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Mössbauer Assessment of Cation Disorder in Columbite–Tantalite Minerals

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We have used X-ray diffraction and Mössbauer spectroscopy to investigate the cationic disorder between crystallographic sites of a columbite–tantalite series of pegmatites. The X-ray results show that the pegmatites have different degrees of crystallographic disorder according to the quarries where the samples come from. Mössbauer spectra allow us to distinguish two Fe^{2+} different sites. A simple model assuming equal *f*-factors and occupation probabilities both for Fe and Mn has been used to turn the relative populations for Fe yielded by Mössbauer spectroscopy into effective site occupancy of the 2+ ions. A well-known empirical formula applied to X-ray results to obtain cationic disorder has been found to correlate within experimental errors with the percentage of cationic ordering obtained by Mössbauer spectroscopy. © 1999 Academic Press

1. INTRODUCTION

Minerals of the columbite–tantalite group are the main source of niobium and tantalum, which are important because of their applications in high-technology products. These oxide minerals have the general formula AB_2O_6, in which the A position is occupied mostly by Fe^{2+}, Mn^{2+}, and, to a lesser extent, Mg^{2+}; the B position is occupied mainly by Nb^{5+}, Ta^{5+}, and, occasionally, Ti^{4+} and Sn^{4+}. The end members of these orthorhombic minerals are ferrocolumbite $FeNb_2O_6$, manganocolumbite $MnNb_2O_6$, manganotantalite $MnTa_2O_6$, and magnocolumbite $MgNb_2O_6$. Ions at A and B sites are coordinated to six oxygen atoms that form distorted octahedra. Octahedra are stacked in a sequence of *ABBABB* layers; those of type A share corners, while those of type B share edges.

Although the 3*d* transition metals occupy mainly the A site, there exists a considerable degree of cation occupation disorder between sites A and B; i.e., Fe, Mn, Nb, or Ta are found to occupy both sites A and B in different proportions. The different cationic occupancy of sites from one member of the series to the other leads to changes in the unit cell dimensions and to distortions in the oxygen octahedra. Cerný and Ercit (1) observed that in several groups of cogenetic columbite–tantalites with variable composition and structural state, the degree of ordering increases with the enrichment in Mn. Komkov (2) found that the **a**/**c** ratio of columbite–tantalite is a suitable parameter to describe the cation order–disorder. Cerný and Turnock (3) found in an **a** vs **c** plot ($3 \times \mathbf{a}$ for disordered phases) that the cell parameters correlate qualitatively with the degree of cationic order and with the approximate Fe/Mn ratio, but that no apparent relationship seems to exist with the Nb/Ta ratio. However, the diagram is of limited quantitative application because the range of cell parameters for fully disordered samples is not known and, in addition, impurity substituents have an unknown influence on those parameters (4). An empirical formula derived by Ercit to estimate the degree of cation order for columbite has been used on some occasions (3–5). In particular, for single crystals of columbite–tantalite pegmatites, Wenger *et al.* (5) found that the degree of cationic disorder obtained after application of

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Ercit's formula (4) correlates well with the site occupancy obtained by refinement of single crystal X-ray diffraction data.

Mössbauer spectroscopy of ^{57}Fe has been successfully applied in mineral studies to find the oxidation state and iron occupation sites. In many cases Fe occupation can be unambiguously assigned based on the magnitudes of the isomer shift and quadrupole splitting. It is usually possible to assess the oxidation state of the iron probe by the value of its isomer shift. The quadrupole splitting is a measure of the charge density deviation from cubic symmetry at the Fe atom site. Generally, for Fe^{2+} ions the larger quadrupole splitting corresponds to a smaller distortion at the probe site (6), although because of the opposite effects that the lattice and valence contributions have on the local electric field gradient (7), there are situations where the assignment is not so straightforward (5).

In this paper we study by X-ray diffraction and Mössbauer spectroscopy a series of tantalite–columbite samples from different pegmatites. We compare the cationic ordering obtained through Ercit's formula with the site population from Mössbauer spectra under simple assumptions and discuss the order correlation obtained by both techniques.

2. EXPERIMENTAL

The Nb–Ta-bearing pegmatites are located in a NNE/SSW belt of rare-element granitic pegmatites of the San Luis range, Argentina, parallel to a stanniferous belt and with the same orientation (8). Columbite–tantalite minerals occur in minor concentrations in these pegmatites and are obtained as a by-product of the exploitation of the main pegmatitic minerals. Samples were collected from three different quarries, "Independencia Argentina" (IA), "La Brillante" (LB), and "Los Chilenitos" (LC), located in separate areas of the belt. The Nb–Ta–bearing pegmatites occur as tabular bodies and usually show a thin external zone and a central bare quartz core. A few pegmatites show more complex zoning; the rest are simple. The pegmatitic bodies mainly consist of quartz, K-feldspar, and plagioclase, with minor muscovite. Accessory minerals found are beryl, spodumene, ambligonite, tourmaline, garnet, and apatite. The ore minerals are columbite–tantalite, chalcopyrite, bismutinite, and pyrite.

Unit cell dimensions were calculated from X-ray powder diffraction (XRD) data obtained with a Rigaku D-Max III powder diffractometer using Ni-filtered Cu$K\alpha$ radiation ($\lambda = 1.542$ Å) and a scan speed of 2° 2θ/min; 2θ readings were automatically recorded by computer. NaCl was used as an internal calibration standard. Indexing and refinement of unit cell parameters were carried out with the modified Werner program (9).

The Mössbauer spectra were taken in a conventional constant acceleration spectrometer of 512 channels with a 50 mCi nominal activity ^{57}Co Rh source in transmission geometry. The heavy ions contained in the samples limit a good signal-to-noise ratio in the spectra, and therefore the method described by Rancourt *et al.* (10) was used to obtain the optimum absorber thickness. This yielded about 28 mg/cm^2 as the ideal amount of sample to prepare the absorbers for the six columbite–tantalite samples analyzed. The data were fitted by a least-squares program that used Lorentzian line shapes with constraints to calculate the hyperfine parameters of the spectra. Isomer shifts were calibrated with an α-Fe foil at room temperature.

3. RESULTS AND DISCUSSION

Columbite–tantalite forms euhedral to subhedral disseminated crystals with thin tabular habit and is usually present as aggregates of parallel to divergent crystals. The mineral is often tarnished iridescent, with metallic to submetallic luster. The crystal size of our samples varied between 1×2 mm^2 and 1.5×3.5 cm^2, but the coarser grains reached up to 7×11 cm^2. No alteration of the mineral was observed. An apparently single generation of columbite–tantalite is dispersed in the pegmatites, replacing mainly feldspar and quartz, pointing to crystallization later than these silicate minerals.

Table 1 shows the unit cell parameters, **a**, **b**, **c**. Table 2 displays the results of the least-squares fittings of the Mössbauer spectra shown in Figs. 1 and 2. For all samples it was necessary to use two quadrupole doublets to fit the spectra. This was the criterion also used to fit the unresolved spectrum of the sample measured by Wenger *et al.* (5). Garg *et al.* (11) and Oliveira *et al.* (12) used only one quadrupole signal to fit their data (although synthetic samples were used in Ref. (11)). However, one-doublet fitting proved inadequate in our case (see Figs. 1 and 2).

The cation order parameter for compounds of formula AB_2O_6 can vary between 100% order (belonging to a situation where all 2+ cations occupy site A and all 5+ cations occupy site B) to 0% order (involving a completely

TABLE 1
Unit Cell Parameters a, b, and c (Å), of Columbite–Tantalite Samples from San Luis Range Pegmatites

Sample	a	b	c
LB1	14.348(6)	5.759(2)	5.086(3)
LC4	14.339(8)	5.742(2)	5.122(2)
LC7	14.339(4)	5.748(1)	5.116(2)
LC8	14.336(5)	5.743(2)	5.114(2)
IA1	14.337(4)	5.748(1)	5.117(1)
IA2	14.287(3)	5.739(1)	5.103(1)

Note. Errors in the least significant figures are quoted between parentheses.

TABLE 2
Mössbauer Parameters of Columbite–Tantalite Samples from San Luis Range Pegmatites

Sample	Δ (mm/s)	δ (mm/s)	Γ (mm/s)	A_{rel} (%)
LB1	2.28 ± 0.03	1.08 ± 0.01	0.43 ± 0.04	20 ± 2
	1.53 ± 0.01	1.15 ± 0.01	0.36 ± 0.01	80 ± 3
LC4	2.25 ± 0.03	1.10 ± 0.01	0.45 ± 0.04	28 ± 4
	1.57 ± 0.01	1.15 ± 0.03	0.40 ± 0.01	72 ± 4
LC7	2.18 ± 0.03	1.09 ± 0.01	0.52 ± 0.04	45 ± 5
	1.49 ± 0.01	1.14 ± 0.01	0.41 ± 0.02	55 ± 4
LC8	2.21 ± 0.04	1.07 ± 0.01	0.52 ± 0.06	41 ± 7
	1.53 ± 0.02	1.14 ± 0.01	0.42 ± 0.03	59 ± 7
IA1	2.29 ± 0.03	1.09 ± 0.01	0.47 ± 0.04	35 ± 4
	1.56 ± 0.01	1.15 ± 0.01	0.42 ± 0.02	65 ± 4
IA2	2.25 ± 0.01	1.09 ± 0.01	0.47 ± 0.02	37 ± 2
	1.55 ± 0.01	1.14 ± 0.01	0.41 ± 0.01	63 ± 2

random distribution of 2+ and 5+ cations in both sites, i.e., 33% of 2+ ions at site A and 66% at site B). The first situation is never observed in real samples, while columbite–tantalite is known in a disordered form (pseudo-ixiolite) (13).

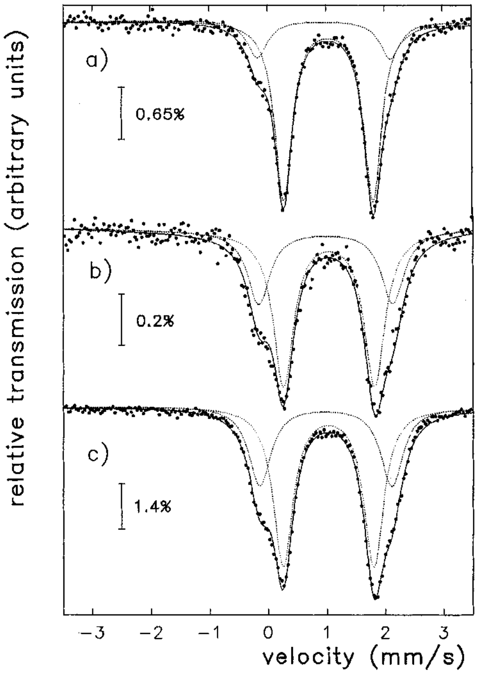

FIG. 1. Mössbauer spectra of columbite–tantalite pegmatites from: (a) LB quarry sample LB1; (b) IA quarry sample IA1; (c) IA quarry sample IA2. Solid lines are the best fits to the data simulated with the parameters of Table 2. Dashed lines are the components of each quadrupole doublet.

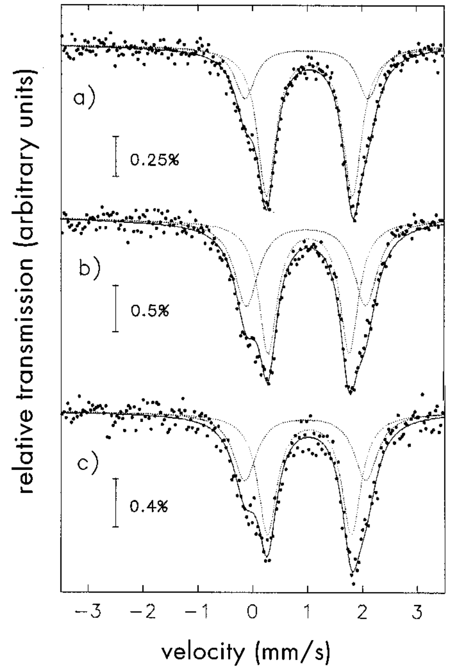

FIG. 2. Mössbauer spectra of columbite–tantalite pegmatites from LC quarry: (a) sample LC4; (b) sample LC7; (c) sample LC8. Solid lines are the spectra simulated with the parameters of Table 2. Dashed lines are the components of each quadrupole doublet.

Using the **a** and **c** parameters obtained by XRD we calculated the percentage of cation order in the current samples following Ercit's formula (4):

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

The results are shown in Table 3. The samples have a degree of order between 48 and 84%, with a mean of 55%. These data show that the columbite–tantalite samples studied have a predominantly intermediate structural state. In ordered columbite the **a**/**c** ratio, with setting conformable with *Pbcn*, ranges from 2.825 (ferrocolumbite) to 2.839 (manganotantalite), while in completely disordered columbite, **a**/**c** varies from 2.76 to 2.77 (2). For our samples, the **a**/**c** ratio varies between 2.79 and 2.82.

To date, the causes of cation disorder in columbite-group minerals are poorly understood, as is the role of impurity elements in the disorder process. Although compositions with low concentrations of these elements show a full range of structural states, compositions with high concentrations of impurity elements show only low to moderate degrees of order (4).

As mentioned above, the cation disorder of the columbite–tantalite group of minerals has been correlated to different structural parameters by several authors (1–4). These are mainly empirical correlations between cell parameters that are influenced not only by the cation disorder but also

TABLE 3

a/c Ratio after X-ray Diffraction Data analysis, Percentages of Cation Order Using Ercit's Formula (4), and Percentages Obtained from Mössbauer Results Assuming Equal *f*-Factors and the Same Probability for Site Occupation of Both Fe and Mn

Sample	a/c	%XRD (± 5%)	%Möss
LB1	2.82	84	71 ± 4
LC4	2.79	48	59 ± 6
LC7	2.80	55	33 ± 7
LC8	2.80	56	39 ± 11
IA1	2.80	52	48 ± 6
IA2	2.79	54	45 ± 3

by the crystallographic, impurity, and structural disorders. In particular, Ercit's formula only describes the distribution of (Fe, Mn) and (Nb, Ta) among the crystallographical distinct *A* and *B* sites in the columbite structure. To our knowledge only one work (5), after refining the X-ray diffraction data obtained from single crystals, relates the site occupancy with the cation disorder.

For reasons probably related to the geothermal history of the mineral, instead of the more favorable *A* sites (energetically lower) the transition metal ions are found to occupy site *B* positions. In these studies the preferences of all transition metal elements for sites *A* or *B* seem to be the same. Indeed, both Fe and Mn play the same role in Ercit's formula.

According to the values of the isomer shifts obtained, all Fe present in the samples is in the 2+ high-spin state. No traces of Fe^{3+} could be observed within the statistics of our data. However, unlike previous works with similar samples (5,11,12), our resolution was enough to sort out two octahedrally coordinated sites with different distortions. The linewidths obtained are similar to values reported in previous works on this type of minerals.

It is well known that in these minerals, the more distorted Fe^{2+} sites have smaller quadrupole splittings. Our two Mössbauer quadrupole signals have Δ values ≈ 2.2 and ≈ 1.5 mm/s, that point toward a greater distortion for the site with the ≈ 1.5 mm/s splitting. Following the same assumptions of Ref. (5), we assign site *A* to the signal of ≈ 1.5 mm/s.

Sample LB1 shows the narrower linewidth, Γ, indicating that the probes are located in equivalent environments, revealing a more regular crystalline structure, in agreement with diffraction data. In samples LC7 and LC8 the higher degree of structural disorder than samples IA1 and IA2 is revealed by the large value of Γ (0.52 mm/s) displayed by Fe atoms occupying *B* sites. In fact, these are the largest linewidths of the whole set of samples analyzed and also those that exhibit the largest degree of cationic disorder. Sample LC4 displays an intermediate situation between IA1, IA2, and sample LB1.

Although sites *A* and *B* have different distortions of the oxygen octahedra, it has been demonstrated (14) that the recoilless fractions depend mainly on the oxidation state of the ion and not so much on its coordination. Therefore, we assume that the recoilless fractions of their Fe^{2+} ions must be very similar. Under this assumption, the relative areas of the subspectra shown in Table 2 should be the same as the Fe^{2+} site occupancy.

In principle, if one technique is able to give the site occupancy, the pure cation disorder can be calculated. Reference (5) makes use of single crystal X-ray results to obtain the occupancy of sites *A* and *B*. It is of interest to investigate whether in this type of mineral it is possible with a technique other than single crystal X-ray diffraction to assess the site occupancy and to establish a correlation between the results yielded by both techniques.

Through Mössbauer data only it is difficult to determine the cation ordering because it is sensitive only to the distribution of Fe but not of Mn. However, assuming that Mn orders the same as Fe does, it would be possible to obtain the site occupancy by Mössbauer spectroscopy. To that end we have used the relative areas A_{rel} of the Mössbauer signals assigned to sites *A* and *B* to calculate the cation disorder x for all samples investigated.

The percentage of cation order x was obtained from the Mössbauer relative areas for the assigned *A* and *B* sites, taking into account that a fully disordered sample would have 33% of Fe^{2+} ions at *A* sites and 66% at *B* sites. Therefore, under the assumption that both Fe and Mn would enter into any crystallographic site with equal probability, the x parameter is obtained with the formula:

$$x(\%) = -50 + 1.515\, A_A,$$

where A_A is the relative area of the Mössbauer subspectrum assigned to probes located at site *A*.

The fact that in no case is the order parameter unreasonable or negative is a support for the site assignment of the Mössbauer signals and for the sensible assumptions of the model used to calculate it.

Table 3 shows that the degree of cation disorder correlates well with that determined through Ercit's formula from X-ray diffraction data. Although Ercit's formula does not take explicitly other factors that influence the cell parameters into account we can say that the percentage order obtained by both techniques is similar for all samples within the experimental errors. This agreement validates the hypothesis that iron and manganese atoms distribute with equal probability among both sites. The agreement is better for samples with the narrower linewidths.

The very small number of samples analyzed here do not allow us to extend this conclusion to all columbite–tantalite minerals, nor to analyze the influence of other parameters, like linewidth, local distortion, presence of diverse ions, or **a/c** ratio. More studies to include a larger number of samples from different quarries are planned along these lines.

4. CONCLUSIONS

Columbite–tantalite shows an increase of order, after application of Ercit's empirical correlation, from LC and IA pegmatites toward LB pegmatite.

Disorder percentages obtained from Mössbauer results assuming equal probabilities for the site occupancy of both Mn and Fe correlate well with empirical formulas that make use of cell parameters obtained by X-ray diffraction.

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