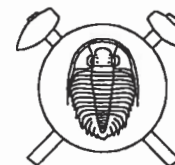


Rietveld refinement of cassiterite: a caveat for meticulous sample preparation



Vypřesnění struktury kasiteritu Rietveldovou metodou: naléhavá výzva k pečlivé přípravě vzorku (Czech summary)

(2 tabs)

MARIANA KLEMENTOVÁ¹ – MILAN RIEDER¹ – ZDENĚK WEISS²

¹ Department of Geochemistry, Mineralogy and Mineral Resources, Charles University, Albertov 6, 128 43 Praha 2, Czech Republic

² Central Analytical Laboratory, Technical University, Tř. 17. listopadu, 708 33 Ostrava-Poruba, Czech Republic

Powder mounts used to collect diffraction data for Rietveld refinements should be prepared with utmost care and maximum skill. Variables modelling preferred orientation may be included in the refinement only if the material is prone to it and if the techniques used in preparing the mount could have allowed or accentuated its presence.

Key words: Rietveld refinement, cassiterite, preferred orientation

Introduction

Cassiterite is a common mineral of tin, it crystallizes with the rutile structure in space group $P4_2/mnm$. Tin occupies Wyckoff position a and is six-coordinated by oxygen (Wyckoff position f). The structure is so simple that it is ideal to be refined by the Rietveld technique: there are two unit-cell parameters, only one free atomic coordinate, and two isotropic temperature factors (six variables for anisotropic temperature factors). Within the mineralogical research performed on a set of samples of cassiterite and associated oxides from mineral deposits of Australia (Klementová 1999), powder data for cassiterite from Herberton were recorded on four conventional diffractometers and on the synchrotron at the ESRF in Grenoble.

The refinements were carried out as part of a standardization routine, because they were expected to differ very little from one another (if at all), but the variety that resulted was alarming and prompted a more thorough examination of the causes.

Instruments and procedures

The diffractometers used were standard instruments with theta - two theta geometry, a summary of instrumental conditions appears in Tab. 1. The sample was packed in

a capillary for the synchrotron and spread on low-background Si sample holder for the conventional diffractometers. There is no *a priori* reason why profile functions should be the same on all instruments, so even though more profile functions were tested, we only give results for calculations with the best reliability factor R (Bragg). All U , V , W halfwidth parameters (for the $\tan^2 \theta$, $\tan \theta$, and constant terms) could only be refined for synchrotron data, diffractometer data warranted only the calculation of the W and V parameters. As expected, W for synchrotron data is about two orders of magnitude smaller than for the conventional diffractometers. These parameters do not play any systematic role in the problem discussed and their values are not tabulated.

Calculations were done using the WYRIET Version 3 program package (Schneider 1994); background was determined by the cursor-picking technique. This was useful not only at the beginning, but it also proved to be the best as calculations advanced. To account for possible anomalous scattering, Δf^r and Δf^i for all radiations were obtained by interpolation in tables by Henke et al. (1993). Scattering factors in the usual nine-parameter representation were used (Revised and Supplementary Tables, *International Tables*, 1974). Monochromator coefficients appropriate for the type of experiment, wavelength, and monochromator were applied.

Table 1. Instrumental details of data collection

No.	data source	radiation / filter, monochromator	two - theta, °			number of hkl	α_2 / α_1	profile function
			from	to	step			
1	synchrotron	0.60261 Å	9.900	49.995	0.005	69	–	Lorentz 2
2	Philips-Mueller ¹	Co / graphite	24.00	157.88	0.02	35	0.55	Pearson VII
3	DRON 2,0 (Burevestnik) ¹	Cu / graphite	24.00	150.00	0.02	50	0.4	pseudo-Voigt
4	Philips ²	Cu / Ni	10.00	75.00	0.05	16	0.5	pseudo-Voigt
5	Philips X'pert MPD ³	Cu / graphite	24.00	150.00	0.02	50	0.55	pseudo-Voigt

¹ Faculty of Science, Charles University, Prague

² Faculty of Mathematics and Physics, Charles University, Prague

³ Czech Geological Survey, Prague

The refinement started out with the scale factor, half-width parameters, zeropoint and unit-cell parameters, which in turn were followed by atomic coordinates, temperature factors, occupancy of Sn, preferred orientation, and additional profile parameters such as asymmetry and shape factors (*NA* and *NB*). The occupancy of Sn was allowed to vary because a chemical analysis of cassiterite from Herberton has shown a significant substitution of tin by iron; the details of the problem are beyond the scope of this paper and will be dealt with elsewhere. As acceptable was considered a stable solution with *all* variables open to variation. The intensity ratio $K\alpha_2 / K\alpha_1$ (where applicable) cannot be refined as such, but when a final stable solution was obtained for each data set, the calculation was repeated for several values of this ratio, and the value given in Tab. 1 was selected according to the lowest reliability factor obtained from the weighted differences in intensity data, *R-WP*.

Discussion

The first round of refinements assumed no preferred orientation, but resulted in a surprisingly poor agreement between data from different instruments. An analysis of diffraction indices of the most disagreeable intensities prompted the introduction of a function for preferred orientation and identified the form as {110}. Subsequent calculations yielded G_i parameters that all calculated with optically small errors, but some data sets had an unacceptably deviant *x* coordinate of oxygen. (In assessing the results, we compared the diffractometer data to the results of a single-crystal refinement by Seki et al. (1984) and the results obtained from our synchrotron data.)

At this point, we examined the techniques used in preparing the powder mount and left out preferred orientation terms for the capillary (used for the synchrotron) and

mounts for two conventional diffractometers in which the formation of a preferred orientation was almost certainly not realistic. Preferred orientation was only calculated for patterns corresponding to mounts prepared by pouring a slurry of ground cassiterite in acetone on the sample holder.

Although this was not a panacea, the disagreement between the structure models calculated from different data sets was reduced substantially. However, two data sets yielded difference intensity curves that at first sight appear rather poor, and none of the parameters of the structural model were able to improve the fit; both solutions are numerically stable. To supplement the subjective optical impression, we turned to the Bragg *R*, Hoppe's (1979) effective coordination number (*ECoN*), and bond valence (Tab. 2). The *ECoN* is a purely geometrical function, whereas the bond valence reflects the geometry as well as cation occupancy (program BONDSTR by J. Rodriguez-Carvajal). According to both approaches, data sets Nos. 3 and 5 must be considered unacceptable, a conclusion that is echoed also by the temperature factors and the occupancy: for diffractometer #3 the temperature factor for Sn exceeds that of oxygen by a factor of four and the occupancy is unrealistically high, whereas for diffractometer #5 the temperature factor calculates as negative. In both cases we apparently deal with data suffering from an instrumental problem that has not yet been identified.

There are two lessons that can be learned from this study. First, sample mounts must be prepared with utmost care and maximum professionalism. Second, variables for modelling of a physical effect like preferred orientation may be introduced only if the material is prone to it and if the techniques used in preparing the mount could have allowed or accentuated its presence. Otherwise, Rietveld refinements of even such simple structures like cassiterite can lead to results that are in serious error.

Table 2. Important results of Rietveld refinement

No.	zeropoint	<i>a</i>	<i>c</i>	<i>x</i> (O)	G_i (preferred orientation on {110})	<i>B</i> (Sn)	<i>B</i> (O)
1	0.0020(1)	4.7384(1)	3.1865(1)	0.3076(5)	none	1.42 (eq)	4.12 (eq)
2	-0.0046(7)	4.7385(1)	3.1865(1)	0.3055(14)	0.960(3)	0.54 (eq)	4.83 (eq)
3	-0.0135(5)	4.7363(1)	3.1851(1)	0.3192(12)	0.827(2)	0.96(2)	0.21(18)
4	-0.020(2)	4.7350(3)	3.1837(2)	0.3096(20)	none	0.53(9)	4.6(9)
5	-0.002(1)	4.7371(1)	3.1857(1)	0.3096(14)	none	-0.64(2)	3.4(3)
		4.736(0)	3.185(0)	0.3053(5)	-	0.29 (eq)	0.46 (eq)

No.	occupancy (Sn)	<i>R</i> % (Bragg)	<i>R-WP</i>	<i>ECoN</i> (Sn)	bond length Sn-O (4×)	bond length Sn-O (2×)	sum of bond valences
1	0.114(1)	4.9	12.30	5.9986	2.050(2)	2.061(2)	4.405(9)
2	0.113(4)	7.3	20.51	5.9986	2.059(4)	2.047(7)	4.429(25)
3	0.215(8)	13.0	24.52	5.7876	2.001(3)	2.138(6)	2.415(11)
4	0.126(7)	11.0	8.15	5.9878	2.040(6)	2.073(10)	4.018(32)
5	0.084(3)	24.3	18.85	5.9880	2.041(4)	2.074(7)	6.010(33)
		2.5		5.9980	2.058(2)	2.045(2)	

G_i , expressing preferred orientation corresponds to the March-Dollase function.

Isotropic equivalents of anisotropic temperature factors are labeled "(eq)".

Full occupancy of Sn in position *a* is achieved at 0.125.

The bottom line represents the single-crystal refinement for synthetic SnO₂ at 295 K (Seki et al., 1984).

Acknowledgements. The sample used was made available by Josef Klomínský of the Czech Geological Survey. The research at ESRF Grenoble was performed in 1999 on beamline BM01B, as part of experiment CH-681; we wish to thank Hermann Emerich and Wouter van Beek who were instrumental in collecting the data. One diffractometer data set was recorded by Ludmila Dobiášová at the Faculty of Mathematics and Physics; critical reading of the manuscript by David Rafaja (from the same Department) resulted in a considerable improvement of argumentation. We are indebted to Roman Skála (Czech Geological Survey) for recording another diffractometer data set and for a careful review of the manuscript that helped eliminate several weak spots.

Submitted February 15, 2000

References

- Henke, B. L. – Gullikson, E. M. – Davis, J. C. (1993): Low-energy X-ray interaction coefficients: Photoabsorption, scattering, and reflection $E = 30\text{--}30,000$ eV, $Z = 1\text{--}92$. Atomic Data and Nuclear Data Tables, 54, 2.
- Hoppe, R. (1979): Effective coordination numbers (ECoN) and mean fictive ionic radii (MEFIR). – Z. Kristallogr., 150, 23–52.
- International Tables for X-Ray Crystallography (1974): Vol. IV, 99–101.
- Klementová, M. (1999): Chemical and structural investigation of cassiterite from some deposits in Australia [in Czech]. – MSc Thesis, Faculty of Science, Charles University, Prague, 124 pp.
- Schneider, M. (1994): Program for Rietveld analysis of X-ray and neutron powder diffraction patterns. – EDV – Vertrieb.
- Seki, H. – Ishizawa, N. – Mizutani, N. – Kato, M. (1984): High temperature studies of the rutile-type oxides, TiO_2 and SnO_2 . – J. Ceramic Assoc. Japan, 92, 219–223.

Vypřesnění struktury kasiteritu Rietveldovou metodou: naléhavá výzva k pečlivé přípravě vzorku

Preparáty určené k měření difrakčních dat pro zpracování Rietveldovou technikou musejí být připravovány s nejvyšší péčí a profesionalitou. Proměnné, které modelují vliv přednostní orientace ve vzorku, smějí být zahrnuty do vypřesnění jediné tehdy, jestliže zkoumaný materiál má k tvorbě přednostní orientace sklon a jestliže technika přípravy preparátu mohla dovolit její vznik.