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Crystal growth and characterization of new-type lead tungstate single crystal

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ABSTRACT

In this work, a new type of lead tungstate crystal (Pb_3WO_6) was synthesized by hydrothermal method under high temperature and high pressure. Crystal structure was characterized by single-crystal X-ray structure determination. Pb_3WO_6 (monoclinic, $P2_1/c$, (No. 14), $a = 7.8643(6)$ Å, $b = 9.2036(8)$ Å, $c = 9.0652(8)$ Å, $\beta = 90.299(5)^\circ$, $V = 656.13(2)$ Å^3, $Z = 4$) exhibited two different layered arrangements of edge-shared octahedral WO_6 with six oxygen coordination along *a* axis. Thermal stability was investigated by TG–DSC and two phase transformations were observed at about 647 and 748 °C, respectively. Finally, VUV excitation and emission spectra of Pb_3WO_6 crystal were studied under the temperature 14 K. The results revealed that samples had weak luminescent properties, which exhibited excitation peak at 285 nm and emission peak at 460 nm at low temperature.

1. Introduction

Lead tungstate ($PbWO_4$) crystals exhibit three kinds of structures: (1) scheelite structure [1] and (2) raspite structure in nature [2]; (3) $P2_1/n$ synthesized under high pressure [3]. However, only scheelite-type $PbWO_4$ crystal could be used extensively in high-energy physics and nuclear medicine as scintillators [4,5] due to its excellent properties such as suitable emission band (420–500 nm) and fast decay time (<100 ns). In the scheelite structure, W atoms are in separated tetrahedral sites and Pb atoms are surrounded by eight oxygen atoms [6]. The strong intrinsic blue emission band is generated by the radiative decay of excitons self-trapped on regular WO_4 groups with Pb contributions and holds the fast component of decay time. The weak green emission band is produced by crystal defects (lack of oxygen, i.e., WO_3 groups) or the raspite-type inclusions and occupies the slow component [7]. Although the origin of the green band in scheelite-type $PbWO_4$ crystal has still been controversial, it could be concluded that lead tungstate has strong structure sensitivity and the absence of crystal defects or raspite-type inclusions makes the serious depression of scintillation properties.

More research works have been carried out to investigate lead tungstate crystals with different structure grown usually by the Czochralski [8] methods, Bridgman methods [9], from the high temperature strain (HTS) [10] and so on, expecting to obtain new structure or modified structure and improve the process of crystal growth for high scintillation properties. Such as $Pb_{0.261}WO_3$ of the tetragonal bronze was grown by cooling method corresponding to the overall composition (Triantafyllou et al., 1996) [11], a bronze phase $Pb_{0.29}WO_3$ in the hexagonal form was synthesized from peroxo-polytungstate precursors (Tatsumi et al., 1997) [12], $Pb_{7.5}W_8O_{32}$ was grown from a melt with a deficiency in PbO by the Czochralski method and proved as a superstructure of scheelite type with partial vacancies on a onefold lead site (Moreau et al., 1999) [13] and so on [14]. But until now, none of these crystals has been reported to exhibit high scintillation properties. The hydrothermal method is particularly beneficial for crystal growth of good-quality crystals while maintaining good control over their composition, such as used for growth of large-sized ZnO crystal [15]. However, this method has not been reported for the growth of large lead tungstate crystal.

In the present work, we reported on the attempt of lead tungstate crystal growth by hydrothermal method at high temperature and high pressure, using alkaline solution as the solvent. A new kind of lead tungstate crystal (Pb_3WO_6) was obtained in millimeter scale. The structure of Pb_3WO_6 crystal was solved from single-crystal X-ray diffraction data. Finally, the thermal stability, phase transformation and scintillation properties of Pb_3WO_6 crystal were investigated systematically.

2. Experiment

2.1. Hydrothermal growth of Pb_3WO_6 crystals

The hydrothermal growth of Pb_3WO_6 crystals was performed in a high-strength nickel alloy autoclave. Because of the high normality of the mineralizing solution, a platinum liner was used to isolate the crystal growth environment from the walls of the autoclave. The crystal growth zone and the dissolution zone were separated by a Pt baffle with an opening ratio of 8–15%. The nutrient was milled from $PbWO_4$

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Table 1
Crystallographic data of Pb_3WO_6 crystal.

Compound	Pb_3WO_6
Crystal system	Monoclinic
Space group	$P2_1/n$
Shape/color	Block, yellow
a (Å)	7.8643(6)
b (Å)	9.2036(8)
c (Å)	9.0652(8)
β (°)	90.299(5)
V (Å^3)	656.13(2)
Z	4
F(000)	1472
ρ_{cal} (g cm^{-3})	9.125
Formula mass	901.44
Diffractometer	Rigaku AFC7 (Mercury CCD)
Radiation	Cu-Kα_1 (λ = 1.54060 Å)
2θ range/°	$6° \leqslant 2\theta \leqslant 64°$
h,k,l	$-11 \leqslant h \leqslant 11$, $-13 \leqslant k \leqslant 12$, $-10 \leqslant l \leqslant 13$
Reflect. coll.	6142
Independ. refl.	2273
$I > 2\sigma(I)$	1866
R_{int}	0.0396
$R1$ [$I > 2\sigma(I)$]	0.0320
$R1$ (all data)	0.0410
$wR2$ (all data)	0.0785
S	1.096

crystal grown by vertical Bridgman method using high pure PbO and WO_3 powder (99.999%). The seeds were long blocks of undoped $PbWO_4$ crystal along (001) orientation from previous Bridgman growth. Aqueous solution of NaOH (3.0 mol/l) was used as a mineralizer solution, which was poured into the liner with the filling quantity of 75–100%. Suitable quantity of distilled water was poured into the volume between the autoclave and the liner for pressure balancing. The temperature of the growth zone was 300 °C, at which the pressure in autoclave was 600–800 bar.

2.2. Characterization

The data collections were carried out by single crystal X-ray diffraction analysis using a Rigaku AFC7 (Mercury CCD) diffractometer (graphite monochromator; Cu-Kα radiation, λ = 1.5406 Å) at ambient temperature. Pb_3WO_6 single crystal was selected under a light microscope for X-ray diffraction investigations. Based on the systematic absences, the space groups $P2_1/c$ (No. 14) was identified. All relevant crystallographic data were listed in Table 1. Direct methods and subsequent Fourier difference analyses were used to locate the atoms. The programs SHELXS-97 [16] included in the program package WinGX [17] were used for structure solutions and refinements. Thermogravimetric analysis and differential scanning calorimeter (TG and DSC) of the samples were carried out at nitrogen atmosphere from room temperature to 800 °C with the rate of 5 °C/min using NETZSCH STA 409 PC/PG. Low temperature VUV (vacuum ultraviolet–visible) spectra were measured under 14 K using beam line 4B8 at Beijing Synchrotron Radiation Laboratory in Beijing, China. X-ray excited luminescence spectra is investigated by Omni Spec spectrometer at room temperature.

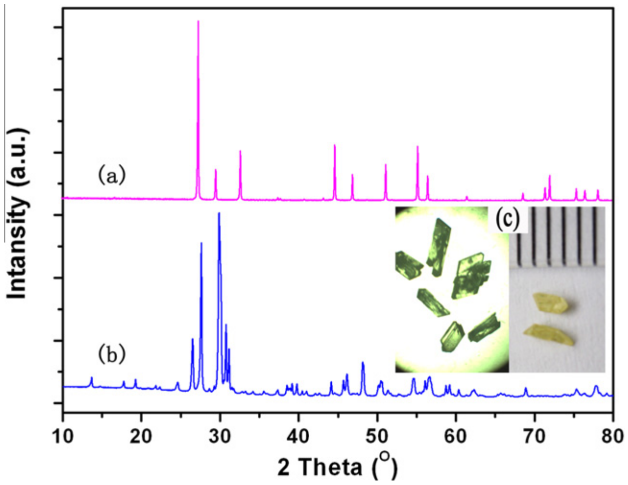

Fig. 1. XRD pattern of scheelite-type $PbWO_4$ (a) and Pb_3WO_6 (b) crystals at room temperature; the picture of Pb_3WO_6 crystal (c) grown by hydrothermal method.

3. Results and discussions

3.1. X-ray diffraction analysis

From the single crystal XRD analysis, it had been observed that Pb_3WO_6 single crystal crystallizes in the space group $P2_1/c$. The XRD pattern and the crystal structure were shown in Figs. 1 and 2, respectively; the refined atom position and standard estimation error for Pb_3WO_6 were listed in Table 2. It was shown that polyhedra composed with two edge-sharing distorted WO_6 octahedra were present separately at the monoclinic structure of Pb_3WO_6 (Fig. 2a). However, the polyhedra arranged in two ways along b axis, exhibiting alternate layers of edge-sharing WO_6 octahedra perpendicular a axis. The W–O distances varied between 1.7706 (0.0076) Å and 2.2400 (0.0076) Å, the mean being 1.9433 Å, and the Pb atoms were five-coordinate.

Tetragonal scheelite $PbWO_4$ (JCPDS card No. 19-0708) was characterized by symmetry group $I4_1/a$ with lattice parameters $a = b$ = 5.462 Å, c = 12.049 Å, and the monoclinic raspite $PbWO_4$

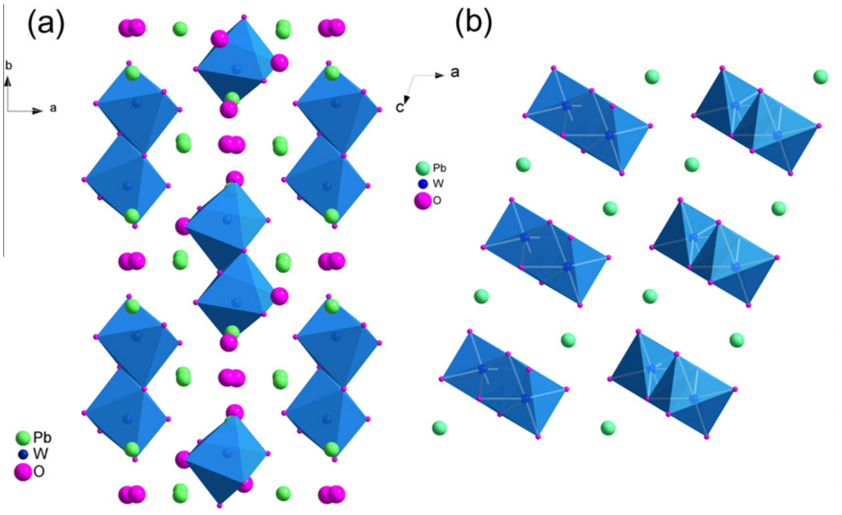

Fig. 2. Arrangement of edge-shared octahedral WO_6 in Pb_3WO_6 (a) and raspite-type $PbWO_4$ (b) crystal.