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Crystal Structures of Bismuth Tellurohalides BiTeX (X = Cl, Br, I) from X-Ray Powder Diffraction Data

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Crystal structures of the bismuth tellurohalides BiTeCl (prepared for the first time), BiTeBr, and BiTeI were refined based on X-ray powder diffraction data using a full-profile Rietveld method. All three phases crystallize in a hexagonal system: BiTeCl; space group $P6_3mc$ (No. 186), a = 4.2426(1) Å, c = 12.397(1) Å, z = 2, R_I = 0.065, R_{Pr} = 0.104; BiTeBr, space group $P\bar{3}m1$ (No. 164), a = 4.2662(1) Å, c = 6.487(1) Å, z = 1, R_I = 0.042, R_{Pr} = 0.082; BiTeI, space group $P3m1$ (No. 156), a = 4.3392(1) Å, c = 6.854(1) Å, z = 1, R_I = 0.054, R_{Pr} = 0.129. Bismuth tellurohalides do not belong to the SbSBr structure type. BiTeBr has a 2H–CdI_2-type structure with tellurium and bromine atoms statistically distributed within a two-layered packing. BiTeI exhibits a distorted variant of the former structure with an ordering of tellurium and iodine atoms in an anionic subcell. In BiTeCl, layers of tellurium and chlorine atoms alternate along the c direction of the unit cell, forming a four-layered $(hc)_2$ packing. Bismuth atoms occupy all octahedral interstices in each second layer. The common feature that the three structures share is the corrugated $(BiTe)^+$ layers which resemble the geometry of bismuth layers in metallic bismuth. The structures are described in terms of a semi-ionic model, according to which bismuth and tellurium atoms form positively charged $(BiTe)^+$ layers, while bismuth–halogen contacts are considered to be ionic.

INTRODUCTION

Since 1962 a complex investigation of SbSI and related compounds has developed rapidly due to the discovery of the ferroelectric properties of SbSI (1). Crystallochemical investigation of thio-, seleno-, and tellurohalides of antimony and bismuth with 1 : 1 : 1 stoichiometry was begun to determine the origin of the ferroelectric properties. A more or less detailed review which summarized the knowledge on this topic appeared in 1980 (2). It was found that SbSI and the majority of the SbSI-related compounds crystallized in a unique orthorhombic structure called the SbSBr structure type (3). Only a few exceptions are known. SbTeI was shown to exhibit a monoclinic distortion (4). Our recent structural investigation showed that BiSeCl, first reported to be orthorhombic (5), crystallized in a monoclinic system and had a $Bi_{11}Se_{12}Cl_9$ composition (6). However, its structural motif is similar to that of compounds of the SbSBr structure type. According to literature data, BiTeBr and BiTeI belong to a CdI_2 structure type (7, 8). The model of the crystal structure of the former compound was proposed on the basis of X-ray powder diffraction data (7). The structure of BiTeI was determined by an X-ray single-crystal technique to have a rather poor R-factor value (R = 0.17) (8). No data on BiTeCl appeared in the literature. Serious difficulties in obtaining suitable single crystals of bismuth tellurohalides are the main reason for applying an X-ray powder diffraction technique to the crystal structure determination of BiTeX (X = Cl, Br, I). In this article we report the preparation of BiTeCl and the X-ray powder diffraction determination of the crystal structures of the three bismuth tellurohalides. Relationships between the structures of BiTeX and of SbSI-related compounds are also discussed.

EXPERIMENTAL

Bismuth tellurohalides were prepared by a standard ampule technique.

For BiTeCl preparation, metallic bismuth, tellurium, and freshly purified bismuth trichloride were mixed in a molar ratio 2 : 3 : 1, placed in a silica tube, and sealed *in vacuo*. The mixture was annealed at 520°C for 10 hr. After the sample was reground it was annealed at 400°C for 10 days. An X-ray diffraction pattern (Guinier FR-552 chamber, Cu$K\alpha_1$ radiation) of the black polycrystalline product did not indicate even traces of the starting materials. As bismuth trichloride is sensitive to moisture, all manipulations were carried out in a glove box, though the product appeared to be resistant against moisture.

BiTeBr was prepared by heating a stoichiometric mixture of bismuth tribromide, bismuth, and tellurium at

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TABLE 1
Data Collection and Refinement Parameters

	Phase		
	BiTeCl	BiTeBr	BiTeI
Space group	$P6_3mc$ (No. 186)	$P\bar{3}m1$ (No. 164)	$P3m1$ (No. 156)
a (Å)	4.2426(1)	4.2662(1)	4.3392(1)
c (Å)	12.397(1)	6.487(1)	6.854(1)
V (Å^3)	193.3(1)	102.3(1)	111.8(1)
Z	2	1	1
ρ_{calc} (g cm^{-3})	6.39(1)	6.76(1)	6.89(1)
μ (cm^{-1})	1543.7	1528.0	1834.2
Data collection mode	Transmission	Transmission	Reflection
Radiation	CuKα_1 (Ge-mono)		CuKα
Wavelength (Å)	1.54056	1.54056	1.54178
Mode of refinement		Full profile	
min 2θ	6.00	10.00	15.00
max 2θ	118.42	115.00	98.30
max intensity (count)	16,460	19,337	17,169
Texture parameter along 001 axis	4.98(4)	3.88(3)	0.149(1)
R_I	0.065	0.042	0.054
R_{Pr}	0.104	0.082	0.129
R_{WP}	0.120	0.101	0.144
Goodness of fit	0.440	0.280	0.501

650°C for 10 hr, followed by annealing at 520°C for 7 days. For the preparation of BiTeI, a stoichiometric mixture of bismuth (III) telluride and bismuth triiodide was annealed at 650°C for 4 hr. The product then was purified by a sublimation *in vacuo* at 520°C. X-ray diffraction patterns showed that BiTeBr and BiTeI were prepared as pure phases.

X-ray raw data were collected on a STADI-P (STOE) automatic diffractometer at 22°C with a step of 0.02° (2θ). Data collection parameters are summarized in Table 1. A reflection mode was applied to BiTeI data collection due to an insufficient total intensity collected when applying a transmission mode. To decrease the influence of the texturing, 30 vol.% of a starch was added to the sample of BiTeI, which led to a change of the intensities ratio of the 001 and 103 reflections in approximately 700 by 700 times.

Crystal structures of bismuth tellurohalides were refined by a full-profile Rietveld method using the CSD program package. Atomic parameters obtained in the last least-squares refinements are listed in Table 2. Selected interatomic distances are listed in Table 3. Figures 1, 2, and 3 show experimental, calculated, and difference profiles for each phase.

CRYSTAL STRUCTURE DETERMINATION

No systematic absences were observed in the X-ray patterns of BiTeBr and BiTeI. The crystal structure of BiTeBr was successfully refined in space group $P\bar{3}m1$ (No. 164), based on a model suggested by Donges (7). We also tried to refine this structure in the space group $P3m1$ (No. 156), taking into account the possible ordering of tellurium and bromine atoms. The refinement showed that these atoms occupied the 1*b* and 1*c* positions with $z = 0.278$ and $z = 0.722$, respectively, and the values of the thermal displacement parameters showed that these

TABLE 2
Atomic Parameters with esd's

Atom	Position	x/a	y/b	z/c	B_{iso}[a]
		BiTeCl			
Bi	2*b*	$\frac{2}{3}$	$\frac{1}{3}$	0.6394(1)	1.67(2)
Te	2*b*	$\frac{2}{3}$	$\frac{1}{3}$	0.2811(1)	1.87(4)
Cl	2*a*	0	0	0.4976(5)	1.44(8)
		BiTeBr			
Bi	1*a*	0	0	0	0.86(3)
Te/Br[b]	2*d*	$\frac{1}{3}$	$\frac{2}{3}$	0.2784(3)	2.16(5)
		BiTeI			
Bi	1*a*	0	0	0.0000	1.13(3)
Te	1*c*	$\frac{2}{3}$	$\frac{1}{3}$	0.6928(2)	2.03(7)
I	1*b*	$\frac{1}{3}$	$\frac{2}{3}$	0.2510(2)	1.44(7)

[a] All atoms are refined isotropically.
[b] Occupations: 0.5 Te + 0.5 Br.

TABLE 3
Selected Interatomic Distances (Å) and Bond Angles (°) with esd's

		BiTeCl	
Bi–Te	3.015(2) (×3)	Te–Bi–Te	89.47(4) (×3)
Bi–Cl	3.015(3) (×3)	Te–Bi–Cl	179.98(8) (×3)
		Te–Bi–Cl	90.54(7) (×6)
		Cl–Bi–Cl	89.46(9) (×3)
		BiTeBr	
Bi–Te/Br	3.054(1) (×6)	Te/Br–Bi–Te/Br	180.00 (×3)
		Te/Br–Bi–Te/Br	91.38(3) (×6)
		Te/Br–Bi–Te/Br	88.62(3) (×6)
		BiTeI	
Bi–Te	3.039(2) (×3)	Te–Bi–Te	83.05(3) (×3)
Bi–I	3.272(2) (×3)	Te–Bi–I	174.43(4) (×3)
		Te–Bi–I	92.79(3) (×6)
		I–Bi–I	91.11(4) (×3)

positions were each statistically occupied by tellurium and bromine atoms with a 1 : 1 ratio. These facts enabled us to suggest that the initial choice of the centrosymmetric group $P\bar{3}m1$ (No. 164) with statistical distribution of tellurium and bromine atoms within the $2d$ position was correct. A comparison of the X-ray patterns of BiTeBr and BiTeI shows that the latter has strong superstructural 002 and 004 reflections (Fig. 3). Such a superstructure can arise due only to an ordering of tellurium and iodine atoms. Taking into account this fact, space group $P3m1$ (No. 156) was chosen for the refinement of the structure of BiTeI and has led to the atomic parameters listed in Table 2. Our attempts to refine this structure in space group $P\bar{3}m1$ have led to unsatisfactory results (R_I = 0.141).

The X-ray diffraction pattern of BiTeCl was indexed in the hexagonal system with unit cell dimensions a = 4.2426(1) and c = 12.397(1) Å. The c parameter appeared to be nearly twice as large as that of BiTeBr and BiTeI. The following systematic absences were observed in an X-ray pattern: hhl, $l \neq 2n$, and if $h - k = 3n$, then $l \neq 2n$. According to these absences and the proposed model of the crystal structure, we chose space group $P6_3mc$ (No. 186), assuming that all atoms occupied special positions $2a$ and $2b$ (9). The refinement was successful in this space group.

DISCUSSION

BiTeBr crystalizes in a CdI_2 structure type with the Te and Br atoms statistically distributed within a two-layered packing. The Bi atoms occupy all octahedral interstices in each second layer. In BiTeI an ordering of the tellurium and iodine atoms occurs that leads to a lowering of symmetry. A two-layered packing is formed by alternating tellurium and iodine atoms along the c-axes.

In the crystal structure of BiTeCl, layers of tellurium and chlorine atoms alternate along the c-axes of the unit cell forming a four-layered $(hc)_2$ packing. Bismuth atoms occupy all octahedral interstices in each second layer. Projections of the crystal structures of the three bismuth tellurohalides onto $11\bar{2}0$ planes are presented in Fig. 4.

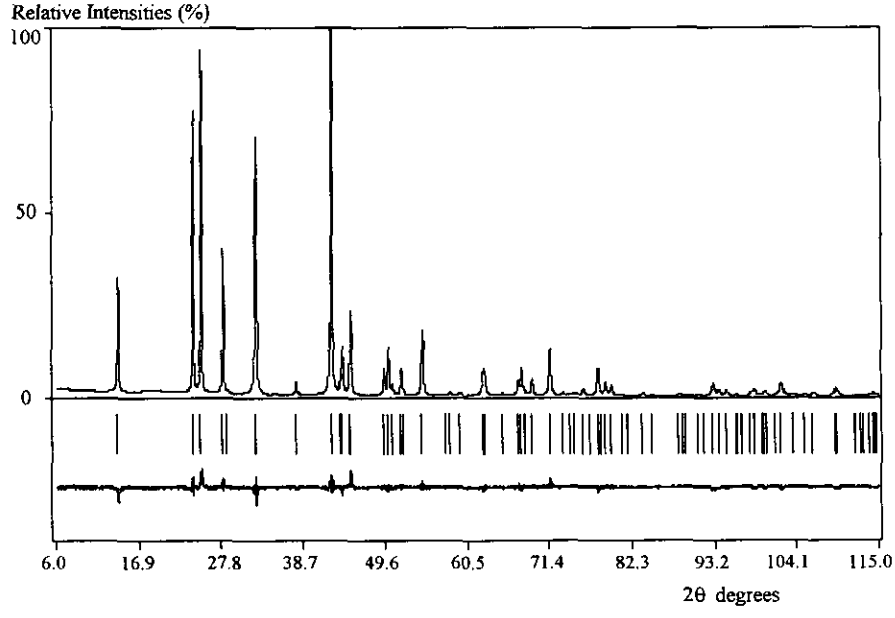

FIG. 1. Experimental and difference profiles for BiTeCl.

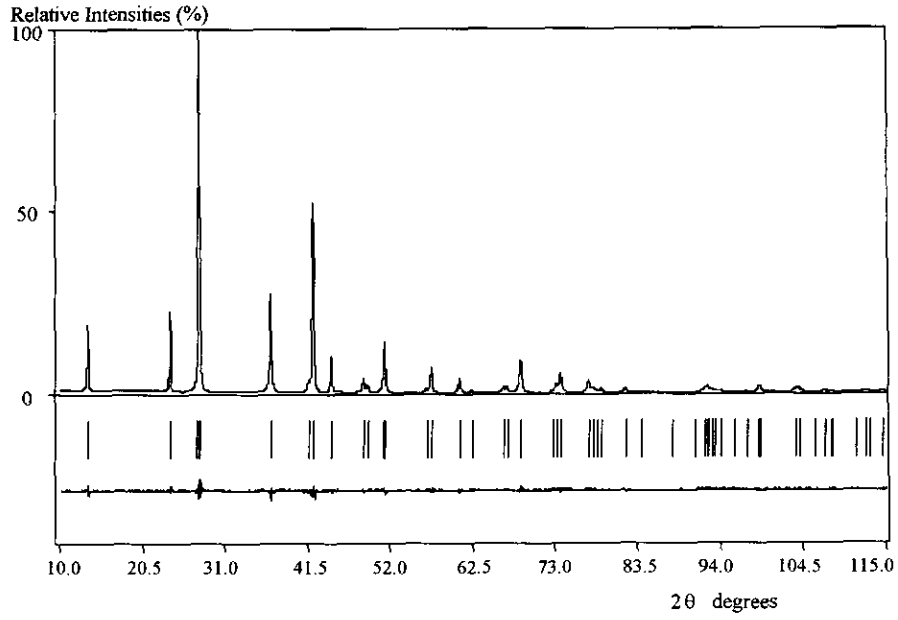

FIG. 2. Experimental and difference profiles for BiTeBr.

In the structures of bismuth tellurohalides the bismuth atoms possess an almost regular octahedral coordination of three tellurium and three halogen atoms. The Bi–Te distances (3.02–3.05 Å) are the same as those in various binary bismuth tellurides, for example, 3.027 Å in Bi_2Te_3 (10), and 3.043 Å in BiTe (11). In contrast, the Bi–X contacts are significantly longer than those in bismuth trihalides (12–14). Such contacts can be more readily compared with Bi–X distances in bismuth thiohalides that crystallize in the SbSBr structure type (15–17). The corresponding distances are compared in Table 4. The unusually long Bi–X distances in the compounds of the SbSBr structure type are explained in terms of a "semi-ionic model" (18). According to this model, metal atoms together with chalcogen atoms compose $(MY)^+$ charged double chains, where M = Sb, Bi and Y = S, Se (Fig. 5); halogen atoms are considered to be X^- anions (X = Cl, Br, I).

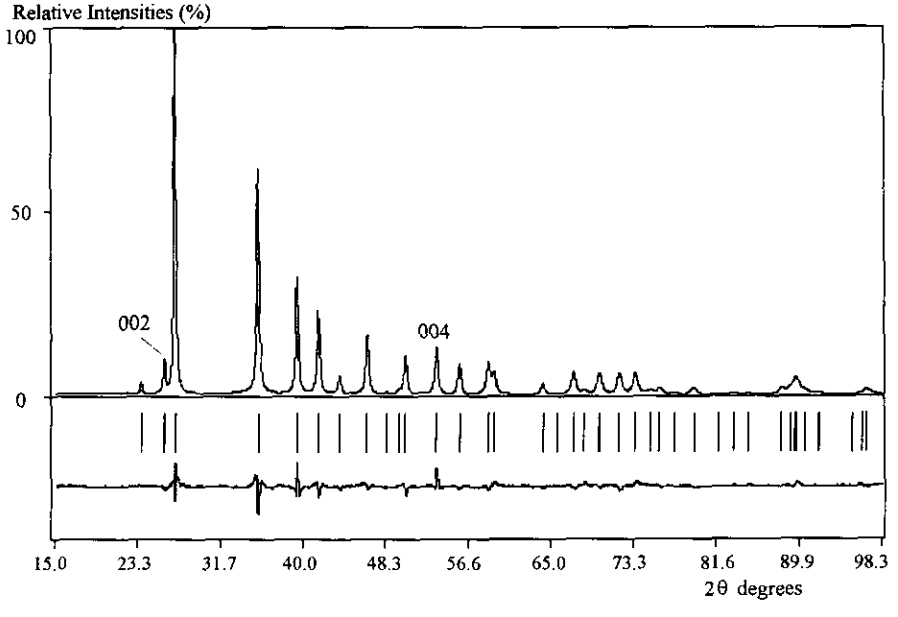

FIG. 3. Experimental and difference profiles for BiTeI. The 002 and 004 superstructural reflections are indicated on the experimental profile.

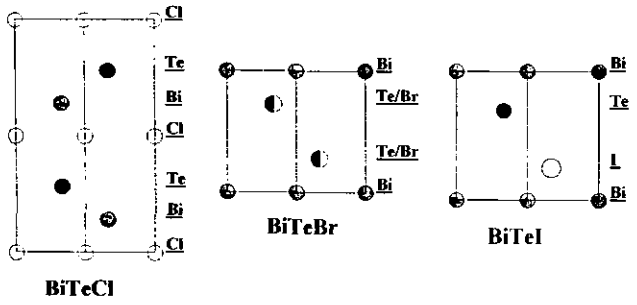

FIG. 4. Projections of the crystal structures of bismuth tellurohalides on the $11\bar{2}0$ planes. Atoms are drawn within the unit cells.

The same semi-ionic model can be adapted for the bismuth tellurohalides. Figure 5a shows a corrugated ($BiTe^+$) layer and I^- anions in the structure of BiTeI. Though a corrugated $(BiTe)^+$ layer differs drastically from the $(SbS)^+$ double chains observed in the structure of SbSBr (19), the coordination of the metal atoms in each shares certain similarities. Thus, each bismuth atom in BiTeX is surrounded by three tellurium atoms, the Te–Bi–Te angles being nearly 90°, and three halogen atoms complete the octahedral coordination of bismuth. In SbSBr, each antimony atom has three sulfur neighbors, the S–Sb–S angles being nearly 90°, but only two halogen atoms complete the coordination of antimony. The application of the semi-ionic model can be useful for an explanation of the differences between the structures of the bismuth tellurohalides. Thus, the Bi–Te covalent and Bi–Br ionic distances being equal, the bromine and tellurium atoms are statistically distributed within the two-layered packing. In BiTeI, the elongation of the Bi–I contact compared with the Bi–Br one leads to an ordering of the tellurium and iodine atoms within the same packing. In BiTeCl, the shortening of the Bi–X contact seems to make a four-layered $(hc)_2$ packing preferable.

The corrugated $(BiTe)^+$ layer possesses the same geometry as bismuth layers in metallic bismuth (20). The bismuth tellurides BiTe and Bi_4Te_3 (11) and bismuth subiodides $Bi_{18}I_4$ (21) and $Bi_{14}I_4$ (22) exhibit the same geometry

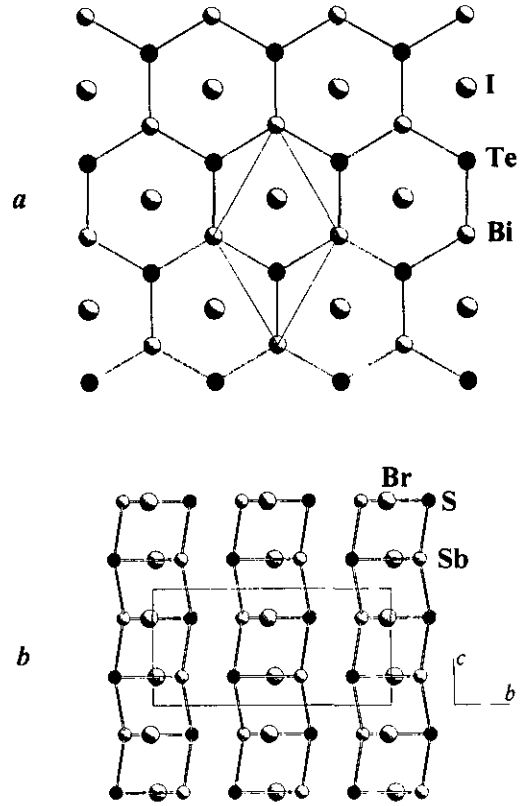

FIG. 5. The crystal structure of BiTeI (a projection on the 001 plane) (a) compared with the crystal structure of SbSBr (a projection on the 011 plane) (b).

of the bismuth layers. The Bi–Bi distances in these phase (3.02–3.09 Å) resemble the Bi–Te distances in BiTeX. The $(BiTe)^+$ and bismuth layers are isoelectronic. Each layer has five electrons per atom, and each atom also has an ns^2 lone pair, no matter how a charge distribution is accounted for. Though it is likely that in BiTeX bismuth atoms are charged positively, as they are bound to the negatively charged halogens, the fact that $(BiTe)^+$ and $(Bi)^0$ layers are isotypical and isoelectronic enables one to treat them as full analogues, and if the term "cluster" is true for the bismuth layers, then the $(BiTe)^+$ layer may

TABLE 4
Bismuth–Halogen Distances in the Trihalides, Thiohalides, and Tellurohalides of Bismuth

Compound	$BiCl_3$	BiSCl	BiTeCl	$BiBr_3$	BiSBr	BiTeBr	BiI_3	BiSI	BiTeI
d_{Bi-X}[a]	2.50 (×3)	2.927 (×2)	3.015 (×3)	2.66[b] (×3)	3.038 (×2)	3.054 (×3)	3.09 (×6)	3.199 (×2)	3.272 (×3)
Ref.	(12)	(15)	[c]	(13)	(16)	[c]	(14)	(17)	[c]

[a] X = Cl, Br, I.
[b] α form.
[c] This work.

be called a "heterocluster." This may give a clue as to why the structures of the bismuth tellurohalides are so different from those of the SbSBr structure type. It is evident that only tellurium can replace bismuth in the bismuth layers to form such a "heterocluster" that preserves the origin geometry of the bismuth layers. If this assumption is true, there could be other compounds with bismuth–tellurium "heteroclusters," but with Bi : Te ratios that differ from 1 : 1. Our preliminary study shows that there exist at least two compounds in the Bi–Te–I system with a Bi : Te ratio greater than 1. Further studies are necessary to establish the composition and the structure of these phases.

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