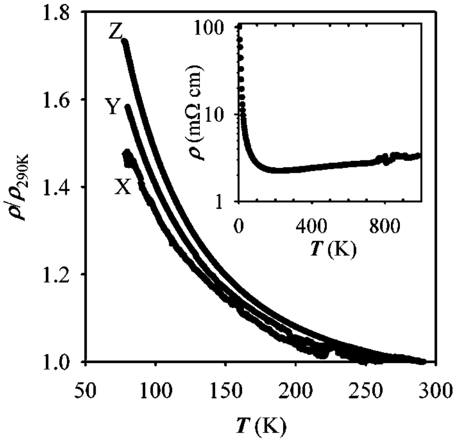

FIG. 2. Normalized *ab*-plane resistivity of BC-222 vs temperature under hydrostatic pressures. The pressure in giga pascal for these curves are changed in this sequence: 0.00 (X), 0.40 (Y), and 1.20 (Z). Inset: Resistivity vs temperature showing change of slope from negative to positive when temperature increases.

about 1 μm in thickness, 10–20 μm in width, and 1–2 mm in length. Since the whiskers have a very small cross section, the intrinsic resistance is inevitably high. More seriously, the contact resistance contributed an even larger portion of the two-wire resistivity, probably due to the anisotropic nature of the whiskers. At ambient pressure, the two-wire resistance across the sample we measured was 10–40 kΩ at room temperature and became higher at lower temperature. This contributed a considerable amount of noise to the signals. We adopted some improvements to our method described in Ref. 15. First, we picked different independent signals to measure. In general, the two thermocouple voltages are on the order of millivolt and the Seebeck voltage measured between the two TN or TP legs is on the order of microvolts. Only three of these four voltages need to be measured and generally only one of the (larger) thermocouple voltages is measured to avoid subtracting two large numbers to yield a small number. However, this is no longer an advantage in the case of a high-resistance sample in which the (smaller) Seebeck voltages are both very noisy. In this experiment, we picked the two (larger) thermocouple signals with low noise and one (smaller) signal between the two TP legs with high noise. Second, we have used a better Fourier-transform routine to handle low signal-noise ratio and the results were satisfactory.

We have measured the resistivity (ρ) of BC-222 (sample No. 1) in *ab*-plane from 4 to 900 K. The inset of Fig. 2 shows the logarithm of ρ vs $1000/T$. The curve shows typical narrow gap semiconductor behavior with the gap $E_g = 3.53$ meV from $T = 30-150$ K. At higher temperatures, the slope of $d\rho/dT$ is positive, as plotted in the inset of Fig. 2. This is not unusual for such a small gap material at low temperature and indicates our BC-222 sample can be roughly categorized as semimetal or very narrow gap semiconductor in the temperature range 4–900 K. Materials with good thermoelectric properties are usually expected to be within this regime.

Figure 2 shows the normalized resistivity of BC-222 (sample No. 2) in *ab*-plane under different pressure. The sample No. 2 has an $E_g = 3.89$ meV at ambient pressure (curve X), which is slightly higher than sample No. 1. As a result, the slope $d\rho/dT$ was always negative, and the resistivity at room temperature is also higher than sample No. 1. The pressure for curve Y and Z were 0.40 and 1.20 GPa, respectively. The pressure increased both resistivity and E_g slightly for sample No. 2. Upon reducing the pressure back to ambient pressure, the resistivity was not reversible but E_g remained unchanged. However, we also observed in another sample that the four-wire resistivity at room temperature was decreased when applying pressure, then increased when further pressure was applied. It is likely that the pressure reduced the intrinsic resistivity at room temperature, but also induced defects in the whiskers. It was noticeable that the two-wire resistance was much higher than the four-wire resistance at ambient pressure, possibly due to the contact was made through c direction of the whiskers and the fact that the resistivity of BC-222 along the c axis (ρ_c) is about 10^2-10^3 times of that in the ab plane (ρ_{ab}). However, the pressure reduced the contact resistance dramatically. Upon applying the pressure, the contact resistance was reduced by 1–2 decades.

Figure 3 shows the thermopower of BC-222 whisker (sample No. 3) versus temperature under high pressure. Curve (a) was measured at ambient pressure. Then pressure

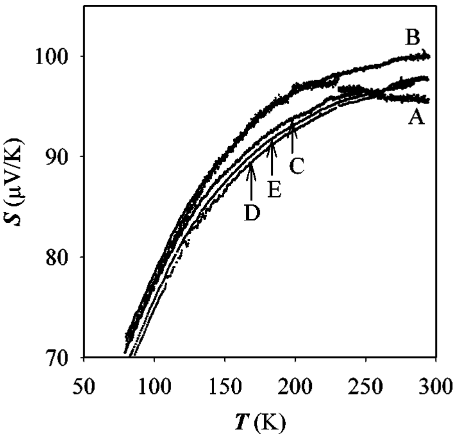

FIG. 3. Thermopower of BC-222 whisker vs temperature under hydrostatic pressures. The pressures in giga pascal for these curves are: 0.00 (a), 0.30 (b), 0.60 (c), 0.90 (d), and 1.20 (e), respectively.

was increased in turn to 0.30 (b), 0.60 (c), 0.90 (d), and then to 1.20 GPa (e). The thermopower data at ambient pressure (a) had lowest quality due to its highest resistance across the whisker. In addition, the whisker is ribbon-like and the internal stress might play an important role at ambient pressure. As a matter of fact, the thermopower measured above 250 K at ambient pressure was not fully repeatable for different runs. Nevertheless, the data below 250 K agrees within different runs very well and the bending over above 250 K shown in curve (a) was always observed although the degree of the bending varied. Upon applying a pressure of 0.30 GPa (b), the two-wire resistance across the sample decreased and the bending over above 250 K shown in curve (a) also disappeared. The $S-T$ curve was also repeatable between different runs. The curves (a) and (b) are almost identical below 250 K. Upon further increase the pressure to 0.6 GPa (c), S at 290 K decreased from 100.0 to 97.3 μV/K and the whole $S-T$ curve shifted downwards noticeably. Further increase of pressure does not have an apparent effect on the $S-T$ curve. We were able to measure the $S-T$ curve after the pressure was reduced to ambient pressure and though consistent with the previous runs, the data resolution was insufficient to determine if S was fully reversible upon release of pressure due to higher resistance between the measuring leads.

For nondegenerate systems, it was shown both theoretically[19,20] and experimentally[14] that the simple formula

$$S=\frac{k_B}{e}\left[\left(r+\frac{5}{2}\right)-\frac{T^*}{T}\right], \tag{2}$$

is meaningful, where k_B is the Boltzmann constant, e is the electron charge, and r is the energy dependence parameter for the electron scattering. The characteristic temperature T^* describes the degree of temperature dependence. At ambient pressure, T^* extracted from our thermopower data is 43.6 K, which corresponds to a k_BT^* of 3.76 meV. This agrees well with the energy gap of $E_g=3.53$ meV and $E_g=3.89$ meV from the resistivity data of sample Nos. 1 and 2. We can conclude from both $S-T$ and $\rho-T$ that under high pressure, the electronic band structure of BC-222 whiskers changes very little.

We observed both increment and decrement of the room temperature resistivity, but the overall trend was dominated by defects in the crystalline induced by applying pressure. As a result, the power factor decreased slightly under high pressure in most of the cases, but less than 20% in all cases. However, the contact resistance was reduced by 1–2 decades when applying pressure. This has great impact from the application point of view. One key factor to reach material limit of ZT in application is to have very small contact resistance. Our experiment demonstrated that pressure can be a useful way to improve the contact resistance with less than 20% poisoning effect to the power factor.

In summary, we extended the studies of thermoelectric properties of $Bi_2Sr_2Co_2O_9$ by applying hydrostatic pressure to the whiskers. The two-wire electrical conductivity increased 1–2 decades under pressure. Meanwhile electronic band structure changes little under high pressure, results in very little poisoning effect to the power factor. The experimental data showed that pressure can be used to improve the efficiency of the thermoelectric devices by reducing the contact resistance. We demonstrated in this letter again the possibility of thermoelectric devices with better efficiency under high pressure in another way, even with unavoidable tradeoff.[14]

This work is supported by Research Grant No. DAAD19-99-1-0001 from the Army Research Office.

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