

Preparation and characterization of Bi-containing ternary chalcogenides with layered composite crystal structure

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(Received May 20, 1991)

Abstract

Bismuth-containing ternary chalcogenides with layered composite crystal structure expressed as $(\text{BiX})_n\text{TX}_2$ or $(\text{BiX})_n(\text{TX}_2)_2$ where $\text{T} \equiv \text{Ti, V, Nb, Ta}$ and $\text{X} \equiv \text{S, Se}$ have been prepared and characterized using powder X-ray diffraction (XRD), electron diffraction and intercalation. The extreme preferred orientation characteristic of this kind of compound has been effectively depressed by treatment of the chalcogenides with an adhesive agent. The lattice constants of both subcells for the Bi-Ta group chalcogenides $(\text{BiS})_{1.09}\text{TaS}_2$, $(\text{BiSe})_{1.09}\text{TaSe}_2$ and $(\text{BiS})_{1.08}(\text{TaS}_2)_2$, have been obtained on the basis of the XRD pattern with depressed preferred orientation. It has been found that the interface of the two adjacent TX_2 sandwiches in the $(\text{BiX})_n(\text{TX}_2)_2$ -type chalcogenides has the character of a van der Waals gap, through the treatment of the chalcogenides with hydrazine monohydrate or aqueous CaCl_2 solution.

1. Introduction

Recently many ternary chalcogenides with layered composite crystal structure have been reported [1]: $(\text{MX})_n\text{TX}_2$ ($\text{M} \equiv \text{lanthanide}$ [2–5], Pb [4,6–8], Sn [9], Bi [10–12], Sb [13]; $\text{T} \equiv \text{Ti, V, Nb, Ta, Cr}$; $\text{X} \equiv \text{S, Se}$; $n \approx 1$). In the compounds whose M is a lanthanide, lead or tin, and whose X is sulphur, it has been found that an MS layer two atoms thick with distorted NaCl structure and a TS_2 sandwich three atoms thick with T in octahedral or trigonal prismatic coordination are stacked alternately, and MS and TS_2 layers form each subcell. The a - b plane of each subcell is perpendicular to the stacking direction. Usually the two subcells have both a axes in common, while the ratio of the length of the b axes (the axes are parallel to each other) is irrational and close to $3^{1/2}$: Wiegiers *et al.* [9] and Guemas *et al.* [14] take the common axis to be the b axis in place of the a axis. Thus both the layer are stacked alternately in a misfit or mutually incommensurate fashion. In addition to the $(\text{MX})_n\text{TX}_2$ -type chalcogenides, a few $(\text{MX})_n(\text{TX}_2)_2$ -type chalcogenides have also been reported [13–16].

We have found for the first time that bismuth forms ternary chalcogenides with a layered composite crystal structure and have given preliminary reports

of this work [10, 11, 15]. We have also found that, in the $(MX)_n(TX_2)_2$ -type chalcogenides, the interface of two adjacent TX_2 layers has the character of a van der Waals gap through treatment with hydrazine monohydrate [13, 15, 16].

In the early stages of our research, it was very difficult to obtain a useful X-ray diffraction (XRD) pattern using the ordinary counterdiffractometer method. That is, owing to an extreme preferred orientation, diffraction lines other than 00 l could not be observed with appreciable intensity. Recently we have found that the problem can be solved to some extent by treatment of the samples with an adhesive agent. It has also been found that exchange of the cation in the van der Waals gap proceeds when the $(BiX)_n(TX_2)_2$, after treatment with hydrazine monohydrate, is treated with an aqueous $CaCl_2$ solution.

In this paper we report some of the results concerning preparation, characterization and intercalation of bismuth-containing ternary chalcogenides of layered composite crystal structure with emphasis on the Bi-Ta group.

2. Experimental details

The bismuth-containing ternary chalcogenides were prepared as follows. Starting materials (powder of bismuth (purity 99.9%), titanium (99.9%), vanadium (99.9%), niobium (99.9%), tantalum (99.9%), sulphur (99.99%), selenium (99.9%)) were mixed together in the atomic ratio of Bi:T:X = 1:1:3 or 1:2:5. In the case of the Bi-Ta group, the ratio was varied according to the assumed formulation of $(BiX)_nTaX_2$ with $X \equiv S$ or Se, or $(BiS)_n(TaS_2)_2$. The mixture was sealed in a silica tube under vacuum. The tube was heated at 500 °C at first for 12 h and then at 800 °C for 2 days. The product was crushed and pulverized and was again heated at 700–800 °C for 2–4 days, depending on the composition. Powder XRD was measured by using the counterdiffractometer method. In order to depress the extreme preferred orientation, the product was mixed with a cyanoacrylate-type adhesive agent and heated at 200 °C for 10 min. Electron diffraction patterns were obtained with crushed samples using a 100 kV electron microscope.

For intercalation, the $(BiX)_n(TX_2)_2$ -type chalcogenides were at first treated with hydrazine monohydrate at room temperature. The solid product was separated by using a centrifuge. The product was neutralized with dilute aqueous HCl solution and was mixed with 4 M aqueous $CaCl_2$ solution.

3. Results and discussion

All the bismuth-containing ternary chalcogenides obtained in the present work were black-greyish microcrystalline powder with a lustre. Their XRD pattern taken with the ordinary counterdiffractometer method consists of several strong peaks and a few weak peaks. The strong peaks are all attributable

to a set of $00l$ diffraction lines. Figure 1(a) shows the pattern for “ BiTaS_3 ”. This suggests that the compound has some layered structure and takes an extreme preferred orientation. Figure 2(a) shows the electron diffraction pattern of “ BiTaS_3 ” with an incident beam parallel to the $[001]$ direction, which is similar to that of other $(\text{MX})_n\text{TX}_2$ samples [4, 7, 10, 17]. The main diffraction spots can be understood as a superposition of a pseudotetragonal

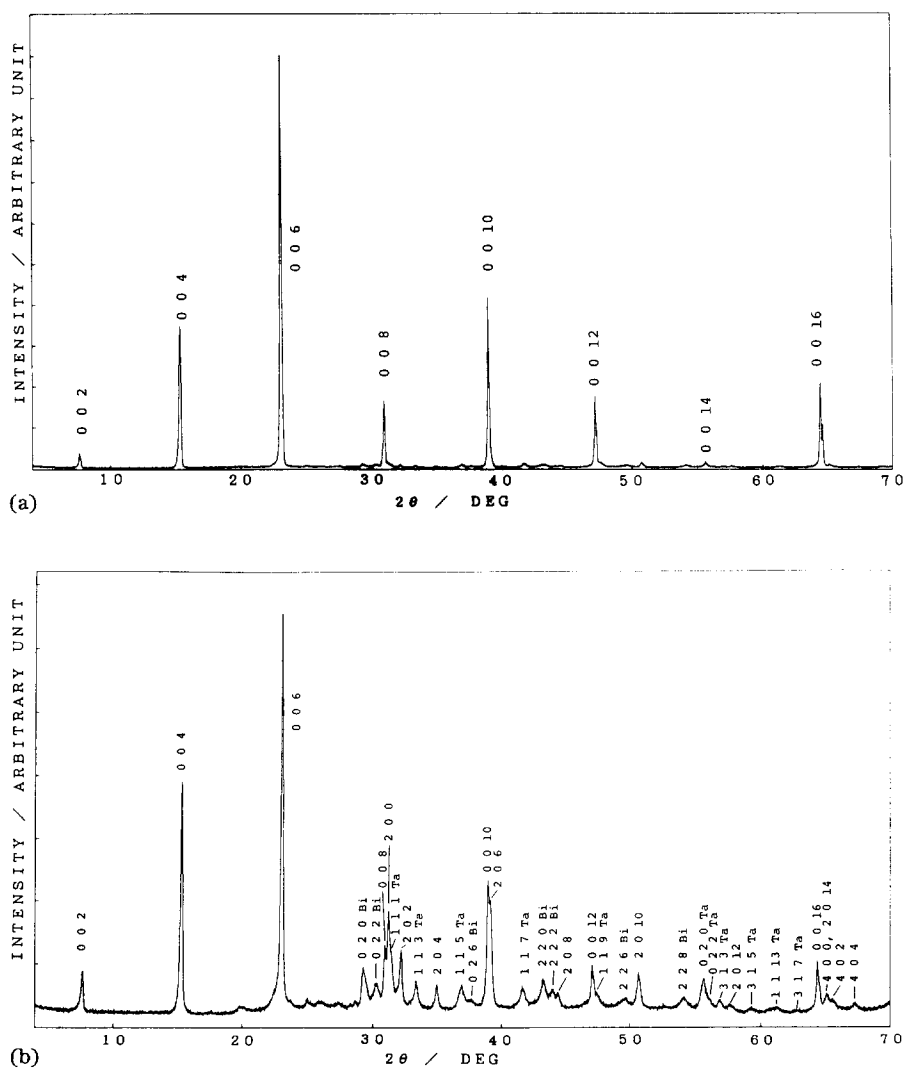


Fig. 1. (a) Powder XRD pattern of $(\text{BiS})_{1.09}\text{TaS}_2$ obtained using the ordinary counterdiffractometer method; only $00l$ diffraction lines are observed owing to the extreme preferred orientation. (b) Powder XRD pattern of $(\text{BiS})_{1.09}\text{TaS}_2$ treated by a cyanoacrylate type of adhesive agent; indices labelled with Bi are attributable to the BiS subcell, those with Ta to the TaS_2 subcell, and the others are common to both subcells.

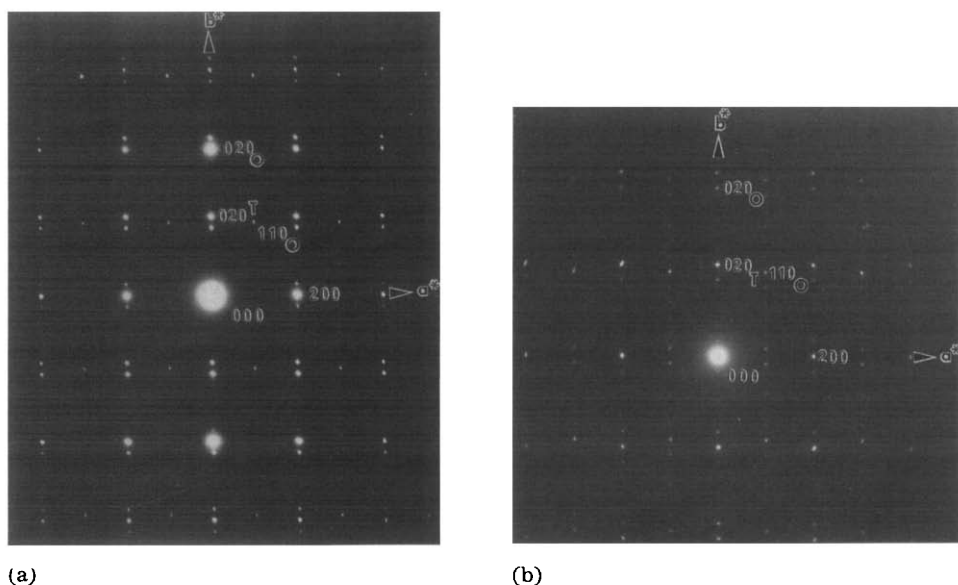


Fig. 2. (a) Electron diffraction pattern of $(\text{BiS})_{1.09}\text{TaS}_2$ with an incident beam along the $[001]$ direction. (b) Electron diffraction pattern of $(\text{BiS})_n\text{VS}_2$ with an incident beam along the $[001]$ direction.

subcell of BiS and a pseudo-orthorhombic (orthohexagonal) TaS_2 subcell. Therefore it is clear that “ BiTaS_3 ” is a composite crystal to be formulated as $(\text{BiS})_n\text{TaS}_2$ with $n \approx 1$ on the basis of analogy with chalcogenides of a similar type with layered composite crystal structure. Figure 2(b) shows the electron diffraction pattern of “ BiVS_3 ”. It is also clear that “ BiVS_3 ” has a similar layered composite crystal structure and should be formulated as $(\text{BiS})_n\text{VS}_2$. Other bismuth-containing ternary chalcogenides with the approximate composition of $\text{Bi:T:X} = 1:1:3$ should also be formulated as $(\text{BiX})_n\text{TX}_2$. These $(\text{BiX})_n\text{TX}_2$ -type chalcogenides seem to consist of a BiX layer two atoms thick and a TX_2 sandwich three atoms thick stacked alternately, by analogy with other $(\text{MS})_n\text{TS}_2$ -type chalcogenides whose crystal structures were determined. Very recently Wulff *et al.* have reported the structure analysis of “ BiTaS_3 ” [12]. They have obtained the formula $(\text{BiS})_{1.08}\text{TaS}_2$ for the sulphide. The TaS_2 part takes a trigonal prismatic coordination like 2H-TaS_2 . The BiS subcell seems to have a distorted NaCl-type structure two atoms thick.

The periodic length in the stacking direction for the bismuth-containing ternary chalcogenides found in our work can be tentatively obtained using the interlayer distance of $00l$ diffraction lines. Table 1 shows the data. The periodic length of the $(\text{BiX})_n\text{TX}_2$ -type chalcogenides is in the range 11–12 Å. On the other hand, the periodic length of BiT_2X_5 -type chalcogenides is in the range 17–18 Å. The difference in periodic length between BiT_2X_5 and $(\text{BiX})_n\text{TX}_2$ coincides well with the periodic length in the layer-stacking direction of the corresponding dichalcogenides as shown in Table 1. Therefore these BiT_2X_5 -type chalcogenides seem to be formulated as $(\text{BiX})_n(\text{TX}_2)_2$ and to

TABLE 1

Periodic length (Å) of $(\text{BiX})_n\text{TX}_2$ and $(\text{BiX})_n(\text{TX}_2)_2$ in the layer-stacking direction

Sample	Periodic length for various T			
	Ti	V	Nb	Ta
I $\equiv (\text{BiS})_n\text{TS}_2$	11.308	11.270	11.511	11.557
II $\equiv (\text{BiSe})_n\text{TSe}_2$	11.838	11.920	12.100	12.162
III $\equiv (\text{BiS})_n(\text{TS}_2)_2$	16.991	—	17.438	17.518
IV $\equiv (\text{BiSe})_n(\text{TSe}_2)_2$	—	—	18.326	—
TS ₂	5.69 ^b	5.73 ^b	5.97 ^c	6.01 ^b
TSe ₂	6.01 ^b	6.10 ^d	6.25 ^b	6.33 ^b
III-I	5.683	—	5.927	5.961
IV-II	—	—	6.226	—

^aThe value of the periodic length seems to correspond to the length of a BiX layer two atoms thick and a TX₂ sandwich three atoms thick for samples I and II, and a BiX layer two atoms thick and two TX₂ sandwiches three atoms thick for samples III and IV [10, 11, 15] (see also the present work).

^bJCPDS numbers: TiS₂, 15-853; VS₂, 36-1139; TaS₂, 2-137; TiSe₂, 30-1383; NbSe₂, 18-923; TaSe₂, 18-1309.

^cAfter ref. 18.

^dAfter ref. 19.

consist of a layer of BiX two atoms thick and two adjacent TX₂ sandwiches three atoms thick stacked alternately.

With ordinary XRD measurement of these chalcogenides using the counterdiffractometer method, it was rather difficult in our earlier work to obtain an XRD pattern free from the extreme preferred orientation. We have recently found that by treatment with an adhesive agent it is possible to depress effectively the preferred orientation. Figure 1(b) shows the XRD pattern after treatment with the adhesive agent. With the assistance of electron diffraction it is possible to index the pattern and obtain the lattice constants of both subcells. The indices are shown in Fig. 1(b) and the lattice constants are presented in Table 2. The lattice constants and number n are a little bit different from those reported by Wulff *et al.* [12] but are basically consistent with their results. The lattice constants of $(\text{BiSe})_{1.09}\text{TaSe}_2$ and $(\text{BiS})_{1.08}(\text{TaS}_2)_2$ were obtained in a similar manner and are also presented in Table 2. The details of powder XRD data and results of electric resistivity measurements will be reported elsewhere.

It is very important to know the character of the structural and electronic interaction between the MX layer and TX₂ sandwich in the $(\text{MX})_n\text{TS}_2$ - or $(\text{MX})_n(\text{TX}_2)_2$ -type chalcogenides with layered composite crystal structure. Wiegiers *et al.* reported for a few $(\text{MS})_n\text{TS}_2$ -type sulphides, through measurement of electrical transport properties, that the electron is transferred from the MS layer into the TS₂ layer and the extent of electron transfer depends on the elements M and T. For example, 0.88 electron per niobium atom is transferred from lanthanum to niobium in $(\text{LaS})_{1.14}\text{NbS}_2$ [20], 0.93–0.96

TABLE 2
Lattice constants of Bi-Ta group ternary chalcogenides with layered composite crystal structure

Chalcogenide	Subcell	Crystal system	a (Å)	b (Å)	c (Å)	β (deg)
(BiS) _{1.09} TaS ₂	BiS	Orthorhombic	5.727(1)	6.088(3)	23.114(6)	
	TaS ₂	Orthorhombic	5.727(1)	3.308(2)	23.114(6)	
(BiSe) _{1.09} TaSe ₂	BiSe	Orthorhombic	5.976(3)	6.313(6)	24.324(6)	
	TaSe ₂	Orthorhombic	5.976(3)	3.435(3)	24.324(6)	
(BiS) _{1.08} (TaS ₂) ₂	BiS	Monoclinic	5.744(2)	6.123(3)	17.545(3)	93.17(3)
	TaS ₂	Monoclinic	5.745(2)	3.313(2)	17.545(3)	93.18(2)

electron per niobium atom is transferred from cerium to niobium in $(\text{CeS})_{1.16}\text{NbS}_2$ [5], and 0.2 electron per tantalum atom from lead to tantalum in $(\text{PbS})_{1.13}\text{TaS}_2$ [6]. The electron transfer from the MX layer to the TX_2 sandwich will have some influence on the TX_2 sandwich. Therefore the physical and chemical properties of the TX_2 sandwich in the ternary chalcogenide with composite crystal structure will be somewhat different from those in the binary system.

We have found that the interface of two adjacent TX_2 sandwiches in $(\text{MX})_n(\text{TX}_2)_2$ has the character of a van der Waals gap and the periodic

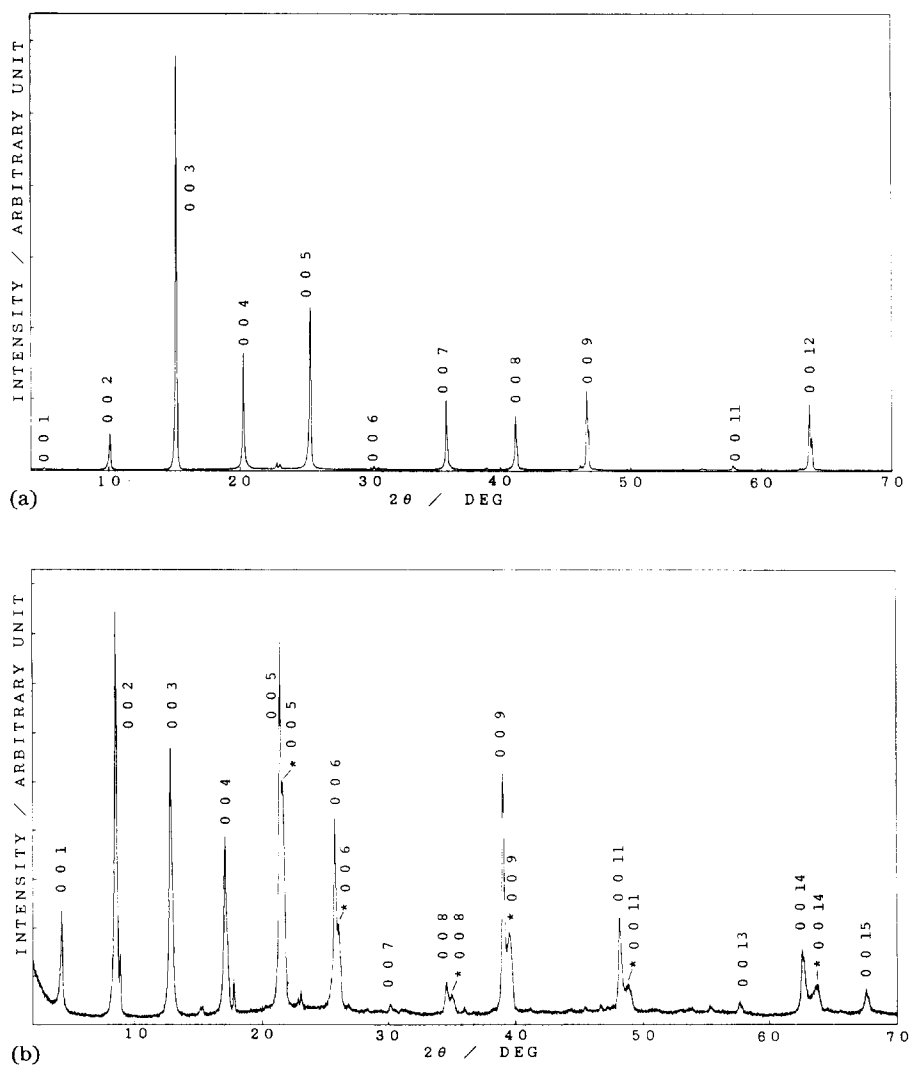


Fig. 3. (a) Powder XRD pattern of $(\text{BiS})_{1.08}(\text{TaS}_2)_2$ with preferred orientation; (b) after treatment with hydrazine monohydrate; (c) after treatment with aqueous CaCl_2 solution.

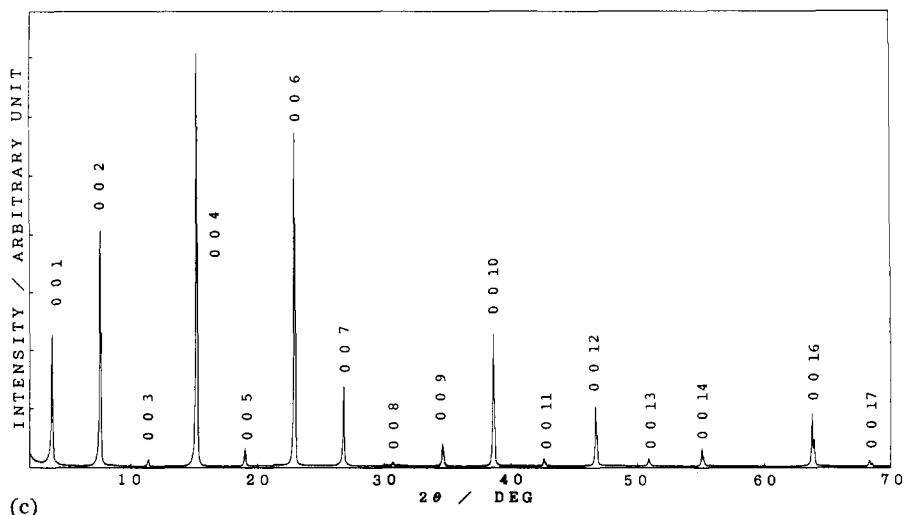


Fig. 3. (continued)

length becomes longer when treated with hydrazine monohydrate [13, 15, 16]. Figure 3(a) shows the XRD pattern of $(\text{BiS})_{1.08}(\text{TaS}_2)_2$ with preferred orientation. When the sulphide was treated with hydrazine monohydrate, the product shows the XRD pattern in Fig. 3(b). We can observe in the pattern two main products whose periodic lengths are 20.73 Å (without an asterisk in front of the indices) and 20.51 Å (with an asterisk in front of the indices). When $(\text{BiS})_{1.09}\text{TaS}_2$ was treated with hydrazine monohydrate, no change in the XRD pattern was observed. Therefore it is clear that a guest species (probably hydrazinium ion) was intercalated into the interface of two adjacent TaS_2 sandwiches and not into the interface of the BiS layer and TaS_2 sandwich. At present, the origin of two kinds of intercalated material is not clear. Some difference in the solvation of the cation may be the reason. Although intercalation using hydrazine is a convenient method, it is not suitable for quantitative discussion because quantitative analysis of intercalated species is not easy in this case. For quantitative analysis, intercalation with hydrated alkaline or alkaline earth ion is more appropriate.

When $(\text{BiX})_n(\text{TX}_2)_2$ treated with hydrazine monohydrate was further treated with aqueous CaCl_2 solution, the periodic length in the layer-stacking direction became about 3 Å longer. Figure 3(c) shows the XRD pattern of the product in the case of $(\text{BiS})_{1.08}(\text{TaS}_2)_2$. The difference in periodic length between $(\text{BiS})_{1.08}(\text{TaS}_2)_2$ and the product treated with aqueous CaCl_2 solution is 5.7 Å. This value is consistent with that when hydrated calcium ion is intercalated into binary TaS_2 (5.8 Å) [21]. These results suggest that the cation exchange reaction (from hydrazinium ion to hydrated calcium ion) occurred in the van der Waals gap of the sulphide. It is known that for each dichalcogenide the maximum amount of intercalated hydrated alkaline or alkaline earth metal ion (corresponding to the negative dichalcogenide layer

charge density) depends on the redox potential (electronic structure) of the host lattice, which must be more positive than that of $\text{H}_2\text{:H}^+$ [22]. It is expected that the electron donated from the MX layer to the TX_2 sandwich will increase the negative charge density of the TX_2 sandwich and decrease the number of intercalated hydrated alkaline or alkaline earth ions. It may be possible to determine the number of electrons transferred from the MX layer to the TX_2 sandwich by determining the decrease in intercalated hydrated alkaline or alkaline earth metal ions, and such a method may supply another way to find the electronic interaction between MX and TX_2 layers.

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