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# Local structure and defect chemistry of $[(SnSe)_{1.15}]_m(TaSe_2)$ ferecrystals – A new type of layered intergrowth compound

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## ABSTRACT

The atomic structure of the family of ferecrystals $[(SnSe)_{1.15}]_m(TaSe_2)$ ($m = 1$, 3, and 6) was investigated by means of transmission electron microscopy. The tantalum in the $TaSe_2$ layers was observed to have trigonal prismatic coordination similar to that found in the 2*H* polytype of bulk $TaSe_2$. The structure of the SnSe constituent was found to be similar to that of orthorhombic α-SnSe. In the compounds with $m = 1$ and $m = 3$, regions with a local ordering of the layers along a commensurate axis, similar to the ordering in conventional misfit layer compounds, were observed. However, on a longer range the ferecrystals were found to exhibit a turbostratically disordered structure. Stacking defects were occasionally found in the samples in which a layer is interrupted and the surrounding layers are bent around these defects, while maintaining abrupt interfaces instead of interdiffusing. Volume defects were found in one sample of $[(SnSe)_{1.15}]_1(TaSe_2)_1$ in which a SnSe layer locally substitutes a part of a $TaSe_2$ layer without interrupting the surrounding layers.

## 1. Introduction

Ferecrystals are a new type of layered intergrowth compounds with a complex crystal structure and remarkable physical properties such as an ultra-low thermal conductivity [1–5]. A ferecrystal consists of two different types of layers, which are alternately stacked in adjustable sequences. The two types of layers consist of different materials, each with a different crystal structure of non-equivalent lattice parameters, which results in a misfit between the two types of layers. Both materials are highly oriented along the stacking direction, i.e. there is a certain crystallographic axis in each layer, which points parallel to the stacking direction. Within the layer plane the two materials show a turbostratic disorder, which means that the crystallites are randomly rotated around the stacking direction and randomly translated perpendicular to the stacking direction [5–8]. This special disorder is suggested to be the decisive factor for the ultra-low thermal conductivity measured parallel to the stacking direction in several types of ferecrystals [1–5]. Adjusting the thicknesses of individual layers and their stacking sequence allows for tuning of the physical properties of the ferecrystals [6]. For a correct interpretation and prediction of the ferecrystal physical properties it is essential to know the atomic structure, including grain size and possible defects. Furthermore, knowledge about the atomic structure can help to understand the formation processes during the synthesis of the ferecrystals and the stabilization mechanism of these materials, which are still both unknown. Whereas X-ray diffraction (XRD) studies of ferecrystals allow for the determination of their average structure [5–8], transmission electron microscopy (TEM) gives additional local information about the material on the atomic scale. Aberration corrected high-resolution transmission electron microscopy (HRTEM) imaging has been a powerful tool for analyzing the crystal structure and lattice imperfections in conventional misfit layer compounds (MLCs) [9]. Thus, we applied aberration corrected HRTEM as well as high-resolution scanning transmission electron microscopy (HRSTEM) to reveal the complex local atomic structure of the ferecrystals. This is the first extensive HRTEM study to investigate the atomic structure of the ferecrystals $[(SnSe)_{1.15}]_m(TaSe_2)$ with $m = 1$, 3, and 6.

## 2. Crystal structure

Ferecrystals and MLCs are described by the general formula $[(MX)_{1+x}]_m(TX_2)_n$, where compounds with $X$ = Se or S, $M$ = Sn, Ca,

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Ba, Bi, Sr, Sb, Pb, or a rare earth metal, and $T$ = Ta, W, Nb, Co, Rh, Cr, V, Mo, Yb or Ti have been reported [1,7–14]. The $MX$ constituent within these composite crystals usually has a distorted rocksalt structure. The other constituent, denoted by $TX_2$, contains $X$–$T$–$X$ trilayers with a hexagonal transition metal dichalcogenide structure. The index $1+x$ is derived from the non-rational ratios of the in-plane periodicities of the $MX$ and $TX_2$ layers in the ferecrystals. For $[(SnSe)_{1.15}]_m(TaSe_2)$ it has been determined as 1.15 using XRD methods [6]. The indices $m$ and $n$ indicate the number of $MX$ and $TX_2$ layers in the repeat unit. In this context one 'layer' of $MX$ stands for two atomic monolayers, and one 'layer' of $TX_2$ stands for three atomic monolayers ($X$–$T$–$X$). The crystal structures of bulk binary 2$H$-$TaSe_2$ and α-SnSe as reported in [16,17] are illustrated in Fig. 1. Binary $TaSe_2$ has a layered structure in which slabs of Se–Ta–Se trilayers are separated by van der Waals (v.d.W.) gaps. It is known that $TaSe_2$ forms many polytypes, e.g. 1$T$, 2$H$, 3$R$, $4H_{(a)}$, $4H_{(b)}$, and 6$R$ [16]. In 1$T$-$TaSe_2$ the Ta atoms are octahedrally coordinated by the Se atoms, whereas in other polytypes a trigonal prismatic coordination or both, trigonal and octahedral coordination are realized. One of the most common polytypes of $TaSe_2$ at room temperature (RT) is 2$H$-$TaSe_2$ (Fig. 1a). Its crystal structure is described by the hexagonal space group $P6_3/mmc$ with trigonal prismatic coordination of the Ta atoms. Bulk binary α-SnSe at room temperature is described by the orthorhombic space group $Pnma$ (Fig. 1b) [17]. $TaSe_2$ and SnSe in the ferecrystals are highly textured: $TaSe_2$[00.1] and SnSe[100] both point parallel to the stacking direction [6]. The two subsystems SnSe and $TaSe_2$ possess different in-plane periodicities. There are two possible in-plane orientations of $TaSe_2$ relative to SnSe in which they are almost commensurate: SnSe[011] || $TaSe_2$[−11.0], and SnSe[0−11] || $TaSe_2$[−11.0]. These two orientations are shown in Fig. 1 inside the α-SnSe [100] projection, with dotted parallelograms indicating the $TaSe_2$ unit cell viewed along stacking direction. In conventional crystalline MLCs both sublattices distort resulting in a perfect commensurate relationship in one of these directions [9–14]. They are incommensurate in all other directions within the layer plane. X-ray diffraction studies and previous TEM studies have shown that in ferecrystals there is a random variation in azimuthal orientations between the different layers, whereas a common constant axis, i.e. SnSe[100] || $TaSe_2$[00.1], is present in the stacking direction (turbostratic disorder) [1,6]. Therefore, the name *ferecrystals*, from the Latin word "*fere*" meaning *almost*, has been introduced for these materials [6]. This turbostratic disorder distinguishes ferecrystals from the well-known conventional MLCs. Conventional MLCs exhibit a strict rotational relation between their constituent layers [9–14]. The reason for this are the different synthesis approaches used for MLCs and ferecrystals: MLCs are synthesized by traditional high-temperature vapor transport methods at 700 °C or higher [10–13], while ferecrystals are synthesized using designed amorphous precursors which are deposited at RT and subsequently annealed at temperatures of 300 °C–400 °C [1–8]. As a result, conventional MLCs are crystalline, thermodynamically stable compounds [10–14] and can be described by means of the superspace concept [15], whereas ferecrystals are metastable with local free energy minima at integer $m$ and $n$ and exhibit a turbostratically disordered structure [1,7,8]. The composition of MLCs is usually confined to $m = 1$ and $n$ = 1, 2 or rarely 3 [10–12], whereas ferecrystals can also be synthesized with larger $m$ and $n$ values [1,4–8].

Crystal structures of MLCs with the composition $[(SnSe)_{1.15}]_m(TaSe_2)$ have not been reported yet. However, there are studies on a $[(SnSe)_{1.16}]_1(NbSe_2)$ MLC [13]. Since 2$H$-$NbSe_2$ and 2$H$-$TaSe_2$ are configurationally isotypic structures [18], it is worth taking a closer look at the well-investigated MLC $[(SnSe)_{1.16}]_1(NbSe_2)$ in order to get information about the possibly similar structure of the $[(SnSe)_{1.15}]_m(TaSe_2)$ ferecrystals. Two projections of the structure model of the MLC $[(SnSe)_{1.16}]_1(NbSe_2)$ as reported in [13] are shown in Fig. 2. The crystal structures of the SnSe and $NbSe_2$ layers in this MLC closely resemble the structures of the respective bulk binary compounds. However, the SnSe subsystem is distorted compared to the bulk structure to create a common crystallographic axis (Fig. 2). This results in a nearly square in-plane unit cell of the SnSe layers instead of the rectangular in-plane unit cell reported for bulk α-SnSe [13]. A square in-plane unit cell of the SnSe subsystem was also found for the $[(SnSe)_{1.15}]_m(TaSe_2)$ ferecrystals by XRD analysis [6]. Interestingly, in bulk SnSe a temperature-dependent distortion occurs as the low-temperature orthorhombic α-SnSe phase continuously converts to the high-temperature tetragonal β-SnSe phase as temperature is increased [17]. In the MLC $[(SnSe)_{1.16}]_1(NbSe_2)$ all of the SnSe and $NbSe_2$ layers are

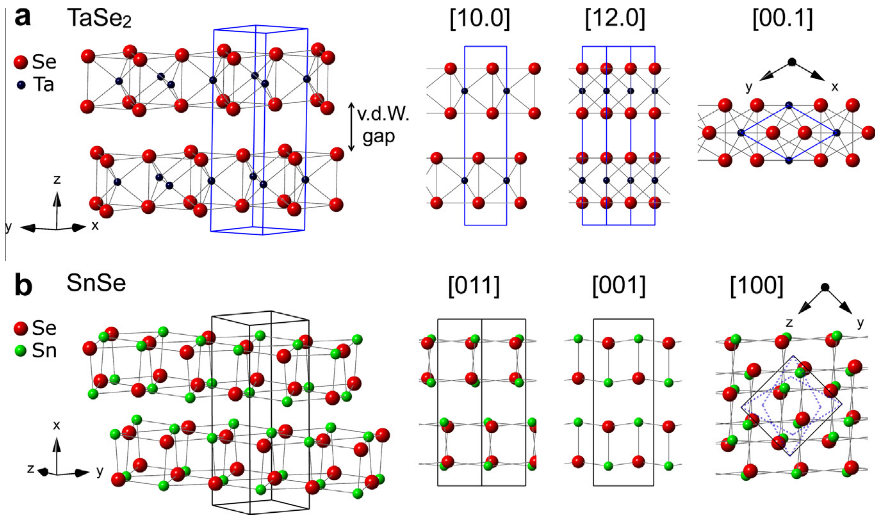

**Fig. 1.** Three-dimensional perspective views and different projections of the crystal structure of: (a) binary 2$H$-$TaSe_2$ (space group $P6_3/mmc$) with projections along $TaSe_2$[10.0], [12.0] and [00.1] according to [16] and (b) binary α-SnSe at RT (space group $Pnma$) with projections along α-SnSe[011], [001] and [100] according to [17]. In a ferecrystal the directions $TaSe_2$[00.1] and SnSe[100] are both parallel to the stacking direction. Inside the drawing of the α-SnSe[100] projection two possible orientations of the $TaSe_2$ unit cell projected along 2$H$-$TaSe_2$[00.1] are shown in dotted lines to point out the two azimuthal orientations of the $TaSe_2$ lattice relative to the SnSe lattice, in which both compounds are almost commensurate. They are incommensurate in all other in-plane directions.