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CATION ORDERING OBSERVED ON  $(\text{Mn}_{0.88}\text{Fe}_{0.09})(\text{Ta}_{0.86}\text{Nb}_{0.14})_2\text{O}_6$ : A MÖSSBAUER AND X-RAY STUDY

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Mössbauer spectroscopy and X-ray powder diffraction are used to show cation ordering on a natural manganotantalite sample. By using electron microprobe analysis the chemical composition  $(\text{Mn}_{0.88}\text{Fe}_{0.09})(\text{Ta}_{0.86}\text{Nb}_{0.14})_2\text{O}_6$  has been determined. The as-received sample is partially ordered, as suggested by the low intensities of the superstructure reflections in the X-ray diffraction pattern and by the existence of two doublets in the Mössbauer spectrum. Heat treatment in vacuum ( $P \approx 10^{-5}$  Pa) at temperature  $T \approx 1320$  K induces cation ordering as shown by the Mössbauer spectrum, and also evidenced by the X-ray diffraction pattern. © 1997 Published by Elsevier Science Ltd. All rights reserved

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## 1. INTRODUCTION

Minerals and synthetic samples of the columbite-tantalite and tapiolite-mossite families, have been extensively studied in the last three decades [1-4]. With the general formula  $\text{AB}_2\text{O}_6$ , where typically  $A = \text{Fe, Mn, Mg}$  and  $B = \text{Ta, Nb}$ , these materials can have minor substitutions of Sn, W and Ti and can also be synthesized with  $A = \text{Co, Ni}$  and  $\text{Cu}$  [5-8]. The tetragonal tapiolite-mossite family, with space group  $P4_2/mnm$ , is an ordered superstructure of the rutile ( $\text{TiO}_2$ ) [2, 9], while the orthorhombic columbite-tantalite family, with space group  $Pbcn$ , is an ordered superstructure of the brookite ( $\text{TiO}_2$ ) [1].

Interest in these materials has recently increased, motivated by their low dimensional magnetic behavior observed in some synthetic end-members of the tetragonal family [10, 11]. In addition, refinement of the crystal structures and phase transformations between columbite-tantalite and related compounds have been the subject of several publications [1-4]. For example, the mineral ixiolite, with general formula  $(A, B)\text{O}_2$  is identified as a substructure of columbite so that completely disordered columbite can be misinterpreted as ixiolite. For a long time, mineralogists have used heating experiments to distinguish these materials. Ixiolite reveals an olivotantalite [1] or wodginite [3] X-ray

powder diffraction (XRPD) pattern upon heating, whereas disordered columbite yields an ordered columbite pattern [1-3], characterized by its superstructure reflections. However, calculation of a theoretical powder diffraction pattern of fully ordered manganocolumbite,  $\text{MnNb}_2\text{O}_6$ , yields only low intensity superstructure reflections [12]. Thus it is difficult to distinguish between ixiolite and partially disordered columbite only by means of their superstructure reflections. Other criteria have been tentatively established to estimate the degree of cation order. For instance, Ercit, cited by Wenger *et al.* [12], derived the following equation for the  $(\text{Fe, Mn})(\text{Ta, Nb})_2\text{O}_6$  system:

$$\% \text{order} (\pm 5\%) = 1727 - 941.6(c - 0.2329a),$$

where  $a$  and  $c$  are the lattice parameters. Wenger *et al.* [12] have suggested that single crystal diffraction data should be used to differentiate between ixiolite and columbite.

Disorder evaluation in synthetic  $\text{AB}_2\text{O}_6$  compounds is also very important because it can have considerable effects on magnetic properties. Thus, this kind of investigation can be used as a control step for the preparation of samples for magnetic properties studies.

In this communication we show that Mössbauer spectroscopy (MS) is an adequate technique to investigate

order-disorder transitions in this kind of materials. Hyperfine interactions are very sensitive to change in the near-neighbour environment and can discriminate site location of Fe ions in columbite-like samples. The analysis by MS is simpler if we want to distinguish between ixiolite and columbite, because in the former material Fe is in valence state 3+, whereas in the latter one it is in valence state 2+. We have analysed 32 samples of the tantalite-columbite and tapiolite-mossite families collected at several Brazilian localities. XRPD and MS measurements of all the samples have enabled us to choose a very pure, partially ordered orthorhombic structure of tantalite type.

## 2. EXPERIMENTAL DETAILS

Electron probe microanalysis (EPMA), XRPD and MS have been used to characterize the selected sample and to investigate the cation-ordering process.

EPMA measurements were performed on the as-collected sample with a wavelength dispersive (WDS) microprobe system (CAMECA SX50). Accelerating potential of 15 kV, beam current of 25 nA and beam size of approximately 1  $\mu\text{m}$  have been used. Pure Nb ( $\text{Nb } L\alpha$ ), pure Ta ( $\text{Ta } L\alpha$ ), synthetic rutile ( $\text{Ti } K\alpha$ ), natural olivine ( $\text{Mn } K\alpha$ - $\text{Fe } K\alpha$ ) and pure W ( $\text{W } L\alpha$ ) were used as standards. The counting time was 20 s for Nb and Ta and 30 s for the remaining elements. The raw data were corrected on-line for drift, deadtime and background using PAP correction programs. The formula was calculated on the basis of six O atoms.

The XRPD patterns were obtained in a Siemens diffractometer with monochromated  $\text{Cu } K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Measurements were performed in the range of  $10 \leq 2\theta \leq 100$  with a scan rate of  $2^\circ \text{ min}^{-1}$ .

For the MS measurements, absorbers with 50 mg of ground (320 mesh) material were prepared in order to satisfy the ideal absorber thickness approximately [13]. The spectra were obtained at room temperature using a constant-acceleration electromechanical drive system with a multichannel analyzer for collecting and storing the data. The hyperfine parameters were obtained by a least-squares procedure assuming Lorentzian line shapes.  $^{57}\text{Co}$  in rhodium was used at room temperature as a source, with nominal activity of 50 mCi.

For the cation ordering experiment, the sample was powdered, pelleted, encapsulated under vacuum ( $P \approx 10^{-5} \text{ Pa}$ ), heated at 1320 K for 48 h and cooled at the rate of  $320 \text{ K h}^{-1}$  to RT.

## 3. RESULTS AND DISCUSSION

Using the EPMA results (Table 1) the sample composition has been calculated to be approximately  $(\text{Mn}_{0.88}\text{Fe}_{0.09})(\text{Ta}_{0.86}\text{Nb}_{0.14})_2\text{O}_6$ . The XRPD pattern of

Table 1. Atomic proportions based on six oxygens, from EPMA measurements

Fe	Mn	Ta	Nb	Ti	W	Total
0.09	0.88	1.72	0.28	0.01	0.01	2.99

the as-collected sample, whose significant part is shown in Fig. 1(a), was indexed to the space group  $Pbcn$ , with cell parameters as displayed in Table 2. For comparison, Table 2 also shows lattice parameters of similar synthetic samples reported earlier [4]. Since there are no spurious reflections on the XRPD diagram and as the EPMA investigation has shown no significant amount of impurities, it is very reasonable to suppose that we have a single-phase manganotantalite sample. The Ercit's equation [12] gives a degree of cation order of 68% for the as-collected sample.

The RT MS spectrum of the as-collected sample is displayed in Fig. 2(a), while the hyperfine parameters obtained from the fitting are shown in Table 3. The spectrum was fitted to two quadrupole doublets, both attributed to  $\text{Fe}^{2+}$  in different octahedrally coordinated sites. This kind of coordination has been confirmed by X-ray structure refinement performed on single crystals of similar samples [12]. These authors investigated the distortions in the metal-oxygen octahedra ( $\text{MO}_6$ ) for the partially ordered columbite ( $\text{Fe}_{0.65}\text{Mn}_{0.30}\text{Ti}_{0.05}$ ) ( $\text{Nb}_{0.75}\text{Ta}_{0.25}$ ) $_2\text{O}_6$ . It was shown from octahedral edge length distortion (ELD) that the  $\text{FeO}_6$  octahedra are more distorted than the  $\text{NbO}_6$  one. Thus we can attribute the outer doublet ( $\Delta E_Q = 2.26 \text{ mm s}^{-1}$ ) to  $\text{Fe}^{2+}$  in the  $\text{NbO}_6$  octahedra, while the inner one ( $\Delta E_Q = 1.54 \text{ mm s}^{-1}$ ) is attributed to  $\text{Fe}^{2+}$  in the more distorted  $\text{FeO}_6$  octahedra. This assignment is justified because the  $\text{Fe}^{2+}$  quadrupole

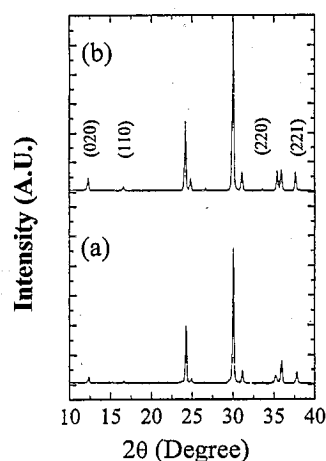


Fig. 1. Representative part of the X-ray powder diffraction patterns for (a) as-collected manganotantalite sample; (b) heat-treated sample.

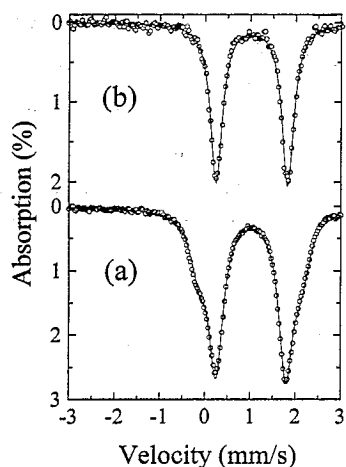


Fig. 2. Mössbauer spectra taken at RT for (a) as-collected manganotantalite sample; (b) heat-treated sample.

splitting is inversely correlated with octahedral distortions [14]. The proportion of Fe<sup>2+</sup> in the FeO<sub>6</sub> octahedra estimated from the spectral areas gives an iron order degree of 71%, very close to the calculated 68% by the Ercit's equation.

The XRPD pattern for the heat-treated sample [Fig. 1(b)] is similar to that obtained for the as-collected one, but showing an increase of the superstructure reflections. The Ercit's equation for the heat-treated sample gives an order degree of 93%. Correspondingly, a dramatic change has been observed in the MS spectrum after the heat treatment as is clearly seen in Fig. 2(b). The hyperfine parameters used to fit the spectrum of Fig. 2(b), shown in Table 3, are almost the same as those attributed to Fe<sup>2+</sup> in the FeO<sub>6</sub> octahedra. The disappearance of the outer quadrupolar doublet suggests that after the heat treatment all the Fe ions are in the "right" octahedra. MS alone does not give direct information on the Mn site location, but the observed increase of the superstructure reflections in the XRPD diagram, the order degree calculated by the Ercit's equation and the significant narrowing of the MS spectrum linewidth after the heat

Table 2. Lattice parameters and Ercit's order parameters for our sample and for some synthetic columbite-tantalite samples [4]

Sample	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Order (%)
Our sample				
As-collected	14.285	5.739	5.089	68
Heat-treated	14.335	5.747	5.074	93
(Fe <sub>0.5</sub> Mn <sub>0.5</sub> )Nb <sub>2</sub> O <sub>6</sub>	14.356	5.748	5.069	102
MnTa <sub>2</sub> O <sub>6</sub>	14.454	5.768	5.097	97
(Mn <sub>0.65</sub> Fe <sub>0.35</sub> )Ta <sub>2</sub> O <sub>6</sub>	14.415	5.761	5.087	98

Table 3. Hyperfine parameters for the as-collected and for the heat-treated sample measured at RT.  $\Delta E_Q$  is the quadrupolar splitting at the iron sites;  $\delta_{Fe}$  is the isomer shift relative to  $\alpha$ -Fe;  $\Gamma$  is the linewidth at half-height; *A* is the relative spectral area

Sample	$\Delta E_Q$ (mm/s)	$\delta_{Fe}$ (mm/s)	$\Gamma$ (mm/s)	<i>A</i> (%)
As-collected	1.54	1.13	0.39	71
	2.26	1.09	0.46	29
Heat-treated	1.58	1.14	0.32	100

treatment, all confirm that an almost total cation-ordering process has occurred.

#### 4. CONCLUSIONS

Mössbauer spectroscopy and X-ray powder diffraction studies were performed on the partially ordered manganotantalite (Mn<sub>0.88</sub>Fe<sub>0.09</sub>)(Ta<sub>0.86</sub>Nb<sub>0.14</sub>)<sub>2</sub>O<sub>6</sub>. Cation ordering induced by heat treatment has been observed. The degree of cation order has been estimated from XRPD data, by Ercit's equation, and from the site population obtained by fitting the MS spectra. Both techniques presented similar results, i.e. degree of cation order about 70% for the as-collected sample and nearly 100% after the heat treatment. These results suggest that MS is a very appropriate technique to be used in routine procedures to evaluate the cation order degree of synthetic samples of the columbite-tantalite family.

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