Mat. Res. Bull. Vol. 9, pp. 141-146, 1974. Pergamon Press, Inc. Printed in the United States.

PRESSURE INDUCED PHASE TRANSFORMATION IN $BaWO_4$

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(Received December 19, 1973; Communicated by M. Nakahira)

ABSTRACT

A new dense form of $BaWO_4$ ($BaWO_4$-II) was prepared under high pressure. The phase boundary between the normal pressure form ($BaWO_4$-I, scheelite structure) and $BaWO_4$-II was determined as $P(kb)=26.7+0.0265T(°C)$, ($T=600-1000$ °c). Crystallographic data were obtained from the single crystal and powder X-ray analyses. $BaWO_4$-II is monoclinic with 8 formula units in the unit cell. The possible space group is $P2_1/n$ and the cell parameters are; $a=13.159$Å, $b=7.161$Å, $c=7.499$Å, $\beta=93.76°$ and the cell volume=705Å^3. The volume decrease upon transformation is estimated to be 12.1%.

Introduction

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 $CaMoO_4$ and $CaWO_4$. 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 $PbWO_4$ 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 $BaWO_4$ was

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

Experimental

Stoichiometric amount of reagent grade $BaCO_3$ and WO_3 was mixed intimately and heated at about 800°C for two days in a platinum crucible. The product was ground again for subsequent firing at 800°C for two days. The final product was a single phase of $BaWO_4$-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 [BiI-II, 25.5kbars; 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

$BaWO_4$-II: In some of the experimental runs, a new phase other than $BaWO_4$-I was obtained as a white powder in the quenched specimen. Under a microscope, this was colorless and transparent as $BaWO_4$-I. Weissenberg and four circle goniometer measurements of a single crystal of about 30microns revealed that the crystal was monolcinic with a possible space group, $P2_1/n$. 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 $7.26 g/cm^3$ with eight formula units per cell. This is in fairly good agreement with the measured density, $7.17 g/cm^3$.

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