MICROWAVE SURFACE RESISTANCE OF Rb-DOPED YBCO CERAMIC

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Abstract **- The influence of Rb_2CO_3 additive on the properties of YBCO was investigated. The primary batch had formula $Y_{1-0.2x}Ba_{2-0.2x}Rb_xCu_3O_y$ where x=0 to 0.60. Only traces of ($2.21x10^{-2}$ wt.%) Rb were found in all samples after final baking. Adding Rb shifted the temperature Ton of the "magnetic transition" towards lower temperatures without affecting the electrical HTSC characteristics and improved the grain size homogeneity.**

Introduction

The main obstacle limiting the practical applications of bulk high-temperature superconducting (HTSC) materials is their granularity and the "weak" bond between the grain in the polycrystalline structure severely worsening their electrical and magnetic parameters compared to the single-crystal materials [1]. This is why the effects of various additives on the process of HTSC polycrystalline structure formation is being intensively studied. For example, small amounts of Ni can be included in the crystal structure of an YBCO HTSC [2], and the presence of Ag during the polycrystalline structure formation can influence the YBaCuO microstructure [3]. The alkali metals group is of particular interest, since the literature data about their influence is controversial. Most authors define the effect of their addition as catalytic [4],[5]. Some of our previous studies showed that adding K in an HTSC affects substantially the microstructure formation [6].

In the present paper we report investigations on the influence of adding Rb in a wide concentration range on the main electrical, magnetic and microstructural parameters of an YBCO material.

Experimental

The samples were prepared following the classical ceramic technology from a starting batch with general formula $Y_{1-0.2x}Ba_{2-0.2x}Rb_xCu_3O_y$, where x changes from 0 to 0.60. The following initial powder compounds were used: Y_2O_3, $BaCO_3$, CuO with 99.99 % purity, and Rb_2CO_3 with 99.90 % purity. After preliminary baking of the batch at 900 °C, 1-μm grain-size powder was used to press pellets with diameter of 10 mm and thickness of 1.5 mm. The samples with $x > 0$ were sintered at 920 °C with isothermal delay of 24 hours and subsequently tempered for 24 hours at 600 °C. From the $x = 0$ composition, samples with good HTSC properties were obtained at final sintering temperature of 980 °C for 60 hours in oxygen atmosphere.

The reaction temperature, decomposition temperature and thermal stability were determined by thermogravimetry (TG) and differential thermal analysis (DTA) in which the mixed powders were heated at 20 C/min in dry air. X-ray diffraction (XRD) data were obtained by powder diffraction utilizing Co(K_α) radiation;scanning electron microscope, energy dispersive X-ray spectra (SEM EDS), were used to study the microstructure and morphology of the crystalline grains in the samples prepared. The compositions of the phases was determined following the standart procedure of electron probe microanalysis (EPMA).

The transition temperature of HTSC samples was determined using the four-probe "resistive" and the contactless "pick-up-coil" techniques. To measure the critical current density J_c and the surface resistance R_s of 10-mm diameter HTSC pellets, we developed our own original equipment. In the J_c measurements, the pellet was placed in a homogeneous a.c. (1 kHz) magnetic field (0 - 15 mT); the dependence was then recorded of the signal from a flat coil (1.5 mm diameter, placed axially on the pellet surface) on the external magnetic field amplitude. This dependence has a well- expressed break point whose location was used to determine the critical current density. Measurements of the surface resistance in the 7 - 15 GHz frequency range were performed using plane copper resonator structures (shaped as circles or 3/4 rings) made on thin dielectric substrates ($\varepsilon = 2.5$), with the pellet being measured serving as a ground plane. All J_c and R_s measurements were carried out at 78 K.

Results and Discussion

Using DTA data, we studied the processes of forming Rb-substituted HTSC as compared to the non-substituted YBCO. Figure 1 shows the DTA curves of $Y_{1-0.2x}Ba_{2-0.2x}Rb_xCu_3O_y$, where x changes from 0 to 0.40. For each sample, data is presented for the initial batch and for one heat-treated at 900 °C (first heat-treatment) were the YBCO phase is about 70-75 wt.% (calculated from the XRD data). In the case of the $Y_1Ba_2Cu_3O_y$ composition, there are endothermic peaks at about 830 °C and 980 °C, which result from decomposition of $BaCO_3$ and partial melting of YBaCuO, respectively. Characteristically, the endothermic processes in Rb-substituted systems start about 760 °C and appears peak at 830 °C (as in pure YBCO) and the new peak about 890 °C. If the endothermic peak at 830 °C can be associated with the processes of $BaCO_3$ decomposition into BaO and CO_2 during the sintering process, the peaks at 760 °C -890 °C are obviously caused by Rb_2CO_3-additive. The optimal sintering temperatures was selected using the DTA data. We found that adding Rb_2CO_3 to the starting batch lowered the sintering temperature of the high-T_c orthorhombic phase down to 920 °C compared to that of pure YBaCuO.

Fig.2 illustrates typical surface structure of the samples prepared using rapid cooling from 850 °C after isothermal delay of 4 hours (x = 0.60). The XRD, SEM EDS and EPMA data indicated the existence of a glass-like Rb_2CO_3 phase at this temperature. This made us suppose that liquid Rb-containing phase exist bettween 760 and 890 C. It participate in polycrystalline structure formation during the second treatment by enhancing the diffusion processes thus helping the CuO- excess move to the surface.

After the first heat-treatment (900 C/24 h), the XRD data showed (SEM EDS and EPMA confirmed it) that in samples with Rb_2CO_3 additive Rb_2O, CuO and $BaCuO_2$ phases existed in the powder.

After the second heat-treatment, the SEM studies demonstrated that samples with Rb-additive possessed a 300-μm low-density surface layer with regions of different grain type. Besides the peaks of the 1-2-3 Perovskite structure, we observed peaks of additional phases in the X-ray patterns of all samples. They were identified as $BaCuO_2$ and CuO using the available powder XRD data [7]. The intensities of their reflexes increased with the increasing of x. Peaks of Rb-additive related phases were not found. When the highly defective surface layer was removed, the XRD data confirmed the presence of only $Y_1Ba_2Cu_3O_y$ phase. Fig.3 illustrates the characteristic stratification of YBCO sample where the Rb-additive in the starting batch was the largest (x = 0.6), as well as the data from the SEM EDS spectra of the zones observed. Scanning of the entire surface of the two zones revealed traces of Rb (about 0.2 wt.%); however, insofar as these data are within the error limits of the analysis, we sought other techniques of detecting Rb. Using AAS (the samples were dissolved in HCl), we studied the Rb content in the surface layer and in the bulk and found that it was practically the same and did not exceed 2.21×10^{-2} wt.% for all compositions (x = 0.2 - 0.6).

The studies of the samples physical properties were performed after the defective multiphase layer was removed through grinding and polishing. Table 1 summarizes the data of the main physical measurements.

Table 1

Physical measurements				
starting composition	$Y_{1-0.2x}Ba_{2-0.2x}Rb_xCu_3O_y$			
	x = 0	x = 0.20	x = 0.40	x = 0.60
density (g/cm^3)	6.0	5.9	6.0	5.8
J_c (A/cm^2)	212	261	217	
surface resistance R_s (mΩ) at f_0=7.3GHz	32	21	27	
at f_0=14.3GHz	51	42	49	

As Table 1 demonstrates, the data for the critical current density for the series of samples investigated vary insignificantly and are in the order of the literature data [8] for polycrystalline untextured YBaCuO substances.

Despite the fact that insignificant amounts of the additive were found in the end-product, differences could be seen in the magnetic and resistive behavior of the samples. Fig.4(a) and (b) allows the comparison of the curves $\chi(T)$ and R(T) for samples with different Rb content in the starting batch. One can see that the final temperature of the superconductive resistive transition coincides with the initial temperature of the magnetic transition. As the content of the additive is increased, the final temperature of the magnetic transition shifts towards the lower temperatures. In contrast, for the resistive transition one can see an increase of the initial temperature as the Rb content in the starting batch is increased (for x = 0.6 we measured an initial temperature in the order of 94.6 K).

The parameter most sensitive to the additive amount was the surface resistance measured at 7.3 and 14.3 GHz. A tendency of reduction was observed and the resistance had its lowest value for x = 0.2. For this sample, the value of the specific resistance at room temperature was 20 % lower. It should be noted that adding Rb allowed reproducible preparation of superconducting structures under relatively mild technological conditions (920 °C/24 hours), while the starting batch (x = 0) had to be treated at a final temperature of 980 °C for 60 hours in oxygen in order to produce good HTSC properties.

To explain the peculiarities observed resulting from adding Rb_2CO_3, we turned to following the changes in the polycrystalline microstructure. Revealing the polycrystalline structure through chemical etching in orthophosphoric acid showed changes in the YBaCuO structure upon adding Rb. Considerable improvement of the structure homogeneity was observed (as compared with pure YBCO) expressed in statistically less internal pores. All the above allow us to suppose that the additive places itself on the grains boundaries which negatively affects the samples magnetic behavior and the higher homogeneity obtained of the polycrystalline structure can only partially compensate for it.

Conclusion

An YBaCuO system was investigated as Rb was introduced in the form of Rb_2CO_3 to a starting batch with general formula $Y_{1-0.2x}Ba_{2-0.2x}Rb_xCu_3O_y$, where x changes from 0 to 0.60. The magnetic and electrical properties of the system were studied as a function of the additive content. As a result, the following conclusion can be drawn:

- Adding Rb allows reproducible preparation of an HTSC material with good physical parameters under milder sintering conditions than in the case of the pure system, namely, lower final temperature (920 °C) and shorter isothermal delay in air.

- The XRD, SEM EDS and EPMA analyses demonstrate that the Rb_2CO_3 introduced to the starting batch in a wide concentration range (x = 0.2 - 0.6) probably participates as a liquid phase in the process of phase formation in the system; moreover, no proof can be found for Rb participating in the Perovskite crystal cell. The Rb additive improves the homogeneity of the system without affecting its electrical HTSC characteristics; indeed, for x = 0.20, the latter were improved. The most important effects are manifested in additive's influence on the final temperature of the transition to non-superconducting state and on the microwave surface resistance. We assume that the worsening of the YBCO magnetic properties after substitution is related to the Rb presence on the grains boundaries.

Figure Captions

Fig.1. Differential thermal analysis (DTA) curves: (a) for the initial batch; (b) for the one heat-treated at 900 C powder of $Y_{1-0.2x}Ba_{2-0.2x}Rb_xCu_3O_y$; A, x=0; B, x=0.20; C, x=0.40.

Fig.2. (a) SEM micrograph, (b) EDS (energy dispersed X-ray spectra) analysis, (c) EPMA data (the unit is at.%) for the $Y_{0.88}Ba_{1.88}Rb_{0.60}Cu_3O_y$ specimen heat treated at 850 °C for 4 hours.

Fig.3. SEM micrograph of a $Y_{0.88}Ba_{1.88}Rb_{0.60}Cu_3O_y$ sample, where (1) is a zone with composition $Y_1Ba_2Cu_3O_y$; (2) is CuO phase; (3) is a zone with $Y_1Ba_2Cu_3O_y + BaCuO_2$ composition and (s) is surface of the sample.

Fig.4. Temperature dependence of the ac susceptibility (a), and resistance (b) for $Y_{1-0.2x}Ba_{2-0.2x}Rb_xCu_3O_y$ with various x values. 1; x = 0. 2; x = 0.20. 3; x = 0.35. 4; x = 0.40. 5; x = 0.60.

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Fig.1

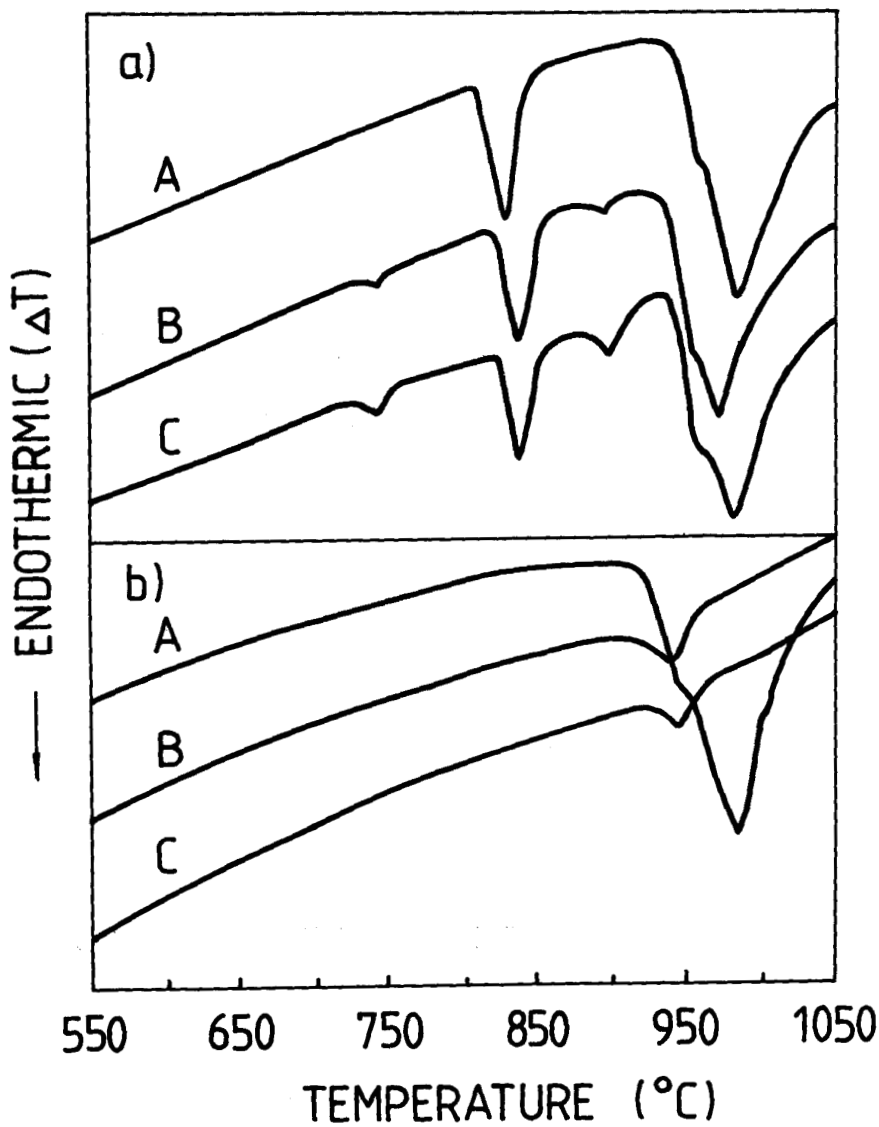
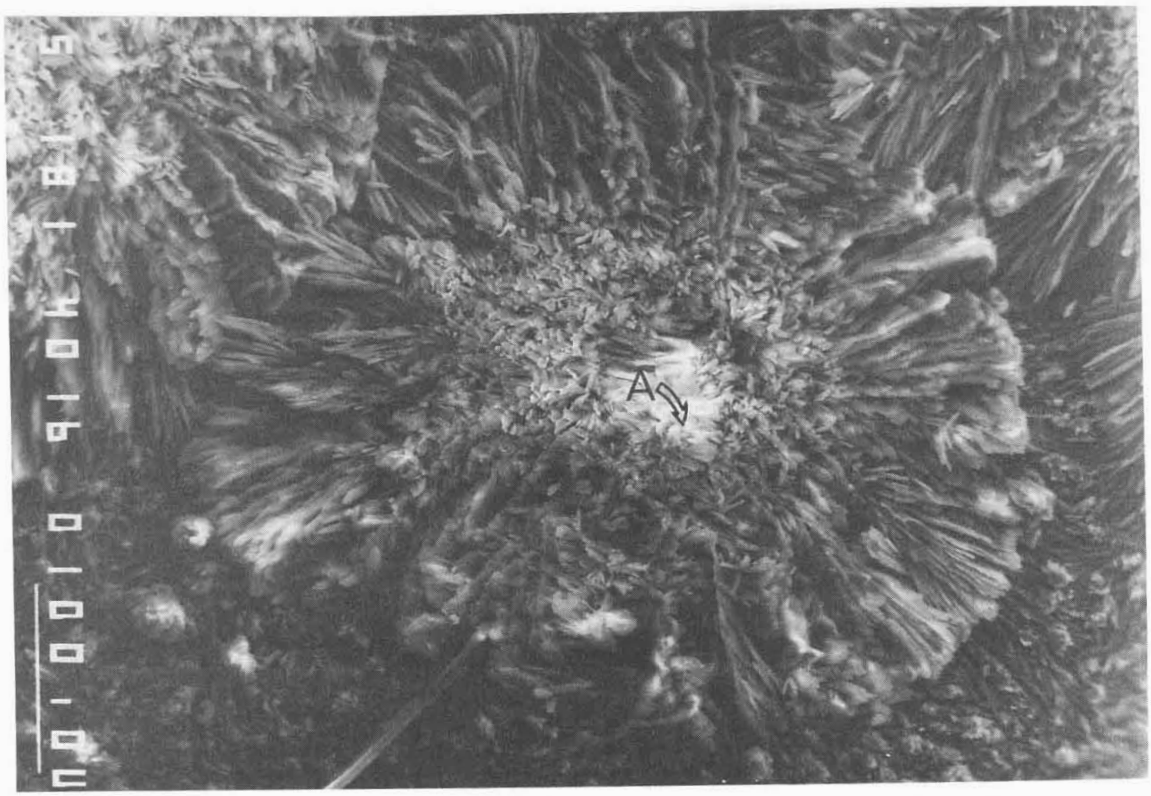
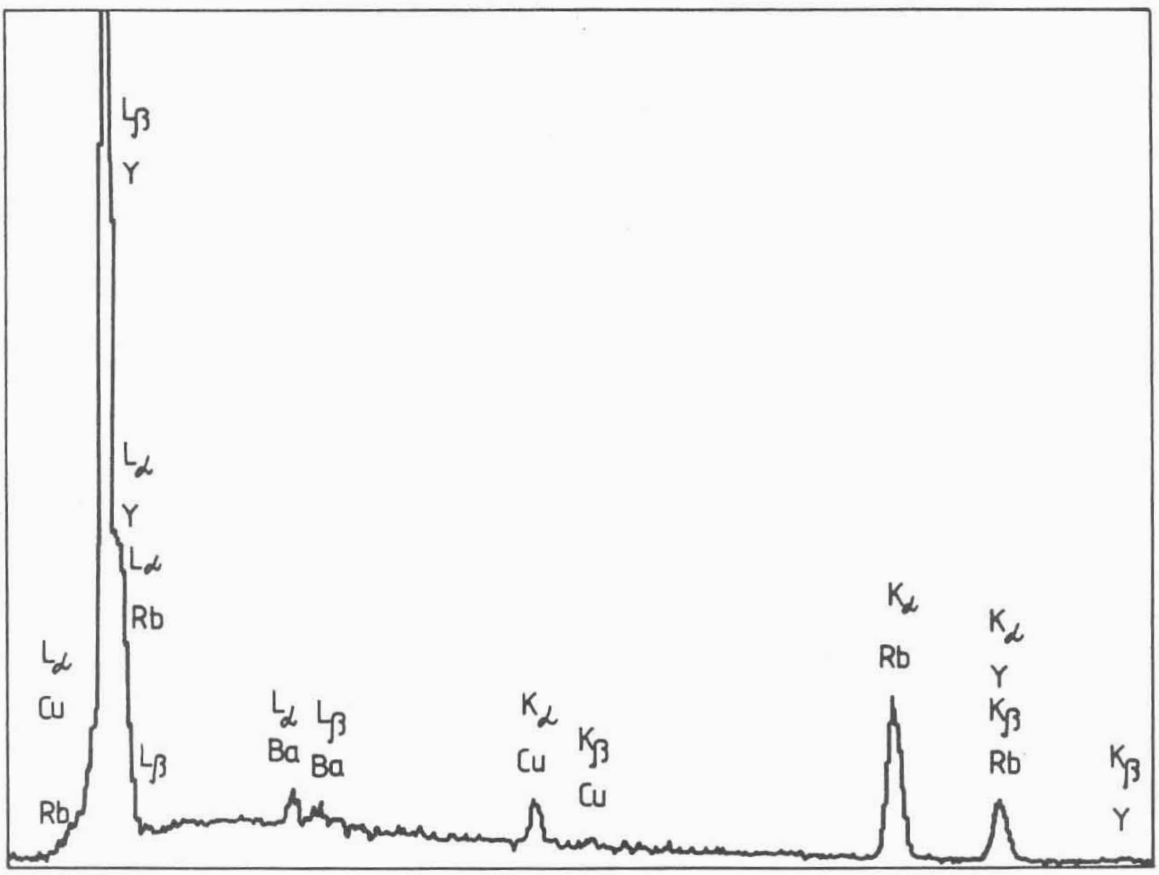

a)
A
B
C
b)
A
B
C
ENDOTHERMIC (ΔT)
550
650
750
850
950
1050
TEMPERATURE (°C)

Fig. 2

a



b



c

phase	Y	Ba	Cu	Rb	O
A	6,85	0,83	1,20	38,40	52,72

Fig.3

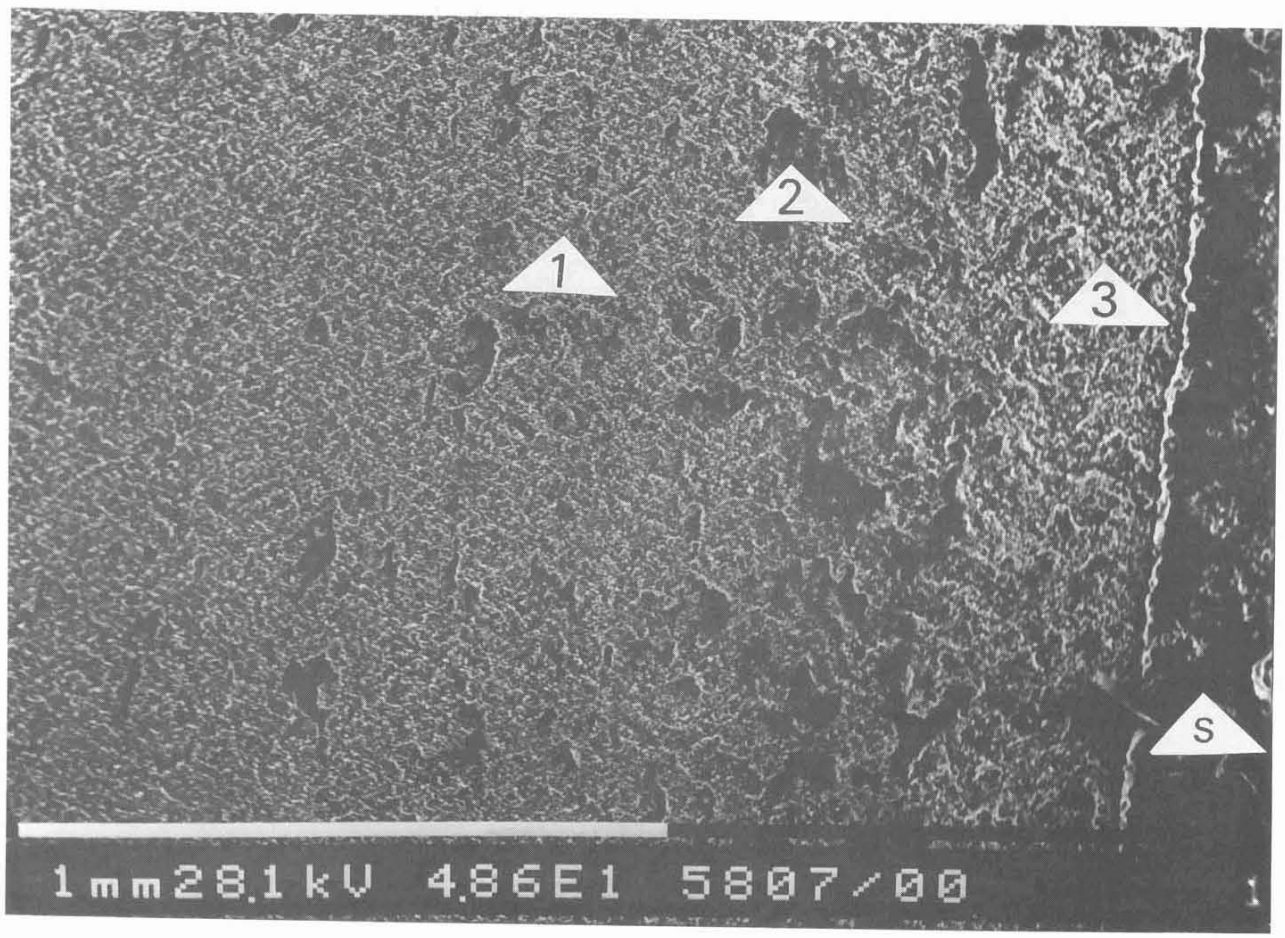
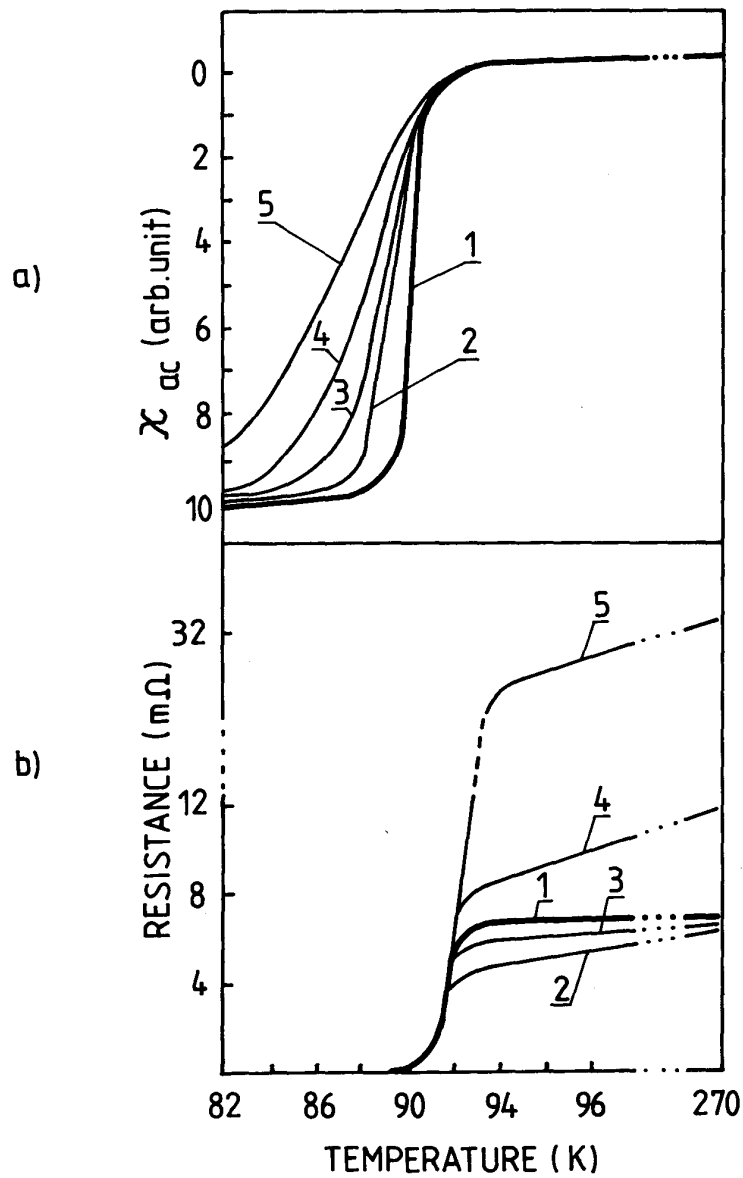


Fig.4


a)
b)
χ_{ac} (arb.unit)
0
2
4
6
8
10
5
1
4
3
2
RESISTANCE (mΩ)
32
12
8
4
5
4
1
3
2
82
86
90
94
96
270
TEMPERATURE (K)