Crystal Structures of the High Pressure Phases ZnAs and CdAs

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The structure of the high pressure compounds ZnAs and CdAs have been determined using Guinier film and counter methods. The compounds are orthorhombic, (space group Pbca; $Z = 8$), with $a = 5.679(2)$ Å, $b = 7.277(4)$ Å, $c = 7.559(4)$ Å and $a = 5.993(4)$ Å, $b = 7.819(6)$ Å, $c = 8.011(6)$ Å respectively.

ZnAs and CdAs are isostructural with the normal pressure phases ZnSb and CdSb, which are related to the high pressure phase Si III. Structural relationships are discussed including the Si III-diamond structure relationship.

Introduction

The previously unknown compounds ZnAs and CdAs could be prepared by high-pressure decomposition of $ZnAs_2$ and $CdAs_2$ or by high-pressure synthesis from Me_3As_2–As mixtures[1]. In the present paper we describe the crystal structures of the new high-pressure phases.

Besides the well-characterized compounds with 1:1 stoichiometry, pressure temperature treatment of $ZnAs_2$ and $CdAs_2$ yielded further quenchable phases whose stability and exact composition are not known[1]. The diffraction data obtained for these phases is presented as an appendix for comparison purposes. All efforts to index this data were without success.

Experimental

The experimental details concerning the synthesis of the high-pressure phases have been discussed[1]. ZnAs could be synthesized practically without impurities, while CdAs still had fair amounts of Cd_3As_2 and As present. However, the diffraction lines due to the impurities were not as sharp, and thus were easy to recognize and remove. The retained phases were fine, well-compacted powders. All efforts to grow single crystals of ZnAs and CdAs under high pressure and temperature using fluxes of ZnI_2 and As were without success.

The diffraction patterns were obtained using a Huber Guinier Camera (film and counter methods) and monochromatized $CuK_{\alpha 1}$ ($\lambda = 1{,}5405$ Å) radiation. The intensity data are for the areas of the peaks (counter methods) and were measured using a planimeter.

Structure Determination

The powder patterns obtained for ZnAs and CdAs are listed in Tables I and II respectively. In each case the observed peaks could be readily indexed using the method of de Wolff[2], and yielded orthorhombic cells with $a = 5.679(2)$ Å, $b = 7.277(4)$ Å, $c = 7.559(4)$ Å and $a = 5.993(4)$ Å, $b = 7.819(6)$ Å, $c = 8.011(6)$ Å, respectively. Systematic absences in both cases indicated that the space group is D_{2h}^{15}-Pbca. From the experimentally determined density for ZnAs of 5.9 g · cm^{-3}, the unit cell must contain 16 atoms. The experimentally determined density of CdAs was less accurate due to the presence of Cd_3As_2 and As. However, the value also indicated that 16 atoms were required in the unit cell. This structural data suggested that the compounds CdAs and ZnAs are isostructural with CdSb and ZnSb[3]. Using the published data for CdSb as a starting model, the structural parameters could be calculated and refined (Table III). The I_{obs} and I_{calc} values are listed in Tables I and II. R-values of 0.121 and 0.137 ($R = \Sigma|I_{obs}-I_{calc}|/\Sigma I_{obs}$) were obtained for ZnAs and CdAs respectively.

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