Journal of Solid State Chemistry 182 (2009) 1944–1949

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

# Structural characterization and electrical properties of $NiNb_{2-x}Ta_xO_6$ ($0 \le x \le 2$) and some Ti-substituted derivatives

M. López-Blanco, U. Amador, F. García-Alvarado *

*Departamento de Química, Universidad San Pablo-CEU, Urbanización Montepríncipe, 28668 Boadilla del Monte, Madrid, Spain*

ARTICLE INFO

*Article history:*
Received 2 January 2009
Received in revised form
2 April 2009
Accepted 28 April 2009
Available online 13 May 2009

*Keywords:*
Columbite
Rutile
Electrical properties
Structural characterization

ABSTRACT

A structural and electrical characterization of the system $NiNb_{2-x}Ta_xO_6$ ($0 \le x \le 2$) is presented. For $x \le 0.25$ materials with the columbite-type structure typical of $NiNb_2O_6$ have been obtained whereas for $x \ge 1$ tri-rutile-like oxides were obtained. The electrical properties are similar in both cases; they are semiconducting with very low electrical conductivity and very high activation energy, though slight differences were found as a function of Ta content. Improvement of conductivity by reducing the stoichiometric materials could not be achieved due to decomposition. In this connection, partial substitution of Nb or Ta by Ti has been carried out in order to create oxygen vacancies. Tantalum was partially replaced by Ti to a significant extent in the tri-rutile structure inducing a slight increasing of conductivity. However, for the columbite case neither Nb nor Ta could be partially replaced. This behavior is quite different from that reported for other similar columbites such as $MnNb_2O_{6-\delta}$, which exhibits high electrical conductivity upon substitution of niobium by titanium.



## 1. Introduction

$AB_2O_6$ (columbite/tri-rutile) type of oxides where $B$ is either Nb or Ta are very interesting materials that have been investigated in view of their dielectric properties and uses in a wide range of related applications [1–5]. Besides, some of them have been proposed as water splitting photocatalyst [6–8] as it is the case of $NiM_2O_6$ ($M$ = Nb, Ta). When $M$ = Nb the oxide crystallizes in the columbite structure whereas for $M$ = Ta a tri-rutile-like material is formed. To our best knowledge, the solubility range of both phases is not known; therefore, we have first investigated the phases present in the system $NiNb_2O_6$–$NiTa_2O_6$. Since the columbite and tri-rutile structures are closely related [9] some degree of solubility could be expected. One of the common features in both structures is that $MO_6$ octahedrons share edges which makes more difficult the formation of oxygen vacancies when compared to corner-sharing based structures (the perovskite for instance). However, we have recently shown that a Nb-based columbite, $MnNb_2O_6$, can be modified by either reduction or substitution in the Nb site, to yield good electronic conductors [10,11]. Even more, oxygen ion conductivity has been detected. These results on columbites are interesting because oxides presenting both electronic and oxygen ion conductivity may be useful as highly efficient electrodes in solid oxide fuel cells. In the case of the columbite $MnNb_2O_{6-\delta}$ [10], it was found that the quantity of oxygen vacancies that can be created is small ($\delta \sim 0.02$). As a novelty it was also found that $MnNb_2O_6$ is affected by an intrinsic instability and instead of the nominal composition two close phases with either lower or higher Mn contents may stabilize. The formation of the latter, $Mn_{1.1}Nb_{1.9}O_6$, is possible because to the oxidation of Mn(II) to Mn(III). Interestingly, when Nb(V) is partially replaced by Ti(IV) this charge-compensating mechanism also operates [11]. The presence of trivalent manganese is responsible of the p-type electronic conductivity observed at ambient $pO_2$. However, at much lower $pO_2$, Mn(III) is reduced and electrical conductivity decreases; further reduction affects Nb(V) or Ti(IV) and n-type conductivity is then observed. Oxygen ion conductivity in this material is low since in the best case a value of $6.0 \times 10^{-5}\,\Omega^{-1}\,cm^{-1}$ at 900°C was found.

In the present paper we present the behavior of another member of the columbite family, $NiNb_2O_6$, for which oxidation of the divalent metal, Ni(II), at ambient $pO_2$ is not likely to occur. On the other hand, we have replaced Nb by Ta to study the series $NiNb_{2-x}Ta_xO_6$ for which the limit members are the columbite $NiNb_2O_6$ [12,13] and the tri-rutile $NiTa_2O_6$ [14], similarly to what occurs for $FeNb_{2-x}Ta_xO_6$ [15]. We aimed to analyze the effects of aliovalent substitution in the pentavalent site of columbite and tri-rutile looking for an improvement of electrical conductivity. In particular, we have replaced $Ti^{4+}$ by either $Nb^{5+}$ or $Ta^{5+}$, similarly to what was made in the case of $MnNb_2O_6$ for which an increasing of electrical conductivity by several orders of magnitude was achieved [11].

* Corresponding author.
*E-mail address:* flaga@ceu.es (F. García-Alvarado).

0022-4596/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2009.04.038

## 2. Experimental

The synthesis of oxides with nominal composition $NiNb_{2-x}Ta_xO_6$ ($0 \le x \le 2$) was carried out at high temperature by reaction of stoichiometric mixtures of $Nb_2O_5$ (99.99%), $Ta_2O_5$ (99.99%) and $Ni(NO_3)_2 \times H_2O$ (20.43% in Ni). First, the blends were heated at 800 °C for 12 h to fully decompose the nitrate; afterwards, they were ground, pelletized and heated up again at temperatures ranging from 1250 °C (for $x = 0$) to 1300 °C (for $x = 1$). Pellets were slowly cooled down to 800 °C and finally quenched in air from that temperature. The same procedure was followed to obtain the Ti-substituted derivatives: $NiNb_{2-y}Ti_yO_6$ and $NiNb_{1.75}Ta_{0.25-y}Ti_yO_6$ ($y = 0.1$, 0.15) and $NiNb_{0.25}Ta_{1.75-y}Ti_yO_6$ ($y = 0.15$ and 0.30).

Structural characterization of the samples was performed by powder X-ray diffraction (XRD) on a Bruker D8 high-resolution diffractometer using a monochromatic Cu$K\alpha_1$ ($\lambda = 1.5406$ Å) radiation obtained with a germanium primary monochromator; diffracted beams were recorded using a position-sensitive detector (PSD) MBraun PSD-50 M. Diffraction patterns were analyzed by the Rietveld method using the program FullProf [16].

Energy dispersive spectroscopy (EDS) has been carried out on a Scanning Electron Microscope JEOL JSM 6400 equipped with an OXFORD INCA EDS detector. Several spectra were recorded in order to analyze the homogeneity of the samples and the eventual presence of different types of particles. This equipment was also used to analyze the morphology on as-prepared pellets obtained by the sintering process described below.

Magnetic susceptibility measurements were made using a SQUID magnetometer (Quantum Design, model MPMS-XL). The temperature dependence of magnetization ($M$) was measured in the temperature range 2–300 K at an applied magnetic field ($H$) of 0.1 T upon heating samples under zero-field-cooled conditions from 2 K (previously cooled at $H = 0$ T). The experimental molar magnetic susceptibility $\chi_{exp}$ ($M/H$) was calculated on the basis of the sample mass and the molecular weight. The molar paramagnetic susceptibility $\chi_m$ was then obtained by subtraction of the diamagnetic contribution from each ion.

Electrical characterization has been performed by impedance spectroscopy (IS) using a FRA Solartron 1260 coupled with a 1290 Dielectric Interface in the 1 MHz–0.1 Hz range in the temperature interval 25–800 °C. Measurements were carried out on pellets whose polished faces were coated with platinum which acts as electrodes.

To get dense pellets, powdery samples were mixed with polyvinyl alcohol, as a binder, compacted into pellets and heated up to 800 °C very slowly (2 °C/min) to decompose the binder. Afterwards, pellets were fired at the synthesis temperature (1250–1300 °C) or slightly above it and slowly cooled down to 800 °C before being quenched in air. The density of pellets was measured by the Archimedes method. Relative densities were find to be the same (approximately 88%) for the whole composition range explored, $NiNb_{2-x}Ta_xO_6$ ($0 \le x \le 2$). On the other hand sintered Ti-substituted samples were found to have relative densities higher than 95%.

## 3. Results and discussion

Samples $NiNb_{2-x}Ta_xO_6$ with $x = 0$, 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75 and 2 have been prepared. The columbite structure has a narrow existence range since only the samples with $x = 0$ and 0.25 were found to be single-phase exhibiting this structure. Fig. 1a shows the XRD pattern for $NiNb_{1.75}Ta_{0.25}O_6$; all the diffraction peaks can be interpreted with the cell and symmetry of columbite [13]. On the other hand, single-phase samples with tri-rutile structure were found for $x = 1$, 1.5, 1.75 and 2. As an example, Fig. 1b shows the XRD pattern for $NiNb_{0.25}Ta_{1.75}O_6$; all the Bragg peaks can be assigned to cells similar to that one of the tri-rutile $NiTa_2O_6$ [14]. On the other hand, for $x = 0.75$ tri-rutile is the main phase but an unidentified second phase is present. This suggests that, in the phase-diagram, the stability region of tri-rutile starts somewhere between $x = 0.75$ and 1. Cell volume per

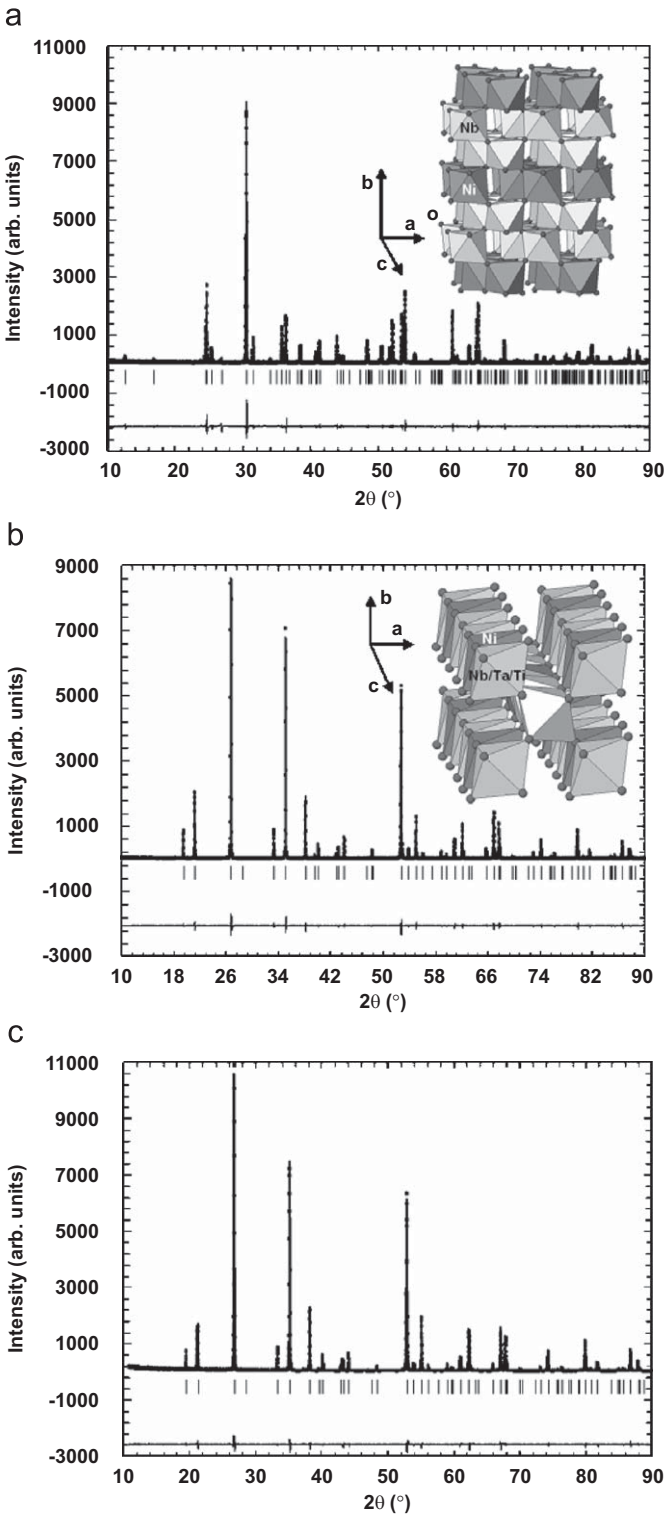


**Fig. 1.** Experimental X-ray diffraction patterns and calculated (profile matching) of (a) $NiNb_{1.75}Ta_{0.25}O_6$ (columbite), (b) $NiNb_{0.25}Ta_{1.75}O_6$ (tri-rutile) and (c) $NiNb_{0.25}Ta_{1.45}Ti_{0.30}O_{6-\delta}$ (tri-rutile). The insets show schematic representations of columbite (a) and tri-rutile (b).