

## Thermoelectric power of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ under pressure up to 9 GPa

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**Abstract.** Thermoelectric power (TEP) of two  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds (with  $\delta = 0.17$  and  $0.21$ ) was measured as a function of quasi-hydrostatic pressure up to 9 GPa at 300 K on samples with low porosity. In both cases TEP decreases with increasing pressure, at a rate  $\sim 0.8 \mu\text{VK}^{-1}/\text{GPa}$ . The data obtained under hydrostatic pressure up to 3 GPa are in good agreement with those under quasi-hydrostatic pressure. The TEP of both compositions is found to decrease linearly at a rate  $0.8 \mu\text{VK}^{-1}/\text{GPa}$  above 1.5 GPa.

**Keywords.** Thermoelectric power; quasi-hydrostatic pressure; hydrostatic pressure

### 1. Introduction

High pressure studies on  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  system have been confined mostly to the measurement of pressure-dependence of superconductivity transition temperature  $T_c$  (Driessen *et al* 1987; Keneko *et al* 1987; Okai *et al* 1987; Akahama *et al* 1987). Attempts have been made to explain the observed weak pressure dependence of  $T_c$ ,  $dT_c/dP$  being  $0.4 \text{ K GPa}^{-1}$ , using the BCS theory, the Cyrot's model and the resonating valence bond model. The measurement of lattice parameters as a function of pressure up to 13 GPa (Fietz *et al* 1987) indicates a normal compression and absence of any phase transition. The thermoelectric power (TEP) as a function of pressure at room temperature has been reported (Kutty and Vaidya 1988) to exhibit a maximum at 1 GPa followed by a monotonic decrease with further increase of pressure. The as-prepared polycrystalline samples are normally highly porous. The bulk properties such as TEP depend critically on the porosity.

In this communication we report the intrinsic pressure dependence of TEP up to 9 GPa at 300 K, as obtained from the measurements on low-porosity specimens.

### 2. Experimental details

The samples were prepared by mixing  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{CuO}$  in required proportions, and heating the mixture in air followed by annealing treatments in oxygen. The X-ray diffraction patterns from the samples indicated the presence of only the orthorhombic phase. The oxygen content was estimated from iodometric titration. The specimen resistance, as measured by the four-lead arrangement, exhibited sharp drop at the superconductivity transition temperature. The lattice parameters and the  $T_c$ -values for the two compositions used in the present measurements are listed in table 1.

The as-prepared samples were highly porous, the bulk density being about 65% of the theoretical density. The density increased to about 80% of the theoretical density on cold-pressing the samples to about 3 GPa. Cold-pressing at still higher pressures did not improve the density further. TEP was measured on as-prepared as well as on cold-pressed samples.

**Table 1.** Data on  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  samples.

Sample No.	$\delta$	$T_c(\text{K})$	Cell parameters		
			$a$	$b$	$c$
1	0.17	94.5	3.8089	3.8796	11.6107
2	0.21	88.5	3.8145	3.8747	11.6034

A tungsten carbide-opposed anvil set-up with 12.5 mm anvil face was used for the high pressure experiments. The technique of TEP measurement described earlier (Singh and Ramani 1978) was slightly modified to accommodate brittle specimens. A stack of three pyrophyllite gaskets was used to contain the specimen, thermojunctions and the heater. The first pyrophyllite gasket (12.5 mm o.d., 5 mm i.d., 0.4 mm thick) with a talc disc (5 mm diameter and 0.4 mm thick) at the centre was placed on the lower anvil. Two pairs of chromel-alumel (0.1 mm dia) thermocouples and a nichrome (0.1 mm dia) heater wire were placed about 1 mm apart. A specimen measuring approximately  $4 \times 1.5 \text{ mm}^2$  and 0.5 mm thick was placed at the centre of the second pyrophyllite gasket (12.5 mm o.d., 5 mm i.d., 0.5 mm thick) and gap around the specimen was filled with talc-powder and epoxy mixture. The epoxy was allowed to set and the gasket-specimen assembly was thinned down to 0.25 mm by working on both sides of the gasket with 600 grade emery paper. The gasket-specimen assembly was placed atop the first such that the specimen lay in contact with the thermojunctions and the heater which was electrically insulated from the specimen by a thin mica sheet. The third gasket (0.25 mm thick) with talc disc at the centre was placed atop the second gasket. The temperature gradient along the length of the specimen was set-up by passing current through the heater. A Leeds and Northrup (K-5) potentiometer and a Keithley-196 multimeter were used to measure respectively the voltage across the two chromel ( $Q_C$ ) and the two alumel ( $Q_A$ ) leads. The TEP was calculated from the relation,

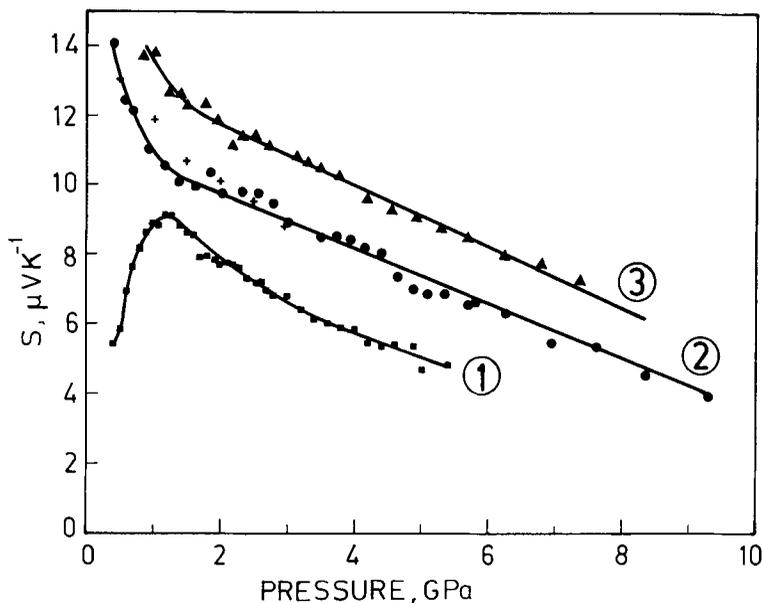
$$S = (S_C - rS_A)/(1 - r)$$

where  $r = Q_C/Q_A$ , and  $S_C$  and  $S_A$  are respectively the TEP of chromel and alumel.

### 3. Results and discussion

The pressure dependence of TEP as obtained for various samples are shown in figure 1. The TEP of as-prepared samples with  $\delta = 0.17$  increases from a value of  $\sim 4 \mu\text{VK}^{-1}$  at 1 atm. reaching a maximum of  $\sim 9 \mu\text{VK}^{-1}$  at 1.2 GPa, and decreases monotonically with further increase in pressure. The TEP of cold-pressed sample ( $\delta = 0.17$ ) decreases linearly above 1.5 GPa. The TEP of cold-pressed sample with  $\delta = 0.21$  is slightly larger than that of sample with  $\delta = 0.17$ , but the pressure dependence of TEP in both cases is nearly the same, being  $0.8 \mu\text{VK}^{-1}(\text{GPa})^{-1}$ . The sign of the TEP is positive indicating a  $p$ -type conduction, which is in agreement with the Hall coefficient measurement (Duan *et al* 1987).

The pressure dependence of TEP of as-prepared samples (porosity 35%) exhibits a shallow maximum at 1.2 GPa. This feature is in good agreement with an earlier



**Figure 1.** TEP vs pressure data for various samples. 1—*as-prepared* sample with  $\delta=0.17$ , 2—*cold-pressed* sample with  $\delta=0.17$ , 3—*cold-pressed* sample with  $\delta=0.21$ . Hydrostatic pressure data are shown by +.

observation (Kutty and Vaidya 1988). However, the TEP data on cold-pressed samples do not exhibit a maximum. It is tempting to suggest that the maximum in the TEP versus pressure data for *as-prepared* samples arises due to the high degree of porosity, which under pressure decreases rapidly leading to an improved inter-particle electrical contact. However, the electrical conductivity of *as-prepared* samples is sufficiently high to provide reasonable electrical contact for the measurement of thermo-emfs, and therefore porosity is not a very likely explanation for the appearance of maximum in TEP-pressure data on *as-prepared* samples.

The stress distribution in the high pressure cell is not truly hydrostatic since a solid pressure-transmitting medium has been used. The stress experienced by the specimen deviates from hydrostatic in two ways. First, there exists a stress (pressure) gradient in radial direction. By optimizing the gasket dimension the gradient can be minimized. For the dimension used in the present experiments the gradient is  $<0.1 \text{ GPa mm}^{-1}$  (Singh *et al* 1983). Secondly, the stress component in the axial direction (which is the direction of loading for pressure generation) is higher than the radial stress component, the difference between the two components, termed uniaxial stress component (Singh and Kennedy 1974), is of the order of the yield stress of the pressure-transmitting medium. For talc the uniaxial component is  $\sim 0.3 \text{ GPa}$  at 9 GPa and proportionately lower at lower pressures.

It is well known that the application of uniaxial load on polycrystalline specimens tends to align the crystallites with *c*-axis parallel to the direction of applied load (Robinson *et al* 1987; Omari *et al* 1987; Murugaraj *et al* 1988; Kanatzidis *et al* 1988; Lusnikov *et al* 1989). The degree of alignment on the surface of the specimen, as measured by X-ray diffraction method, is 2 to 3 times larger than that in the bulk specimen, as obtained from magnetization studies. The TEP is highly anisotropic,

being 2 and  $10 \mu\text{VK}^{-1}$  respectively in the *ab*-plane and in the *c* direction for  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (Wang and Ong 1989). As small uniaxial stress component is always present in an opposed anvil set-up with solid pressure medium, one would expect the degree of alignment of the crystallites in the specimen to change with pressure. If so, then the observed pressure dependence of bulk TEP will consist of two factors, the intrinsic pressure dependence of TEP, and the changes in TEP arising from pressure-dependent degree of alignment (because the magnitude of uniaxial stress component depends on pressure). The second factor will lead to a decrease in TEP. The measurements of degree of crystallite alignment by X-ray diffraction technique in as-prepared and the pressurized specimens indicate that no appreciable crystallite alignment takes place on pressing the specimens up to 9 GPa.

The TEP data obtained under hydrostatic pressure up to 3 GPa using piston-cylinder apparatus and teflon cell assembly (Shubha and Ramesh 1986) agree well with those obtained with the opposed anvil set-up. This indicates that the stress distribution in the opposed anvil set-up used in the present experiments is close to hydrostatic. The observed decrease in TEP with increase in pressure above 1.5 GPa is therefore largely an intrinsic effect. Further investigations are in progress to establish the pressure dependence of TEP in the low pressure region ( $< 1.5$  GPa).

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