Superconductivity above 20 K in barium-niobium-oxide compounds

V. A. Gasparov,[1)] G. K. Strukova, and S. S. Khassanov
Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russia

(Submitted 11 August 1994)
Pis'ma Zh. Eksp. Teor. Fiz. **60**, No. 6, 425–428 (25 September 1994)

Superconductivity above 20 K has been observed in multiphase bulk samples of a barium-niobium-oxide compound. Preliminary ac susceptibility, electrical, and structural properties of this compound are presented. We believe that this compound may be the basis for a new family of high-temperature superconducting oxides. © *1994 American Institute of Physics.*

Since the discovery of high-temperature superconductivity in cuprates by Bednorz and Müller,[1] the question has arisen why only copper oxides exhibit high-temperature superconductivity, while other oxides do not. Indeed, only bismuth oxide compounds ($Ba_{0.6}K_{0.4}BiO_3$) have been observed to be superconducting, with T_c of about 27 K (Ref. 2). High-temperature superconductivity has been reported in nonoxide systems: fullerens[3] and recently at 23 K in multiphase bulk samples of a quaternary, intermetallic, yttrium palladium boride carbide.[4] The discovery of high-temperature superconductivity in copper-free oxide systems may give new insights into the mechanism of high-temperature superconductivity.

There are many oxide and nitride superconductors based on niobium, with the highest T_c (15 K) for cubic NbN.[5] Niobium oxide (cubic NbO) is metallic and has a very low transition temperature of less than 1.2 K, and niobium dioxide NbO_2 is an n-type semiconductor.[6] $Ba_{0.6}NbO_3$ bronzes sintered at 1100 °C are known to be semiconducting with rather low resistivity and a perovskite cubic structure.[7] Nevertheless, we were able to synthesize, at a rather low temperature (about 500 °C), a $Ba_xNbO_{2-\delta}$ multiphase metallic compound, for which both the ac susceptibility and the resistivity measurements confirm the presence of superconductivity with an onset temperature above 20 K.

Powder samples of $Ba_xNbO_{2-\delta}$ were prepared by mixing appropriate amounts of Nb (99.99% purity) and BaO_2 (99.9% purity) powders in an agate mortar. This mixture was pressed into discs about 1 mm thick and 10 mm in diameter. The pellets were rapidly heated to about 500 °C in a quartz crucible in air, hydrogen, vacuum, or mixtures of oxygen and argon at various partial pressures, followed by quick burning due to a solid-state reaction. The samples were then rapidly cooled to room temperature. They consist of a mixture of black and yellow ceramic phases. Samples for magnetic and resistivity measurements were cut from these sintered materials using a diamond saw. It was observed that the heating and cooling rates, the time, the temperature, and the composition of the atmosphere used for annealing strongly affect the transition temperature.

The ac susceptibility studies have been carried out with samples of various shapes using the radio-frequency (5–10 MHz) method, which was recently used for investiga-

 © 1994 American Institute of Physics

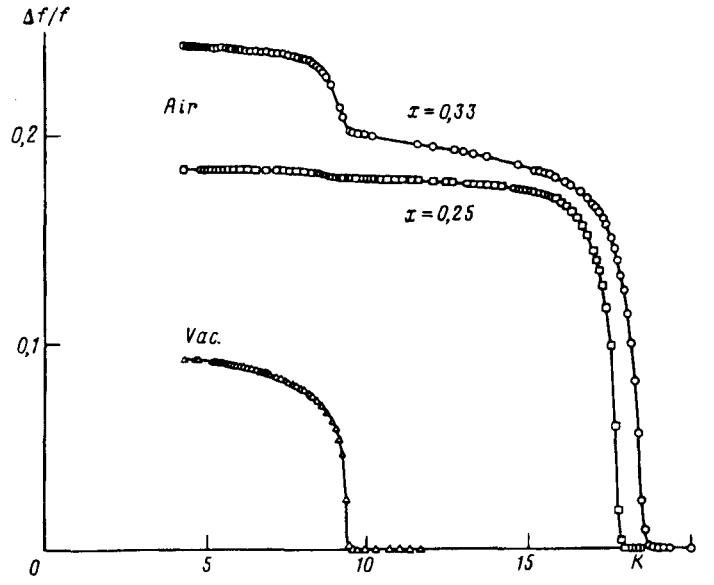

FIG. 1. The temperature dependence of $\Delta f/f$ ($f \simeq 6$ MHz), for samples with $x=0.33$ and 0.25, and size about $2\times2\times1$ mm prepared in air. The analogous curve for a sample prepared in vacuum with size $1\times1\times0.5$ mm is also presented.

tions of the magnetic penetration depth in ceramics, thin films, and single crystals.[8,9,10] Briefly, the sample is placed inside the inductance coil of an LC circuit, and the resonant frequency of this circuit is monitored as a function of temperature. The temperature dependence of the coil inductance $L(T)$ causes changes in the resonant frequency $f(T)$ of the circuit: $\Delta L/L=-2\Delta f/f \propto \eta X'$, where X' is the real part of the ac magnetic susceptibility $X=X'+iX''$, and η is the filling factor. The resistivity was measured by a standard four probe ac (9 Hz) method.

Figure 1 shows the temperature dependence of the value $\Delta f/f=[f(T)-f(25\ K)]/f(T)$, which is proportional to $-X'(T)$. The data shown are for $Ba_xNbO_{2-\delta}$ samples prepared in air with $x=0.25$ and 0.33, and for an $x=0.33$ sample prepared in vacuum (the same transition was found for samples sintered in hydrogen). It is obvious that the diamagnetic transition occurs at transition temperatures of 18.6 and 9.3 K. Note that the filling factor η and the sample volume of these samples are different and therefore the value $\Delta f(0)/f$ reflects a Meissner volume fraction only qualitatively. The skin depth in the normal state $\delta(T>T_c)$ is less than the sample thickness in the frequency range measured and therefore the $\Delta f(T)/f$-vs-T curve is due to the temperature dependence of the penetration depth $\lambda(T)$ (Ref. 8).

When the $Ba_xNbO_{2-\delta}$ samples, with $0.2<x<1$, were prepared in air, they showed strong evidence of a superconducting transition at 18.6 K. Decreasing x results in a decrease in the value of $\Delta f/f$ at the 9.3-K superconducting transition. The higher transition temperature clearly decreases with a decrease in x. These two-step transitions were

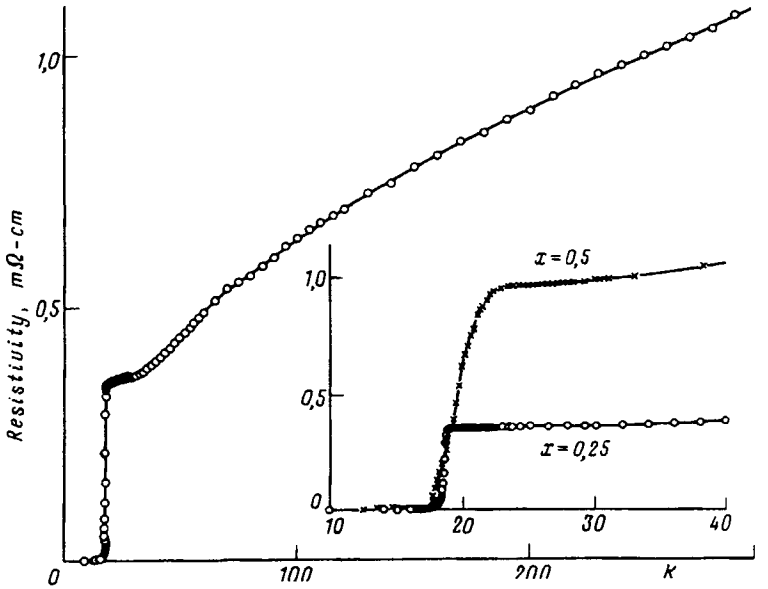

FIG. 2. The resistivity-versus-temperature curve for a sample with $x=0.25$, prepared in air. The inset shows the low temperature part of this dependence on an extended scale, together with the resistivity transition for a sample with $x=0.5$.

confirmed by direct magnetization measurements; however, the temperature control of the latter was less precise than for the ac susceptibility measurements.

Subsequent annealing of these samples in flowing oxygen at 400 °C produces powder-like samples with no superconducting transition. Annealing the superconducting samples under low oxygen presssure (200 Torr) at $T>350$ °C did not change the appearance of the sample, but eliminated the superconducting transition. Vacuum annealing of these samples, however, did not change the superconducting transition at temperatures up to 900 °C. Higher temperatures resulted in the loss of the higher T_c transition. Samples sintered in vacuum and in hydrogen exhibited only one transitiion temperature of 9.3 K, apparently due to metallic niobium.

The plot of the typical resistivity versus the temperature for $Ba_{0.25}NbO_{2-\delta}$ samples is shown in Fig. 2. Note the rapid, classical metallic decrease of the resistivity below room temperature, with the resistivity ratio $\rho(300\ \mathrm{K})/\rho(23\ \mathrm{K})\simeq 3$, and a rather low resistivity. The inset in Fig. 2 shows in more detail the resistive superconducting transition for samples with $x=0.5$ and $x=0.25$. The 10–90% transition for the $x=0.25$ sample is about 1 K and the onset temperature is 18.6 K. For the $x=0.5$ sample, the onset temperature of the transition is even higher (about 22 K), but the width of the transition is also much larger.

X-ray diffraction data, shown in Fig. 3, reveal a multiphase system. Detailed structural studies will require single-phase materials. Notice, however, the presence of an fcc phase of the NbN type with a lattice constant 4.40 Å and the presence of the $Ba_4Nb_2O_9$

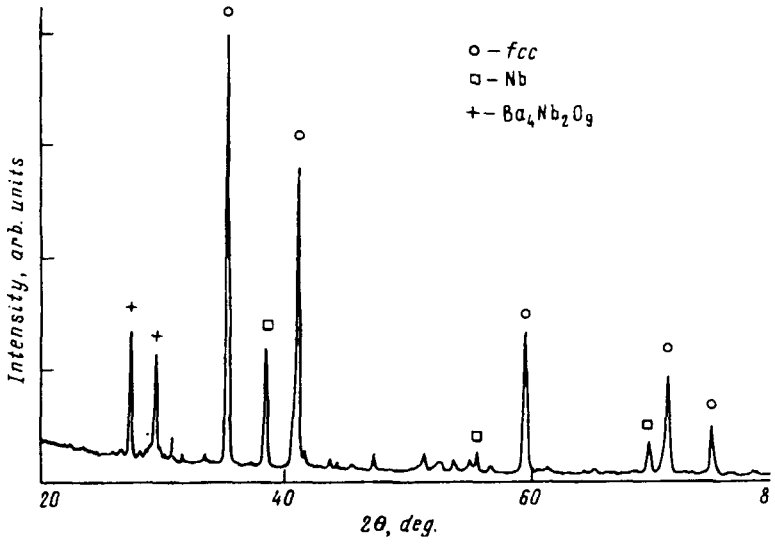

FIG. 3. Typical x-ray diffraction patterns for the $Ba_xNbO_{2-\delta}$ samples with $x=0.25$, sintered in air.

phase. Auger spectroscopy showed, however, that nitrogen was absent on most of the surface of the sample. It comprised only about 10% of those regions in which it was present, compared to a 40% oxygen content, which was found to be distributed uniformly in the sample. This clearly proves that the NbN phase is not responsible for the higher-T_c transition. The presence of slightly shifted metallic Nb peaks in the XRD spectra indicate metallic Nb, which is also seen on the $X'(T)$ curves.

Microprobe study of samples with $x=0.33$ showed the presence of multiple phases, with the average composition $Ba_{0.6}Nb_{0.8}O_{1.1}$. The close composition was found from Auger spectroscopy. This phase is similar to the niobium bronze oxide $Ba_{0.5+x}NbO_3$ ($0.2<x<0.5$) with a cubic perovskite structure and lattice constant $a=4.08$ Å (Refs. 7 and 11), but it contains much less oxygen. Note, however, that niobium bronze samples are semiconducting and red in color, in contrast with our yellow and black metallic samples. A Nb oxide superconductor $(Sr_{1-x}Ln_x)Nb_2O_{6-y}$ (Ln: La, Nd, Pr, Ce, Gd), with an orthorhombic structure, was recently reported.[12] Its onset temperature, however, is only about 12 K.

In summary, the ac susceptibility and resistivity measurements provide strong evidence for superconductivity above 20 K in multiphase $Ba_xNbO_{2-\delta}$ compounds. This transition temperature is much higher than that obtained previously in Nb-based oxides and nitrides. Thus, we feel that the synthesis and structural study of single-phase materials is essential.

We thank I. F. Shegolev for interest and stimulating discussions, S. F. Kosterev and V. D. Gurova for the magnetization study, A. V. Polisskii for help with the resistivity measurements, I. M. Shmyt'ko for the x-ray study, I. M. Ovchinnikov for the Auger

spectroscopy study of the samples, and R. A. Batto for help in the preparation of this manuscript.

[1)]E-mail: vgasparo@issp.chg.free.net

---

[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).
[2] R. J. Cava *et al.*, Nature **332**, 814 (1988).
[3] A. F. Hebard *et al.*, Nature **350**, 600 (1991).
[4] R. J. Cava *et al.*, Nature **367**, 146 (1994).
[5] R. E. Pessal *et al.*, J. Phys. Chem. Sol. **29**, 19 (1968).
[6] H. R. Khan *et al.*, Mat. Res. Bull. **9**, 1129 (1974).
[7] F. Studer *et al.*, J. Phys. Chem. Sol. **41**, 1187 (1980).
[8] V. A. Gasparov, R. Huguenin, D. Pavuna *et al.*, Sol. St. Comm. **69**, 1147 (1989).
[9] V. A. Gasparov, Physica C **178**, 449 (1991).
[10] V. A. Gasparov *et al.*, Physica C (1994, in press).
[11] R. R. Kreiser and R. Ward, J. Sol. St. Chem. **1**, 368 (1970).
[12] J. Akimitsu *et al.*, Jpn. J. Appl. Phys. **30**, L1155 (1991).

Published in English in the original Russian journal. Reproduced here with stylistic changes by the Translation Editor.