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Determination of the crystal structure of lead tungstate by neutron diffraction

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Abstract

The crystal structure of lead tungstate, $PbWO_4$, is tetragonal, scheelite type, space group $I4_1/a$. This compound, du to the difference in the vapour pressure of the two raw oxides, WO_3 and PbO, used in the crystal growth, is frequently subjected to lead deficiency. It has been reported by one group 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 $P\bar{4}$.

We report here on neutron diffraction measurements performed on three different single crystals, two of them being presented to us as possibly presenting the lead deficient phase. Our measurements do not show any indication of structural distortion, even at 70 K for one of the samples. The existence of a lead deficient structure remains unconfirmed.

Keywords : Lead tungstate, crystal structure, neutron diffraction

1. Introduction

Lead tungstate, $PbWO_4$, occurs in nature as tetragonal stolzite, of scheelite type [1] and monoclinic raspite [2]. The common form for the industrial crystals used in particle detection is the scheelite type, space group $I4_1/a$. Following X-ray diffraction studies on lead deficient crystals, a distortion of this structure, described by the space group $P4/nnc$, has been described by Moreau *et al.* [3]. The corresponding composition is $Pb_7W_8O_{(32-x)}$. Further neutron diffraction investigation on powdered samples leads the same authors to a third tetragonal structure, space group $P\bar{4}$, with the composition $Pb_{7.5}W_8O_{32}$ [4]. However these distorted lead deficient structures have not been observed elsewhere, even in precise studies around stoichiometry [5].

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 [6]. The existence of a specific crystal structure for lead deficient $PbWO_4$ 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) [6].

A structural transition has also been suggested in lead tungstate at 220 K [7], but no indication on the character of this transition has been reported.

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.

2. Experimental

To clarify the problem, we have undertaken neutron diffraction measurements on single crystals. This technique is particularly adapted to observe small displacements of oxygen atoms. Three lead tungstate samples, about 10 mm^3, were measured. The first sample comes from the early crystals synthesised in 1994. The two last are issued from the crystals grown for CMS R&D at Bogoroditsk, and were presented to us as possibly presenting the distorted tetragonal structure.

Data collection was performed on the 5C2 neutron four-circle diffractometer installed at the hot source beamline of the reactor Orphée, Saclay (France). All samples were measured at room temperature. One of them was also tested at 120 and 70 K.

3. Results

Table 1 reports the refinement results and parameters. In all cases, the quality of the crystal was found excellent. The diffraction patterns were examined in the *P* cell, to check about reflections forbidden in the scheelite symmetry. No reflection peak, with $I > 3s(I)$, was observed that could not be interpreted in the $I4_1/a$ space group.

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

	space group	**a (Å)**	**c (Å)**	**wavelength (Å)**	**reflections measured**	**independent reflections**	**R**	**Rw**	**goodness of fit**
sample 1 293 K	$I4_1/a$	5.456	12.02	1.1056 (Ge 311)	450	385	2.04 %	1.91 %	0.9222
sample 2 (CMS #1655) 293 K	$I4_1/a$	5.46(1)	12.04(2)	0.8305 (Cu 220)	196	176	1.96 %	2.11 %	1.0868
sample 3 (CMS #1830) 293 K	$I4_1/a$	5.46(1)	12.05(2)	0.8305 (Cu 220)	463	401	2.80 %	2.71 %	1.0002
sample 3 (CMS #1830) 120 K	$I4_1/a$	5.46(1)	12.01(2)	0.8305 (Cu 220)	406	328	3.33 %	3.19 %	1.0949
sample 3 (CMS #1830) 70 K	$I4_1/a$	5.46(1)	12.01(2)	0.8305 (Cu 220)	404	337	3.15 %	2.94 %	1.0587

4. Conclusion

No deviation from the scheelite structure has been observed in the samples measured. No phase transition has been observed above 70 K. The crystal structure of the single crystals studied in this work is undoubtedly of the scheelite type. Up to now, the existence of a specific crystal structure for lead deficient $PbWO_4$, such as $Pb_7W_8O_{(32-x)}$ or $Pb_{7.5}W_8O_{32}$ remains to be confirmed.

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