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Hf₂Se₃, a new structure in the binary Hf–Se system

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Abstract

Hf₂Se₃ was synthesized and its structure determined using the Rietveld method with X-ray powder diffraction data (Ti₅S₈ type, space group: *P6₃mc*, *a* = 3.7165(1) Å, *c* = 12.4304(2) Å, *Z* = 2 for Hf_{1.35}Se₂, *R_p* = 0.0600, *wR_p* = 0.0811). The Se atoms form a closed packed array of the h.c. type, the Hf atoms occupy octahedral interstices in alternating fully and 35% occupied layers.

Keywords: Hafnium; Selenium

1. Introduction

In the course of the investigation of ternary systems involving Hf and Se, a new phase was found and its structure was refined using the Rietveld X-ray powder method. The existence of this phase was suggested in 1958 by McTaggart and Wadsley [1], who were not able to index the 'complex' powder pattern. No experimental details of this powder pattern were given. To our knowledge there is no other reference to this phase.

The sesquichalcogenides and their neighboring phases of the Group 4 transition metals M₂X₃/M₃X₄ (M = Ti, Zr, Hf, and X = S, Se and Te) form an interesting class of materials and much work has been done on the characterization of the titanium sulfides and the zirconium sulfides and selenides [2]. In all compounds a close packing of anions forms the framework of the structure, with metal atoms occupying 2/3 (3/4) of the octahedral sites. The variety of structures results from the different ways of stacking the hexagonal anion layers (f.c.c. = c, h.c.p. = h, or intermediates like h.c., h.h.c., etc. [3]), and from the way metal vacancies are arranged within this framework.

Frequently metal atom layers are alternately fully and partially occupied. These structures are related to the intercalation compounds of the transition metal dichalcogenides A_xMX₂ (A = alkali metal or late 3d transition metal, M = transition metal, X = chalcogen). If the metal atom vacancies order within these partially occupied layers, more complex structures are found.

A distinct case of ordering of the metal vacancies is realized in the cubic structure of Zr₅S₄ [4] in which vacancies occur in all metal layers.

2. Experimental details

Hf₂Se₃ was prepared from a stoichiometric mixture of Hf metal and HfSe₂, which itself was previously prepared from the elements in a sealed fused silica tube at 750 °C. A pressed pellet was melted for a short time in an arc furnace on a water-cooled copper hearth. Further annealing for 20 h at 1250 °C decreased the line widths of the diffraction lines only slightly. Guinier powder diffraction using Si as an internal standard was used to identify phases in the sample. A finely ground sample was mounted in a shallow cavity of a zero-background single-crystal quartz mount and diffraction data were collected on a Scintag Powder diffractometer with 5 s per 0.02° steps over the range 23°–160° in 2θ at room temperature using Cu Kα radiation. The data were corrected for coincidence effects prior to Rietveld refinement.

3. Structure solution and refinement

The observed lines in the Guinier powder diffraction pattern could be assigned to either the known HfSe phase (WC type) [5], or could be indexed on the basis of a hexagonal unit cell with *a* = 3.7151(2) and

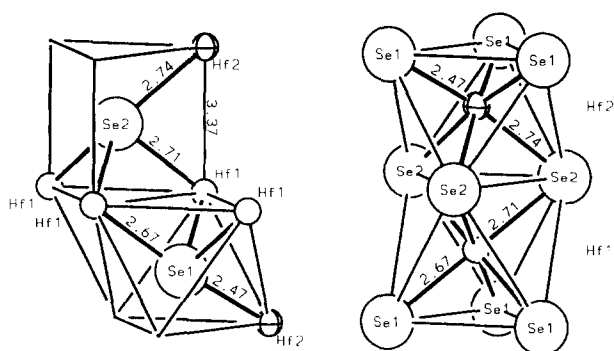


Fig. 3. Coordination geometries around Se and Hf atoms in Hf_2Se_3 . The partial occupancy of Hf(2) leads to the indicated fourfold (average) coordination of selenium atoms.

occupied. The TiAs type itself is an intermediate between the NaCl type (all nonmetals in octahedral coordination) and the NiAs type (all nonmetals in trigonal prismatic coordination). To our knowledge there are only two more examples with the Ti_5S_8 type structure displaying alternately fully and partially occupied metal layers, namely Ti_5S_8 and Zr_2Se_3 [2,8].

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