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Synthesis and electrical properties of solid solutions $BaNb_{1-x}Ti_xO_3$ with $0 < x < 0.8$

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Abstract

The cubic perovskite $BaNbO_3$ has been prepared in sealed ampoules from mixtures of $Ba_5Nb_{14}O_{15}$ and Nb. Solid solutions $BaNb_{1-x}Ti_xO_3$ have been prepared from mixtures of $BaTiO_3$ and $BaNbO_3$ fired at 1300°C under purified argon flow. Between $0 < x < 0.7$, electrical resistance measurements from 4.5 K to 250 K indicate that these compounds behave as metals. For $x = 0.8$, a metal–non-metal transition occurs, not explained by semiconducting behaviour. © 1997 Elsevier Science S.A.

Keywords: Solid solutions Ba(Nb,Ti)O_3; Electrical resistance

1. Introduction

Following the ideas which guided Bednorz and Muller to the superconductivity, compounds such as ternary oxides containing d^1 ions (Ti^{3+}, V^{4+} or Nb^{4+}) may favour strong electron-photon coupling and could be candidates for high-T_c superconductivity.

Analogies exist between d^0 (as Cu^{2+}) and d^1 ions, replacing a full plus-one hole by an empty one plus one electron. The d^1 ternary oxides would be in way opposite to cuprates and could eventually lead to electron superconductivity. This behaviour is observed in $Li_xTi_2O_4$, Li_xTiO_2, Li_xNbO_2 or tungsten bronzes and seemed to be confirmed by Akimitsu et al. [1], who pointed out the discovery of superconductivity at 11.5 K in $Sr_{0.9}Nd_{0.1}Nb_2O_6$, but their results were not confirmed.

Studies on d^1 ternary have been focused essentially on compounds of composition ABO_3 with a crystal structure derived from the cubic perovskite. The series $RETiO_3$ (RE = rare earth) has been extensively investigated and presents a remarkable variation in physical properties [2,3].

On the other hand, superconductivity occurs at a metal–non-metal transition in Ba(Pb,Bi)O_3 and (Ba,K)BiO_3. This kind of transition is found in complex oxides of transition with mixed valence states, which exhibit interesting transport properties including, in some cases, superconductivity and related to the occupation of the d bands. Control of the filling of the d bands can be done for solid solution systems (RE,A)MO_3 with perovskite-like structures; A are divalent alkaline earth ions and M is Ti or V [4]. A similar method consists of modifying the valence states of metals such as Nb by variation of the ratio Nb^{4+}/Nb^{5+} in $Na_{1-x}Sr_xNbO_3$ and $K_{1-x}Ba_xNbO_3$ [5–7]. Unfortunately, no superconductivity has been found in these systems.

The aim of the present work is to obtain a metal–non-metal transition by mixing two different transition cations Ti^{4+} (d^0) and Nb^{4+} (d^1) in solid solutions $BaNb_{1-x}Ti_xO_3$ rather than from solid solu-

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tions of mixed valence states of a single transition metal.

2. Experimental procedure

2.1. Synthesis

2.1.1. $BaNbO_3$

This perovskite was synthesized in two steps [7,8]:

$$5BaCO_3 + 2Nb_2O_5 \rightarrow Ba_5Nb_{14}O_{15} + 5CO_2$$

in air at 1000°C and

$$Ba_5Nb_{14}O_{15} + Nb \text{ in excess} \rightarrow 5BaNbO_3$$

(ratio Ba:Nb = 1:1.08) red purple

in evacuated silica ampoule at 1100°C.

X-ray analysis (Fig. 1) showed typical diffraction patterns corresponding to a perovskite structure. All reflections were indexed on a cubic cell with a parameter, $a = 4.085$ Å, in good agreement with the results of Casais et al. [8] and Kopnin et al. [9].

2.1.2. Solid solutions $BaNb_{1-x}Ti_xO_3$ with $0.05 < x < 0.8$

Appropriate amounts of $BaNbO_3$ and pure Aldrich $BaTiO_3$ were thoroughly mixed and fired at 1300°C under argon flow, passing through Ti–Zr alloys turnings used as a getter. The samples were kept under these conditions for 12 h several times and we obtained blue compounds. X-ray analysis showed typical diffraction patterns corresponding to a perovskite structure. All reflections were indexed on a cubic cell with small variations of the a parameter, varying linearly from 4.085 Å for $BaNbO_3$ to 4.031 for $BaTiO_3$.

2.2. Electrical resistance measurements

For electrical resistance measurements, the samples were prepared from fine powders mixed, ground together and pressed into pellets of 10 mm in diameter and 3 mm in thickness. The pellets were then sintered for 15 h under purified argon flow at 1300°C. The samples' resistance was measured by the four-wires DC method with a Keithley 181 nanovoltmeter and a Keithley 224 programmable current source. The temperature was monitored in the range 4.5–250 K by a Lake Shore DRC 93 temperature controller associated to a Cernox temperature sensor. The whole process was driven under Labview by a desktop computer.

3. Results

We have plotted the results concerning pure $BaNbO_3$ and samples with 30, 50 and 70% Ti (Fig. 2).

3.1. $BaNbO_3$

This oxide has a non-empty 3d band and, assuming a cubic perovskite structure, must have a metallic behaviour. The experimental values are in good agreement with the results of Casais et al. [8] who found a Pauli-like metallic perovskite. The DC conductivity may be estimated at approx. 100–200 Ω^{-1} cm^{-1}, which is below the Mott minimum (300 Ω^{-1} cm^{-1}) [9]. As it was pointed out by Crandles et al. [10], the nature of the conduction mechanism of such oxides is unclear and often inexplicable in terms of one electron band models.

Nevertheless, the behaviour of our sample is not strictly metallic. In fact plotting R vs. $T^{3/2}$, we obtain a straight line which implies that the carriers are scattered by charged imperfections (Fig. 3).

3.2. $BaNb_{1-x}Ti_xO_3$ with $x = 0.05, 0.3, 0.5$ and 0.7

To compare the different resistances, we have plotted the normalized resistances (Fig. 4), dividing the values of the resistances by the value of R at 150 K. We observed low values of the electrical resistance increasing with T, characteristic of a metallic behaviour. The metallic character increases from $x = 0.05$ to 0.7. In fact for $x = 0.7$, we see that with increasing temperature from 4.5 K, the resistance increases, reaches a maximum and then decreases. The same behaviour has been observed in $Y_{1-x}Ca_xTiO_3$ by Tokura et al. [11] and was attributed to a slight (macroscopic) inhomogeneity of the sample. This behaviour was not observed for $0.05 < x < 0.5$ and we think that it is the beginning of the mechanism explaining the behaviour of the following composition (80%).

3.3. $BaNb_{0.2}Ti_{0.8}O_3$

The experimental results are plotted in Fig. 5. The resistivity decreases with increasing temperature which implies apparently an activation energy. To verify this assumption, we have plotted $\ln(1/R)$ vs. $1/T$ in Fig. 6. The curve is not a straight line but an hyperbole. Such a behaviour has been observed by Ellis et al. [6], in the system $Na_{1-x}Sr_xNbO_3$.

The general hyperbolic shape of the curve $\ln(1/R)$ vs. $(1/T)$ led us to plot $\ln(1/R)$ vs. T. As can be seen in Fig. 7, there is a large temperature range in which $\ln(1/R)$ varies linearly. This behaviour has been explained by McKinnon et al. [12] using a model in which carriers can jump from one site to another by an incoherent tunnelling rather than by a thermally activated hopping. Basically, this model assumes that the tunnelling is a direct function of the magnitude of

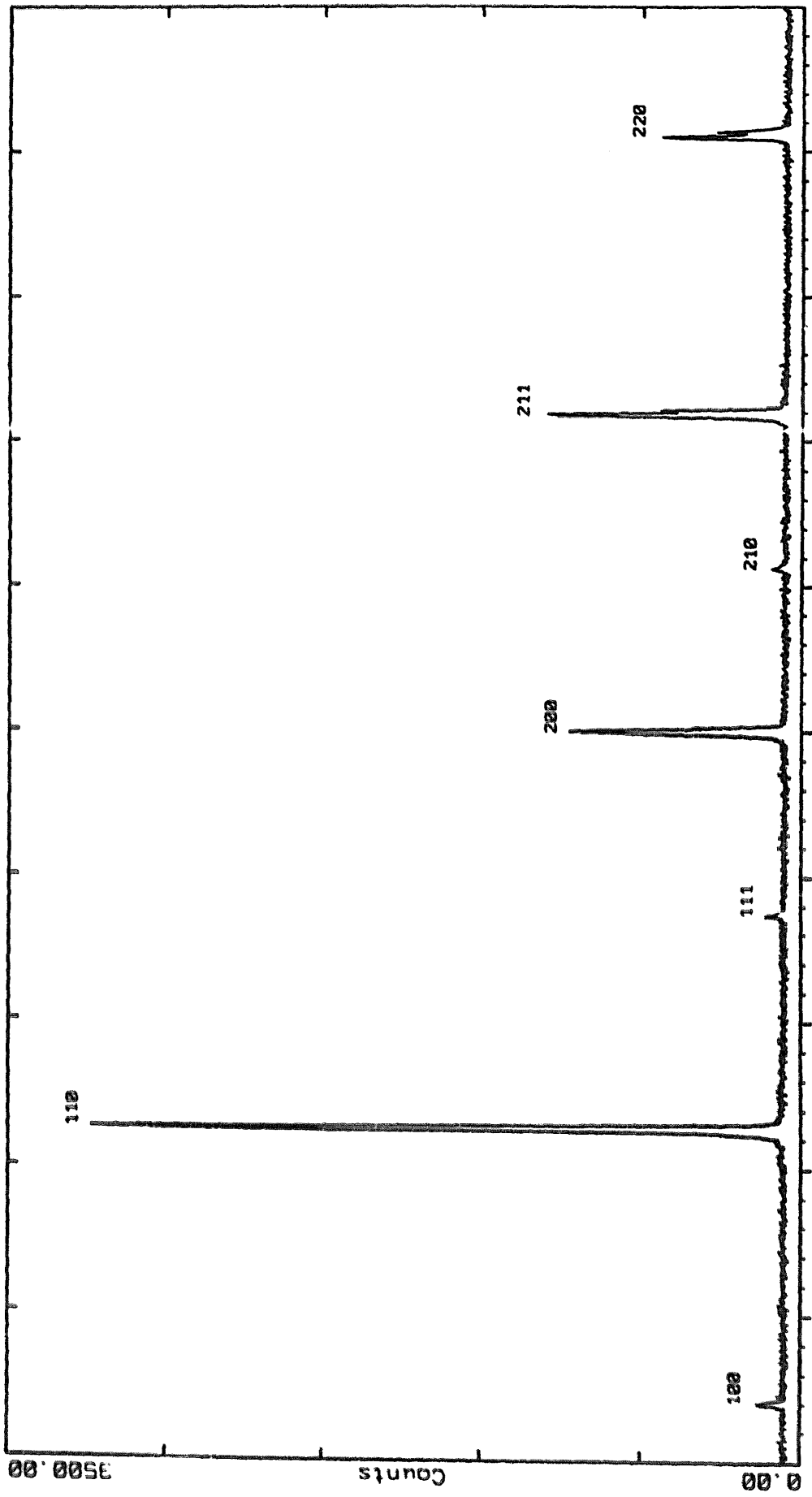

Fig. 1. X-ray powder pattern using CuK α radiation for $BaNbO_3$.

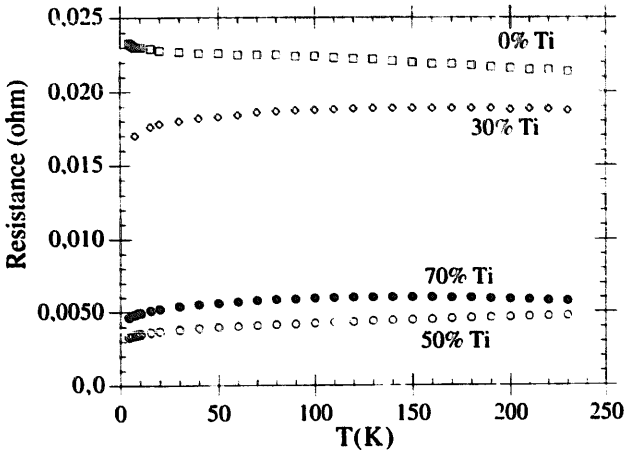

Fig. 2. Electrical resistance R of samples $BaNb_{1-x}Ti_xO_3$ with $x = 0$, 0.3, 0.5 and 0.7 vs. temperature.

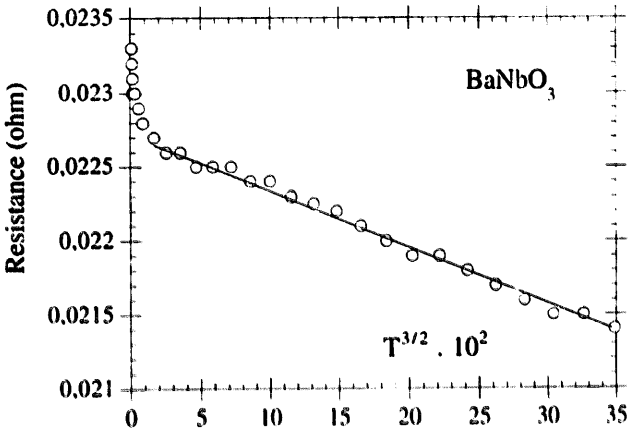

Fig. 3. Electrical resistance R of pure $BaNbO_3$ vs. $T^{3/2}$.

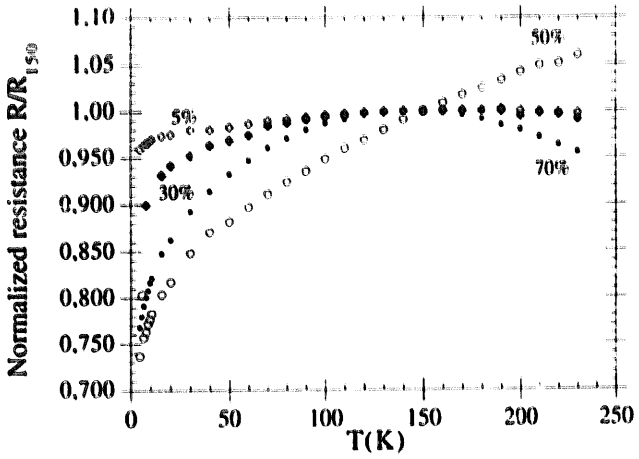

Fig. 4. Normalized resistance $R/R_{150\ K}$ of $BaNb_{1-x}Ti_xO_3$ with $x = 0.05$, 0.3, 0.5 and 0.7 vs. temperature.

the overlap integral between nearest neighbour ions and thus that it will be enhanced upon increasing the temperature since this enlarges the amplitude of vibrations in the lattice.

4. Conclusion

The perovskites $BaNbO_3$ and the solid solutions

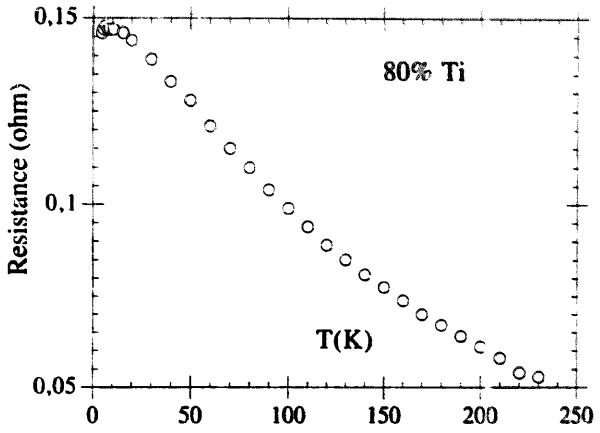

Fig. 5. Electrical resistance R of $BaNb_{0.2}Ti_{0.8}O_3$ vs. temperature.

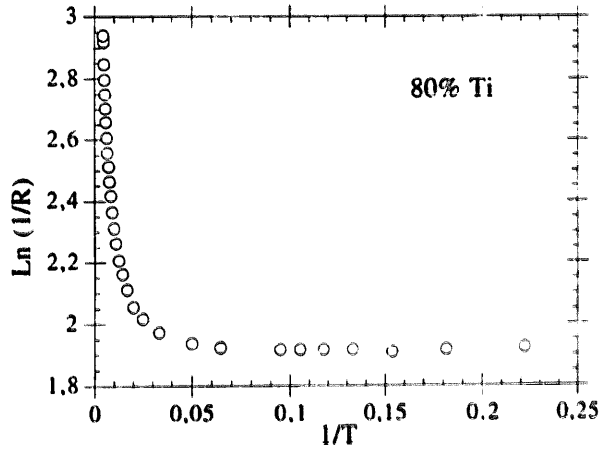

Fig. 6. $Ln(1/R)$ vs. $1/T$ for $BaNb_{0.2}Ti_{0.8}O_3$.

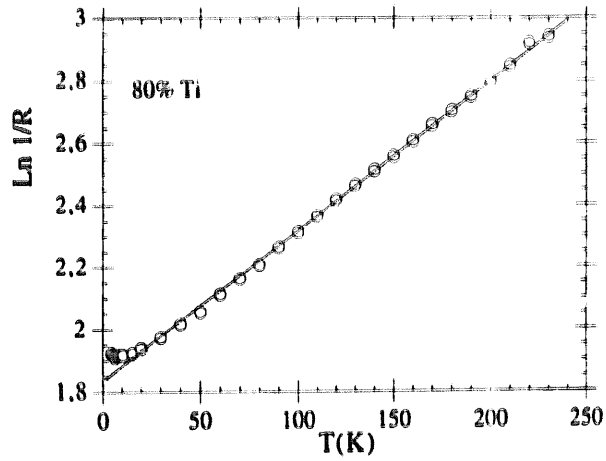

Fig. 7. $Ln(1/R)$ vs. T for $BaNb_{0.2}Ti_{0.8}O_3$.

$BaNb_{1-x}Ti_xO_3$ with $0 < x < 0.8$ present a metallic electrical conductivity. Between $x = 0.7$ and $x = 0.8$, a transition metal–non-metal appears which can be explained by a model of jumping from one site to another by an incoherent tunnelling.

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