Refinement of Monoclinic ReO_2 Structure from XRD by Rietveld Method

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Received on 9 January, 2004. Revised version received on 30 January, 2004

ReO_2 presents two crystalline variants, with monoclinic and orthorhombic structures. The former is metastable and irreversibly transforms to an orthorhombic structure above 460°C. The structure of the latter was determined from studies on monocrystalline samples, whereas for the monoclinic variant there are no single crystals available so far. It was found only one monoclinic variant and the structure associated with this variant is based on studies on polycrystals. We analyzed a monoclinic oxide powder sample by X-ray diffraction and refined its pattern by means of the Rietveld Method. We obtained that the monoclinic variant belongs to space group $P2_1/c$, with lattice parameters $a = 5.615(3)$, $b = 4.782(2)$, $c = 5.574(2)$ Å, $\beta = 120.13(1)^o$.

Introduction

ReO_2 (configuration $5d3$) is found in two crystalline variants: monoclinic (α-ReO_2) and orthorhombic (β-ReO_2). The former is stable only below 300°C [1]. The crystals obtained in the usual production conditions for this monoclinic variant are not large enough for a single crystal analysis. The second variant exists at higher temperatures and shows up during an irreversible transformation of the monoclinic phase above 460°C [2].

The two ReO_2 variants present crystalline (metallic) conductivity and Pauli paramagnetism [3]. The structures of rhenium oxides were extensively studied by Magnéli [4]. He points to the existence of Re-Re bindings, that influence greatly the arrangement of ReO_6 octahedrons and the physical properties of rhenium oxides. Magnéli determined the β-ReO_2 structure from single crystal analysis and restated the structure for the α-ReO_2 based on several papers on polycrystals [2]. This structure is the same as the one of MoO_2 with slightly modified parameters, as originally proposed by Zachariasen [5], based on the great similarity between these two oxides.

There is no data on α-ReO_2 in the ICSD (Inorganic Crystal Structure Database - 2000). In the PDF2-ICDD (Powder Diffraction File - International Centre for Diffraction Data - 2000) one only entry (# 17-600) is found, presenting some crystallographic information obtained by Tribalat [6] in 1964, using a Debye-Scherrer chamber. He proposed the $P2_1/c$ space group, with $a = 5.58$, $b = 4.81$, $c = 5.50$ Å and $\beta = 119.55^o$. Some objections on these results were raised by Colaïtis [7] in 1972.

Experimental

As initial experimental procedure, the ReO_3 (99.9%, AlfaAesar n^o 62109) was used as calibration compound in order to know the X-ray diffractometer set-up profile. The crystalline parameters of ReO_3 was found in ICDD # 33-1096. The ReO_3 X-ray diffraction pattern (CuKα) was measured in order to obtain a good ReO_2 initial FWHM input parameters (U,V,W). The experimental set-up used for all measurements was a Rigaku DMAX2000 X-ray diffractometer, with Bragg-Bretano geometry, and with pyrolitic carbon monochromator in the diffracted beam. The goodness-of-fit of the ReO_3 Rietveld final refinement is represented by S(R_{wp}/R_{exp}), and it has shown $S = 1.33$ as the best fit result. Furthermore, all ReO_3 crystalline parameters were confirmed by X-ray absorption measurements, which were performed for Re in the L_{III} edge (10.525keV) at the XAFS station of National Braziliam Laboratory (LNLS-Campinas-Brasil) [9].

The study of ReO_2 started after we had known the U,V,W initial parameters. The structure of α-ReO_2 was investigated by X-ray diffraction powder pattern measurements using a 99,9% pure sample, from AlfaAesar (Johnson Matthey Company). The X-ray diffraction pattern was obtained in the Rigaku DMAX2000 X-ray diffractometer setup described before. CuKα radiation was employed. Data acquisition time was approximately 90 h for the range of 5° to 150°, leading to good statistics, and with 0.01° step, allowing excellent definition to reflection peaks.

Rietveld analysis

The information on PDF2 (#17-600) was employed for this initial structure refinement. As the atomic positions of rhenium and oxygen were not known, we have used high simmetry values as initial inputs, namely Re1 (0,0,0), Re2 ($^1/_2$,0,0) for rhenium atoms and O1 ($^1/_3$,$^1/_4$,$^1/_6$), O2 ($^5/_6$,$^1/_4$,$^1/_6$) for oxygens.

The refinement was performed using the DBWS code, version # 9807 (2000) [8]. Pseudo-Voigt (pV) profile function was used for the fit of reflection peaks; $\eta > 1$ indicated that the peak shape is strongly Lorentzian. As described before, the initial FWHM parameters (U,V.W) were obtained from the ReO_3 study [9]. The profile asymmetry caused by the axial divergence of the beam was corrected by means of the model by Riello, Canton and Fagherazzi, which is available in this version of the code. No effects due to surface roughness nor preferable orientation were detected during refinement process. The Fig. 1 shows a graphical representation of the final Rietveld refinement, the experimental data and the difference between them.

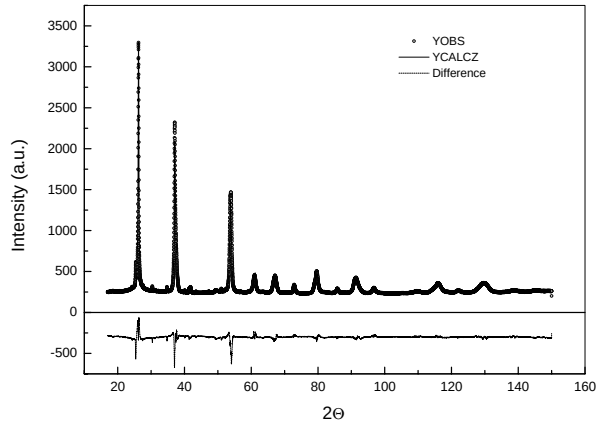

Figure 1. Final Rietveld refinement (line), data experimental (circle) and difference between both.

Results and conclusions

Our results led to the conclusion that α-ReO_2 belongs to space group $P2_1/c$, with lattice parameters $a = 5.615(3)$, $b = 4.782(2)$, $c = 5.574(2)$ Å, $\beta = 120.13(1)^o$ [10] and [11] . The goodness-of-fit, represented by S(R_{wp}/R_{exp}) was $S = 1.42$. The parameters, which represents the quality of the Rietveld refinement, are in the Table I.

Table I - Rietveld quality parameters refinement

Parameter	Value
R-P	11.12%
R-WP	15.09%
R-Expected	27.27%
S	1.42
D-WD	0.03
N-P	13301
Derived Bragg R-Factor	7.54
Derived R-F	5.97
FWHM	$U = 0.028600(6)$
	$V = -0.00373(2)$
	$W = 0.054980(8)$

The α-ReO_2 structure may be described by an arrangement of ReO_6 octahedrons forming straight chains, which are connected one another by the octahedrons having a common vertex, as in rutile. In the rutile the octahedral arrangement presents the metallic atoms equally spaced along the a-axis, whereas in α-ReO_2 the rhenium atoms present a spacing modulation along the a-axis, with alternate distances. Through the refinement of the position of the Re2 site we obtained the distance between atoms in the Re-Re coupling, along the a-axis, inside the octahedron chains. Re-Re distances alternate between 2.622(6) and 2.993(6) Å along the chains, which causes the undulation suggested by Gibart in 1967 [4]. Fig. 2 shows the 2D view of the ReO_2 structure along the [010] direction. We also performed the refinement of oxygen positions and extracted the relative distances between all pairs of oxygen (O1 and O2) and rhenium (Re1 and Re2) sites. Fig. 3 shows the 2D view along the [001] direction of monoclinic ReO_2structure.

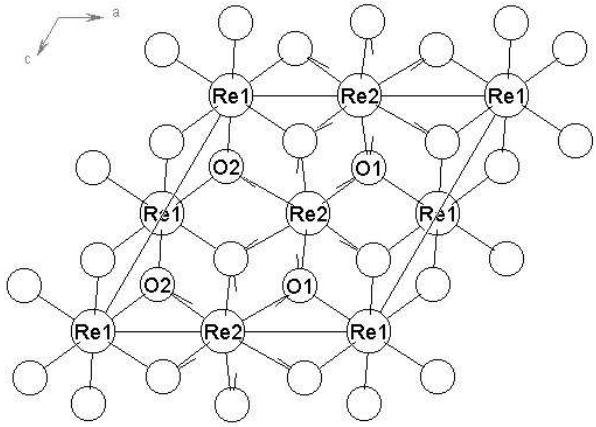

Figure 2. The 2D view of ReO_2 structure along the [010] direction.

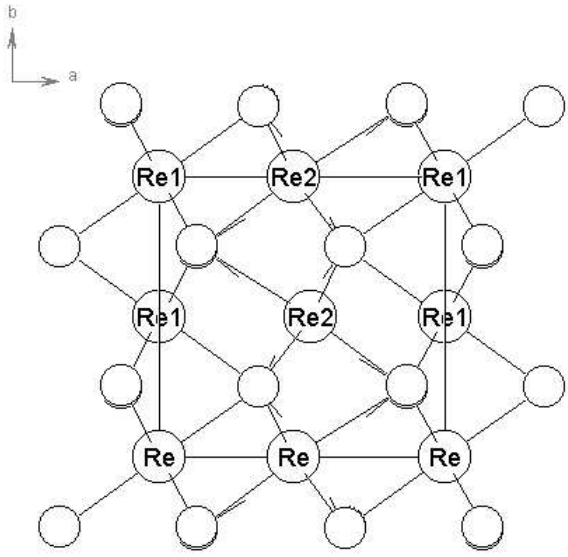

Figure 3. The 2D view of ReO_2 structure along the [001] direction.

Table II summarizes the crystalline data description resulting from the final Rietveld refinement.

Table II - Crystal Parameters

Crystal data

Formula sum	ReO_2
Formula weight	218.21
Crystal system	monoclinic
Space group	$P2_1/c$ (nr. 14)
Unit cell dimensions	$a = 5.615(3)$ Å
	$b = 4.782(2)$ Å
	$c = 5.574(2)$ Å
	$\beta = 120.13(1)^o$
Cell volume	129.45(76) Å^3
Z	4
Density, calculated	11.196 g/cm^3
Temperature	293(2) K

Atomic coordinates

Atom	Ox.	Wyck.	Occ.	x	y	z
Re1	+4	2a		0	0	0
Re2	+4	4e	0.5	0.467(1)	0.00000	0.00000
O1	-2	4e		0.346(3)	0.248(2)	0.192(2)
O2	-2	4e		0.133(1)	0.754(3)	0.302(2)

Selected interatomic distances (Å)

Re1-Re2	2.622(6)	Re2-O1$^{(iii)}$	2.187(17)
Re2-Re1$^{(i)}$	2.993(6)	Re2-O2$^{(iv)}$	2.033(13)
Re1-O1$^{(ii)}$	2.059(15)	Re1-O2$^{(iv)}$	2.020(13)

Symmetry codes: (i) $1 + x, y, z$; (ii) $-x, -y, -z$; (iii) $1 - x, -y, -z$; (iv) $x, 0.5 - y, -0.5 + z$.

Acknowledgments

Research performed at LNLS - National Synchrotron Light Laboratory, Brazil (project # XAS 827/01). The authors would like to thank the Bazilian Agencies CNPq, CAPES and FINEP. Thanks to the Companhia Vale do Rio Doce and Companhia Siderurgica de Tubarão.

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