Crystal structure of lead tungstate at 1.4 and 300 K

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Abstract

The crystal structure of lead tungstate, PbWO₄, is tetragonal, scheelite type, space group $I4_1/a$. This compound is frequently subjected to lead deficiency, due to the difference in the vapour pressure of the two oxides, WO₃ and PbO, used in the crystal growth. One group has reported that lead vacancies can order in a crystal structure derived from the scheelite type, but of lower symmetry and described by the space group P4/nnc or $P\overline{4}$.

We report here on neutron diffraction measurements performed on three different powdered samples. Our measurements do not show any indication of structural transition between 1.4 and 300 K. The structure is undoubtedly the tetragonal one. The existence of a lead deficient structure remains unconfirmed.

Keywords : Lead tungstate, crystal structure, neutron diffraction

1. Introduction

Lead tungstate, PbWO₄, is a scintillator now widely used in particle and nuclear physics [1] and intense research and development works are under way. It occurs in nature as tetragonal stolzite, of scheelite type, space group $I4_{1/a}$ [2] and monoclinic raspite, space group $P2_{1/a}$ [3]. A high pressure form, with space group $P2_{1/n}$ has also been reported [4]. The common form for the industrial crystals used in particle detection is the scheelite type. Following X-ray diffraction studies on lead deficient crystals, a distortion of this structure described by the space group P4/nnc has been suggested by Moreau *et al.* [5]. The corresponding composition was Pb₇W₈O_(32-x). Further neutron diffraction investigation on powdered samples leads the same authors to a third tetragonal structure, space group $P\overline{4}$, with the composition Pb_{7.5}W₈O₃₂ [6]. However these distorted lead deficient structures have not been observed elsewhere, even in precise studies around stoichiometry [7].

A structural transition has also been suggested in lead tungstate at 220 K [8], but no indication on the character of this transition has been reported.

It is largely admitted that non-stoichiometry, especially lead vacancies, has a large influence on the spectroscopic and optical properties of lead tungstate and on its behaviour under radiation [9]. The existence of a specific crystal structure for lead deficient PbWO₄ is a key point in the interpretation of the properties of lead tungstate, for example the occurrence of a second maximum of radiation resistance when lead content decreases (the first being at exact stoichiometry) [9].

Thus the confirmation, or not, of the existence of the phase $Pb_7W_8O_{(32-x)}$ or $Pb_{7.5}W_8O_{32}$ would be of great importance. In a first study on single crystals performed at LLB, no evidence of any distorted phase was found between 70 and 300 K [10].

2. Experimental

After discussion of the problem with the Russian crystal growers, we obtain from them two samples from one of the last batches of crystal production for CMS. They are issued from the same piece, one from the top side, near seed, ("top sample"), the second from the bottom side of the crystal bar ("bottom sample").

We performed powder diffraction measurement on the two samples. Data were collected on the G4.1 two axes-multidetector powder diffractometer installed at the cold source beamline of the reactor Orphée, Saclay (France), the neutron wavelength being 2.4266 Å. The samples were measured at room temperature and at 1.4 K. We also measured at room temperature a sample ("yellow sample") issued from a crystal of yellowish aspect coming from the early stage of the industrial R&D for CMS [11]. Diffraction spectra were refined using the program Fullprof [12], also used to simulate the spectra for the five published structures : the usual scheelite, the two distorted scheelite-like structures proposed in [5,6] and the two monoclinic phases, raspite $P2_1/a$ [3] and "high pressure form" $P2_1/n$ [4].

3. Results

In all cases, the structure is very well described by the scheelite $I4_1/a$. Table 1 reports the refinement results for lattice parameters and oxygen atomic positions. Oxygen positions do not vary significantly between samples and with temperature. They are very close to the published data. Refinement results are compatible with the exact stoichiometry. However, for the refinement calculation, the occupation factors for O and Pb are correlated to the temperature factors *B* and it is difficult to conclude precisely on the exact composition.

The comparison between measured and calculated spectra excludes clearly the distorted phases in all samples at all temperatures. No phase transition is found as well in the range 1.4 - 300 K. Figure 1 shows for example the spectra measured at 290 and 1.4 K for the top sample. The simulated spectra for the low symmetry structures are shown in Figure 2.

The lattice parameters vary obviously significantly between 290 and 1.4 K. The relative variation is approximately $6 \ 10^{-6} \ K^{-1}$ for *a* and 17 $10^{-6} \ K^{-1}$ for *c*. One notes that a small but significant diminution of the lattice parameters from top sample to bottom or yellow samples. This may be related to the lead content, that one may suppose decreasing from top to bottom and be lower in the old sample, but this remains to be measured.

Table 1 : Results and parameters of the structure refinements for lead tungstate samples measured at LLB.

	a	С	Oxygen position		
	(Å)	(Å)	x	У	z
Published data [5]	5.456(2)	12.020(2)	0.2388	0.1141	0.0429
Тор @ 290 К	5.46979(52)	12.06339(117)	0.23170(65)	0.11220(58)	0.04300(36)
Bottom @ 290 K	5.46462(49)	12.04787(109)	0.23168(60)	0.11200(53)	0.04324(33)
Yellow @ 290 K	5.43241(48)	12.04817(106)	0.23416(56)	0.10844(48)	0.04083(31)
Top @ 1.4 K	5.45961(52)	12.00222(114)	0.23109(63)	0.11017(60)	0.04326(35)
Bottom @ 1.4 K	5.45565(46)	11.99235(102)	0.23102(56)	0.11004(53)	0.04248(33)



Figure 1 : Powder diffraction spectra and comparison to Fullprof calculation for PbWO₄, "top sample", at 290 K (a), and 1.4 K (b).



Figure 2 : Simulation with the program Fullprof of the spectra that would have presented the low symmetry phases : pseudo-scheelite P4/nnc and $P\overline{4}$ (crystal data from [5,6]), raspite $P2_1/a$ (data from [3]), and "high pressure form" $P2_1/a$ (data from [4]).

4. Conclusion

No deviation from the scheelite structure has been observed in the samples measured. The occurrence of structural transition is also excluded between 1.4 and 300 K. The crystal structure of the samples studied in this work is undoubtedly of the scheelite type. Up to now, the existence of a specific crystal structure for lead deficient PbWO₄, such as Pb₇W₈O_(32-x) or Pb_{7.5}W₈O₃₂ remains to be confirmed. It seems evident that such eventual lead deficient phase, if it exists, does not play the stabilising role attributed to it in [9].

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[1] see for example :

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