

## PRESSURE INDUCED PHASE TRANSFORMATION IN $\text{BaWO}_4$

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### ABSTRACT

A new dense form of  $\text{BaWO}_4$  ( $\text{BaWO}_4$ -II) was prepared under high pressure. The phase boundary between the normal pressure form ( $\text{BaWO}_4$ -I, scheelite structure) and  $\text{BaWO}_4$ -II was determined as  $P(\text{kb}) = 26.7 + 0.0265T(^{\circ}\text{C})$ , ( $T = 600$ - $1000^{\circ}\text{C}$ ). Crystallographic data were obtained from the single crystal and powder X-ray analyses.  $\text{BaWO}_4$ -II is monoclinic with 8 formula units in the unit cell. The possible space group is  $P2_1/n$  and the cell parameters are;  $a = 13.159\text{\AA}$ ,  $b = 7.161\text{\AA}$ ,  $c = 7.499\text{\AA}$ ,  $\beta = 93.76^{\circ}$  and the cell volume  $= 705\text{\AA}^3$ . The volume decrease upon transformation is estimated to be 12.1%.

### Introduction

$\text{ABO}_4$  compounds, where the B-cation is W or Mo, generally crystallize in either scheelite- or wolframite-structure. In the structure, average coordination number of the A and B cations is six and of the oxygen three. Based on high pressure Raman spectra measurements, Nicol and Durana(1) described a transformation from scheelite to a wolframite-like structure in  $\text{CaMoO}_4$  and  $\text{CaWO}_4$ . Sleight(2) also indicated a possibility of the pressure induced phase transformation from scheelite to wolframite. With larger A-cations in these compounds, a high pressure form of  $\text{PbWO}_4$  was reported by Chang(3). Although the structure of this high pressure form was different from wolframite, no detailed crystallographic data was given. In the present work, the high pressure phase transformation of scheelite-type  $\text{BaWO}_4$  was

studied and a new high pressure form was characterized by the single crystal analysis.

### Experimental

Stoichiometric amount of reagent grade  $\text{BaCO}_3$  and  $\text{WO}_3$  was mixed intimately and heated at about  $800^\circ\text{C}$  for two days in a platinum crucible. The product was ground again for subsequent firing at  $800^\circ\text{C}$  for two days. The final product was a single phase of  $\text{BaWO}_4$ -I as examined by X-ray, and was used as the starting material for high pressure runs. The specimen was sealed in a platinum capusule in order to avoid chemical contamination(4). A cubic-anvil type apparatus was used for the high pressure experiments. Pressure value was calibrated on the NBS scale [ $\text{BiI-II}$ , 25.5kbars;  $\text{BaI-II}$ , 55kbars](5). Temperature was measured with a chromel-alumel thermocouple without any correction for the pressure effect on the e.m.f. Identification of phases in the quenched specimen was made mainly by the X-ray powder analysis.

### Results and Discussions

$\text{BaWO}_4$ -II: In some of the experimental runs, a new phase other than  $\text{BaWO}_4$ -I was obtained as a white powder in the quenched specimen. Under a microscope, this was colorless and transparent as  $\text{BaWO}_4$ -I. Weissenberg and four circle goniometer measurements of a single crystal of about 30microns revealed that the crystal was monoclinic with a possible space group,  $\text{P2}_1/\text{n}$ . The lattice parameters were refined by the least square method using the high-angle diffraction data obtained from the four circle goniometer. Table 1, includes these parameters along with the powder diffraction data. In the table, the calculated d-spacings are based on these parameters. The intensities as observed in the powder diffraction were in good agreement with those of the single crystal measurements.

Based on the present unit cell, the calculated density is  $7.26\text{g/cm}^3$  with eight formula units per cell. This is in fairly good agreement with the measured density,  $7.17\text{g/cm}^3$ .

The general characteristics of powder pattern is quite different from that of the wolframite. Comparison is made of



TABLE 1

Observed and Calculated d-spacings and Unit Cell  
Dimensions of  $\text{BaWO}_4$ -II

h	k	l	$d_{\text{obs}}$	$d_{\text{calc}}$	$I_{\text{obs}}$
2	0	0	6.588	6.565	M
0	1	1	5.188	5.174	VW
$\bar{2}$	1	1	4.163	4.154	M
2	1	1	3.980	3.977	VW
0	2	0	3.582	3.581	VW
$\bar{2}$	0	2	3.349	3.346	S
4	0	0	3.284	3.283	S
0	2	1	3.232	3.230	S <sub>-</sub>
2	0	2		3.163	
$\bar{1}$	2	1	3.162	3.157	S <sub>+</sub>
4	1	0	2.985	2.984	M
$\bar{2}$	2	1	2.933	2.931	M <sub>-</sub>
2	1	2	2.895	2.893	M <sub>-</sub>
2	2	1	2.868	2.866	M
$\bar{4}$	1	1	2.831	2.830	M <sub>-</sub>
4	1	1	2.717	2.717	W
3	2	1	2.565	2.564	W
$\bar{5}$	1	1	2.387	2.386	VW
$\bar{4}$	2	1	2.336	2.336	W

$$a=13.159\pm0.012\text{\AA}, b=7.161\pm0.003\text{\AA}, c=7.499\pm0.006\text{\AA}$$

$$\beta=93.76\pm0.05^\circ, V=705.2\pm1.0\text{\AA}^3, Z=8$$

Space group ;  $P2_1/n$

these patterns as depicted in Fig.1, between the wolframite structure ( $\text{CdWO}_4$ ) and the present high pressure  $\text{BaWO}_4$  and also  $\text{PbWO}_4$  of high pressure form. In the figure, I and II stand for the high pressure forms of  $\text{BaWO}_4$  and  $\text{PbWO}_4$ , respectively, and III for  $\text{CdWO}_4$ . The pattern of  $\text{PbWO}_4$  is similar to that of  $\text{BaWO}_4$ . These patterns strongly suggest that the structure of high pressure  $\text{BaWO}_4$  is different from the wolframite one. We, therefore, tentatively name the present high pressure product as  $\text{BaWO}_4$ -II.

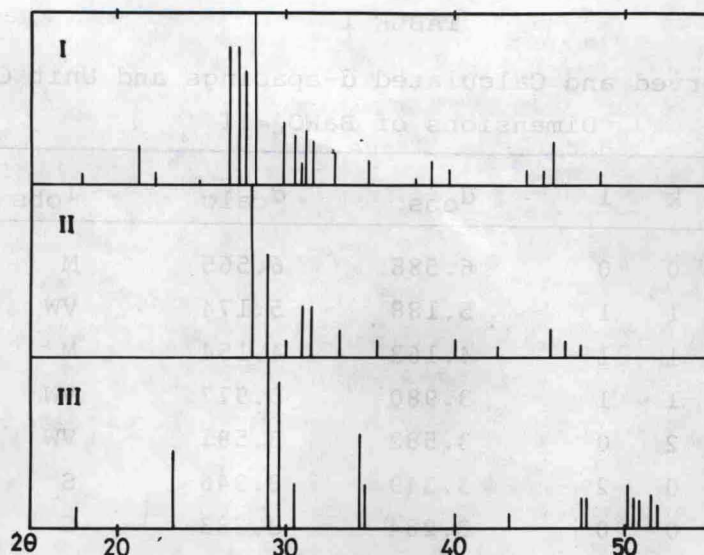


FIG. 1

Comparison between the powder patterns ( $\text{CuK}\alpha$ ) of  $\text{BaWO}_4$ -II, high pressure form of  $\text{PbWO}_4$  (3) and the wolframite structure ( $\text{CdWO}_4$ ) (6).

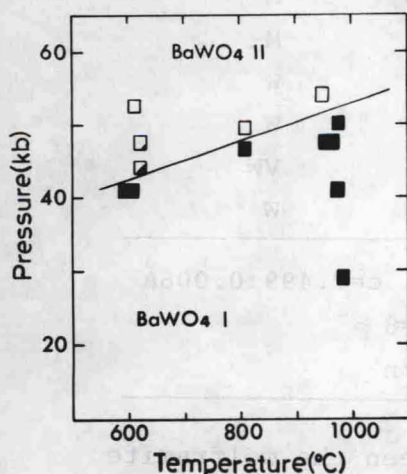


FIG. 2

Pressure-Temperature  
diagram of  $\text{BaWO}_4$

suggests that the transformation is reversible.

Phase diagram: Throughout the entire experimental runs, the product was always either a mixture of the I and II forms or a single phase of the respective one. This enables us to establish

These statements are further confirmed by the structure analysis based on the four circle goniometer data. Although the details of the structure will be reported in a separate paper, it is worthwhile noting here that the average coordination number of the cations has increased as compared with that of either the wolframite- or the scheelite-structure.

Although  $\text{BaWO}_4$ -II was quenchable as described above, this was completely transformed to  $\text{BaWO}_4$ -I upon heating in air at  $800^\circ\text{C}$ . This

a pressure-temperature diagram as shown in Fig.2. When the product was a mixture of the two phases, their relative quantity was estimated from the intensities of powder diffraction peaks. From the figure, the equilibrium phase boundary can be expressed in terms of the equation;  $P(\text{kbar}) = 26.7 + 0.0265T(^{\circ}\text{C})$ .

Considerations: The pressure induced phase transition of  $\text{ABO}_4$  compounds has been examined by several researchers(7,8,9,10). Among them, Nicol and Durana(1) claimed through their high pressure Raman spectra measurements that  $\text{CaWO}_4$  and  $\text{CaMoO}_4$  transformed reversibly to a high pressure form at about 20kbars which was of similar structure to wolframite. On the other hand, Sleight(2) showed that the quenched specimens of  $\text{CaWO}_4$ ,  $\text{CdWO}_4$ ,  $\text{CaMoO}_4$  and  $\text{CdMoO}_4$  did not reveal any high pressure form. It was therefore considered that these wolframite-like high pressure phases are not quenchable. In comparison with those observations, it is interesting to note that the high pressure forms are obtained in quenched products for  $\text{PbWO}_4$ (3) and  $\text{BaWO}_4$  where the A-cations are relatively large. As Fig.2 shows, the  $dP/dT$  is positive in the transformation of  $\text{BaWO}_4$ -I to  $\text{BaWO}_4$ -II. This is similar to the behaviors of the high pressure form of  $\text{PbWO}_4$ .

In the  $\text{BaWO}_4$ -I  $\rightarrow$   $\text{BaWO}_4$ -II transformation, the volume of the unit cell decreases by 12.1% of the I-form( the cell volume of the II-form is normalized to a four formula unit cell). If the transformation is of a scheelite  $\rightarrow$  wolframite structure, no change in the average coordination number may result in much smaller volume decrease. Shannon and Prewitt(11) discussed an empirical tendency that a larger decrease of cell volume is associated with an increase of coordination number. In fact, the present case, the decrease amounting to 12.1% is associated with an increase in the average coordination number in the high pressure phase.

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