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Nature of low dimensional structural modulations and relative phase stability in Re$_x$Mo(W)$_{1-x}$S$_2$ transition metal dichalcogenide alloys


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We report on the various types of Peierls like two dimensional structural modulations and relative phase stability of 2H and 1T poly-types in the Re$_x$Mo$_{1-x}$S$_2$ and Re$_x$W$_{1-x}$S$_2$ alloy system. Theoretical calculation predicts a polytype phase transition cross over at $\sim$50 at. % of Mo and W in ReS$_2$ in both monolayer and bulk form, respectively. Experimentally, two different types of structural modulations at 50% and a modulation corresponding to trimerization at 75% alloy composition are observed for Re$_x$Mo$_{1-x}$S$_2$ and only one type of modulation is observed at the 50% Re$_x$W$_{1-x}$S$_2$ alloy system. The 50% alloy system is found to be a suitable monolithic candidate for metal semiconductor transition with minute external perturbation. ReS$_2$ is known to be in the 2D Peierls distorted 1Td structure and forms a chain like superstructure. Incorporation of Mo and W atoms into the ReS$_2$ lattice modifies the metal-metal hybridization between the cations and influences the structural modulation and electronic properties of the system. The results offer yet another effective way to tune the electronic structure and poly-type phases of this class of materials other than intercalation, strain, and vertical stacking arrangement. Published by AIP Publishing.

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INTRODUCTION

Atomically thin transition metal dichalcogenides (TMDs) are considered to be the next generation platform for future electronics and offer numerous novel device applications based on their unique excitons, spin, and valley properties. The most explored members in the family i.e., MoS$_2$ and WS$_2$ possess a direct band gap in the monolayer form but undergo transition to an undesirable indirect band gap material for a number of layers two and more. The stable crystal structure of MoS$_2$ and WS$_2$ is 2H (space group 194: P6$_3$/mmc) with a direct band gap of 1.88 and 1.9 eV, respectively, for the monolayer. On the other hand for ReS$_2$, the band gap remains direct even in the bulk form due to weak interlayer van der Waals and electronic coupling. The stable crystal structure of ReS$_2$ is 2D-Peierls distorted 1T$_d$ (space group 2: P1) where chains made of Re$_4$ clusters form the quasi two dimensional superstructure with a band gap of 1.55 eV for the monolayer. The metastable unmodulated 1T phase of MoS$_2$ is demanding due to its metallicity that is indispensable for carrier transport, injection and in the modulated 1T$_d$ form shows excellent hydrogen evolution activity (HER). The most stable configuration in the modulated 1T form of MoS$_2$ and WS$_2$ is a 2a $\times$ a superstructure as in the case of ReS$_2$. These superstructures are reported to have a band gap of 0.1–0.2 eV and 0.14 eV, for MoS$_2$ and WS$_2$, respectively. Throughout the text “1T$_d$” is used to represent the chain like superstructure in all cases.

As already mentioned above, the 1T and modulated 1T$_d$ poly-types of both MoS$_2$ and WS$_2$ are metastable. However, due to their useful properties, various attempts have been made to stabilize these poly-type structural forms. Most of the reports are based on intercalation method using alkali metals, e.g., Li, and K where structural transitions between various poly-types take place during loading of alkali metals at the interlayer spacing with the end application as rechargeable batteries. Among various reports, Li and alkali metal intercalation was reported to stabilize the 1T$_d$ form of both MoS$_2$ and WS$_2$ through hybridization between metals forming a quasi 2D chain. Li intercalation of MoS$_2$ powders in water formed a 2a $\times$ 2a superstructure as confirmed by X-ray diffraction. On the other hand, K intercalation stabilizes two different forms of the modulated structure of MoS$_2$ depending on the K concentration, i.e., trimerization of Mo with superstructure $\langle a, 3 \times a, 3 \rangle$ (x $\approx$ 0.3) and tetramerization of Mo with superstructure $2a \times 2a$ (x $\leq$ 0.3). The presence of two different superstructures in this case was confirmed by a scanning tunneling microscopy (STM) technique. Relative stability of various types of superstructure modulations in Li intercalated MoS$_2$, i.e., LiMoS$_2$ was previously investigated by first principles calculations. It was found that the $(2a \times 2a)$ superstructure formed by tetramerization of cations was more stable (by 0.5 eV) compared to trimerized $(a, 3 \times a, 3)$ structural modulation. This opened a band gap of about 1 eV. However, later studies based on both experimentation and theory revealed that it is $2a \times a$ type periodicity forming chain like structure the most stable modulated form of MoS$_2$. It was also pointed out that a
charge density wave (CDW) phenomenon was at the origin of such structural modulation that was associated with a partially nested Fermi surface and the stabilization is localized around the Fermi level. The destabilization due to strain occurs mainly in the 3p of the Sulphur part which is compensated by electronic stabilization in the 3d of the Molybdenum part. Although energetically least stable, the trimerized modulated structure was predicted to be the thinnest ferroelectric material.24

There is a lot of interest in the community to understand and control various structural poly-types of monolayer TMDs by different means for their efficient utilization in energy, optoelectronics, and novel devices apart from immense interest in fundamental science.3–8,23–26 Among recent reports, intermediate steps of structural transition from trigonal prismatic 2H to octahedral 1T phases have been studied by electron microscopy.20 Three different types of distortions or sub-structures are observed by HRTEM as transient states involving a shear mechanism. These are (2 × 1), (2 × 2) and (3 × 1) and the combinations between them. The d electron system for various superstructures changes as follows, d^2 for 2 × 1 (zigzag clustering), d^d for (3 × 1) (ribbon chain clustering), and d^d for 2 × 2 (diamond chain clustering). In another report, Li intercalated MoS2 shows the presence of a bi-phase structure, i.e., both 2H and combination of 1T and 1Td (2 × 1).3 Different structural phases form coherent interface at the boundary. The structure changes from 1Td to 1T by e− beam exposure. The transition from 1Td to 2H is a multi-step process and goes via different metastable structures. In the case of WS2, 1T is found to be more stable than MoS2. After annealing at different temperatures, the structure does not transform to the 2H phase completely and defects are believed to stabilize the residues of the 1T phase.

Formation of a metastable tetramer diamond unit along with zigzag chains with a new orientation formed by e− beam irradiation of the zigzag 1T phase of Li intercalated WS2 has been reported.17 In the 1T zigzag starting phase, both tetramer and triangular clusters were present. The presence of triangular clusters in K intercalated 2H-MoS2 has already been predicted theoretically18 and experimentally confirmed.29 Theoretically, the energy difference between the two meta-stable structures is found to be 0.1 eV per formula unit. The stabilization of the local tetramer in the present case is due to the electronic charging effect. It was argued that the observed distortion is not a charge density wave (CDW) phenomenon but rather Jahn Teller (JT) type introduced by a weakening of the W-S bonds leading to electronic instability. However, ReS2 is not a Jahn Teller type as argued before because the gap opens in the d bands at the Fermi level as confirmed by modern first principles calculations.10,13,29

Thus, in the present report, stabilization of 1Td structural form of Re0.5X0.5S2 and Re0.5W1−xS2 alloys has been explored by both theory and experiment. Theoretically, a structural cross over is observed at approximately 50% alloy composition in both monolayer and bulk form. In this context, the stability of the metallic 1T phase of MoS2 upon 25% Sn substitution was predicted theoretically.30 There are some reports where Re incorporation into MoS2 forms nanotubes, fullerene, and nanoparticles reported to show beneficial effects on HER activity.31–36 Taking theory as a guide experimentally, only 50% alloy composition is synthesized in both the cases. However, for the ReMo1−xS2 alloy, two different compositions, i.e., 50% and 75% and for the ReW1−xS2 case mostly homogeneous 50% alloy composition was obtained after the synthesis procedure. In the case of the ReMo1−xS2 alloy, two different types of modulations, i.e., tetramer (type I) and trapezoid like modulations (type II) or two different modulations between two different cations for 50% and a trimer modulation, are observed for 75% alloy composition. The observation of stable trimerized structural modulation is important as this could be useful as a thinnest platform for ferroelectric devices.24 On the other hand in Re0.5W1−xS2, the alloy formation is homogeneous and only one type, i.e., tetramer modulation (type I) is observed along with some areas with different modulation vectors probably due to slightly varying composition in these areas. The energy difference between the metallic and semiconducting ground states with slightly differing structural parameters is found to be very small; 90 and 40 meV for the 50% ReMo1−xS2 and Re0.5W1−xS2 alloys, respectively. This could be an excellent monolithic candidate for the metal-semiconductor transition with minute external perturbation suitable for application as a nanoscale switching device. Overall, the results show that the alloy can be formed between these important material systems with a differing stable structural form of the terminal compounds, i.e., 2H and 1Td and the various structural modulations observed offer yet another way to controlling the electronic structure of this system other than intercalation, strain, and vertical stacking arrangement. While high resolution electron microscopy revealed the details of such modulated structures, the density functional theory (DFT) based calculations throw light on the implications on the electronic properties of such an alloy system.

MATERIALS AND METHODS

Re0.5X0.5S2 (X = Mo and W) alloys were synthesized following a similar synthetic procedure reported earlier for ReS2.13 In short, rhenium (wire, 1.0 mm diameter, 99.97%, Alfa Aesar), molybdenum/tungsten (powder, 99.9%, Sigma Aldrich/powder, 99.8%, Sigma Aldrich) and sulfur (powder, −325 mesh, 99.5%, Alfa Aesar) were taken in the stoichiometric ratio (1:1:4) and sealed in an evacuated (10−8 mbar) quartz tube. The tube was then heated to 200 °C at the rate of 10°C/h followed by annealing at that temperature for 2 h in order to avoid any possible explosion due to the high vapor pressure of sulfur. Next, the temperature was increased to 900°C at a rate of 20°C/h and annealed for 120 h after which the furnace was shut down and the sample was allowed to cool to room temperature naturally. The final product was fine black powder.

All the high resolution phase contrast transmission electron microscopy (HRTEM, in ICMS, India) and Z-contrast high angle annular dark field imaging (HAADF, in KAUST, Saudi Arabia) were performed in a FEI TITAN aberration
corrected 80–300 keV TEM. Powder alloy samples were sonicated for 40 min to exfoliate monolayer materials for TEM imaging and energy dispersive spectroscopy (EDS) analysis.

**Computational method**

The electronic structure calculations were performed using density functional theory (DFT) as implemented in Wien2k code.\(^{37}\) Wien2k uses linearized augmented plane waves as the basis and considers all electrons into the calculation. We have used the following structures for the present calculation: monolayer and bulk form of 2H and 1T MoS\(_2\), WS\(_2\), ReS\(_2\), and various alloys between them and also considering structural modulations for ReS\(_2\) and some of the intermediate alloy composition. (The schematic of calculated structures is shown in various figures while describing the results and also some in the supplementary material). For the construction of bulk (1T/2H) and monolayer (1T/2H) Re\(_x\)Mo(W)\(_{1-x}\)S\(_2\) alloy structure, various sizes of supercells depending on Re concentrations were constructed, e.g., (i) 4 \(\times\) 4 \(\times\) 1 supercell for 6.25% Re, (ii) 4 \(\times\) 2 \(\times\) 1 for 12.5% Re, (iii) 2 \(\times\) 2 \(\times\) 1 for 25% and 75% Re, and (iv) 2 \(\times\) 1 \(\times\) 1 for 50% Re. A \(\Gamma\) centered 30 \(\times\) 30 \(\times\) 1 and 30 \(\times\) 30 \(\times\) 18 \(k\) point mesh was used for a single formula unit cell of monolayer and two formula unit cell of bulk. The number of the \(k\) mesh points was reduced proportionally for the larger supercell.

For bulk MoS\(_2\) and WS\(_2\) calculation, a unit cell consisting two formula units was considered with Bernal stacking along the \(c\)-direction. DFTD\(_3\) was introduced for dispersion correction which considers van der Waals interaction between the layers.\(^{38}\) In the case of monolayer calculation, 16 Å vacuum was added between the layers in order to prevent interlayer coupling. The optimization of lattice parameters and atomic position for the MoS\(_2\), WS\(_2\) and distorted ReS\(_2\) model was performed using the generalized gradient approximation (GGA) exchange-correlation functional of Perdew, Burke, and Enzerhof (PBE).\(^{39}\) The criteria of convergence for force, energy and electronic charge were set below 1 mRy/a.u., 0.0001 Ry and 0.0001 e, respectively. The relaxed lattice parameters of MoS\(_2\), WS\(_2\), modulated ReS\(_2\), and all other alloy structures considered for the present calculations are shown in Table 2 (supplementary material). The muffin tin radii and RMT were chosen in such a way that they do not overlap. The \(K_{\text{max}}\) was set at 7.00/RMT.

**RESULTS AND DISCUSSION**

We begin with the experimental structural description and associated superstructures observed by high resolution transmission electron microscopy in both Re\(_x\)Mo(W)\(_{1-x}\)S\(_2\) and Re\(_x\)W\(_{1-x}\)S\(_2\) alloy systems. As mentioned earlier, the most stable structure of ReS\(_2\) is 1Td (space group 2: \(P\overline{1}2_1\overline{1}\)) and for MoS\(_2\) and WS\(_2\) it is 2H (space group 194: \(P6_3/mmc\)). ReS\(_2\) is known to be in a 2D Peierls distorted 1Td structure where four Re atoms hybridize to form Re\(_4\) clusters. Incorporation of Mo and W atoms into the ReS\(_2\) lattice modifies the metal-metal hybridization between the cations and influences the structural modulation and electronic properties of the system. Figure 1(a) is the typical 1Td ReS\(_2\) structure where four Re atoms together hybridize to form a tetramer Re\(_4\) cluster forming a quasi two dimensional chain like superstructure. The calculated superlattice spots corresponding to 1T (one of the S hexagons is rotated by 30° with respect to other Re and S hexagons) and periodic modulations/superstructure (2\(a\times a\)) are indicated with two different color circles. The lattice parameter of monolayer ReS\(_2\) is \(a = 6.4308\) Å, \(b = 6.4912\) Å, and \(c = 119.03°\). The typical stable 2H and distorted 1T structure of MoS\(_2\) and WS\(_2\) is shown in Figures 1(b) and 1(c). Kindly note that the length of the edges and
the angle between them of the modulated structural units can be different along different directions for the same superstructure periodicity depending on the alloy composition. Therefore, in order to distinguish such modulations between different alloy systems, we take help from the geometry by drawing a rhombus with four cations at the corners as shown in Figure 1(d). Two different directions are defined as $a_1$ and $a_2$, with an obtuse angle between them as $\gamma$. Another two parameters are defined as $a'_1$ and $a'_2$ along the original $a_1$ and $a_2$ directions, which will define the distance between the hybridized units along the two different directions. The supercell lattice parameters of the system are also defined in terms of repeat vectors $a$ and $b$ (Fig. 1(d)). This is helpful to describe in detail the nature of modulation vectors and their strength along distinct directions, which in the literature either various nomenclature or dimensionality of modulations (1D or 2D) was used to define such structures. However, distortions can be quasi 2D with different lattice vectors and strength along different directions and therefore, we have used this definition to distinguish the various structural distortions observed in both the alloy systems. Additionally, the bonding lines between cation-cation represent hybridization and various types of hybridization possibilities are also indicated in the same figure. For both the alloys, all the structures are found to be the 1T$_d$ poly-type form with different types of superstructures depending on the alloy composition. All the structural parameters obtained from theoretical and experimental observations are given in the supplementary material.

Alloy of Re$_x$Mo$_{1-x}$S$_2$

Three different types of structural modulations or superstructures are observed in this alloy system depending on the composition. Out of three, two different modulations are observed for the same 50% and the third one with a trimeler type modulation for 75% Re$_x$Mo$_{1-x}$S$_2$ alloy case. Percentage numbers in the alloys indicate the composition in terms of either Mo or W in the host ReS$_2$ lattice. There are areas where pathways of poly-type structural transition are observed due to gradual changes in Re concentrations and are also described. The EDS analysis for 50% alloy is shown in the supplementary material (Fig. S7).

Type I modulation of 50% Re$_x$Mo$_{1-x}$S$_2$

Figure 2(a) shows the modulation for the monolayer alloy. Alternate rows are filled by either Re and Mo atoms. This gives rise to the different modulations of lattice parameters along different directions. This is schematically shown in the inset. The Mo-Mo, Re-Re, and Re-Mo distances are 2.88, 2.80, and 2.68 Å, respectively. The acute angle $\gamma$ of the rhombus is $74^\circ$. $a'_1$ and $a'_2$ are 2.9, and 2.7 Å. The FFT (fast Fourier transformation) equivalent to the periodic diffraction pattern of the image is shown in Figure 2(d). FFT also shows the signature of the 1T$_d$ phase. The superlattice spots corresponding to the 1T$_d$ phase are strong along one of the directions that correspond to the parallel planes containing only Re and Mo atoms. The observed modulation in this case is similar to the ReS$_2$ but with different lattice vectors. The Z-contrast line scan profile identifying Re and Mo in a column is shown in Figure S2 (supplementary material).

Type II modulation of 50% Re$_x$Mo$_{1-x}$S$_2$

For the same 50% alloy composition, a unique structural modulation is observed in some areas particularly near the surface regions and to the best of our knowledge this type of structural modulation is not known in the literature.
(Fig. 2(b)). Two consecutive parallel lines are marked along which modulation of cations is different, i.e., one short and another large distance of periodic structural modulation. This can also be thought of in terms of two independent 1D Peierls distorted atomic chains or 2D type with doubling the edge of one side of the supercell unit. Considering all four atoms from the consecutive rows, a trapezoid-like geometry can be identified or in other words the structural parameters can be described using two numbers of rhombuses and doubling the side along one direction (inset of Figure 2(b)). The lattice parameters are shown in the same figure. FFT also reflects the corresponding symmetry (Fig. 2(e)). The distances between the atoms, which are short and long, are 2.42 Å and 2.69 Å, respectively. This trapezoid structure can be stabilized in both tetramer type of modulation like Re₄ in ReS₂ (2D chain) and NN configurations (1D chain) depending on Re concentration as shown in Figure S3.1 (supplementary material).

**Trimerized modulation of 75% ReₓMo₁₋ₓS₂**

In this case, a trimerized modulation is observed as shown in Figure 2(c). The triangles are indicated in the figure along with the schematic (inset in Fig. 2(c)) and the length of the edges is equal to each other and is 3.2 Å. At the center of the large hexagon, the Re atom is occupying the site as marked with the blue circles. The structure can also be described by two parallel lines with one of them completely occupied by Mo and another one is alternately filled by Mo and Re atoms. The distance between the Mo-Re atoms is 2.8 Å. The γ is 109° in this case. The FFT shows the signature of the 1Td phase along with structural modulation (Fig. 2(f)). The observation of stable trimer modulation is significant in the sense that such a structure was predicted to be the thinnest ferroelectric in the case of MoS₂. The present alloy offers a stable trimer system without an intercalation route and might be amenable for a possible thinnest ferroelectric device fabrication. The Mo-Mo distance in the trimer is ~3.2 Å. The Re-Mo or Re-Re bond distance in the trimer is ~2.8 Å–2.9 Å as shown in the HRTEM images in Figure S4 (supplementary material).

In some areas, pathways of phase transition between 2H to 1T₄ structure are observed due to gradual changes in Re concentrations as shown both HRTEM and HAADF images (Figs. 3 and 4). This is an accidental finding and involves different intermediate phases depending on local Re distributions. Four distinct intermediate transition phases have been identified as shown in Figure 3. The transition from 2H to 1T₄ takes place via simultaneous rotation and gliding of one of the two S planes of the 2H crystal structure. As mentioned before, the Re-Re, Re-S bond length is shorter compared to Mo-Mo, Mo-S counterpart because of the smaller ionic radius of Re. The gradual decrease in the Metal-S bond length due to introduction of Re atoms at Mo sites can be observed for the intermediate phases in going from 2H to 1T₄ and these are indicated and tabulated in the same figure. The intermediate phase IV is similar to the intermediate stripe phase reported earlier for the hydrogenated 2H MoS₂ surface. As already mentioned, the presence of four different phases is due to different distribution of Re in the MoS₂ lattice which can clearly be observed in the Z contrast image and the route from 2H to 1T₄ transition is indicated by arrows in Figure 3. This image shows clearly the movement of the S plane due to Re incorporation into the lattice and extent to which the plane will move depends on the local population of Re. Figures 4(b)–4(e) are showing the atomically resolved images from areas with single Re substitution, two Re atoms forming a dimmer, three Re atoms forming a trimer, and four Re atoms forming a tetramer, respectively. The various metal-metal and metal-S bond lengths are also mentioned. It is found that the smallest Re-S bond length in mono atomic doping is 1.39 Å (Re₁-S₁) and for dimmer is 1.42 Å (Re₂-S₃) and 1.65 Å (Re₁-S₃). The area where four Re atom forming tetramer the metal-metal distance is 2.7 Å and 2.9 Å which is similar to the Re-Re distance in ReS₂. Example line profiles identifying two different metals for various clustering are shown in the inset. A gradual S plane rotation (along with gliding of the plane) is observed from 2H to 1T₄ phase and associated modulation of the structure due to hybridization between cations. A detailed schematic representation showing the correlation between the movements of the S plane with Re content for various intermediate phases observed experimentally is given in Figure 3 and this contain very rich structural variation in this 2D alloy system. The continuation of Figure 3 is clearly visible in the HAADF STEM image in Figure S5 (supplementary material). It is worth investigating the electronic properties of such intermediate phases, which is part of further work. The simulated diffraction pattern of distorted 1T phases from the theoretical crystal structure is well compared with selected area diffraction (SAD) in Figure S9 (supplementary material).

**Alloy of ReₓW₁₋ₓS₂**

In this case, the alloy composition (i.e., 50%) is homogeneous in most of the regions probed and no variation in structural modulation is observed unlike the ReₓMo₁₋ₓS₂ alloy system except few areas where the deviation in modulation is observed probably due to slight variation in composition. This is due to good mixing between W and Re atoms as they are next to each other in the Periodic Table and have an almost equal atomic size. This slight variation in the composition cannot easily be determined between W vs. Re atoms, unlike Mo vs. Re atoms where the atomic number difference is high. We describe the detailed observation below:

**Type I modulation of 50% ReₓW₁₋ₓS₂**

This is exactly similar to the 50% ReₓMo₁₋ₓS₂ alloy system described earlier with alternating layers of W and Re atoms as indicated in Figure 5(a). This gives strong superlattice spots in the FFT image which corresponds to the parallel planes containing mono-type atoms (Fig. 5(b)). This is a quasi 2D system and the geometrical parameters are given in Table 3 in the supplementary material which are slightly different compared to the MoS₂ counterpart. The angle γ is 80° between the a₁ and a₂ directions. The W-W, Re-Re, and Re-W distances are 2.78, 2.68 Å, and 2.43 Å, respectively. We
do not observe type II modulation in this case like in the Re0.5Mo0.5S2 alloy system.

Variation in type I modulation in RexW1-xS2

In some areas, variation in the lattice parameters of superstructure modulation is observed (Fig. 5(c)). This may be because of slight variation in W composition in the alloy in these areas. The two different areas are marked corresponding to regions with more 1D and 2D like modulation (Fig. 5(c)). The modulation vectors and lattice parameter for the supercell are indicated. The mechanism for 1D to 2D transition is shown in Figure S3 (supplementary material).

Density functional theory based calculation was carried out as a function of Mo and W concentration for RexMo1-xS2 and RexW1-xS2 alloy systems in both monolayer and bulk form (Fig. 6). The data of cohesive energy against alloy composition for monolayer for two different alloys are given in Figures 7(a) and 7(b) (see supplementary material for the bulk). The cohesive energy corresponding to 2H and unmodulated 1T polytypes is indicated by different colors points. All the 1T forms of unmodulated alloys are metallic and expected to have imaginary phonon mode similar to 1T MoS2 or ReS2 and render them unstable and undergo 2D Peierls structural modulation. Therefore, for some alloy composition, e.g., 25, 50, and 75 at. %, modulated 1Td structural calculation was carried out to investigate the relative stability with respect to its un-modulated and 2H counterparts. One can observe that at ~50 at. % alloy composition a structural cross over between 2H and 1Td takes place and the modulated structure is the most stable beyond that composition (see the data for 75%). Therefore, it can be expected that for this composition range the alloy would be stable in the modulated 1Td form. Experimental results suggest that for the Re0.5Mo0.5S2 alloy system, the 1Td modulated structure is stable even at 75 at. % in addition to 50 at. %, however, with a trimer type modulation. The initial calculations do not suggest the formation of such structural modulations.
and defects might be playing a role stabilizing such structure through the electronic charging effect. It will be worth investigating both theoretically and experimentally the electronic properties of such an alloy superstructure for the stable in-plane dipole domain structure for thinnest ferroelectric devices and beyond the scope of the present discussion. Similarly, it will also be worth investigating any novel properties arising from the type II or trapezoid type modulation for the 50% RexMo1-xS2 alloy system as part of the future exploration. The relative energy difference between the 2H and 1Td form of structural poly-types at 50% alloy composition is 90, 40 meV for monolayer RexMo1-xS2 and RexW1-xS2 alloys, respectively. The relative energy difference between the 2H semiconductor and 1T metallic phase of MoS2 and WS2 is 0.25 eV and 0.35 eV, respectively, which are one order of magnitude higher than the 50% alloy case. The relative stability of the 1T phase in the SnS2-MoS2 alloy system investigated earlier reported a cross over at 60 at. % of Sn in the MoS2 lattice and all the alloys are found to be metallic in nature. The modulated 1Td structure corresponding to 50% alloy composition for both the cases (Re0.5Mo0.5S2 and Re0.5W0.5S2) is shown in Figure 7. The lattice parameters are indicated with the help of rhombus geometry defined earlier. The structure is semiconducting with a band gap of

![FIG. 4. (a) The STEM HAADF images show the phase transition from 2H to 1Td through intermediate metastable phases. This is equivalent to Figure 3 but with the direct detection of Re atoms in the lattice. (b) Is the 1Td phase and the (g) corresponding line scan showing two S peaks in between two metal atoms. (c)–(f) Show monoatomic, two, three, and four (tetramer geometry, Re4) atom clusters in Re doped MoS2. The figure (g), (h), and (i) are the line scan showing Re dopant corresponding to figure (b), (c), and (d), respectively. The scale bars are 0.5 nm for (a), and 0.2 nm for (b)–(f).](image1)

![FIG. 5. (a) HRTEM image and (b) corresponding FFT showing the 1Td phase with structural modulation for XRe = 50% RexW1-xS2 alloy. This is similar to Type I modulation observed in the case of Re0.5Mo0.5S2. (c) Some areas show strength of structural modulation along different directions, i.e., 2D vs. 1D, probably due to slight variation of W/Re concentration and the corresponding FFTs are shown in (d) and (e). The scale bar is 1 nm.](image2)
0.317 eV and 0.115 eV for Re$_{0.5}$Mo$_{0.5}$S$_2$ and Re$_{0.5}$W$_{0.5}$S$_2$ alloys, respectively (Figs. 7(b) and 7(c)).

However, with slightly different atomic configurations for the same composition, both metallic and semiconducting states are also found to be stable with a smaller energy difference (supplementary material). The difference between these later structural states and the most stable structural configuration is the atomic distances between two different cations. The most stable configuration is obtained if the Mo-Mo (or W-W) and Re-Re distances are different than the single value and this is because of the different sizes of the atoms which are also reflected in different lattice parameters of the individual crystals. The energy difference between semiconducting and the metallic ground states is also small, 90 and 40 meV for Re$_{0.5}$Mo$_{0.5}$S$_2$ and Re$_{0.5}$W$_{0.5}$S$_2$ alloys, respectively. This is extremely important in the sense that by small external stimuli, e.g., strain, charge or photon energy can tune the conductivity of such a system with the slight modification of atomic arrangement within the same host lattice. This can be useful as a switch, sensors, and many novel...

FIG. 6. Relative stability of 2H vs. 1T polytype of monolayer (a) MoS$_2$-ReS$_2$ and (b) WS$_2$-ReS$_2$ alloys as a function of Re concentration. Compositions and the corresponding energy values are marked with different colors. Approximately, at X$_{Re} = 50\%$, a structural cross over is observed between 2H and 1T and 2H and 1T$_d$ polytypes. Also, (a) shows the energy values of different structural ground states for 50\% Re$_x$Mo$_{1-x}$S$_2$ alloys. The inset is the zoomed energy values for 50\% alloy composition for various structural configurations.

FIG. 7. The most stable 1T$_d$ structure of X$_{Re} = 50\%$ (a) Re$_x$Mo$_{1-x}$S$_2$, (d) Re$_x$W$_{1-x}$S$_2$ alloy. Both the structures are semiconducting and the corresponding band structure and density of state are given (b) and (c), (e) and (f) for Re$_{0.5}$Mo$_{0.5}$S$_2$ and Re$_{0.5}$W$_{0.5}$S$_2$ alloys, respectively.
nanoscale electronic devices through metal-semiconductor transition. Although similar possibility exists between structural polytypes, i.e., between 2H and 1T1Td in the family, the energy difference is significantly higher, i.e., ~0.25–0.35 eV and only an alkali metal intercalation route has been shown to be able to control such structural transitions in a reversible way. This is in contrast to irreversible transitions in the SnS2-MoS2 based alloy reported earlier where the similar transition is composition dependent. The reversible metal-semiconducting transitions between H and T* phases of W0.67Mo0.33Te2 by charge mediation were also predicted theoretically with the small energy difference between the two structural polytypes.

The nature of valence and conduction bands for 50% RexMo1-xS2, RexW1-xS2 alloy cases is briefly described below. The conduction band maximum (CBM) and the valence band maximum (VBM) of MoS2 are made of Mo dxy orbital. In the case of ReS2, both the VBM and CBM have significant contributions from dxy and dx2-2y2 orbitals. In the case of MoS2, the direct transition occurs from K (VBM) to K (CBM) and for ReS2, it is from Γ (VBM) to Γ (CBM). For the two alloy cases, we have found a stable semiconductor state for both Re0.5Mo0.5S2 and Re0.5W0.5S2 with the triclinic state having P1 crystallographic symmetry. The Brillouin zone and the symmetry points used for plotting band structure are shown in the supplementary material (Fig. S10). The VBM energy value at M point is comparable with R point but the CBM energy at M point is lowest for Re0.5Mo0.5S2. The Re0.5Mo0.5S2 structure shows a fundamental and direct band gap of 0.317 eV with fundamental transition between M and M (Fig. 7(b)). An indirect transition from M to X having band gap of 0.115 eV is found for Re0.5Mo0.5S2 (Fig. 7(e)). Figures 7(c) and 7(f) show that for Re0.5Mo0.5S2, the fundamental direct band transition has significant contribution from Mo dx2−2y2 and dx2−y2−2 orbitals at VBM and dx2−y2 orbital at CBM and similarly the fundamental indirect band transition for Re0.5Mo0.5S2 is primarily due to the Re dx2−2y2 orbital at the VBM and W dx2−2y2 orbital at the CBM. The band structure and DOS for other stable configurations are shown in Figure S8 and the related lattice parameters are listed in Table 2 (supplementary material).

CONCLUSIONS

In summary, alloy formation, 2H vs. 1T1Td structural stability, and electronic structure between MoS2/WS2 and ReS2 have been explored both by theory and experiment. Theory indicates a structural cross over between 2H and 1T1Td at approximately 50% alloy composition for both the system. Experimentally, two different structural modulations for 50% and a trimerized modulation are observed in Re0.25Mo0.75S2 and only tetramerized modulation is observed for WS2-ReS2 alloy systems. The trimer modulation could offer the stable thinnest platform to explore the ferroelectric device. The 50% alloy system is found to be a suitable monolithic candidate for metal semiconductor transition with minute external perturbation. The results show yet another way to tune the various structural types and the corresponding electronic structure in this important class of material systems.

SUPPLEMENTARY MATERIAL

See supplementary material for HRTEM, Z-contrast STEM HAADF image, schematic model, EDS, Band structure and DOS, table contains lattice parameter of the Re0.5Mo0.5S2 and Re0.5W0.5S2 alloy system.

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