

LETTER TO THE EDITOR

Nitride Formation by Air Ignition

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It was recently reported that a new barium-niobium oxide, prepared by the ignition in air of a mixture of barium peroxide and niobium metal powders, was superconducting below temperatures of about 20 K. This finding, if true, would be of considerable significance because the highest superconducting transition temperature (T_c) previously found for a niobium-based oxide is 5.5 K. We have reproduced this synthesis, and we conclude from X-ray diffraction, electron microprobe, and magnetic susceptibility studies that the superconducting phase in this product is basically niobium nitride. Ignition of niobium metal powder in air leads only to niobium oxide, but ignition in air of Ta plus BaO₂ leads to the formation of Ta₂N. Apparently, there have been no previous reports of nitride formation by any ignition reaction in air. © 1995 Academic Press, Inc.

Although many superconducting compounds containing niobium are known, attempts to produce superconducting oxides of niobium have been generally disappointing. The only binary oxide of niobium known to be superconducting is NbO with a T_c of 1.2 K (1), and the only ternary niobium oxide showing superconductivity is Li_{0.45}NbO₂ with a T_c of 5.5 K (2). Phases of the type A_xNbO₃ where A is Ba or Sr (3) as well as phases containing the Nb₆O₁₂ cluster (4) seemed to be good candidates for superconductivity, but neither family has yet shown any such indications. Although a T_c of 12 K has been reported for oxides of the type Sr_{1-x}R_xNb₂O₇, where R is a rare earth (5), this result remains unconfirmed despite determined efforts (6).

Our synthesis conditions were the same as those given by Gasparov *et al.* (7). Barium peroxide (BaO₂) and niobium metal powder were intimately mixed by grinding in

an agate mortar. A BaO₂-to-Nb ratio of 0.33 was used for most experiments. This BaO₂-Nb mixture in an alumina boat was placed into a muffle furnace preheated to 600°C. When ignition commenced, the sample quickly became red hot. It was removed from the furnace either immediately or after 5 sec. These experiments were repeated using SrO₂ instead of BaO₂. They were also repeated using Nb powder alone.

The X-ray powder patterns of the products showed some unreacted niobium in all cases. When BaO₂ was a reactant, the product contained Ba₄Nb₂O₉ and Ba₆Nb₃O_{13.5}. When SrO₂ was a reactant, the product contained Sr₄Nb₂O₉ and SrNb₂O₆. Regardless of whether the oxide reactant was BaO₂ or SrO₂, a prominent phase in the product showed a face-centered-cubic (fcc) pattern with a cell edge of 4.392 ± 0.002 Å. Considering the size difference between Ba and Sr, this result suggests that significant amounts of Ba or Sr are not present in the fcc phase. When pure niobium metal powder was ignited in air, the product contained only Nb₂O₅ in addition to unreacted niobium.

Our X-ray diffraction results in the barium/niobium system are essentially identical to those of Gasparov *et al.* They attributed superconductivity to the fcc phase; indeed, this is the only phase present which could be responsible for the superconductivity well above 9 K. The X-ray pattern of this fcc phase is essentially the same as reported for NbN (8). However, Gasparov *et al.* claim, based on Auger analysis, that the fcc phase cannot be NbN. Also, ignition of niobium metal powder in air does not lead to any NbN or to any superconducting product. Furthermore, Gasparov *et al.* report a T_c of about 20 K, whereas the T_c of pure niobium nitride does not exceed 16 K.

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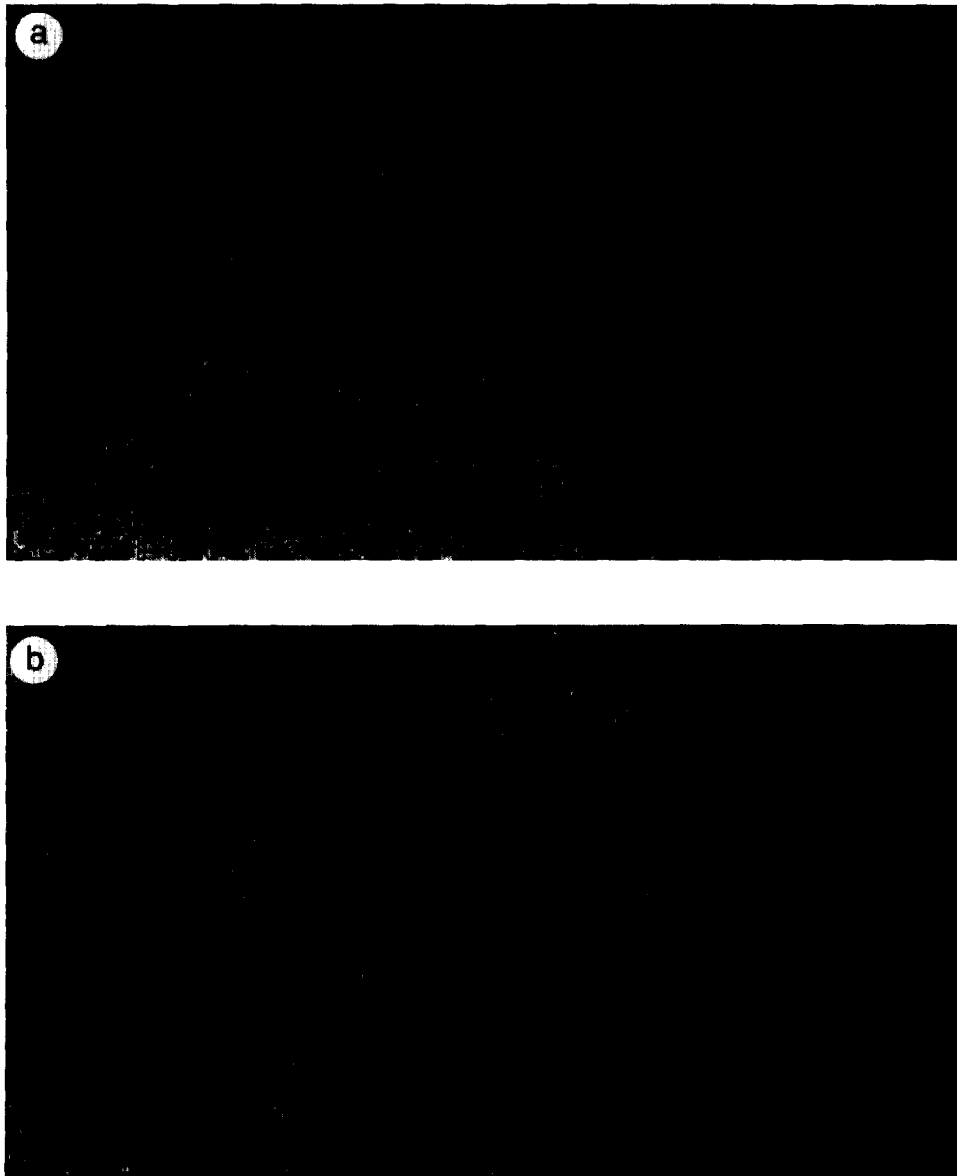


FIG. 1. Compositional mapping from electron microprobe. Niobium is shown in (a) where black indicates no niobium; the brightest areas indicate niobium metal and the lightest gray areas are oxide phase. The intermediate contrast regions in (a) are NbN as shown by the nitrogen mapping in (b).

Wavelength dispersive microprobe analysis was conducted on our samples to determine the chemical composition of the phases present. For the most difficult aspect of this analysis, the quantification of the nitrogen concentration, a synthetic multilayer diffracting crystal (PC1, 60 Å, d spacing) was used. Calibration for nitrogen employed an AlN standard. Clear evidence for niobium nitride was found (Fig. 1). Precise quantification is difficult, but the nitrogen-to-niobium ratio approached one in most of the areas where nitrogen was observed.

Our results can be rationalized as follows. On ignition

of a BaO₂/Nb or SrO₂/Nb mixture in air, the most exothermic and fastest reaction involves formation of barium or strontium niobates. This quickly consumes so much oxygen so quickly that the remaining unreacted niobium powder is temporarily exposed to an atmosphere of nearly 100% nitrogen. It is known that niobium metal powder will react with nitrogen to form NbN at the temperatures used in this work. It is also known that NbN is oxidized only very slowly by air under these conditions. Our proposed reaction scenario is supported by the texture of our products. These products consist of nodules of niobium

metal and barium- or strontium-niobium oxides surrounded by reaction halos of NbN (Fig. 1). These nitride halos are extremely friable and are easily crushed and lost during handling. This may explain why Gasparov *et al.* observed only very low levels of nitrogen in their samples.

Superconductivity in our samples was evaluated using a Lakeshore ac susceptometer. The results were the same, regardless of whether BaO₂ or SrO₂ was a reactant and regardless of whether time in the furnace was 5 sec or less than 1 sec. There were increases in susceptibility at 16 K and another at 9 K. We attribute these transitions to NbN and Nb, respectively.

An explanation of our results is straightforward. No new phase was formed. The observed superconductivity is due to Nb and NbN. The formation of niobium nitride under these conditions is, however, surprising. We know of no previous example of nitride formation occurring in air. Our X-ray diffraction results are consistent with those reported by Gasparov *et al.*, but we find a lower T_c . We can only speculate about the higher T_c reported by Gasparov *et al.* The fcc phase they produced might be NbN containing some carbon. The source of this carbon might be a barium carbonate impurity in their barium peroxide reactant. The addition of carbon to NbN could result in a T_c of about 18 K. Gasparov *et al.* do not report

zero resistance at temperatures above 18 K; however, they claim onset behavior somewhat above 20 K in some, but not all, of their samples.

Air ignitions of BaO₂ with Ti, Zr, Mo, W, and Ta were also conducted. The pyrotechnic displays were interesting, but only the ignition with Ta produced a prominent nitride phase, Ta₂N.

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