Supporting Information of

Polytypism and superconductivity in the $NbSe_2$-$TiSe_2$ Solid Solution

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This SI includes:

- Figure S1. Representative PXRD patterns with Rietveld fits.
- Figure S2. Elementary composition analysis of a selected area of $Nb_{0.98}Ti_{0.02}Se_2$ from STEM-EDS.
- Figure S3. Elementary composition analysis of selected areas of representative $Nb_{1-x}Ti_xSe_2$ samples with SEM-EDS.
- Figure S4. Temperature-dependent magnetic susceptibility of $Nb_{1-x}Ti_xSe_2$ with x = 0.25, 0.5, and 0.75.
- CCDC deposition numbers for the $Nb_{0.5}Ti_{0.5}Se_2$ structure.

Rietveld refinements are conducted on the powder X-ray diffraction (PXRD) patterns via GSAS II, to provide an estimated wt.% value of each polytype for reference. Preferred orientation has been considered during the refinement (Spherical harmonic model with harmonic order of 8-10) due to the layered structure,[1] as the strong preferred orientation affects the peak intensity distribution and the peak shape. According to the HR-STEM results, 2H (*P*63*/mmc* (#194) with metals on the 2b site, Se on the 4f site), $4H_b$ (*P*63*/mmc* (#194) with metals on the 2a and 2b sites, and Se on two 4f sites), and/or 1T (*P*-3*m*1 (#164) unit cell with metals on the 1a site, Se on the 2d site) polytype models are adopted in the refinements of different samples. Ti and Nb were refined as a mixed site with the stoichiometric fractions on each site, with the equivalent U_{iso}. The wR% of the refinements is acceptable for most of the refinements, with the GOF (goodness of fit) ranging from 2 to 6, according to the degree of preferred orientation and the complexity of the phase formation. The obtained weight percentage for the different polytypes can be considered as an estimation and is used as a reference for the qualitative analysis of the phase composition.

Reference:

1 B. H. Toby and R. B. Von Dreele, *J Appl Cryst*, 2013, **46**, 544–549.

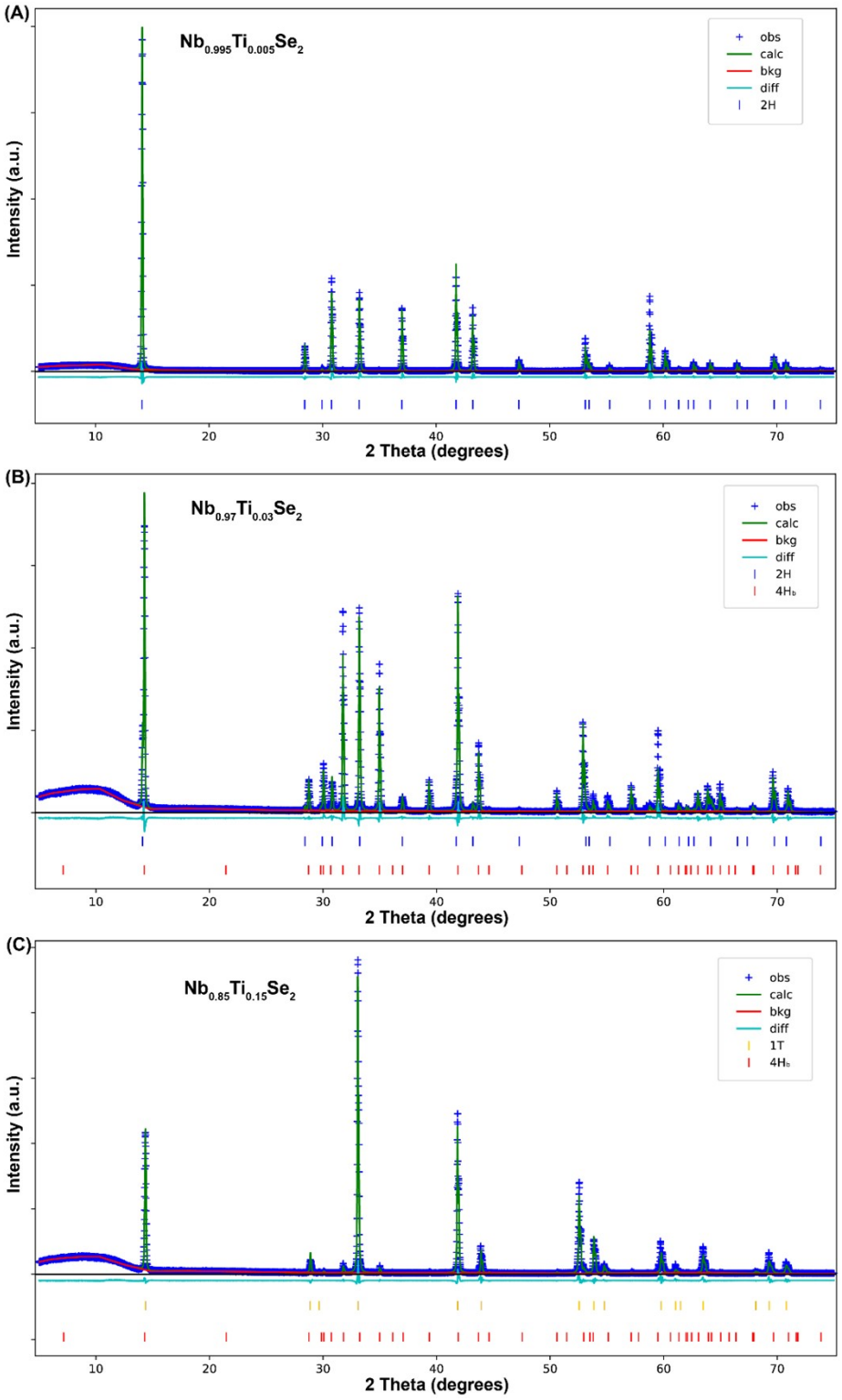

Figure S1. Representative Rietveld refinements of $Nb_{1-x}Ti_xSe_2$ powder samples annealed at 850 °C, with (A) x = 0.005, with mainly the 2H phase, wR% = 19.1%, GOF = 5.1; (B) x = 0.03, with the 2H phase at around 14% and the $4H_b$ at 86% (wt.%), wR% = 17.6%, GOF = 3.9; and (C) x = 0.15, with the $4H_b$ phase at around 8% and the 1T at 92% (wt.%), wR% = 17.8%, GOF = 3.6.

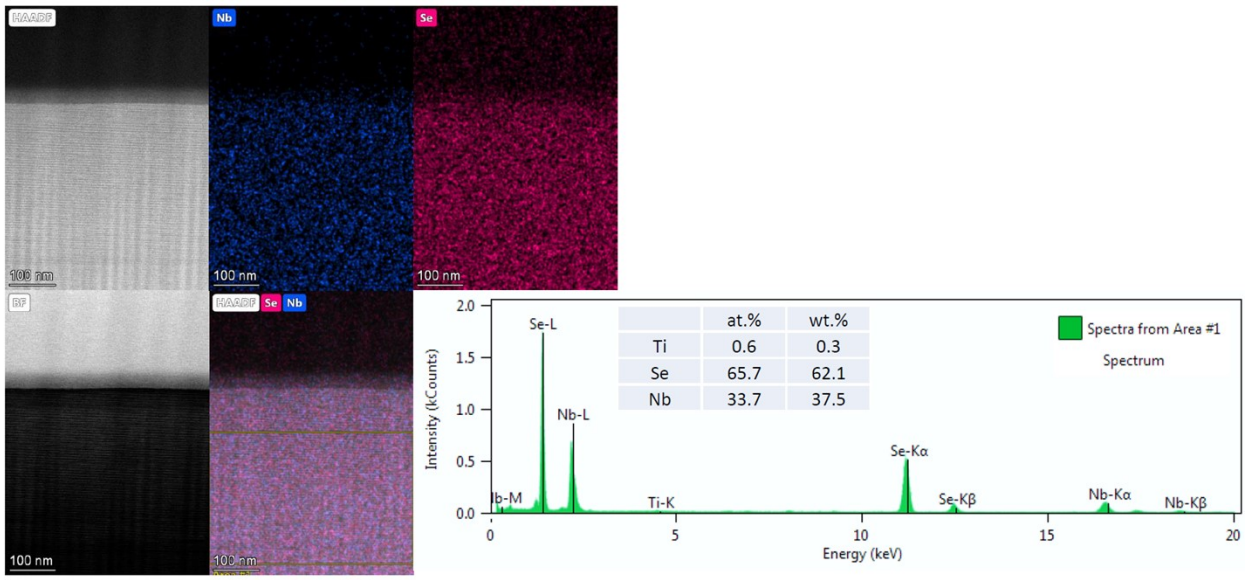

Figure S2. Elementary composition analysis of a selected area of $Nb_{0.98}Ti_{0.02}Se_2$ from STEM-EDS. In general, the elements are uniformly distributed and the average composition is close to the starting material stoichiometry.

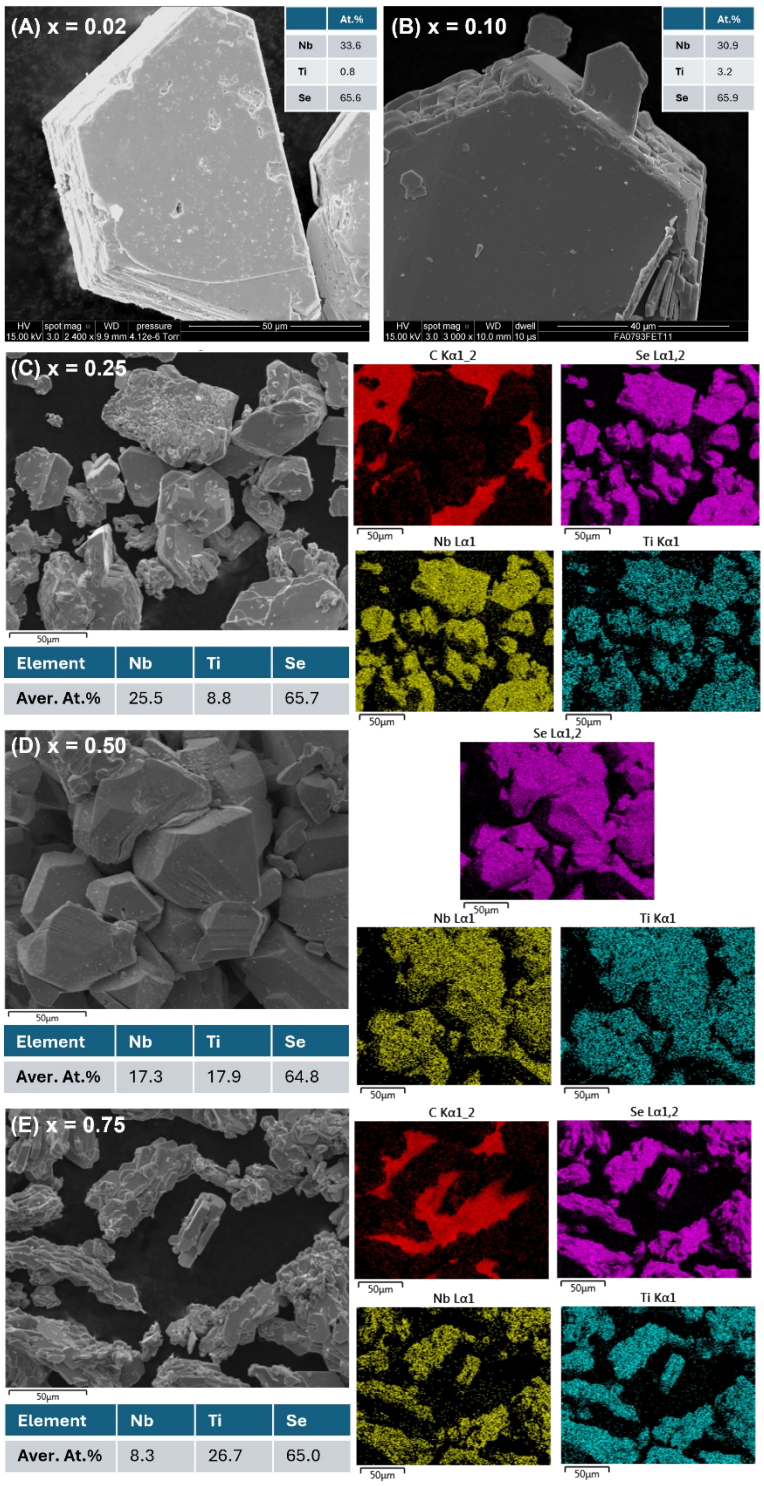

Figure S3. Elementary composition analysis of selected areas with SEM-EDS, of representative $Nb_{1-x}Ti_xSe_2$ samples with (A) x = 0.02 and (B) x = 0.10 annealed at 850 °C, and (C) x = 0.25, (D) x = 0.50, (E) x = 0.75 at 900 °C. EDS mapping is used to show the uniform distribution of the elements (some undetectable dark area is due to the angle issue of the detector), and average EDS results are listed respectively.

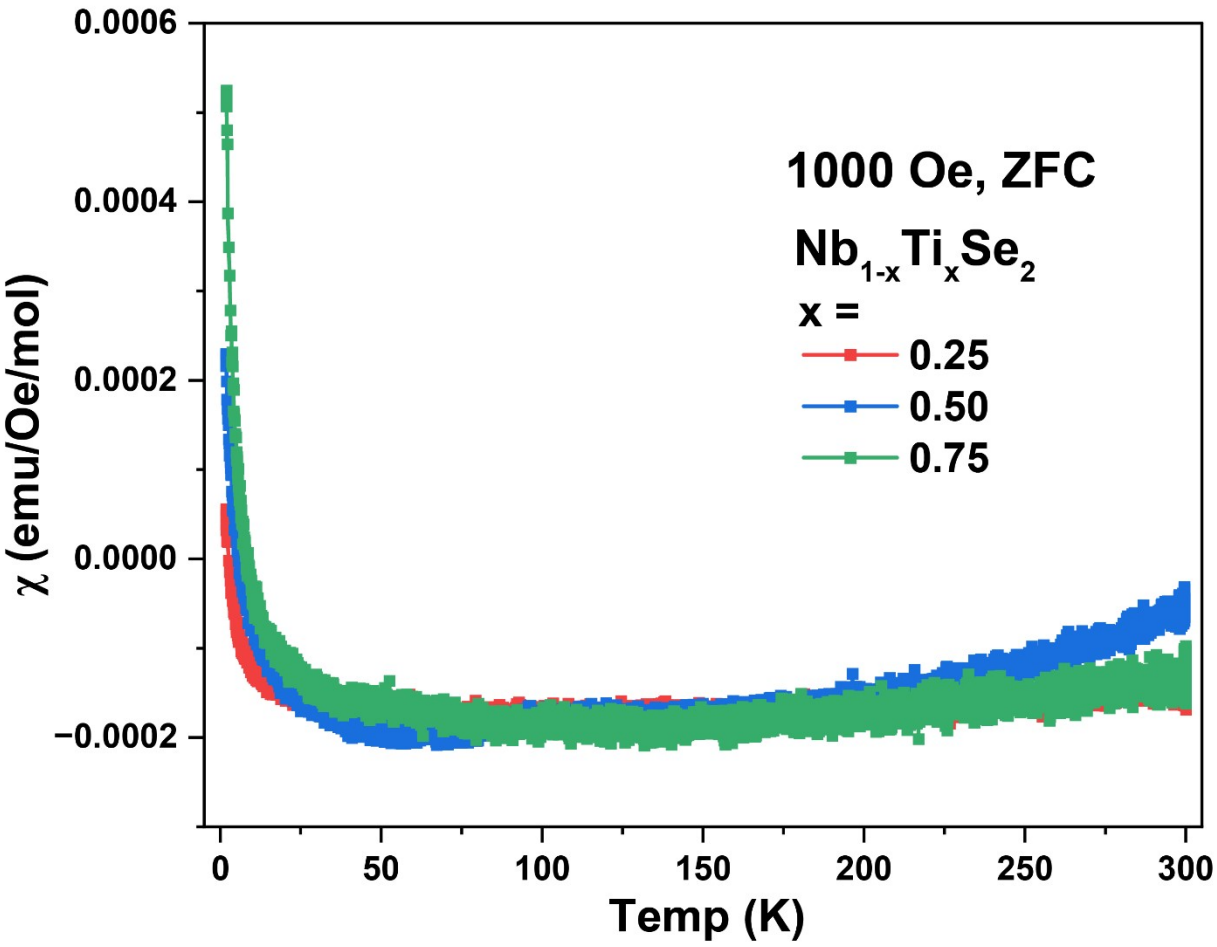

Figure S4. Temperature-dependent magnetic susceptibility of $Nb_{1-x}Ti_xSe_2$ with x = 0.25, 0.5, 0.75, annealed at 900 °C.

Supplementary Text

CCDC Deposition Number 2516559 contains the crystallographic data of $Nb_{0.5}Ti_{0.5}Se_2$ structure, which can be obtained free of charge.