Growth, Structure, Micro-structure and Magneto-transport of an Easy Route Synthesized Bulk Polycrystalline TiSe₂

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Abstract
This article reports an easy route synthesis of bulk polycrystalline TiSe₂. Phase purity and micro-structure are determined through powder X-ray diffraction (PXRD) and field emission scanning electron microscopy (FESEM) respectively. Vibrational modes of TiSe₂ as being analyzed by Raman spectroscopy show the occurrence of both A₁g and E₂g modes. Charge density wave (CDW) is observed in transport measurements of TiSe₂ with a hysteresis in cooling and warming measurements at around 180 K. Furthermore, studied TiSe₂ showed negative magnetoresistance (MR) below the CDW and a small positive MR above the CDW.

Keywords Charge density wave · Structural details · Raman spectroscopy · Magnetoresistance

1 Introduction
Transition metal dichalcogenides (TMDCs) are a class of layered materials, having an atomic layer of transition metal being sandwiched between two atomic layers of chalcogen atoms. The adjacent layers of TMDCs are stacked via van der Waals forces [1–3], and thus qualifying them to be the members of van der Waals compounds family [4–6]. TMDCs are metallic, semimetallic or semiconducting, depending on the choice of the insertion of transition metal and chalcogen [7]. This class includes semiconductors such as MoS₂ and WS₂ [8], and semimetals, e.g. WTe₂ and TiSe₂ [9, 10]. Also, some TMDs like NbSe₂ are found to show superconductivity as well [11]. TiSe₂ is one of the most studied materials in TMDCs family. Di Salvo et al. first reported a commensurate 2×2×2 charge modulation or CDW in TiSe₂ at 200 K accompanied by a periodic lattice distortion [12]. The theoretically calculated bulk electronic band structure showed that TiSe₂ must be a semimetal, with non-trivial topological properties [13]. Due to the presence of both semi-metallic nature and topological properties, TiSe₂ is regarded as a topological semimetal (TSM) [13]. TiSe₂ is found to show direct correlation between observed CDW and bulk electronic band structure as being evidenced by angle-resolved photo-electron spectroscopy [14].

There have been several studies on CDW characteristics of TiSe₂ [15–18]. CDW is known to get suppressed with doping or intercalation of foreign atoms [15–18]. Apart from doping of foreign atoms, CDW can be altered by different growth mechanism or by surface oxidation [19, 20]. TiSe₂ is also found to show Kondo effect on doping of 3d transition elements, which acts as a spin flip centres in the TiSe₂ unit cell [15]. More interestingly, TiSe₂ is found to show superconductivity with doping of Cu atoms and Pd atoms [16, 21]; this result was interesting in itself as the observed superconductivity was accompanied by suppressing of CDW with increased doping. Although CDW is the most prominent feature of TiSe₂, yet its origin is different from most of the materials showing the same property. In most of the material, CDW emerges from Fermi surface nesting, while the same reason is not valid in the case of TiSe₂ [16]. All in all, TiSe₂ is an interesting material with some exceptional properties. This motivates us to write this short letter on an easy route synthesis and brief physical properties of TiSe₂.

In this short letter, we report synthesis of polycrystalline TiSe₂. The synthesized sample is examined in context of phase purity and elemental composition through XRD and energy-dispersive X-ray analysis (EDAX) techniques respectively. Raman modes are also observed for polycrystalline
TiSe$_2$ through Raman spectroscopy. The signature feature of TiSe$_2$, i.e. CDW, is observed at around 180 K, with a hysteresis in warming and cooling data. Magneto-transport measurements show positive MR above CDW temperature and the same is negative below the CDW temperature.

2 Experimental

Polycrystalline samples of TiSe$_2$ were prepared using an easy self-flux method. The stoichiometric amounts (1:2) of Ti (99.99%) and Se (99.99%) powders were taken and ground thoroughly in MBRAUN glove box in argon atmosphere. The obtained mixed powder was pressed into a rectangular pellet using the hydraulic press under an approximate pressure of 2 gm/cm$^3$ and was sealed in a quartz tube under a vacuum of $5 \times 10^{-5}$ Torr. The vacuum quartz tube was placed into PID controlled muffle furnace and heated to 650 °C at a rate of 120 °C/h, and at this point, Ti atoms react with Se atoms. After this, the obtained pre-reacted powder was grounded again and heated to a higher temperature of 950 °C at a ramp rate of 120 °C/h. Sample is heated at a higher ramp rate to minimize the loss of Se. The sample was kept at 950 °C for 48 h and subsequently cooled down to 650 °C with rate of 2 °C/h. During this period, TiSe$_2$ phase starts to develop and this phase is stabilized by keeping the sample at 650 °C for 24 h and was finally cooled to room temperature. Figure 1a, b show the schematic of both of the stages of synthesis process of polycrystalline TiSe$_2$.

The structural analysis for checking the phase purity was done through room temperature XRD (X-ray diffraction) using Rigaku Miniflex II X-ray diffractometer equipped with Cu-K$\alpha$ radiation of wavelength 1.5418Å. Full prof software is used for Rietveld refinement of PXRD pattern and VESTA software is used to extract unit cell based on refined parameters from Rietveld analysis. Surface morphology and EDAX spectra were taken using Zeiss EVO-50 FESEM. Raman spectra of bulk TiSe$_2$ polycrystalline are taken at room temperature using the Jobin Yvon Horiba T64000 Raman Spectrometer for a wavenumber range of 55–400 cm$^{-1}$. Magneto-transport measurements were carried out using Quantum Design Physical Property Measurement System (QD-PPMS), a standard four-probe method that is used to measure the transport properties of synthesized TiSe$_2$ polycrystalline sample.

3 Result and Discussion

Figure 2a shows Rietveld refined PXRD pattern of synthesized TiSe$_2$ polycrystalline sample. Rietveld refined PXRD pattern confirms that the synthesized TiSe$_2$ sample is
crystallized in trigonal crystal structure with P -3 m 1 (164) space group. The synthesized sample seems to be phase pure through PXRD pattern as all the peaks are found to be indexed with their corresponding planes in TiSe₂ crystal structure. No XRD peak corresponding to any impurity peak is detected. The quality of fit is determined through calculating goodness of fit parameter, i.e. $\chi^2$ parameter, which is found to be 5.63. The Rietveld refined lattice parameters along with the atomic positions are tabulated in Table 1. The unit cell of TiSe₂ is drawn by using VESTA software, which employs crystallographic information file generated through Rietveld refinement of PXRD pattern. The same is shown in Fig. 2b; it is clear that the studied TiSe₂ polycrystalline sample exhibits a layered structure composed of van der Waals layers. Each van der Waals layer contains tri-layers arranged in Se-Ti-Se order, in which the Ti atom is surrounded by six Se atoms in the octahedral configuration. The presence of van der Waals gap in between the trilayer makes the compound easily cleavable and provides opportunity to the host and the dopant material for various intercalations and the possible charge transfer.

FESEM image of synthesized TiSe₂ sample is shown in inset (a) of Fig. 3. The elemental composition is determined through EDAX measurements and the same is shown in inset (b) of Fig. 3. Both the constituent elements, viz. Ti and Se, are found to be in a near stoichiometric ratio, signifying the purity of the sample. Also, the EDAX spectra shown in Fig. 3 show the peaks only for Ti and Se atoms, which shows that the synthesized sample is free from any foreign contamination. Figure 4 presents the room temperature Raman spectra of synthesized bulk TiSe₂ polycrystalline sample. Raman vibration modes are observed at 150 cm⁻¹ and 255 cm⁻¹ respectively. These vibrational modes are identified as $A_{1g}$ and $E_g$ modes of TiSe₂ and are in accordance with the previous report on 1 T phase of TiSe₂ [22]. In 1 T phase of TMDs, transition element is octahedrally bonded with the chalcogen atoms. The schematic of vibrational modes observed in TiSe₂ is shown in inset of Fig. 4. $A_{1g}$ modes of TiSe₂ comprise in-plane vibrations of Se atoms, while the $E_g$ modes show out of plane vibrations of Se atoms around Ti atoms. This is clear from inset of Fig. 4.

Figure 5a shows $\rho$-$T$ measurements result of TiSe₂ polycrystalline samples. An interesting anomaly, in terms of insulator to metal transition, is observed in a temperature range of 150–200 K. Charge carriers get ordered and thus the observance of CDW at around 180 K. This result is in accordance with the earlier reported results on the same compound [15–20]. Furthermore, clear hysteresis is observed in CDW in both warming and cooling data, which is the characteristic of a first-order phase transition. The reason behind this hysteresis is vested in dual electrical conductivity of TiSe₂. TiSe₂ shows two electronic phases, namely at higher temperatures, i.e. above CDW, the insulating phase starts to dominate over the metallic phase across CDW, as revealed in Fig. 5a. At CDW, this insulting phase is maximized but the metallic phase does not disappear. The coexistence of two electronic phases results in the hysteresis in warming and cooling cycle.

Figure 5b shows MR% vs applied field (up to ± 10 T) plot of synthesized TiSe₂ sample at 2 K, 100 K, 200 K and 290 K. MR% is calculated by following the formula.

$$\text{MR\%} = \left[ \frac{\rho(H) - \rho(0)}{\rho(0)} \right] \times 100$$

![EDAX spectra of synthesized TiSe₂ polycrystalline sample in which inset (a) is showing the FESEM image and the inset (b) is showing the atomic composition of constituent elements](image-url)
MR% is calculated at two temperature points below the CDW transition, viz. 2 K and 100 K, and same way above CDW transition, i.e. at 200 K and 290 K. MR% behaviour is different in both the regions. TiSe2 is found to show positive MR at temperatures above the CDW transition and a negative MR at temperatures below the same. The negative MR is found to be around 3.5% at 2 K and 1% at 100 K. This negative MR is related to the correlation between CDW and magnetic field. CDW tends to suppress with applied magnetic field and eventually demolished when Pauli spin energy surpasses the CDW condensation energy. This argument has been suggested to be the reason for observed negative MR below CDW transition [23, 24]. Another possible reason for negative MR below CDW could be the possible Kondo effect; however, that is not the case here, as in Kondo effect MR shows parabolic dependence on applied magnetic field and not linear [25]. Above CDW, MR is positive but very small around 0.4%. The possible reason for the observed behaviour of MR can be related to simultaneous existence of two electronic phases in TiSe2. The insulating electronic phase tends to increase gradually as the temperature is reduced down to CDW transition, and this insulating electronic phase of TiSe2 results in small but a positive MR above CDW transition. But at the temperatures below the CDW transition, metallic phase tends to increase with lowering the temperature and a negative MR is observed below CDW transition. In insulating region, MR is very low (<1%) and nearly constant at both the temperatures, viz. 200 K and 290 K, which is obvious as the insulating phase of a material shows much lesser effect of magnetic field on resistivity, while, in metallic phase, the observed negative MR shows stronger temperature dependency, as it is increased to 3.5%

4 Conclusion

In this work, we synthesized TiSe2 polycrystalline sample, which is well characterized through PXRD, FESEM and Raman spectroscopy. Raman spectroscopy confirms 1 T phase of TiSe2. This 1 T TiSe2 is found to show ordering of carriers at around 180 K in terms of CDW, which further show hysteresis in warming and cooling cycles. Magnetoresistance measurements show interesting behaviour as the synthesized sample is found to show positive MR above CDW transition and negative MR below CDW transition.
Our motive through this short letter is to inspire the condensed matter scientists to study more about the MR properties at above and below CDW transition.

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