

**INFLUENCE OF POLYCRYSTALLINE STRUCTURE IN YBaCuO
HIGH-T_c SUPERCONDUCTING CERAMIC ON SURFACE RESISTANCE**

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Abstract - The samples were prepared using the primary batch formula: $Y_{1-0.2x}Ba_{2-0.2x}Cu_3(Me)_xO_y$, where Me - alkali metal (Na, K, Rb); $x = 0$ to 1.2. The presence of alkali carbonates during the technological process allows one to influence the YBCO grain size and improve the homogeneity of the structure. Despite the large concentration range of additives on the initial batch after second treatment in the temperature higher than $900\text{ }^\circ\text{C}$ only traces of the alkali metals were revealed. The influence of Na-, K- and Rb-impurities in concentrations for Na about 5×10^{-1} wt.%; for K to 4×10^{-2} wt.% and Rb to 2×10^{-2} wt.% in polycrystalline YBCO was investigated. For Rb and K the $R(T)$ transitions are comparable to that of pure YBCO. The microwave R_s is least influenced by the impurities, but strongly depends on the grains size and homogeneity. Each impurity has a specific effect on $\chi(T)$ and J_c which is related to the grain-boundary structure.

INTRODUCTION

Investigating the influence of the different impurities on the magnetic and electrical HTSC properties is of interest, as much for the understanding of the intergranular phenomena, as for solving technological problems. However, to our knowledge, only a few isolated papers have appeared on the alkali metals impurities in YBCO [1,2] and the data published are controversial. There have been reports on obtaining $T_c=135$ K in a YBCO system substituted with K [3]. For the K-additive, where relatively more detailed studies have been carried out, the opinion predominates that its effect is due to the formation of a KCu-compound participating indirectly in the YBCO-phase formation process [2].

Our recent work [4] showed that K_2CO_3 may be added to the initial batch in significant quantities without causing deterioration of the general HTSC properties; we also attributed this fact to the KCu-compound.

The aim of this work is to compare the polycrystalline structures of HTSC Na-, K- and Rb- containing samples and the influence of the microstructure on their magnetic and electrical properties.

EXPERIMENTAL

The samples were prepared using the primary batch formula: $Y_{1-0.2x}Ba_{2-0.2x}Cu_3(Me)_xO_y$, where Me - alkali metal (Na, K, Rb); $x=0$ to 1.2. Attention was paid to the purity of the initial components: the basic content of Y_2O_3 was 99.99%; of $BaCO_3$, 99.99% and CuO , 99.99%. The additives were introduced as alkali carbonates with high purity (more than 99.9 wt.%). After preliminary baking of the batch at 900 °C, 1- μ m grain- size powder was used to press pellets which were then sintered once more. The final temperature was different for each additive (from 900 °C to 980 °C for 50 h) and was selected using the differential thermal analysis (DTA) data. The single-phase YBCO ($x=0$), which we use to compare the doped systems, were obtained via final sintering treatment consisting in baking at 980 °C for 60 hours in oxygen atmosphere; its HTSC properties were close to the best quoted in the literature for polycrystalline untextured YBCO.

The phase content and polycrystalline microstructure were characterized using X-ray powder diffraction (XRD) and scanning electron microscopy (SEM) with X-ray microanalyser (EPMA). The resistivity $R(T)$ and ac magnetic susceptibility $\chi(T)$ transitions were measured using the four-probe "resistive" (measuring current value 100 mA) and the contactless "pick-up coil" techniques (magnetic field 0-25 mT). To determine the surface resistance R_s at 15 GHz we developed our original equipment described in [5].

RESULTS AND DISCUSSION

Our investigation showed that the Na_2CO_3 , K_2CO_3 and Rb_2CO_3 influence was well pronounced when the carbonates were in significant concentrations, for Na_2CO_3 , $x=0.40$, (1.42 wt.%) to 1.20, (4.37 wt.%); for K_2CO_3 , $x=0.40$, (2.38 wt.%) to 0.95, (5.69 wt.%) and for Rb_2CO_3 , $x=0.20$, (2.57 wt.%) to 0.40, (5.07 wt.%). The case of additives concentrations below these limits are well described on the literature [1, 2]. When these ranges are exceeded, it is difficult to obtain reproducible single-phase samples with HTSC properties. Our investigation was, therefore, focused on the ranges mentioned of additives concentrations.

After the first heat-treatment (900 °C/24h) the YBCO phase is about 75 wt.% and the XRD data showed (and SEM and EPMA confirmed it) that in samples with Na₂CO₃ and Rb₂CO₃ additives Na₂O, Rb₂O and CuO phases existed in the powder, while for the case of K₂CO₃, the analysis revealed the presence of K₃CuO₂ phase.

For each additive can be drawn a specific influence on the final temperature-treatment compared with pure YBCO -generally, the sintering temperature decreases. HTSC samples for Na additive (x>0.4) were obtained at 940 °C, for K (x>0.4) at 950 °C and for Rb (x>0.2) at 920 °C. The SEM and EPMA data indicated the differences on the microstructure after second treatment. The YBCO was basic structure. For samples with Na-additive on the range of additive concentration the CuO-excess remained in the material as second phase and from 2 to 5x10⁻¹ wt.% Na (Na₂O) was found on the end-product. The two additional phases were dispersed in the sample.

For the K₂CO₃ additive, the XRD and EPMA data revealed the existence of K₃CuO₂ phase which evaporated above 900 °C and only traces were revealed on the surface of the samples. To explain the disappearance of the K and Cu-excess from the samples after 950 °C we analysed the crucibles after sintering. Atomic absorption spectroscopy (AAS) study shows about 0.66 wt.% of Cu (as compared with 0.00024 wt.% in zero-content sample) and 13.8 wt.% (sample with x=0.75).

The XRD, SEM and EPMA data showed the existence of a glass-like Rb₂CO₃ phases at 850-890 °C. This made us suppose that liquid alkali- containing phases participate in polycrystalline structure formation during the second treatment by enhancing the diffusion processes thus helping the CuO - excess move to the surface. On the other hand alkali-containing phases evaporated above 900 °C. AAS study of crucible walls were the Rb-doped (x=0.4) sample were baked proves about 14.1 wt.% of Rb.

Fig.1 illustrates typical surface structure. Five phases were identified in the specimens: for undoped sample; (A) with basic structure Y₁Ba₂Cu₃O_y crystals, for Na-doped sample; (A) with basic structure Y₁Ba₂Cu₃O_y crystals, (B) dark-Na₂O and (C) gray-CuO, for the Rb- and K-doped samples; (D) dark-K₃CuO₂, (E) dark-Rb₂O and (A) with basic structure Y₁Ba₂Cu₃O_y crystals. The composition was determined by EPMA. The resultant composition is listed in Table 1.

The measurement accuracy of EPMA method for metal ion analysis is 0.5% and for the single-phase YBCO chemical analyze [6] for oxygen ion is 5%. Chemical formula for the phase A (undoped sample) was estimated to be Y₁Ba₂Cu₃O_{6.54}. The SEM studies proved that samples with K- and Rb-additives possessed a low-density surface layer and its thickness is about 200-µm. Its chemical content depended on the alkali carbonate added: according to the EPMA data, for Rb-doped the layer consisted of YBCO and Rb and Cu oxides; for K, we found K₃CuO₂ (see fig.1). When this layer was removed, the XRD showed that the basic structure was single-phase YBCO. Using atomic absorption spectroscopy (AAS) we revealed only traces of the alkali additives: about 4x10⁻² wt.% K and 2x10⁻² wt.% Rb, which remained as impurities at the grain boundaries. To avoid the influence of the low-density layer, we polished the sample surface before the HTSC measurements.

Table1. Composition of the undoped and alkali metal doped YBCO specimen, determined by EPMA. The unit is at. %

Specimen	Phase	Y	Ba	Cu	Me	O
Undoped	A	8.41	15.45	24.04	0.00	52.10
Na-doped	A	8.22	15.47	24.25	0.00	52.06
	B	0.43	0.94	3.40	60.17	35.05
	C	0.45	0.23	49.21	0.00	50.11
K-doped	A	8.43	15.56	23.91	0.00	52.11
	D	3.85	27.20	5.82	16.23	46.90
Rb-doped	A	9.62	14.85	23.15	0.00	52.39
	E	1.59	0.66	1.68	36.39	59.58

We accumulated a large amount of data about the Rb, Na and K additives influence on the HTSC properties in a wide concentration range. We presented here the more characteristic results for comparable concentration limit (mentioned above) to illustrate the influence of different impurities on the HTSC properties. The term "impurities" was chosen because only traces (to 4×10^{-2} wt.% for K and Rb and 5×10^{-1} wt.% for Na) were found of alkali metals after the second-treatment and surface layer removal. The studies allowed us to assume that they are located at the grain boundaries. Despite the fact that insignificant amounts of the additives were found in the end-product, differences could be seen in the magnetic and resistive behaviour of the samples as illustrated by fig.2(a) and (b). In a large concentration range, the $R(T)$ superconducting transitions were similar and better (for Rb, the initial temperature was in the order of 94.6 K and for K 93.4 K) than those of pure YBCO. The resistance at T_{end} was highest in Na-containing YBCO where the impurities phases (Na_2O and CuO) were more significant.

It is difficult to explain is the $\chi(T)$ dependence. Each impurity had a specific influence (see fig.2b). The Na and Cu oxides impurities worsened the (χ) HTSC transition. The inferior impurities of Rb_2O in grain boundaries shifted the transition-onset temperature towards the lower temperatures. In the case of K_3CuO_2 -content boundaries for samples with best $R(T)$ transition ($x=0.75$ in the initial batch). we observed T_{end} as high as in pure YBCO, but ΔT was larger. The different $\chi(T)$ behaviour from Rb and K-doped samples where the impurities concentration is similar confirm the importance of the grain-boundary structure which is responsible for the different $\chi(T)$ behaviour.

To explain this behaviour we investigated the parameters more sensitive to the grain structure, namely R_s . Table 2 summarizes the data.

Table 2

System: $Y_{1-0.2x}Ba_{2-0.2x}Cu_3(Me)_xO_y$					
Added element: Me = Na					
x	0	0.40	0.75	0.95	1.20
wt. %	0	1.42	2.69	3.43	4.37
R_s, mΩ at f=14.3 GHz	51	51	51	55	49
Density, g/cm³	6.0	5.8	5.4	5.3	4.9
Added element: Me = K					
x	0	0.40	0.75	0.95	
wt. %	0	2.38	4.49	5.69	
R_s, mΩ at f=14.3 GHz	51	58	62	97	
Density, g/cm³	6.0	5.9	5.4	4.9	
Added element: Me = Rb					
x	0	0.20	0.35	0.40	
wt. %	0	2.57	4.45	5.07	
R_s, mΩ at f=14.3 GHz	51	42	45	49	
Density, g/cm³	6.0	5.9	6.0	6.0	

The microwave measurement showed that R_s depended weakly on the grain-boundary impurities, while being strongly affected by the grain-size and homogeneity. Using SEM photographs, we carried out a statistical analysis of the grain-size on doped samples in comparison with pure YBCO polycrystalline structure. The YBCO grains had the specific shape of a parallelepiped. We compared the grains with different longitudinal and similar transverse dimensions and calculated the average longitudinal dimension. Fig.3 shows the grain-size distribution in doped and undoped samples. It is clear that adding Na_2CO_3 allowed to obtain a polycrystalline structure with small average grain-size and high homogeneity. These samples exhibited the best R_s , despite the low density of those with Na_2O and CuO impurities. The K_2CO_3 -additive kept relatively higher grain-size which worsened R_s , but resulted in high homogeneity which was probably responsible for

the good $R(T)$ transition data. We assumed, furthermore, that the worse J_c in K-doped samples had to do with different grain-boundary structure. The influence of Rb impurity on the microstructure we related with the liquid phase existence by the technological process and the enhancing recrystallization process responsible for the highest grain size, density and texture which reflected on the best electrical properties. This impurity was most insignificant in the end-product and only $\chi(T)$ behaviour were sensitive to them existence in the grain-boundary.

CONCLUSIONS

The following conclusions can be drawn:

- 1) The presence of alkali carbonate additives in specific concentration limits during the technological process of samples preparation allows one to influence the YBCO grain-size and improve the homogeneity of the structure.
- 2) The alkali additives react differently with CuO excess in the initial batch. Na_2CO_3 does not remove this excess; CuO and Na_2O phases remain disseminated in the entire sample. Rb_2CO_3 enhances the CuO diffusion towards the sample surface. The carbonate it self dissociates at 890 °C, with only traces of Rb_2O remaining as impurity at the grains boundaries after the second heat-treatment. When the defective surface layer is removed, the samples have good HTSC properties. The K_2CO_3 reacts with the CuO excess and forms a KCu- compound which diffuses towards the surface and evaporates above 900 °C. Only traces of K (in the order of 4×10^{-2} wt.%) remain at the grain boundaries.
- 3) For Rb- and K-doped samples with similar impurities in the order of $2-4 \times 10^{-2}$ wt.%, $R(T)$ transitions are comparable to the best one of pure YBCO. Each additive has a specific effect on $\chi(T)$ transition which is related to the grain-boundary phase structure. Inferior quantity of Rb_2O deteriorate the $\chi(T)$ transition and the same concentration of KCu-compound improve T_{end} of YBCO.
- 4) The HTSC parameter most sensitive to the impurities is J_c . Only in the case of Rb, impurities at the grain boundaries in the order of 2×10^{-2} wt.% virtually do not affect J_c . The experiments demonstrated that R_s is least influenced by the impurities, but strongly depends on the grains size and homogeneity.

CAPTIONS

Fig.1 SEM photograph for (a) pure YBCO, (b) Na-, (c) K-, (d) Rb-doped samples - surface layer.

Fig.2 (a) $R(T)$ transitions and (b) $\chi(T)$ transition for pure YBCO compared with Na-, K- and Rb-doped $Y_{1-0.2x}Ba_{2-0.2x}Cu_3(Me)_xO_y$ samples.

Fig.3 The statistical analysis for grain-size distribution in polycrystalline YBCO obtained from initial batches include Na-, K- and Rb-additive in concentration about 4.5 wt.%.

REFERENCES

- [1] R.J.Cava, J. Krajewski, W.Peck, B.Batlogg, Jr.Rupp, R.Fleming and A.James, *Lett. to Nature* 338, 328,(1989)
- [2] Y.Saito, T. Noji, A.Endo, N.Higuchi, K.Fugimoto, T.Okawa and A.Hattori, *Physica C* 148B, 336 (1987)
- [3] Y.Khan, *J.Mater.Sci.Lett.* 7, 53 (1988)
- [4] I.Dragieva, Nedkov I., *IEEE Trans.MAG* 26, 1433 (1990)
- [5] I.Nedkov,A.Veneva, S.Miteva, T.Nurgaliev and V.Lovchinov, accepted EMMA'93, M2-P-18 (1993)
- [6] T.Nedelcheva, A.Stoyanova-Ivanova and L.Kostadinova, *J.Anal.Chem.*342, 196 (1992)

Fig.1

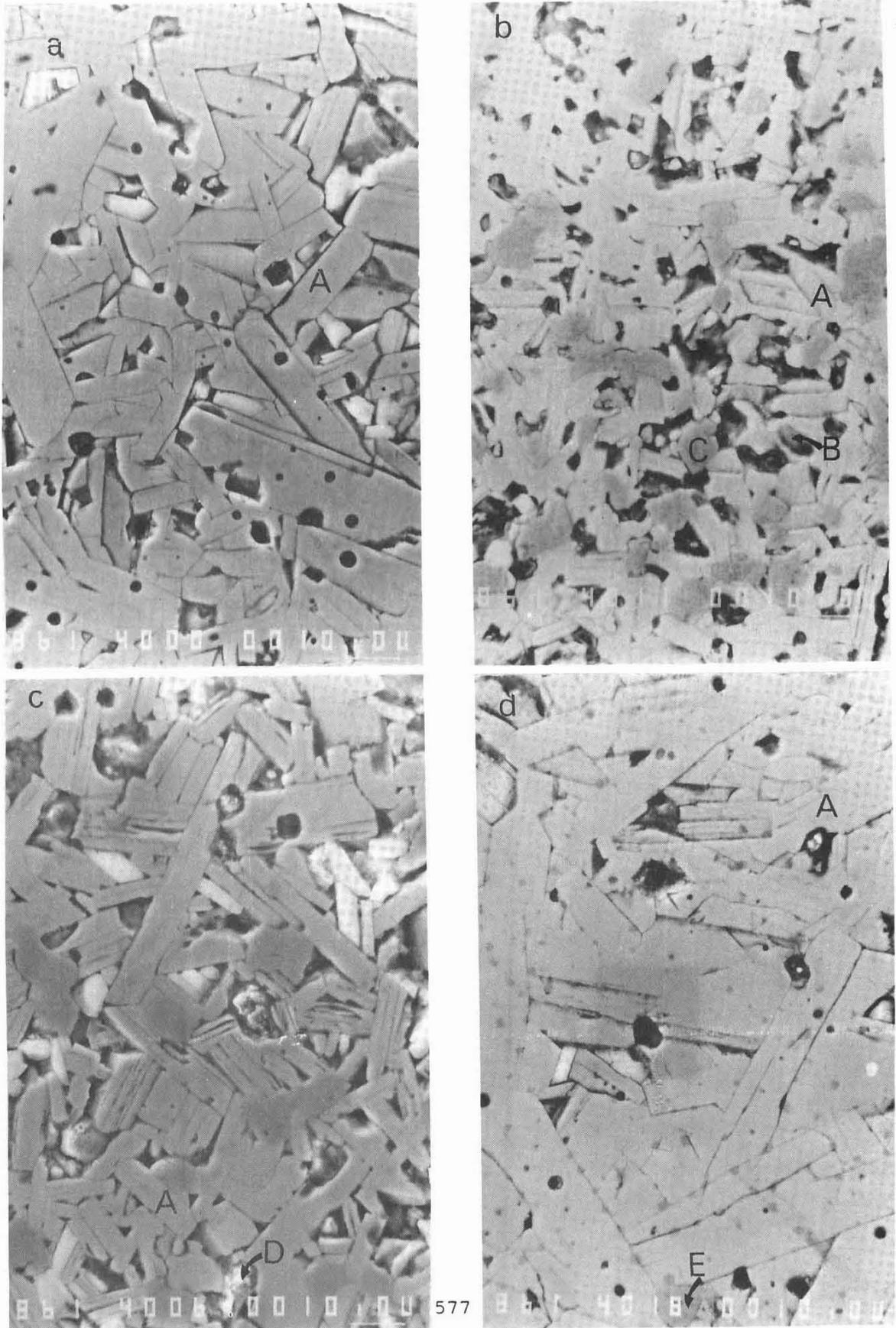


Fig.2

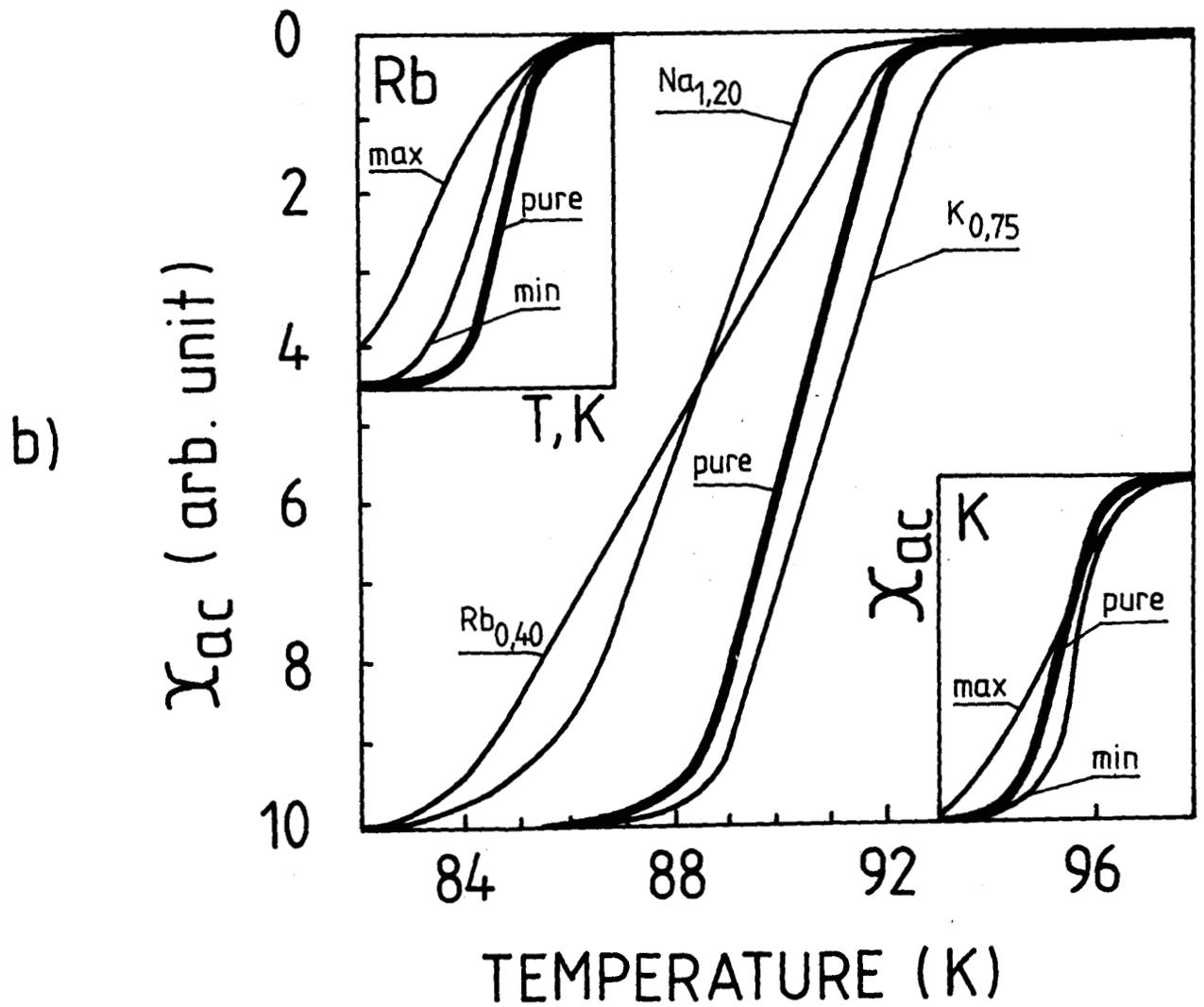


Fig.2

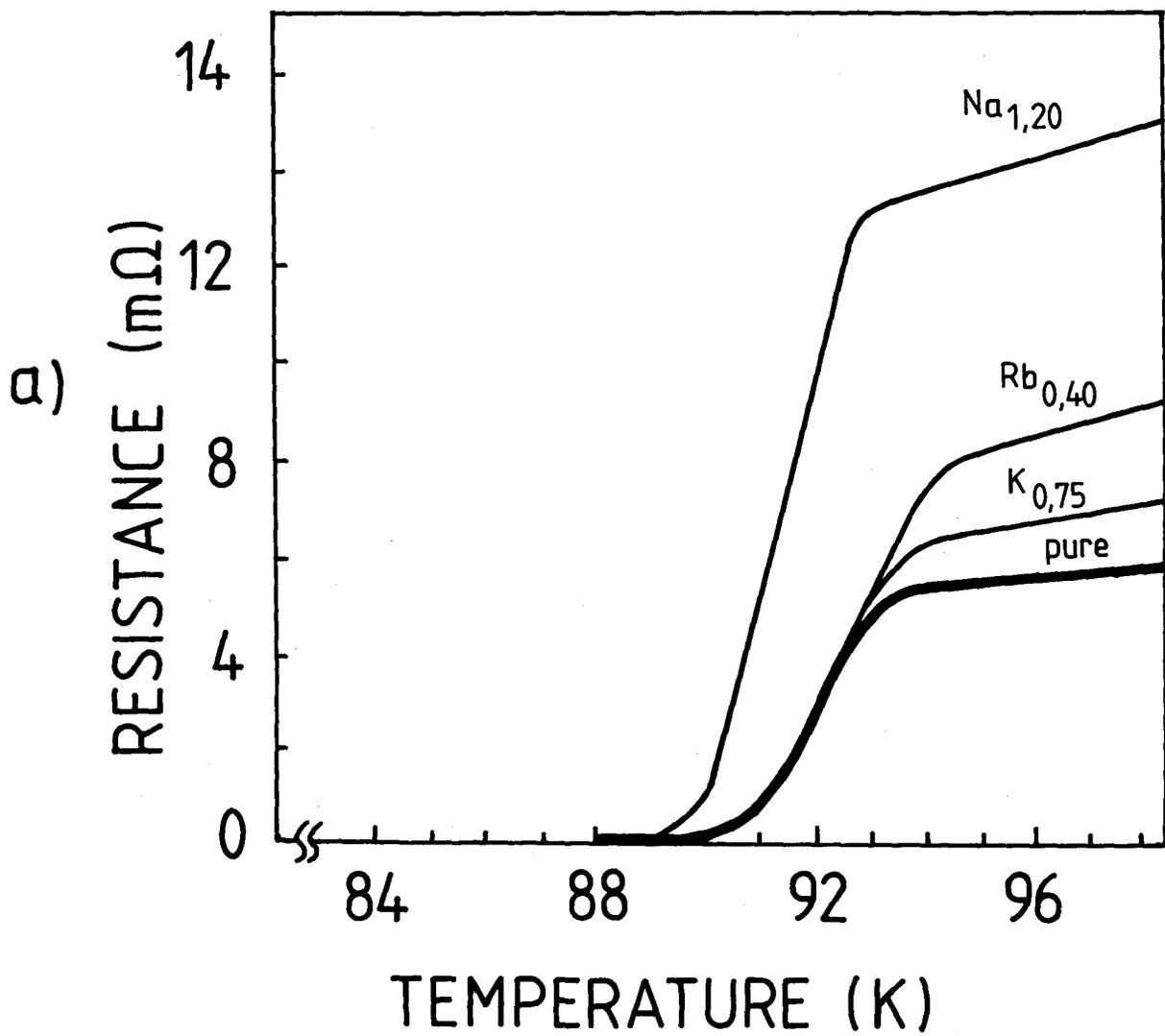


Fig.3

