ELSEVIER
Journal of Alloys and Compounds 317–318 (2001) 127–131
Journal of ALLOYS AND COMPOUNDS
www.elsevier.com/locate/jallcom

Synthesis, characterization, electrical and magnetic properties of $CrTa_2O_6$ and $CrNb_2O_6$

V. Guillen-Viallet[a,b,*], J.F. Marucco[a,b], M. Ghysel[a]

[a] *Laboratoire d'Etude des Matériaux Hors d'Equilibre, CNRS UMR 8647, bâtiment 415, Université de Paris-sud, 91405 Orsay cedex, France*
[b] *Service de Physique de l'Etat Condensé, DRECAM, CEA Saclay, 91191 Gif sur Yvette, France*

Abstract

Compounds $CrTa_2O_6$ and $CrNb_2O_6$ were synthesized. The former presents a slightly distorted trirutile structure and the latter has a tetragonal structure. Both are semiconducting oxides with an activation energy of 0.5 eV. Magnetism measurements are in good agreement with Cr^{2+} in $CrTa_2O_6$, contrary to $CrNb_2O_6$, which contains Cr^{3+} corresponding to a charge transfer between Cr^{2+} and Nb^{5+}. At the present time, $CrTa_2O_6$ remains the only oxide with divalent chromium. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Trirutile $CrTa_2O_6$; Tetragonal $CrNb_2O_6$; Semiconducting oxides

1. Introduction

$CrTa_2O_6$ is the only example of an oxide containing divalent chromium. Actually, compounds of Cr^{2+} are found in halides and CrO has been reported but not confirmed. $CrTa_2O_6$ belongs to the oxide family $Ta_2M^{2+}O_6$ presenting a trirutile structure, with M=Mg, Ni, Fe, Co. It was first synthesized by Bernier et al. [1,2], who pointed out its antiferromagnetic properties and a static Jahn–Teller distortion as expected for high-spin Cr^{2+}. More recently, the structure and magnetism were studied by neutron diffraction by Saes et al. [3], who confirmed the trirutile structure. This compound shows long-range antiferromagnetic order below 10.3 K with a complex magnetic structure. On the other hand, no electrical measurements have been carried out on this material. The aim of the present work was to synthesize this compound in order to measure its electrical conductivity and to determine the nature of the conduction. We also present the preparation and the electrical and magnetic characterization of $CrNb_2O_6$. This compound was an attempt to prepare another oxide containing Cr^{2+}.

2. Experimental procedure

2.1. Synthesis

2.1.1. $CrTa_2O_6$

The synthesis of this trirutile was achieved according the reaction described by Bernier et al. [2]. Stoichiometric amounts of Cr_2O_3 (Koch-light, 99.995%), Ta_2O_5 (Johnson-Matthey, 99.99%) and very fine chromium metal powder (Koch-Light, 99.2%) were mixed according to the following reaction:

$$3Ta_2O_5 + Cr + Cr_2O_3 \rightarrow 3CrTa_2O_6$$

The intimately ground mixture was heated at 1050°C for 48 h, under argon flow, passing through Ti–Zr alloy turnings used as a getter. The product was ground and heated three times to obtain an X-ray spectrum without impurities.

2.1.2. $CrNb_2O_6$

The synthesis of this compound was achieved according to the same reaction substituting Ta_2O_5 with Nb_2O_5 (Johnson-Matthey, 99.99%). The experimental procedure was the same as described above.

---

*Corresponding author. Laboratoire d'Etude des Matériaux Hors d'Equilibre, CNRS UMR 8647, bâtiment 415, Université de Paris-sud, 91405 Orsay cedex, France.

PII: S0925-8388(00)01328-1

2.2. Chemical analysis

Chemical analyses were performed with a LEICA 260 scanning electron microscope (SEM) equipped with a Tracor Noran energy dispersive X-ray microanalyzer (EDX).

2.3. X-ray measurements

X-ray diffraction patterns were obtained on a Philips PW 1840 diffractometer (using Cu Kα radiation) equipped with a back monochromator.

2.4. Electrical resistance measurements

The samples used for electrical resistance (R) measurements were prepared from fine powder, pressed into the shape of a parallelepiped bar and sintered in purified argon at 1050°C. The length of the sample was 20 mm and the section 5×5 mm. The resistance R was measured by the four-wire DC method with a Keithley 191 multimeter. These measurements were carried out in a purified argon flow from room temperature to 900°C by increasing and decreasing the temperature.

2.5. Magnetic measurements

The magnetic measurements were carried out by SQUID magnetometry (Cryogenic Limited, S 600) in a magnetic field of 100 G. The susceptibility measurements were performed on powder samples. Classical zero field cooled (ZFC) and field cooled (FC) procedures were used.

3. Results

3.1. Chemical analysis and X-ray diffraction

3.1.1. $CrTa_2O_6$

The SEM analysis gives a perfect stoichiometric composition, Ta/Cr=2. The X-ray diffraction pattern of $CrTa_2O_6$ shown in Fig. 1 shows that a single phase is obtained. This oxide presents a slightly distorted trirutile structure, and the unit cell constants determined according to a monoclinic structure ($P2_1/n$) are $a = 4.707(3)$, $b = 4.730(3)$, $c = 9.318(5)$ and $\beta = 90°89(3)$, deviating slightly from the results obtained previously [2,3].

3.1.2. $CrNb_2O_6$

This compound is more contentious, but several careful analyses led to the conclusion that the Nb/Cr ratio is also 2. On the other hand, the X-ray diffraction pattern (Fig. 2) is the same as the pattern observed by Ben-Dor et al. [4] for $Cr_{0.4}Nb_{0.6}O_2$. The unit cell constants determined according to a tetragonal structure ($P4_2/mnm$) are $a = 4.682(3)$ and $c = 3.002(7)$, which are in good agreement with the results of the above authors: $a = 4.6833(5)$ and $c = 3.0070(4)$.

3.2. Electrical conductivity

The conductivity σ was calculated from the resistance measurements and the geometry of the sample. The conductivity results for the two oxides are plotted in Fig. 3. We observe that the conductivity of $CrNb_2O_6$ is larger than that of $CrTa_2O_6$ at high temperature. Plots of $\ln \sigma$ versus $1/T$, where T is the absolute temperature, are shown in Fig. 4 for $CrTa_2O_6$ and Fig. 5 for $CrNb_2O_6$. Both compounds present semiconducting behavior and a phase

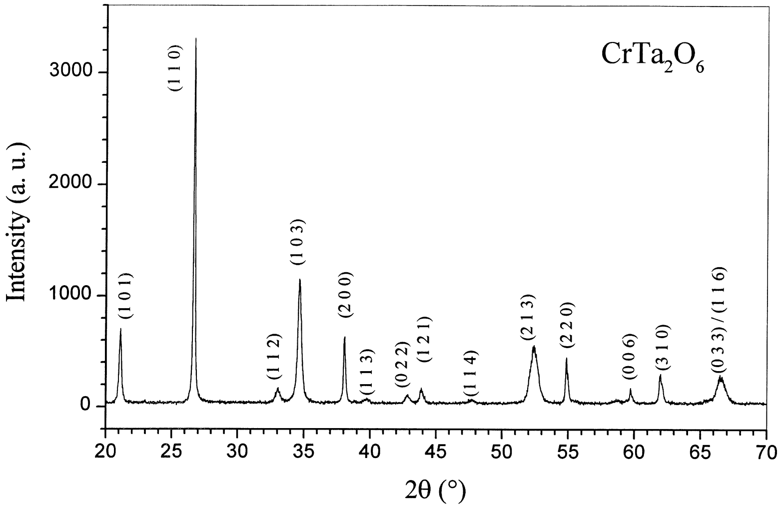

Fig. 1. X-ray diffraction pattern (Cu Kα radiation) for the trirutile $CrTa_2O_6$.

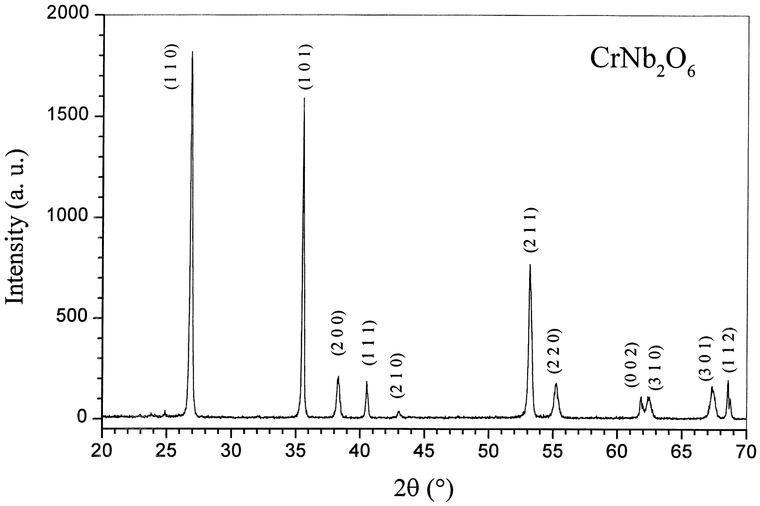

Fig. 2. X-ray diffraction pattern (Cu Kα radiation) for tetragonal $CrNb_2O_6$.

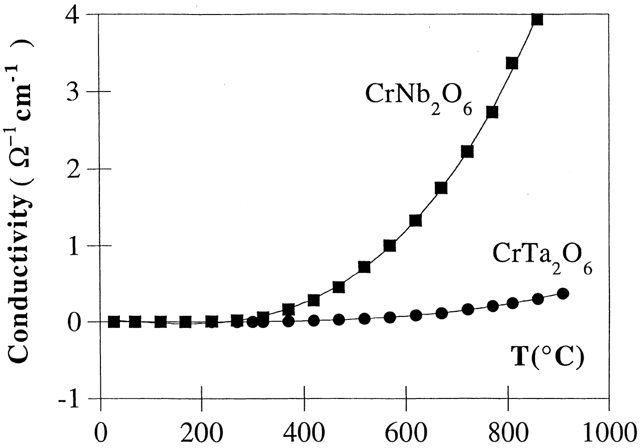

Fig. 3. σ vs. temperature (°C) for $CrTa_2O_6$ and $CrNb_2O_6$ between 25 and 900°C.

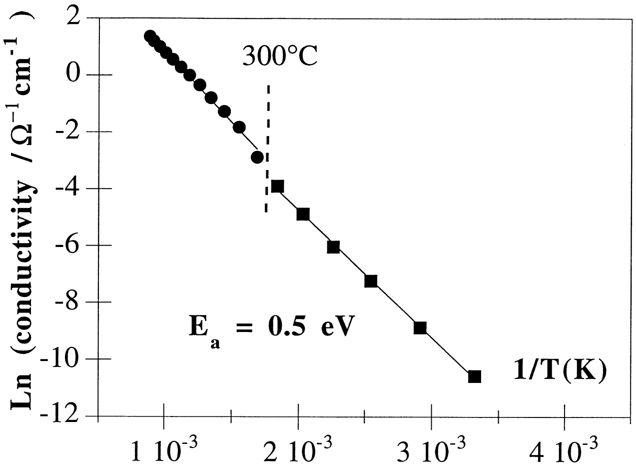

Fig. 5. Ln σ vs. $1/T$ for $CrNb_2O_6$.

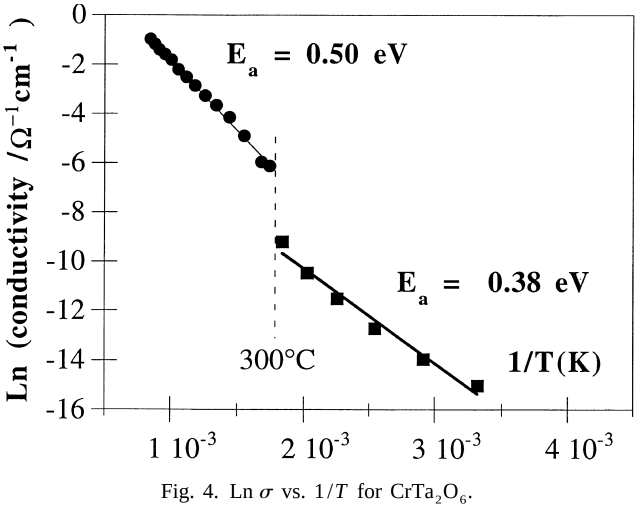

Fig. 4. Ln σ vs. $1/T$ for $CrTa_2O_6$.

transition at 300°C. In the case of $CrTa_2O_6$ the transition is sharp, whereas for $CrNb_2O_6$ the transition is very reduced. For the former compound, two domains are displayed. There is a high-temperature range with an activation energy of 0.5 eV and a lower-temperature range with an activation energy of 0.38 eV.

3.3. Magnetic measurements

Fig. 6 shows the temperature dependence of the magnetic susceptibility of $CrTa_2O_6$ over the range 8 to 150 K. These results are in good agreement with the results of Bernier [2] and Saes [3], and confirm the presence of Cr^{2+} and an antiferromagnetic transition at 10 K. Fig. 7 shows the temperature dependence of the magnetic susceptibility of $CrNb_2O_6$ over the range 5–300 K. The Curie law holds down to low temperatures and μ_{eff} = 3.94 Bohr Magnetons

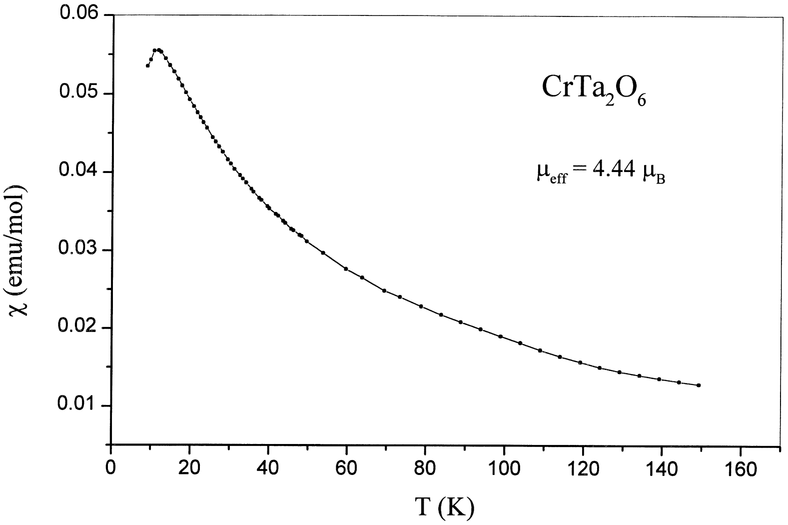

Fig. 6. Magnetic susceptibility χ versus temperature between 8 and 150 K for CrTa$_2$O$_6$, confirming the antiferromagnetic transition.

can be derived from the Curie constant, which is consistent with the presence of Cr^{3+}.

4. Discussion

We compared two oxides presenting a rutile structure, CrTa$_2$O$_6$ and CrNb$_2$O$_6$. The former is an ordered trirutile with planes containing either Ta or Cr, the latter is a simple tetragonal rutile with Cr and Nb distributed at random. This difference may be related to the presence of ions having different charges and different ionic radii. In the former, the large difference between Cr^{2+} (94 pm) and Ta^{5+} (78 pm) implies an ordered trirutile. On the contrary, in the latter, the small difference between Cr^{3+} (76 pm), Nb^{4+} (82 pm) and Nb^{5+} (78 pm) leads to a disordered simple rutile structure. This behavior may also be related to the differences between the chemical behavior of Ta (a single valence state) and Nb (several oxides), as was observed in pyrochlores Cd$_2$Nb$_2$O$_7$ and Cd$_2$Ta$_2$O$_7$, or between LiNbO$_3$ and LiTaO$_3$. This difference was pointed out by Sleight et al. [5] and Rao et al. [6] and attributed to the more covalent Nb–O bonds. On the other hand, the thermodynamic properties of Cr^{2+} in oxides are unknown and seem to be reducing for Nb^{5+}. Therefore, to synthesize compounds containing divalent chromium, this cation must

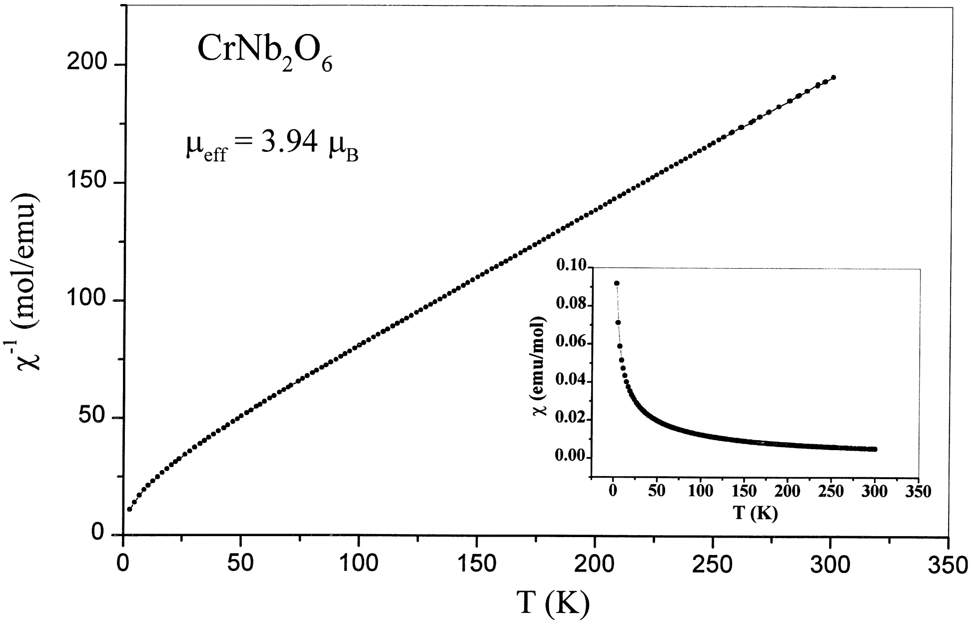

Fig. 7. Reciprocal magnetic susceptibility (1/χ) plotted versus temperature (K) between 5 and 300 K for CrNb$_2$O$_6$. The inset shows the susceptibility χ versus temperature (K) between 5 and 300 K.

be associated with another transition cation having a single ionization state such as Ta, Zr or Hf. We tried to synthesize double perovskites, implying Cr with Zr or Hf, but we were unsuccessful.

On the other hand, the sharp transition of ln σ vs. $(1/T)$ for $CrTa_2O_6$ suggests two different conduction mechanisms. For $CrNb_2O_6$, the two domains have the same activation energy. The identical values determined for $CrNb_2O_6$ and $CrTa_2O_6$ above 300°C suggest the same mechanism related to the same structure. So we can assume that, above 300°C, $CrTa_2O_6$ becomes a simple rutile. Nevertheless, the larger conductivity of $CrNb_2O_6$ is also related to charge hopping between Cr and Nb, contrary to $CrTa_2O_6$, in which hopping between Cr^{3+} and Ta^{5+} is impossible, and implies a more favorable conductivity in the disordered material.

5. Conclusion

Two oxides having the rutile structure, $CrTa_2O_6$ and $CrNb_2O_6$, were synthesized. The former has an ordered trirutile structure. Its magnetic properties are in agreement with the presence of divalent chromium. On the contrary, the latter has a disordered simple rutile structure and the magnetic susceptibility can be explained by the presence of trivalent chromium, implying a charge transfer between Cr and Nb. Both are semiconductors with an activation energy of 0.5 eV and a higher conductivity for the Nb-containing material.

References

[1] J.-C. Bernier, C.R. Acad. Sci. Paris 273 (Ser. C) (1971) 1166.
[2] P. Massard, J.-C. Bernier, A. Michel, Ann. Chim. 6 (1971) 41.
[3] M. Saes, N.P. Raju, J.E. Greedan, J. Solid State Chem. 140 (1998) 7.
[4] L. Ben-Dor, J. Shimony, J. Cryst. Growth 43 (1978) 1.
[5] A.W. Sleight, J.D. Bierlein, Solid State Commun. 18 (1976) 163.
[6] C.N.R. Rao, K.J. Rao, Phase Transitions in Solids, McGraw-Hill, New York, 1978.