

## The structure of hessite, $\text{Ag}_2\text{Te-III}$

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With 3 figures

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### Auszug

Als Raumgruppe eines einheitlichen Hessitkristalls ( $\text{Ag}_2\text{Te-III}$ ) von Bótes, Transsylvanien, wurde  $P2_1/c$  gefunden; die Gitterkonstanten wurden zu  $a = 8,09$ ,  $b = 4,48$ ,  $c = 8,96$  Å,  $\beta = 123^\circ 20'$  bestimmt. Die Elementarzelle enthält 4  $\text{Ag}_2\text{Te}$ . Alle Atome befinden sich in allgemeinen Lagen; ihre Parameter sind:

$$\begin{aligned}x &= 0,018, \quad y = 0,152, \quad z = 0,371 \text{ für Ag(I),} \\x &= 0,332, \quad y = 0,837, \quad z = 0,995 \text{ für Ag(II),} \\x &= 0,272, \quad y = 0,159, \quad z = 0,243 \text{ für Te.}\end{aligned}$$

Symmetrie und Dimensionen der Zelle stimmen nicht mit den Literaturangaben überein. Es wird angenommen, daß die früheren Untersuchungen an verzwilligten Kristallen durchgeführt wurden.

### Abstract

The space group of a single crystal of naturally occurring hessite ( $\text{Ag}_2\text{Te-III}$ ) from Bótes, Transylvania, was found to be monoclinic  $P2_1/c$ ; the cell constants were determined as follows:  $a = 8.09$ ,  $b = 4.48$ ,  $c = 8.96$  Å,  $\beta = 123^\circ 20'$ . There are 4 ( $\text{Ag}_2\text{Te}$ ) per cell, and all atoms lie on the following fourfold general positions: Ag(I) at  $x = 0.018$ ,  $y = 0.152$ ,  $z = 0.371$ ; Ag(II) at  $x = 0.332$ ,  $y = 0.837$ ,  $z = 0.995$ ; and Te at  $x = 0.272$ ,  $y = 0.159$ ,  $z = 0.243$ .

This cell and the symmetry differ from those previously reported for hessite in the literature. It is believed that the other recent determinations have been based upon misleading data from twinned crystals.

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### Introduction

The mineral hessite,  $\text{Ag}_2\text{Te}$ , and its polymorphs have been the subject of several crystallographic investigations. Results have been conflicting and confusing. Part of the confusion arises out of the notation used to identify the different polymorphs. In this paper the notation used by KRACEK and KSANDA<sup>1</sup>, utilizing Roman numerals, will be followed. The polymorph whose stability range lies between  $690^\circ$  to  $802^\circ\text{C}$  and the melting point will be referred to as  $\text{Ag}_2\text{Te}$ -I. The polymorph stable between  $105^\circ$  to  $145^\circ$  and  $690^\circ$  to  $802^\circ\text{C}$ , listed as  $\alpha$ -hessite or  $\alpha$ - $\text{Ag}_2\text{Te}$  in many texts, will be called  $\text{Ag}_2\text{Te}$ -II. The polymorph stable from room temperature up to  $105^\circ$  to  $145^\circ\text{C}$ , called  $\beta$ - $\text{Ag}_2\text{Te}$  in earlier literature, will be labeled  $\text{Ag}_2\text{Te}$ -III. These labels should not be confused with the notation used by ROWLAND and BERRY<sup>2</sup>, where  $\text{Ag}_2\text{Te}$  "type I" and "type II" refer to morphological examples.

A conflict exists in that the symmetry and unit-cell dimensions reported by three different investigators for  $\text{Ag}_2\text{Te}$ -III do not agree; nor does the lattice type arrived at by two workers for  $\text{Ag}_2\text{Te}$ -II. There has been no crystallographic study of  $\text{Ag}_2\text{Te}$ -I reported in the literature.

### $\text{Ag}_2\text{Te}$ -III: hessite

The most recent crystallographic investigation of the room-temperature polymorph,  $\text{Ag}_2\text{Te}$ -III, is that of ROWLAND and BERRY<sup>2</sup>. From material synthesized from aqueous sodium-sulfide solution in a graphite-lined steel bomb at several different temperatures from  $350^\circ$  to  $490^\circ\text{C}$ , crystals were obtained from which morphological data and some single-crystal x-ray data could be taken. It is to be noted that the temperatures utilized were at least  $200^\circ\text{C}$  above the stability range of  $\text{Ag}_2\text{Te}$ -III at normal pressures. Unless the effect of the pressure that existed within the steel bomb was to increase the stability range of  $\text{Ag}_2\text{Te}$ -III by more than  $200^\circ$ , it seems unlikely that the morphology of the crystals grown under these conditions represents the morphology of the  $\text{Ag}_2\text{Te}$ -III phase. However, as the powder diffraction record of the products of these runs was identical with that of natural

<sup>1</sup> F. C. KRACEK and C. J. KSANDA, A paper on the Ag—Te system; in preparation.

<sup>2</sup> J. F. ROWLAND and L. G. BERRY, The structural lattice of hessite. Amer. Mineral. **36** (1951) 471—479.

hessite, there is little doubt that the internal structure at room temperature was that of  $\text{Ag}_2\text{Te}$ -III.

From one of these crystals exhibiting orthorhombic morphology, ROWLAND and BERRY obtained Weissenberg and rotation films that lead to the following unit-cell and space group: orthorhombic  $Immm$ ;  $a = 16.28$ ,  $b = 26.68$ ,  $c = 7.55$  Å. But here again it must be pointed out that since the crystals were grown at temperatures above the stability field of  $\text{Ag}_2\text{Te}$ -III, there is a possibility that, during the transformation, twinning took place that resulted in additional symmetry and an apparent cell larger than that which would be exhibited by a true single crystal.

ROWLAND and BERRY's cell does not agree with that described by TOKODY<sup>3,4</sup>. TOKODY found  $\text{Ag}_2\text{Te}$ -III to be monoclinic with a cell size of  $a = 6.57$ ,  $b = 6.14$ ,  $c = 6.10$  Å,  $\beta = 61^\circ 15'$ . From the cell content of 3 ( $\text{Ag}_2\text{Te}$ ) he concluded that the space group must be  $Pm$ ,  $P2$ , or  $P2/m$ . However, this cell was determined principally from the powder diffraction record, and to index all the reflections it was necessary to consider that some reflections were due to  $\beta$  radiation. Powder photographs taken on natural samples during the present investigation indicate that the lines considered by TOKODY to be due to  $\beta$  radiation were clearly due to  $\text{CuK}\alpha$ . THOMPSON<sup>5</sup> also reports that the powder pattern of hessite could not be indexed on the monoclinic elements of TOKODY.

### Structure determination

Small crystals of hessite from Bótes, Transylvania, obtained both from the U. S. National Museum (U. S. N. M. No. R 9556) and from the Harvard University Museum (No. 99348), were found to contain small inclusions of petzite<sup>6</sup>. By fracturing these small crystals at liquid nitrogen temperatures, it was possible to obtain fragments of hessite free from any petzite. The diffraction record of these fragments showed them to be single, undeformed crystals. The x-ray powder diagram

<sup>3</sup> L. TOKODY, Über Hessit. Z. Kristallogr. **82** (1932) 154—157.

<sup>4</sup> L. TOKODY, Berichtigung zu meiner Mitteilung „Über Hessit“. Z. Kristallogr. **89** (1934) 416.

<sup>5</sup> R. M. THOMPSON, The telluride minerals and their occurrence in Canada. Amer. Mineral. **34** (1949) 342—382.

<sup>6</sup> A. J. FRUEH, The crystallography of petzite,  $\text{Ag}_3\text{AuTe}_2$ . Amer. Mineral. **44** (1959), in press.

