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Effect of synthesis process and substrate on electrical and thermal transport properties of Bi-2212

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Abstract

Resistivity, thermoelectric power and thermal conductivity have been measured for a Bi-2212 system synthetised from a glassy precursor, either with a commercially Al_2O_3 substrate or with a home-made $BaZrO_3$ substrate. Those measurements show that the $BaZrO_3$ substrate gives better superconducting properties to the Bi-2212 than the Al_2O_3 substrate. The effect of (1.0 T) weak magnetic field has been searched for. The thermal magnetoconductivity and the contributions of the magnetic field to the thermoelectrical power are studied and compared through fine measurements. An electronic contribution seems to appear already well above the critical temperature and to exist up to 200 K. The onset temperature is thus deduced.

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1. Introduction

The glassy matrix method is sometimes used to enhance the synthesis of Bi-2223 phase against the 2201 and 2212 phases [1]. However the effect of contamination by the crucible is an important problem in such a method. The contamination of aluminum in the Bi-based (BSCCO) compounds has several negative implications on the thermal and electric properties of the sample [2]. In order to avoid the aluminum contamination induced by the chemical reaction between the melt and the conventional alumina substrate, $BaZrO_3$ substrates can be used in YBCO synthesis [3-6].

Here we report how the technologically attractive Bi-2212 phase has been synthesized from a glassy precursor by using two different substrates, i.e. Al_2O_3 and $BaZrO_3$ at the synthesis time in order to check whether the latter substrate *in fine* enhances the superconducting properties of Bi-2212 as it is the case for the YBCO compounds. Both synthesis ways are thus compared in view of the resulting electrical and thermal properties. Some related work on $BaZrO_3$-BSSCO composite has already been reported by the Geneva group [7].

Since a good sample of Bi-2212 will be found to be synthetised, thanks to the $BaZrO_3$ crucible, physically relevant informations may be extracted from the data such as the onset temperature, the range of fluctuations, and the electronical contribution to the heat transport, all parameters asking for intensive research at this time.

In Sect. 2, the synthesis of the two types of samples is detailed. The experimental set-up for the resistivity measurement and the simultaneous measurements of the thermoelectric power and thermal conductivity are explained in Sect. 3. The results and analyses are given in Sect. 4. A discussion is found in Sect. 5. Conclusion is drawn in Sect. 6.

2. Synthesis

Powders of Bi_2O_3, $SrCO_3$, $CaCO_3$, CuO and PbO_2 have been mechanically mixed together using an agathe mortar starting from a 2234 stoechiometric composition in order to obtain a large amount of pure 2212-BSCCO. An excess of calcium and copper has been used here in order to increase the diffusion of the reactive species for enhancing the formation of the intended 2212 stoichiometry. This mixture has been next decarbonated at 800C for 20h and melted in an alumina crucible at 1075C for 30 minutes in air. The liquid has been quenched between two room temperature copper blocks to form a glass. After grinding the glass, the powder has been pressed into pellets. The pellets have been finally heated in oxygen atmosphere on either alumina or barium zirconate substrates at 860C for 50h. The open porosity of the home-made barium zirconiate substrate allows the elimination of the excess liquid phase during the thermal treatment by capillarity effect.

Optical polarized light microscopy and scanning electron microscopy with an Energy Dispersive X-ray microanalysis system have been used in order to identify the crystalline phases and to determine their chemical composition [6].

No interaction has been found between the $BaZrO_3$ substrate and the Bi-based material. Notice that we have also detected by EDX analyses that some grains do contain a concentration of copper and calcium higher than that expected for the Bi-2212 stoichiometry, thus still approaching the 2223 stoichiometry. However in the case of the Al_2O_3 substrate, a strong interaction has been found in between the sample bulk and the substrate. This chemical interaction is responsible for the formation of an « eye-slope » reaction layer at the interface beetween the alumina substrate and the Bi-based materials (Fig.1b).

We conclude that the BSCCO compounds do not stick to the $BaZrO_3$ substrate (Fig.1a). This is not the case for the Al_2O_3 substrate for which the diffusion and contamination of the sample by Al corrosion is clearly visible (see Fig.1b).

3. Experimental set up

A small (10mm length, $1mm^2$ cross section) bar was cut from each pellet near its center (a) grown on Al_2O_3 (b) grown on $BaZrO_3$ respectively. They were glued on the sample holder and introduced into a cryogenic system made of a compressor and a double stage cold CTI - 20 model. In fact due to the at first surprising observation of different conductivity behaviours (Fig. 2), i.e. a semiconductor-like one and a metallic-like one respectively, different contact configurations were used in case (a), i.e. faces, sides, nature. No effect was seen for these tests, and the semiconducting, superconducting-free behaviour is confirmed.

Electrical and thermal transport properties have been measured down from 200K to 20K. During the experimental run, the cooling power is obtained through a Gifford - Mac Mahon cycle. The electrical resistivity was measured using the four - point method with current reversals [8].

The thermal conductivity and the thermopower were simultaneously measured using the steady state longitudinal heat flux method and the differential method respectively. The details and the accuracy of the technique taking into account the thermal losses are fully described in refs. [8,9].

It has been discussed in [8,9] that the relative error on the thermal conductivity is estimated to be ca. 8%. It is due mainly to the applied power, the thermal losses, the temperature gradient, the distance between thermocouples and the cross section area of the sample. The estimated error for measuring the thermopower is estimated to be ca. 2%, to be compared with the relative error for the electrical resistivity estimated to be ca. 3%.

4. Results

In Fig.2(a-b), the resistivity ρ of both samples obtained either with an alumina substrate or with a barium zirconate substrate respectively is represented versus temperature T. The opened circles represent the measurements without any applied magnetic field. The dark circles have been obtained with a 1.0 T magnetic field applied at high temperature perpendiculary to the current.

For the BSCCO sample obtained with the Al_2O_3 substrate, the resistivity exhibits a typical insulator behavior. The resistivity very mindly depends on the magnetic field. On the other hand, the sample which has been grown on the $BaZrO_3$ substrate shows a superconducting transition near the so-called critical temperature T_c= 85 K estimated from the inflexion point. At high temperature, the resistivity is linear with a 10μΩ.m resitivity value at 0K and is about 40μΩ.m at 225K. When a magnetic field is applied, the resistivity transition midpoint is shifted towards lower temperature, ca. 80 K for a 1.0 T field. Fluctuation effects seem to smear out the transition on both sides of the inflexion point.

In Fig.3 (a-b), the thermoelectric power S and the thermal conductivity κ are given versus temperature both for the sample obtained on the Al_2O_3 substrate case and the $BaZrO_3$ case. In the inset, those quantities are represented on a large scale of temperature in order to observe the high temperature behavior. The downward pointing triangles represent the field free thermal conductivity and the squares the field free thermoelectric power. The upward pointing triangles and the diamonds represent the thermal conductivity and the thermoelecric power respectively when a 1.0 T magnetic field is applied at high temperature perpendiculary to the thermal gradient.

(i) In the alumina substrate case, the thermal conductivity increases monotically with temperature above T_c and reaches 4 W/mK at 250 K. A change of slope is found at 60K and 50 K without and under the applied magnetic field respectively. A bump occurs like a maximum at 30 K. The applied magnetic field has a weak effect discussed below.

The thermoelectic power has a value of 140 μV/K at 250 K, decreases slowly with decreasing temperature and sharply drops to zero below 60 K. Inflexion points are found at 50 K and 45 K without and under the applied magnetic field respectively.

(ii) As far as the BSCCO grown on $BaZrO_3$ substrate is concerned, at high temperature, κ exhibits a power law behavior. An angular point is found near 85 K which is the defined critical temperature. A maximum occurs at 70 K. When a magnetic field is applied, the behavior is similar to the zero field case but a marked absolute value difference occurs between both curves especially at high temperature.

The thermoelectric power has an inflexion point at 85 K with and without magnetic field. Notice that the curves S(H=0) and S(H=1T) cross each other at 85 K. The influence of the magnetic field is large below the critical temperature and well marked at high temperature.

In order to evaluate the influence of the magnetic field on the thermoelectric power and the thermal conductivity, normalized quantities as $\kappa^*=(\kappa(B)-\kappa(0))/\kappa(0)$ and $S^*=(S(B)-S(0))/S(0)$ are reported versus the temperature in Fig.4a and Fig.4b respectively for the compound synthesized with the $BaZrO_3$.

The so-called thermal magnetoresistivity κ^* shows a 2% maximum at 150 K, while inflexion points occur at 100 K and 190 K. At high temperature, κ^* is finite and is a 1% constant till 80K equal to about, but is close to 0% at lower temperature. That indicates that the magnetic field has the strongest influence near 150 K. At 100 K, the magnetic field influence decreases to a quasi zero value at and below 75 K.

The influence of the magnetic field on S is represented in Fig. 3b. S^* is nearly constant and equal to 2 % above 80K. S^* changes sign at 85 K. A sharp decrease occurs at 85 K up to 200%, increases below 75 K and reaches 0% at 50 K.

In both cases, the values above 280K might be influenced by radiation effect [3,10] however an intrinsic effect like pair existence [11] has not to be *a priori* rejected.

5. Discussion

The results of the resistivity ρ measurements obviously show that the BSCCO phase grown on the $BaZrO_3$ substrate is much better electrically conducting than the one from the Al_2O_3 substrate as far as superconducting properties are concerned. The disappearance of the superconductivity transition in the Al_2O_3 substrate case may be attributed to the strong contamination of the BSCCO phase by aluminum which deeply modifies the microstructure and composition. On the other hand, the $BaZrO_3$ substrate does not mask the Bi-2212 superconducting phase. The usually expected linearity of the resistivity at high temperature is well observed.

Similar results are found in the thermoelectric power and in the thermal conductivity effect measurements for both substrate cases. Nevertheless a transition is still found in S and κ in the Al_2O_3 case near 50 K. This indicates that in such an insulating-like material, the electrons are not much available for the superconducting mechanism. Therefore the S and κ behaviour trully probe here the contribution of the change in phonon mean free path due to the establishment of a superconducting (coherent) phase throughout the material [12,13,14]. This change in phonon mean free path is irrelevant for the electrical conductivity here. The conclusion that only electrons lead to some structure in the thermal conductivity below T_c is here unfounded [15]. One can see that the electronic contribution is about 21% at 150 K and 36% at $2T_c$. However the structure (peak) itself is certainly governed by the electronic contribution (mean free path, Van Hove singularities and gap effect)[14,16,17].

In the BSCCO sample on Al_2O_3 substrate, the influence of the magnetic field is less than 1% of the total signal for the thermal conductivity and the thermoelectric power. On the other hand, in the $BaZrO_3$ case, the influence of the magnetic field is of the order of 1% in the thermal conductivity. Even though error bars do exist we consider the differences to be meaningful. This implies that a non negligible electronic contribution is found, since the phonon contribution is not expected to be much influenced by the magnetic field. Since $\kappa(B)$ is smaller than $\kappa(0)$, at high temperature, the magnetic field is considered to decrease the electron mean free path. The bump in κ^* at 150 K indicates that electrons are accumulating (in pairs) close to the Fermi level before much condensing below the inflexion point at 100 K. This condensation process begins near the inflexion point at 190 K which is defined as the onset temperature. It might also be the temperature at which there is a pseudogap opening [18]. The field influence becomes very small at low temperature because of shielding of pairs and of flux pinning. The fact that the critical temperature is different from the lowest inflexion point may be considered as due to a fluctuation effect [19]. This gives support to the work of Houssa et al. who considered the gap effect as the most relevant contribution for the thermal conductivity features when Van Hove singularities exist in the density of states [20,21].

As for the influence of the magnetic field on S, it can be noticed that this influence is quite constant at high temperature and then shows a sharp transition at 85K. The magnetic field on S exhibits a change of sign of S at 85 K. The origin of such a links serving as Josephson junctions for d-wave type superconductivity is studied at this time [22].

At high temperature, the magnetic field influences the electron mean free path because of the curvature of the charge carrier path and the scattering by grain boundaries. Below the critical temperature, the magnetic field breaks pairs, a non-zero density of states of normal electrons remains. The relative influence of B on S^* is then very obvious as seen.

6. Conclusion

$BaZrO_3$ as substrate does not react with BSCCO phases and does not destroy the superconducting properties of the Bi-2212 phase. Moreover, the quality of the Bi-2212 as synthetized allows to finely analyze thermal transport phenomena. A non negligible electron contribution is found even for weak field at high temperature. From measurements under a magnetic field an onset temperature near 190 K can be discerned. It is about twice the critical temperature and can be nowadays attributed to a temperature at which a pseudogap opens up.

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Figure Captions

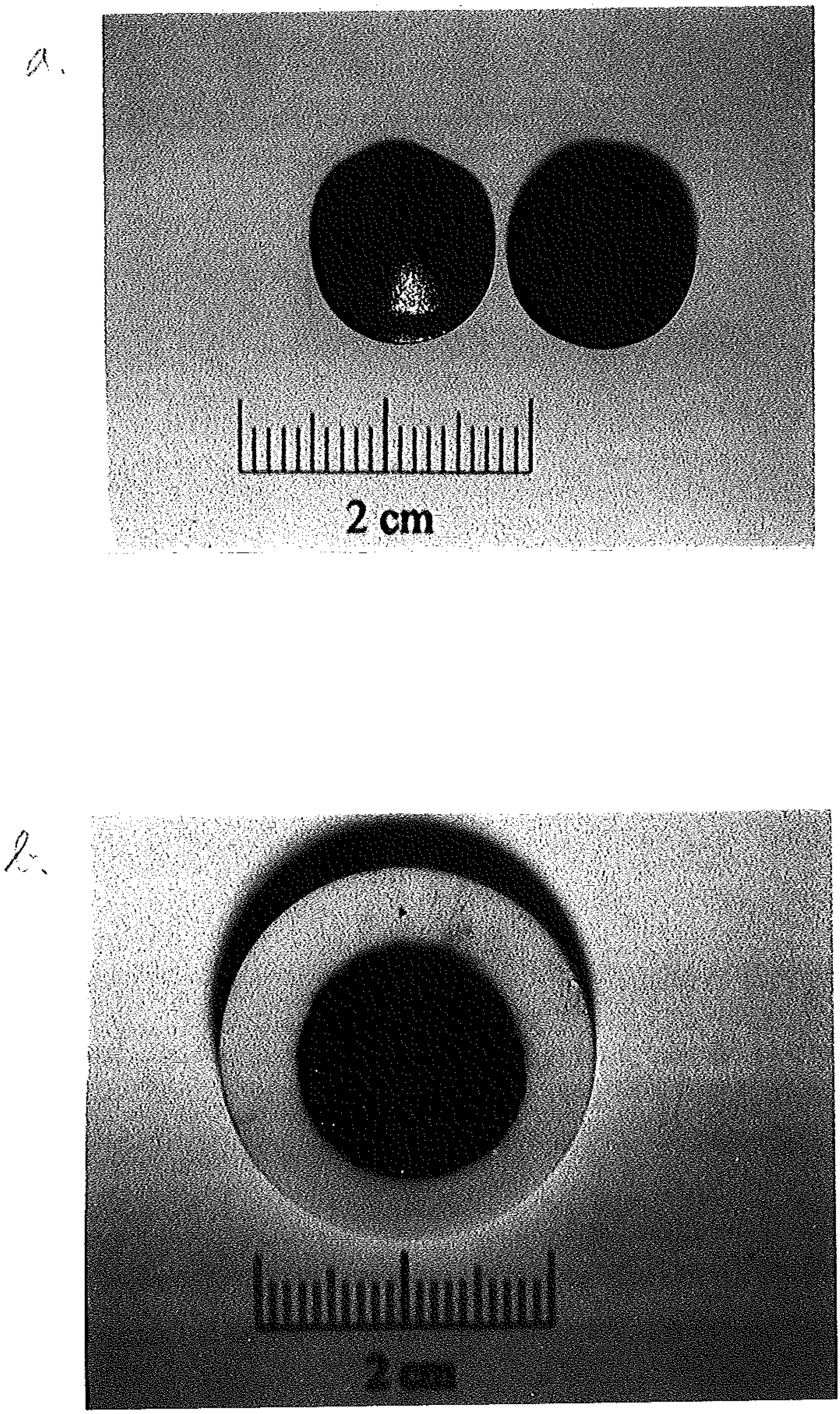
Fig.1 : Optical micrograph of Bi-2223 glassy presursor annealed on (a) $BaZrO_3$, and (b) Al_2O_3. The interaction layer between the alumina substrate and the Bi-based pellet is clearly visible.

Fig.2 : Resistivity of Bi-2212 phase grown on a) Al_2O_3 substrate and b) $BaZrO_3$, the opened circles and the full circles represent the resistivity measured in absence or presence of a 1.0T magnetic field respectively.

Fig.3 : Thermoelectic power S and thermal conductivity κ of Bi-2212 phase grown on a) Al_2O_3 substrate and b) $BaZrO_3$, the triangles and the squares represents κ and S respectively in the field free case. The up triangles and the diamonds are κ and S obtained under a 1.0 T magnetic field.

Fig.4 : Normalized magnetic contribution to a) the thermal conductivity κ^* and to b) the thermoelectric power S^* versus temperature (see text for definition)

1.



Optical micrograph of the Bi-2223 glassy precursor annealed on (a) $BaZrO_3$, and (b) Al_2O_3. The interaction layer between the alumina substrate and the Bi-based pellet is clearly visible.

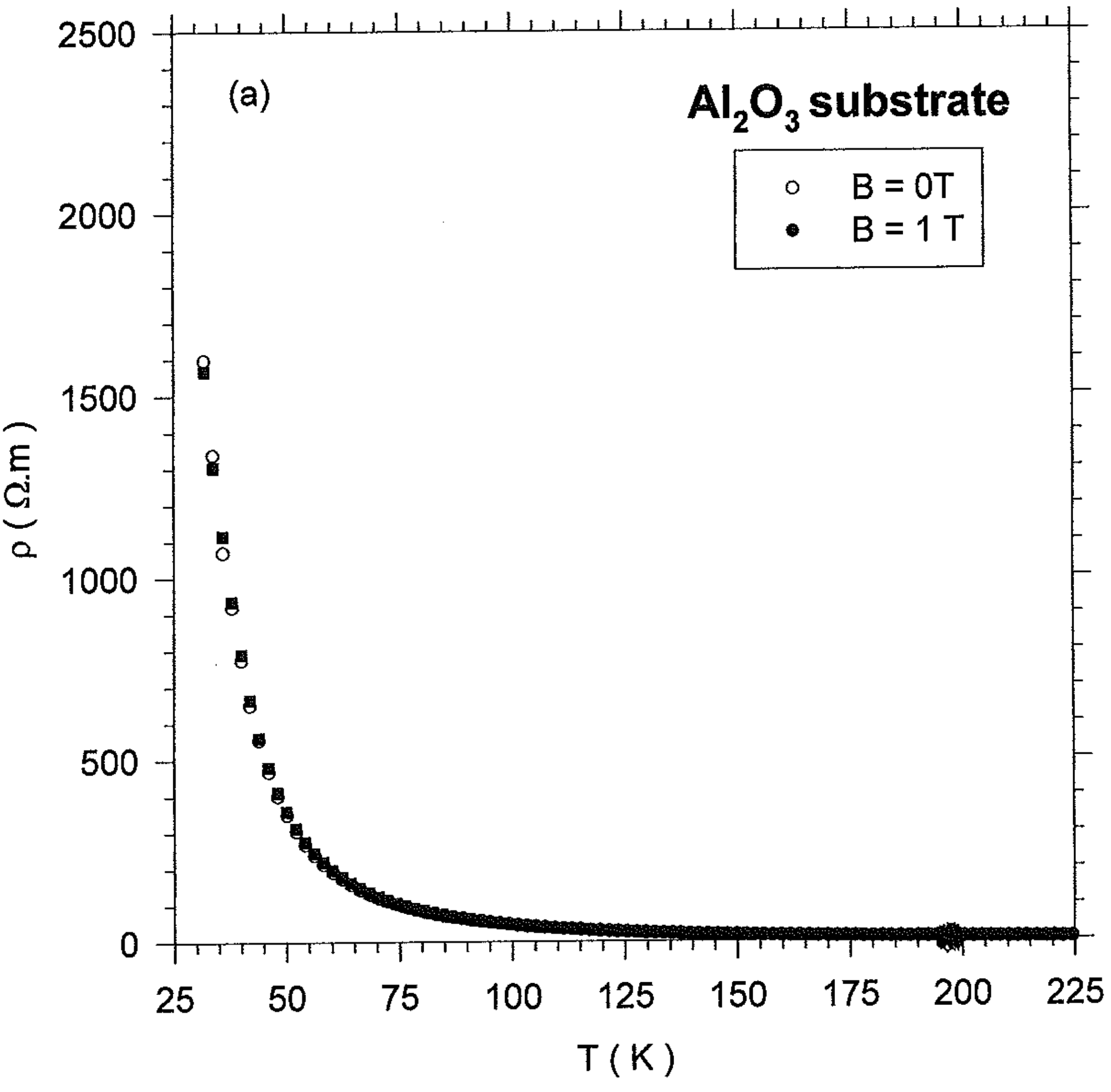

(a)
Al_2O_3 substrate
○ B = 0T
● B = 1 T
ρ (Ω.m)
2500
2000
1500
1000
500
0
25
50
75
100
125
150
175
200
225
T (K)

Fig 2a

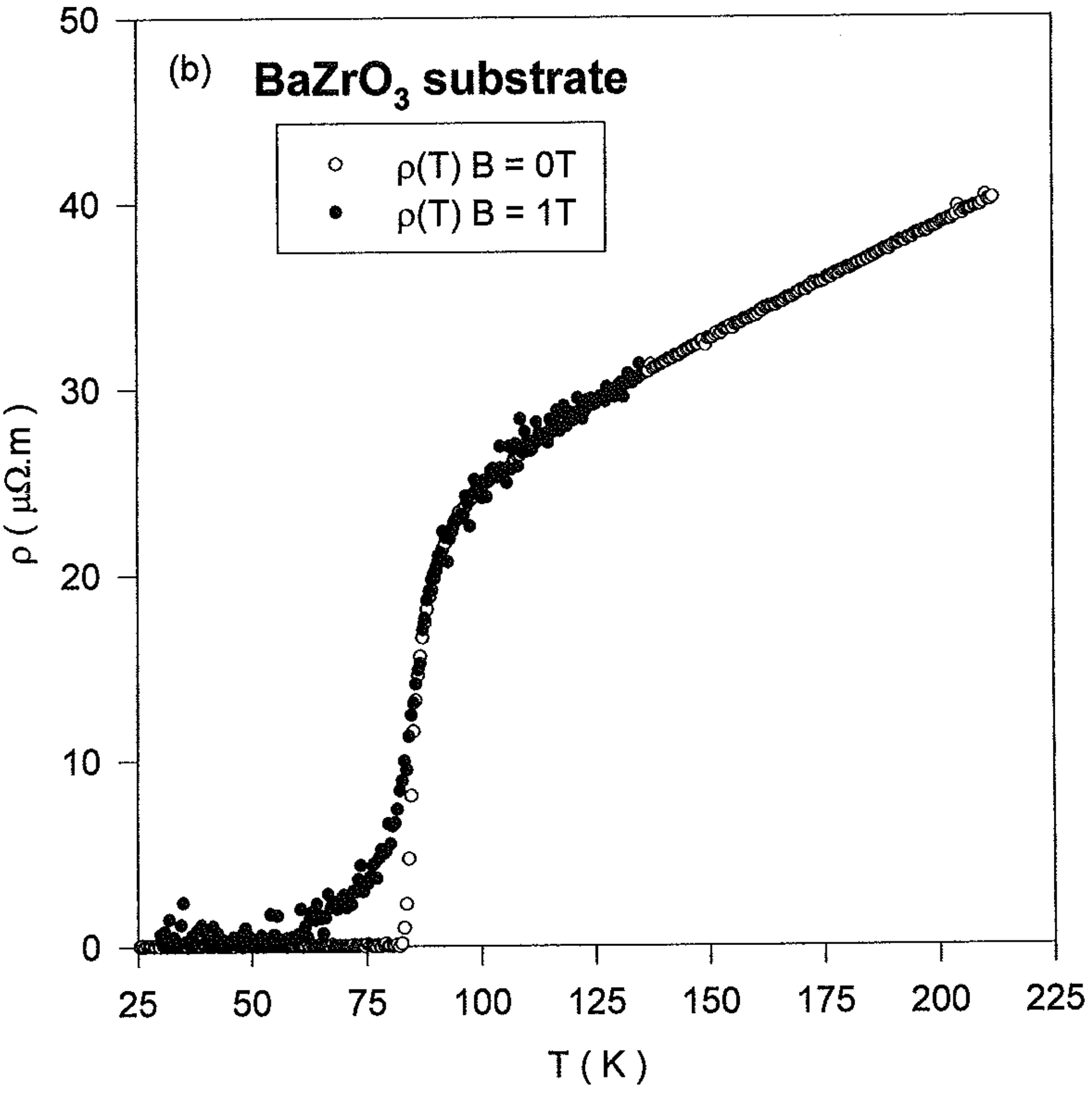

(b)
BaZrO$_3$ substrate
○ ρ(T) B = 0T
● ρ(T) B = 1T
ρ (μΩ.m)
0
10
20
30
40
50
25
50
75
100
125
150
175
200
225
T (K)

Fig 2b

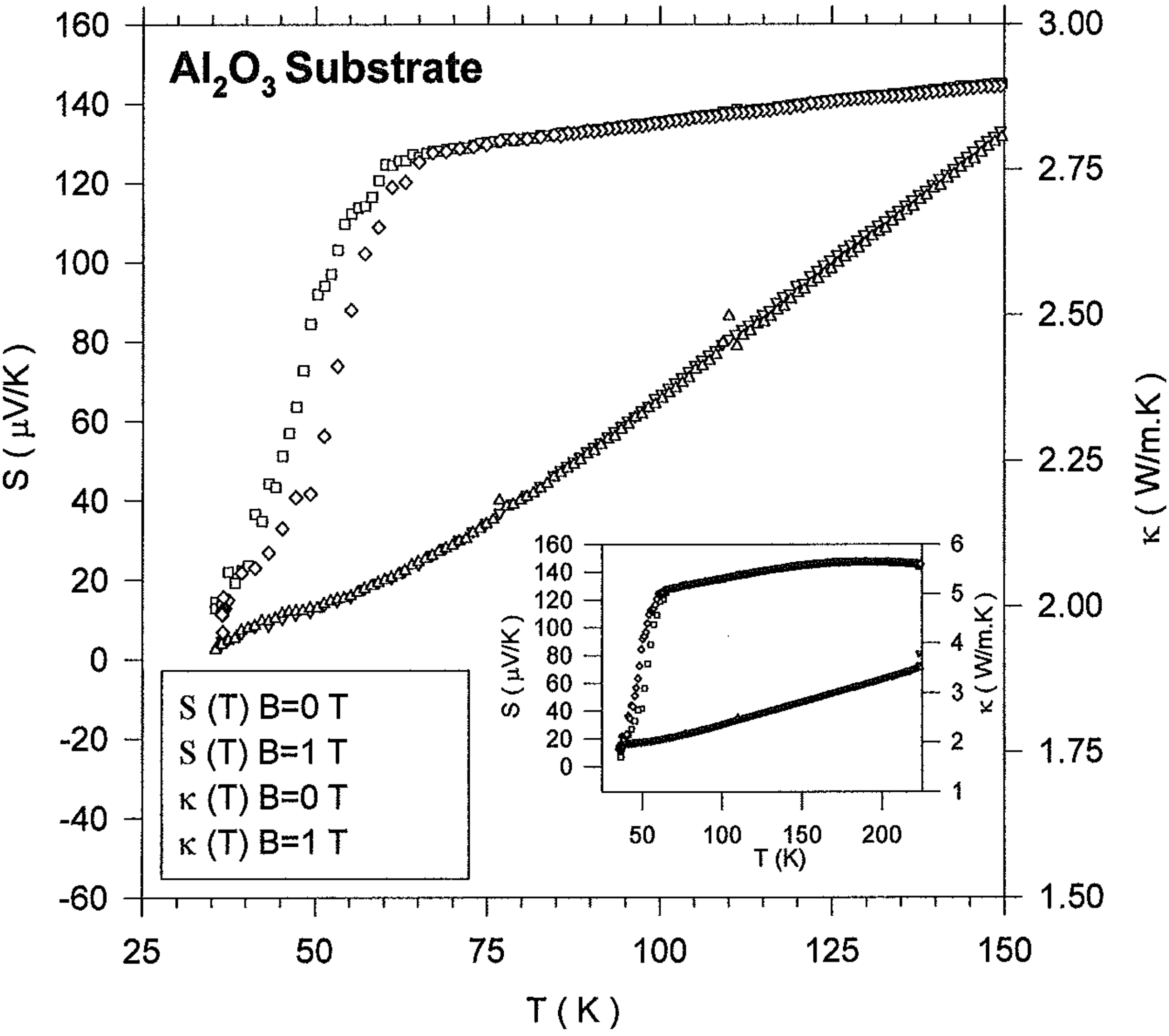

Al$_2$O$_3$ Substrate
S (µV/K)
κ (W/m.K)
T (K)
160
140
120
100
80
60
40
20
0
-20
-40
-60
3.00
2.75
2.50
2.25
2.00
1.75
1.50
25
50
75
100
125
150
S (T) B=0 T
S (T) B=1 T
κ (T) B=0 T
κ (T) B=1 T
S (µV/K)
κ (W/m.K)
T (K)
160
140
120
100
80
60
40
20
0
6
5
4
3
2
1
50
100
150
200

Fig 3a

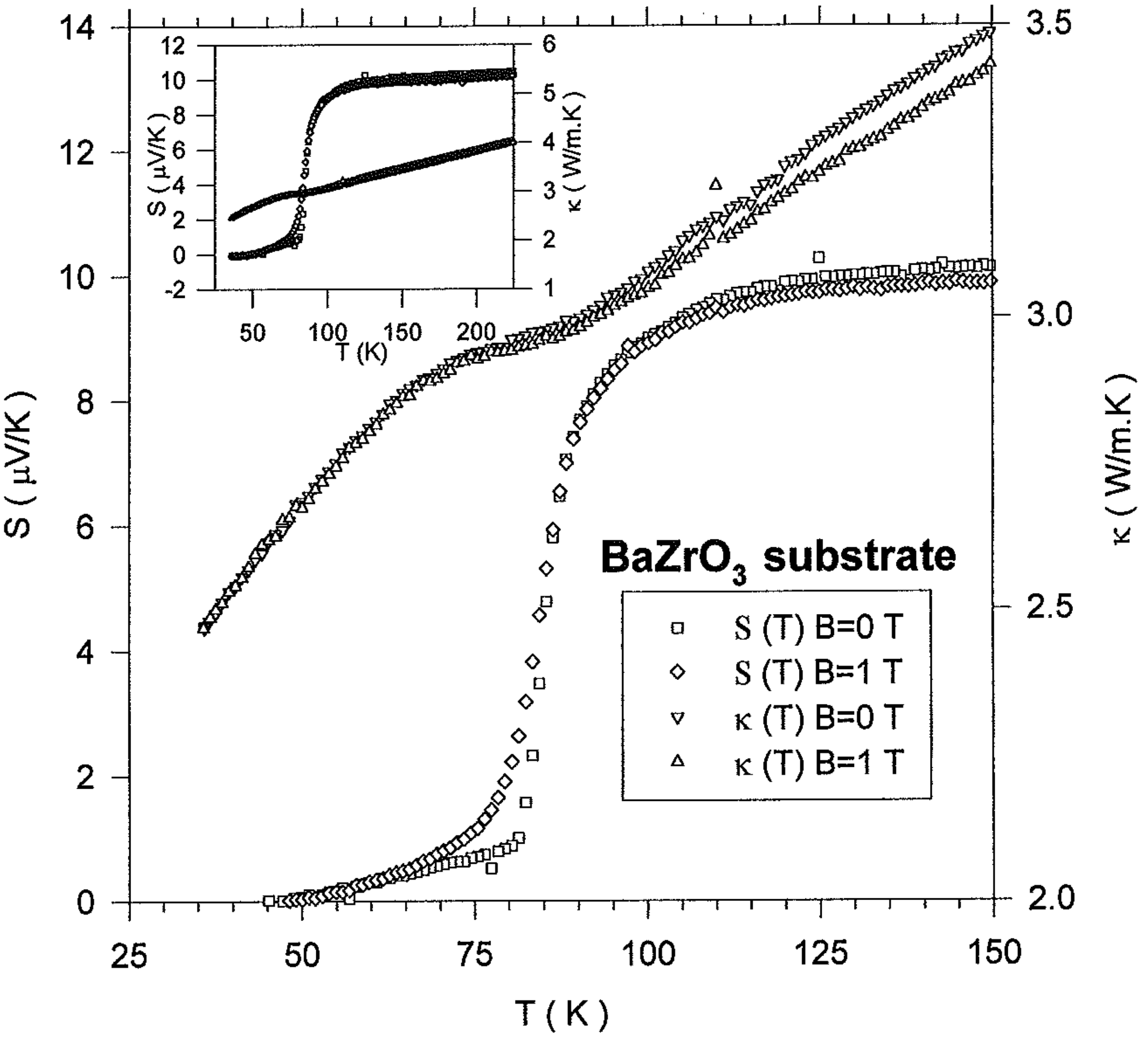

14
12
10
8
6
4
2
0
S (μV/K)
3.5
3.0
2.5
2.0
κ (W/m.K)
25
50
75
100
125
150
T (K)
BaZrO$_3$ substrate
S (T) B=0 T
S (T) B=1 T
κ (T) B=0 T
κ (T) B=1 T
12
10
8
6
4
2
0
-2
S (μV/K)
6
5
4
3
2
1
κ (W/m.K)
50
100
150
200
T (K)

Fig 3b

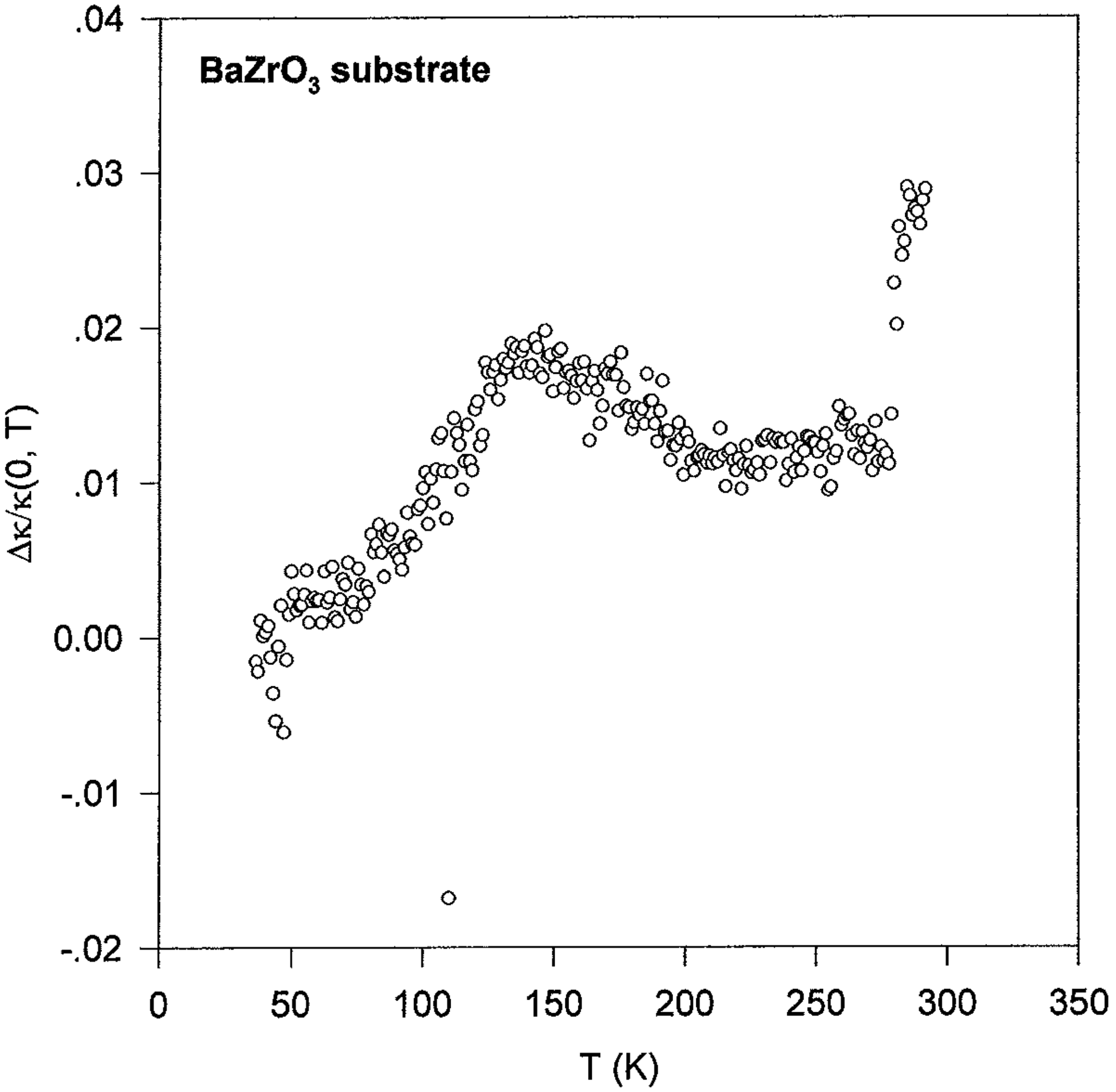

BaZrO$_3$ substrate
Δκ/κ(0, T)
.04
.03
.02
.01
0.00
-.01
-.02
0
50
100
150
200
250
300
350
T (K)

Fig 4

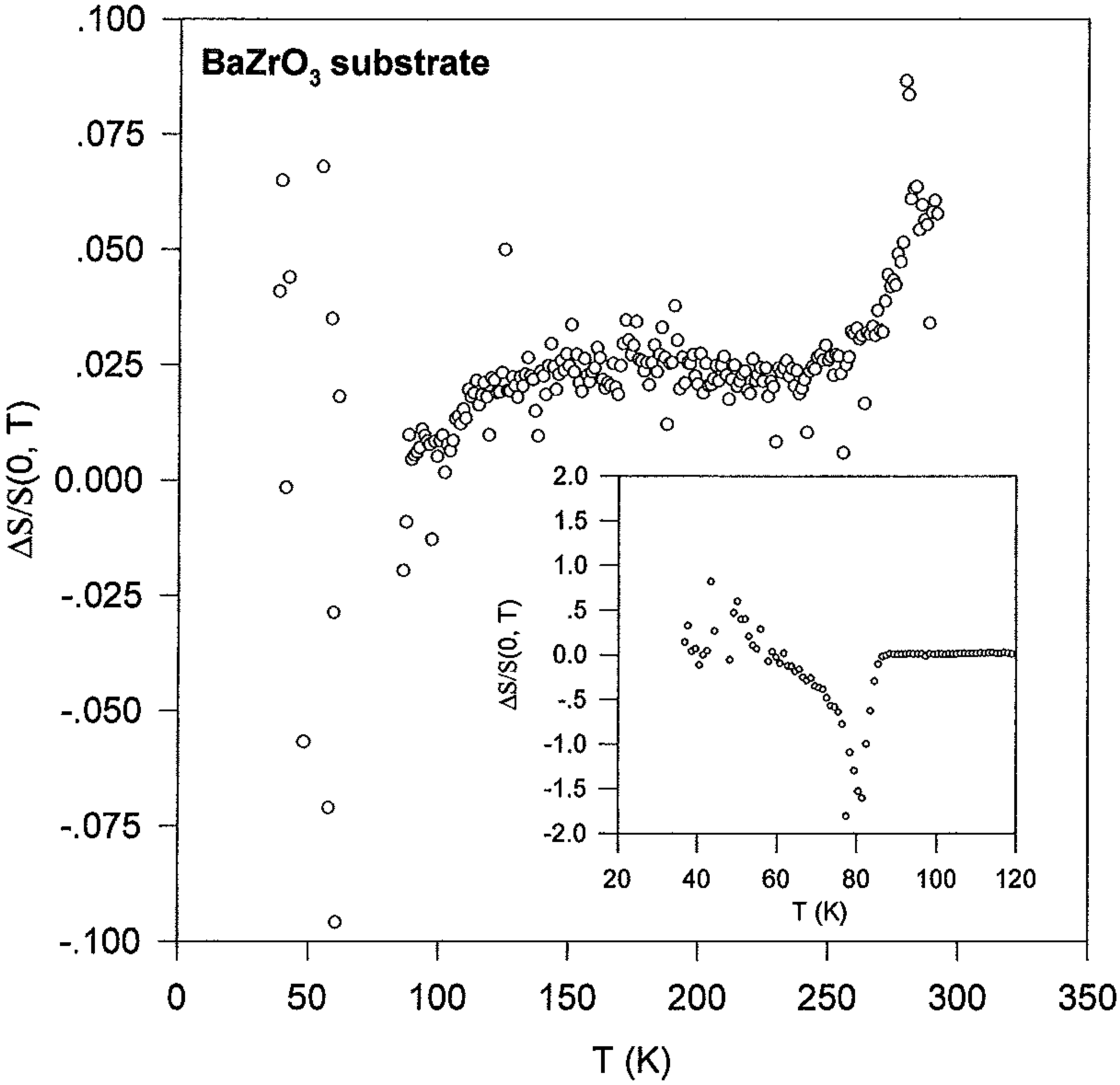

BaZrO$_3$ substrate
.100
.075
.050
.025
0.000
-.025
-.050
-.075
-.100
ΔS/S(0, T)
0
50
100
150
200
250
300
350
T (K)
2.0
1.5
1.0
.5
0.0
-.5
-1.0
-1.5
-2.0
ΔS/S(0, T)
20
40
60
80
100
120
T (K)

Fig 4A