Enhanced Thermoelectric Properties of Se Deficient Layered $TiSe_{2-x}$: A Charge Density Wave Material

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Supporting information:

I. **X-ray diffraction Reitveld refinement**

The x–ray powder diffraction (XRD) measurements at room temperature have been used for structural characterization of the compounds. Figure S1 presents the Rietveld refined (using the FULLPROF program) room temperature XRD patterns of hot pressed and cold pressed compounds. It is evident from the fitted XRD patterns that all the compounds are in single crystalline phase. The crystal structures of the compounds are indexed with a hexagonal structure

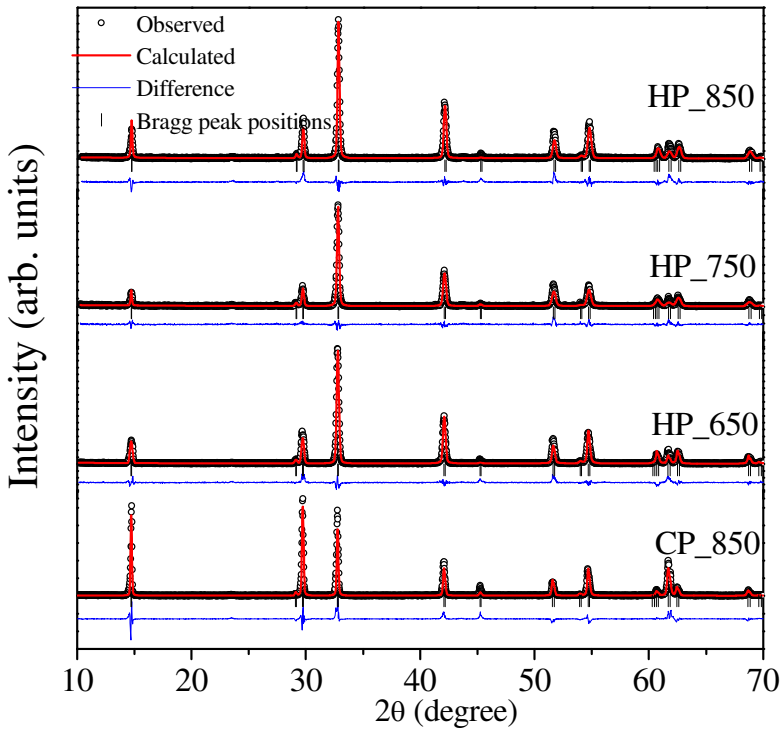

Fig. S1 Fitted XRD pattern for CP_850, HP_650, HP_750 and HP_850.

of the space group $P\bar{3}m1$. The important structural parameters, such as atomic coordinates, and lattice constants, derived from the Rietveld analysis of XRD, are shown in Table S1 for all the compounds.

Table S1 Structural parameters of Reitveld refined XRD patterns of $TiSe_{2-x}$ samples. (*x*, *y* and *z* denote the fractional coordinates).

Sample	Elements	*x*	*y*	*z*	*a=b*	*c*	*c/a*
CP_850	Ti	0	0	0	3.541(2)	6.009(4)	1.697(2)
	Se	0.333	0.666	0.257(2)			
HP_650	Ti	0	0	0	3.537(2)	6.006(5)	1.698(2)
	Se	0.333	0.666	0.258(2)			
HP_750	Ti	0	0	0	3.534(6)	6.003(1)	1.699(3)
	Se	0.333	0.666	0.251(3)			
HP_850	Ti	0	0	0	3.533(5)	6.003(6)	1.699(4)
	Se	0.333	0.666	0.251(3)			

II. X-ray photoelectron spectroscopy analysis

The x-ray photoelectron spectroscopy (XPS) data for all the $TiSe_{2-x}$ samples has been recorded using Mg Kα (1253.6 eV) x-ray source. The energy calibration was made against the C 1s peak. Figure S2(a) and S2(b) shows the XPS spectra for all the samples corresponding to Ti and Se.

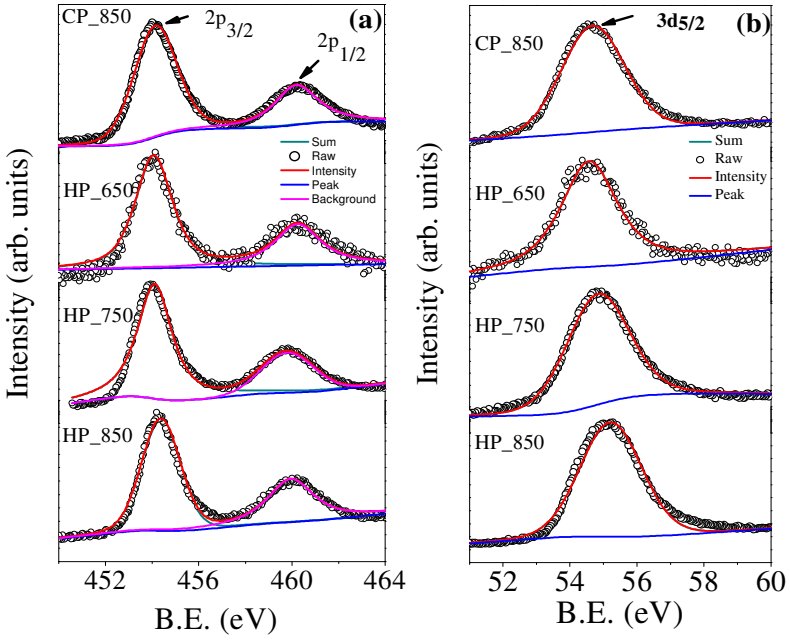

Fig. S2 Fitted XPS spectrum of samples (a) CP_850 and (b) HP_850.

The observed peaks in Ti at binding energy (BE) of 455.8 eV and 461.7 eV corresponds to the Ti $2p_{3/2}$ and $2p_{1/2}$. Observed slight shift of 1.8 eV towards higher binding energy side with respect to pure Ti (454 eV for $2p_{3/2}$) is due to the Ti-Se bond formation. The analyses of Ti and Se XPS spectra indicate that the BE position of Ti $2p_{3/2}$ peak in CP_850 and HP_850 samples are at 455.7 and 455.3 eV, respectively. This shift in BE of Ti from 455.7 eV to 455.3 eV is attributed to the increased Se deficiency in the sample. The XPS spectra corresponding to Se $3d_{5/2}$ exhibits peak at BE of 54.8 eV which correspond to the selenide. In case of Ti or Se oxide formation the BE energy should shift to 458.8 eV (TiO_2) with respect to Ti and between 58.9 eV to 59.8 eV (SeO) with respect to Se. In present study, the observed BE of Ti and Se does not give any signature of the oxide formation.