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SUPERCONDUCTIVITY ABOVE 20 K IN BARIUM-NIOBIUM-OXIDE COMPOUNDS

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We report the observation of superconductivity above 20 K in multiphase bulk sqmples 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.

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 about 27 K [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 succeeded in preparing, at a rather low temperature (about 500° C), a $Ba_xNbO_{2-\delta}$ multiphase metallic compound for which both *ac*-susceptibility and resistivity measurements confirm 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 up 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 solid state reaction. The samples were then rapidly cooled to room temperature. They consist 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 rates of heating and cooling, the time, temperature, and composition of the atmosphere used for annealing strongly affect the transition temperature.

Ac-susceptibility studies have been carried out on samples of various shapes using the radio-frequency (5-10 MHz) method, which was recently used for investigations of 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

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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.

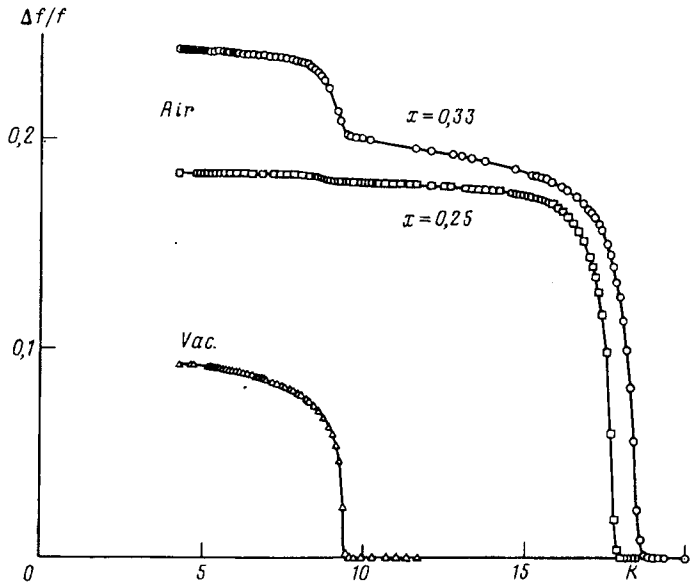

Fig. 1. The temperature dependence of $\Delta f/f$ ($f \simeq 6$ MHz), for samples with $x = 0.33$ and 0.25, and size about 2 x 2 x 1 mm prepared in air. The analogous curve for a sample prepared in vacuum with size 1 x 1 x 0.5 mm is also presented

Fig. 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 with transition temperatures of 18.6 and 9.3 K. Notice, that the filling factor η and the sample volume for these samples was different and therefore the value $\Delta f(0)/f)$ reflects a Meissner volume fraction only qualitatively. The skin depth value in the normal state $\delta(T > T_c)$ was less than the sample thickness at the frequency range measured and therefore the $\Delta f(T)/f$ vs T dependence is due to the temperature dependence of the penetration depth $\lambda(T)$ [8].

When they were prepared in air, $Ba_xNbO_{2-\delta}$ samples with $0.2 < x < 1$ showed strong evidence for 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 confirmed by direct magnetization measurements; however, the temperature control for the latter was less precise than for the *ac* susceptibility measurements.

Subsequent annealing of these samples in flowing oxygen at 400° C results in powder-like samples with no superconducting transition. Annealing the superconducting samples under low oxygen pressure (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 for 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 transition temperature of 9.3 K, apparently due to metallic niobium.

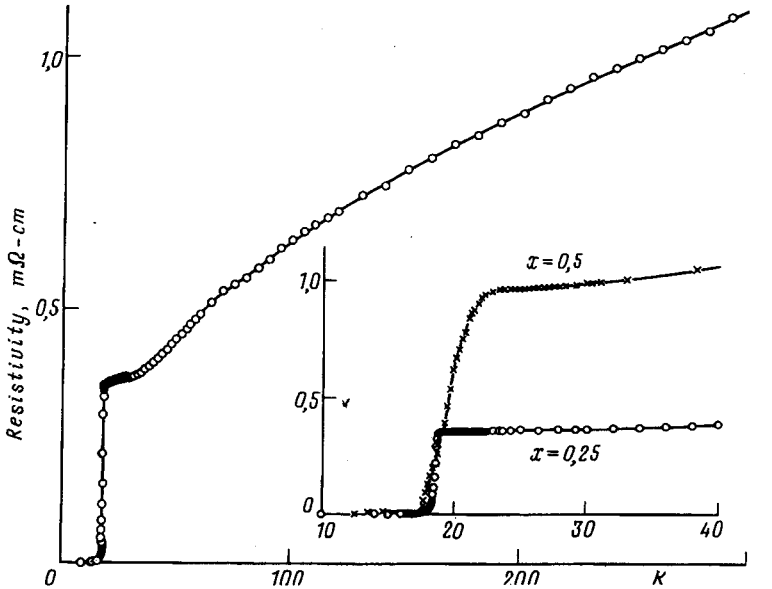

Fig.2. The resistivity-versus-temperature curve for a sample with $x = 0.25$, prepared in air. The inset shows the low temperature part of this dependence on an extended scale, together with the resistivity transition for a sample with $x = 0.5$

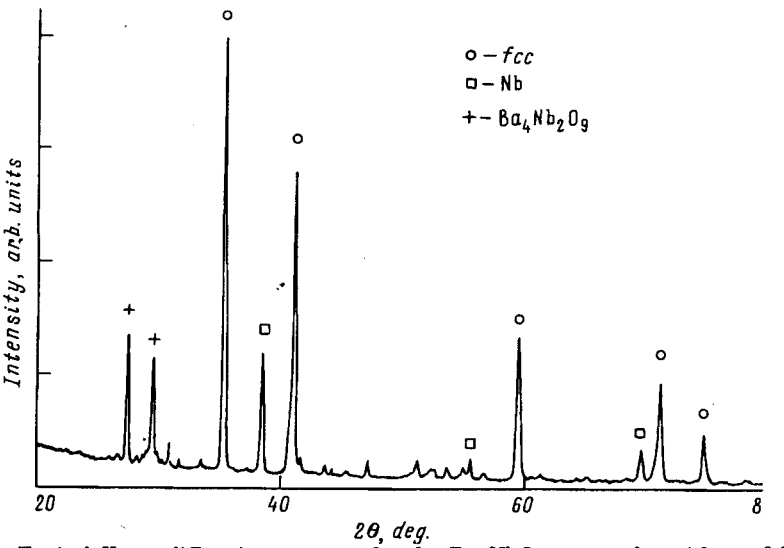

Fig.3. Typical X-ray diffraction patterns for the $Ba_xNbO_{2-\delta}$ samples with $x = 0.25$, sintered in air

The typical resistivity versus temperature for $Ba_{0.25}NbO_{2-\delta}$ samples is presented in Fig.2. Note the rapid, classical metallic decrease of the resistivity below room temperature, with the resistivity ratio $\rho(300\,K)/\rho(23\,K) \simeq 3$ and rather low resistivity. The inset to 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 are presented in Fig.3 and reveal a multiphase system. Detailed structural investigations will require single-phase materials. Notice, however, the presence of the *fcc* phase of type NbN with lattice parameter 4.40Å and of the $Ba_4Nb_2O_9$ phase. However, Auger spectroscopy showed that nitrogen was absent over most of the sample surface and made up only 10% or less of those regions in which it was present, compared to the 40% oxygen content found to exist uniformly throughout the sample. This clearly proves that it is not NbN phase that is 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 cubic perovskite structure and lattice parameter $a = 4.08$Å[7, 11], but contains much less oxygen. Notice, however, that niobium bronze samples were red in colour and semiconducting, in contrast to our yellow and black metallic ones. A Nb-oxide superconductor $(Sr_{1-x}Ln_x)Nb_2O_{6-y}$ (Ln: La, Nd, Pr, Ce, Gd) with orthorombic structure, was recently reported [12], but with onset temperature about 12 K only.

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

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