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# Structural Properties and Interlayer Interaction in $(MX)_x TX_2$-Type Ternary Chalcogenides with Layered Composite Crystal Structure

Yoshito Gotoh [a], Junji Akimoto [a] & Mitsuko Onoda [b]

[a] National Institute of Materials and Chemical Research, Higashi 1-1, Tsukuba, Ibaraki, 305-8565, Japan

[b] National Institute for Research in Inorganic Materials, Namiki 1-1, Tsukuba, Ibaraki, 305-0044, Japan

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# Structural Properties and Interlayer Interaction in $(MX)_xTX_2$-Type Ternary Chalcogenides with Layered Composite Crystal Structure

YOSHITO GOTOH[a], JUNJI AKIMOTO[a] and MITSUKO ONODA[b]

[a]*National Institute of Materials and Chemical Research, Higashi 1–1, Tsukuba, Ibaraki 305–8565, Japan and* [b]*National Institute for Research in Inorganic Materials, Namiki 1–1, Tsukuba, Ibaraki 305–0044, Japan*

Structural properties and interlayer interaction in mutually incommensurate $(MX)_xTX_2$-type ternary chalcogenides with layered composite crystal structure have been investigated on the basis of structure analysis including superspace group symmetry. It has been confirmed that charge transfer between substructures occur in $(LaS)_xTiS_2$ from the results of Ti *K* XANES spectra. The lattice stability and interlayer interaction in the $(MX)_xTX_2$ have been discussed with the use of bond-valence-sum (BVS) method by considering modulated structure analysis.

*Keywords:* composite crystal; modulated structure; interface modulation

## INTRODUCTION

The $(MX)_xTX_2$-type ternary chalcogenides ( M = Pb, Sn, Bi, Sb, rare earth elements; T = Ti, V, Nb, Ta, Cr; X = S, Se; $x$ = 1.07-1.25 ) are composed of three-atom-thick $TX_2$ sandwiches and two-atom-thick MX double layers, alternately stacked[1]. In general, the $TX_2$ sandwiches and the MX double layers are mutually incommensurate because the ratio of the in-plane lattice constants of the average structures of the two subsystems is irrational. The mutually incommensurate structure is also called composite crystal because more than two sets of diffraction vectors are observed. It is possible to describe the

composite crystal as modulated structure including intersubstructure interaction with the use of $(3+d)$-dimensional superspace group[2-4].

In the $(MX)_xTX_2$ series with layered substructures, interlayer interactions such as interface modulation and charge transfer show attractive properties. In the present study, we will investigate the structural properties and interlayer interaction in some $(MX)_xTX_2$-type layered composite crystal structures with superspace group symmetry.

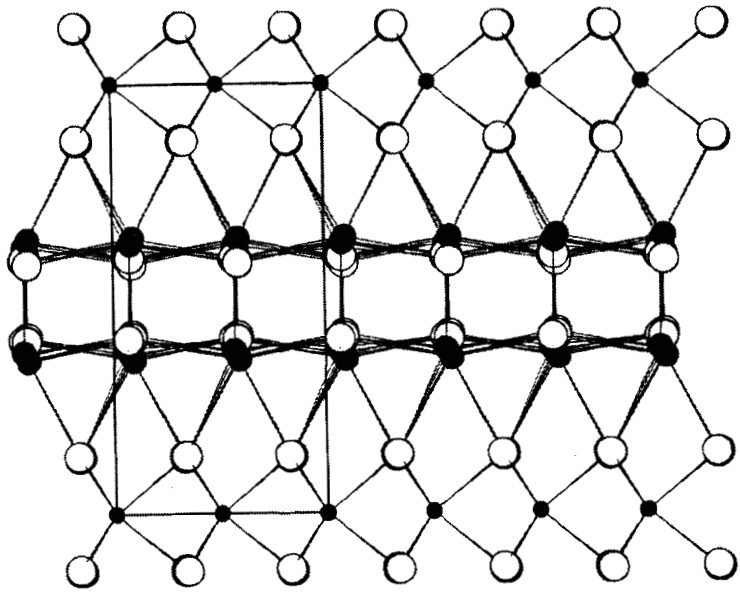

FIGURE 1 Projection of the modulated structure of $(SnS)_{1.17}NbS_2$ along the mutually incommensurate direction.

## RESULTS AND DISCUSSION

The projection of the incommensurately modulated structure of $(SnS)_{1.17}NbS_2$ is illustrated in Fig. 1. It is clearly seen that all of the Sn atoms in strongly

modulated SnS double layers are protruded toward the S atoms in the $NbS_2$ sandwiches[5]. Therefore we can expect the charge transfer from the MS substructure to the $TS_2$ one and the variety of structural interaction between substructures.

In the present work, XANES spectra at Ti *K*-edge have been obtained for selected compounds of $(MS)_xTiS_2$ series in Fig. 2. It can be seen qualitatively that the valence state of Ti in $(LaS)_xTiS_2$ is considerably lower than those in $(PbS)_{1.18}TiS_2$ and $TiS_2$. Then, it is confirmed that the charge transfer between La in LaS double layers to Ti in $TiS_2$ sandwiches undoubtedly occur. The slight difference between the spectra of $(PbS)_{1.18}TiS_2$ and $TiS_2$ may suggest that a small amount of charge is transferred to $TiS_2$ sandwiches in $(PbS)_{1.18}TiS_2$.

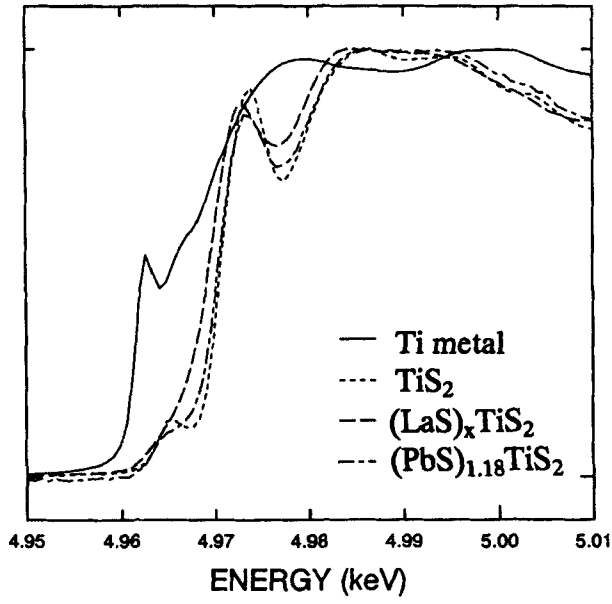


FIGURE 2 XANES spectra at Ti *K*-edge for some selected compounds in $(MS)_xTiS_2$ series.

To estimate the strength of the interlayer interaction in $(MS)_xTS_2$ series, we have calculated the bond-valence-sum (BVS) at the interface between the M atom in the MS substructure and S atom in the $TS_2$ one. The interface BVS of the $i$-th atom in the $\mu$-th subsystem $V^{int.}{}_{i\mu}(t)$ is described as

$$V^{int.}{}_{i\mu}(t) = \Sigma_{\nu \neq \mu} \Sigma_j s_{i\mu j\nu}(t) = \Sigma_{\nu \neq \mu} \Sigma_j \Sigma_g \exp[\{r_0 - r_{i\mu j\nu}(t, g)\} / B]$$

where $s_{i\mu j\nu}$ and $r_{i\mu j\nu}$ are the bond-valence and the interatomic distance between the $i$-th atom in the $\mu$-th substructure and $j$-th atom in the $\nu$-th substructure, respectively. The $t$ is the internal parameter and $g$ is the symmetry operations of $j$-th atom in $(3+d)$-dimensional superspace. The parameter $r_0$ and $B$ are selected from ref. [6]. As we can see clearly in Table I, the interface interaction between the MS double layers and the $TS_2$ sandwiches in $(LaS)_xTS_2$ is considerably stronger than those in $(PbS)_xTS_2$ and $(SnS)_xTS_2$. From the results of modulated structure analysis[5,7,8], it has been revealed that La atom in the LaS is coordinated by mainly three S atoms in the $TS_2$, whereas Pb and Sn atoms are coordinated by mainly two S atoms in the $TS_2$. In the $(MS)_xTS_2$ series, then, $(LaS)_xTS_2$ show the most stable stacking sequences of substructures, compared with $(PbS)_xTS_2$ or $(SnS)_xTS_2$.

It should be noted that there is the correlation between the values of superconducting transition temperature $T_c$ and the periodic distance $I_c$ along stacking direction or $V^{int.}{}_{M}(t)$ in $(MS)_xNbS_2$ series. The degree of charge transfer and structural modulation seem to affect the superconductivity of $(MS)_xNbS_2$ series. In fact, the structural modulation in the $NbS_2$ sandwiches in $(LaS)_{1.14}NbS_2$ is slightly larger than that in the $NbS_2$ ones in $(SnS)_{1.17}NbS_2$. The modulation amplitude of the interatomic distances between Nb atoms of the $NbS_2$ sandwiches in $(LaS)_{1.14}NbS_2$ and $(SnS)_{1.17}NbS_2$ are 0.4 Å and 0.15 Å, respectively.

Succeeding our first report of $(PbS)_{1.12}VS_2$[9], all of the $(MS)_xVS_2$ compounds, in contrast to our expectation, do not show superconductivity nor

metallic properties[1]. This is because the structure of the $VS_2$ sandwiches in $(MS)_xVS_2$ compounds are strongly modulated. It should be noted that the average structure of the $VS_2$ sandwiches in $(MS)_xVS_2$ are quite similar to the binary $VS_2$ which is metastable compound with metallic property. We can say that displacive modulation in the $VS_2$ sandwiches in $(MS)_xVS_2$ is considerably larger than those in the $NbS_2$ in $(MS)_xNbS_2$ and influence the electronic structure of $(MS)_xVS_2$ essentially.

TABLE I The periodic distance $I_c$ along stacking direction, superconducting transition temperature $T_c$ and the average values of the interface BVS of the M atom in the MS substructure $V^{int.}{}_M(t)$ for some selected $(MS)_xNbS_2$ and $(MS)_xVS_2$ compounds.

| Compound | $I_c$ Å$^{-1}$ | $T_c$ K$^{-1}$ | Average $V^{int.}{}_M(t)$ |
|---|---|---|---|
| $(PbS)_{1.14}NbS_2$ | 11.90[1] | 2.72[1] | |
| $(SnS)_{1.17}NbS_2$ | 11.76[1] | 2.76[1] | 0.24 |
| $(BiS)_{1.11}NbS_2$ | 11.50[10] | 0.42[11] | |
| $(LaS)_{1.14}NbS_2$ | 11.52[8] | –[1] | 0.93[8] |
| $(PbS)_{1.12}VS_2$ | 11.83[7, 9] | –[9] | 0.30 |
| $(SnS)_xVS_2$ | unknown | | |
| $(BiS)_{1.16}VS_2$ | 11.31[12] | – | |
| $(LaS)_{1.18}VS_2$ | 11.15[13] | – | ~1.0 |

## CONCLUSIONS

In the present study, we have investigated the structural properties and interlayer interaction in $(MX)_xTX_2$-type ternary chalcogenides with layered composite crystal structure. It has been confirmed that the charge transfer between La in the LaS double layers to Ti in the $TiS_2$ sandwiches undoubtedly occur in $(LaS)_xTiS_2$. To estimate the strength of the interlayer interaction in

**$(MS)_xTS_2$ series, we have calculated the bond-valence-sum at the interface between the substructures. In the $(MS)_xTS_2$ series, $(LaS)_xTS_2$ show the most stable stacking sequences of substructures, compared with $(PbS)_xTS_2$ or $(SnS)_xTS_2$.**

## *References*


[1] G. A. Wiegers, *Prog. Solid State Chem.*, **24,** 1 (1996) and references therein.
[2] A. Janner and T. Janssen, *Acta Crystallogr.*, **A36,** 408 (1980).
[3] K. Kato, *Acta Crystallogr.*, **B46,** 39 (1990).
[4] A. Yamamoto, *Acta Crystallogr.*, **A48,** 476 (1992).
[5] Y. Gotoh, J. Akimoto, Y. Oosawa and M. Onoda, in *Aperiodic '97; Proceedings of the International Conference on Aperiodic Crystals,* edited by M. de Boissieu, J. L. Verger-Gaugry and R. Currat (World Scientific, Singapore, 1999), Chap. 3, p.309.
[6] I. D. Brown and D. Altermatt, *Acta Crystallogr.*, **B41,** 244 (1985).
[7] M. Onoda, K. Kato, Y. Gotoh and Y. Oosawa, *Acta Crystallogr.*, **B46,** 487 (1990).
[8] S. van Smaalen, *J. Phys.: Condens. Matter.*, **3,** 1247 (1991).
[9] Y. Gotoh, M. Goto, K. Kawaguchi, Y. Oosawa and M. Onoda, *Mat. Res. Bull.*, **25,** 307(1990).
[10] Y. Gotoh, J. Akimoto, M. Goto, Y. Oosawa and M. Onoda, *J. Solid State Chem.*, **116,** 61 (1995).
[11] A. Nader, A. Briggs and Y. Gotoh, *Solid State Commun.*, **101,** 149 (1997).
[12] Y. Gotoh, J. Akimoto, Y. Oosawa and M. Onoda, *Jpn. J. Appl. Phys.*, **34, L** 1662 (1995).
[13] K. Friese, O. Jarchow and K. Kato, *Z. Kristallogr.*, **212,** 648 (1997).