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Syntheses and Characterization of Two New Layered Ternary Chalcogenides NaScQ_2 (Q = Se and Te)

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Electronic Supplementary Information (ESI)

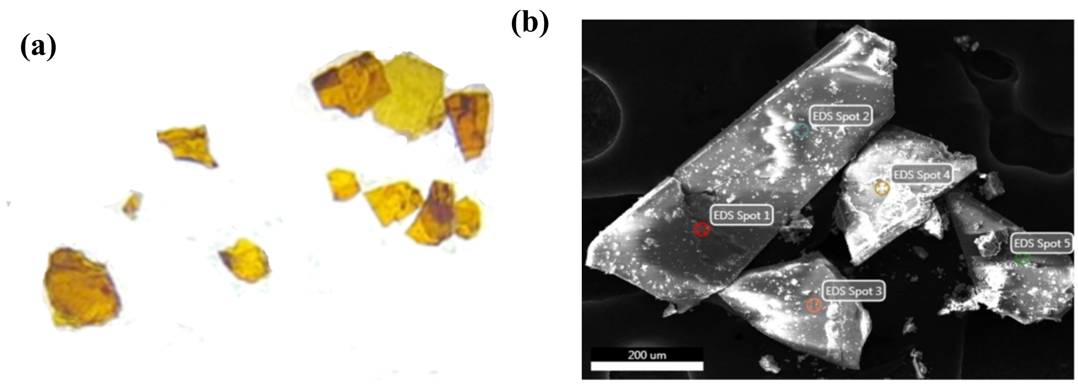

Fig. SI1 An **(a)** optical microscopic image and **(b)** SEM image of a few crystals of the $NaScSe_2$.

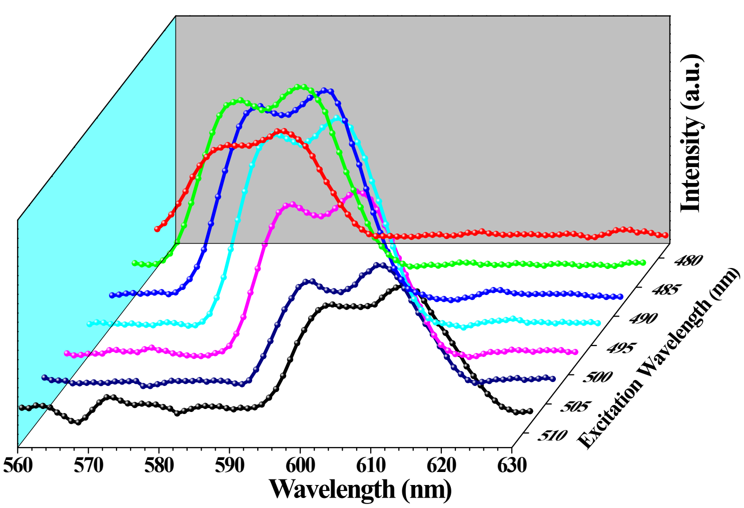

Fig. SI2 The fluorescence spectroscopic datasets of the polycrystalline $NaScSe_2$ at different excitation wavelengths.

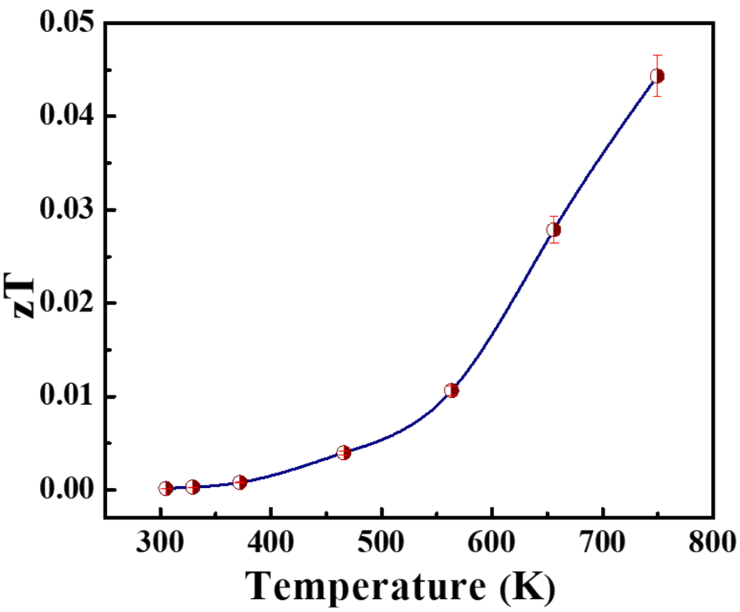

Fig. SI3 The thermoelectric figure of merit (*zT*) of the polycrystalline $NaScTe_2$ sample.

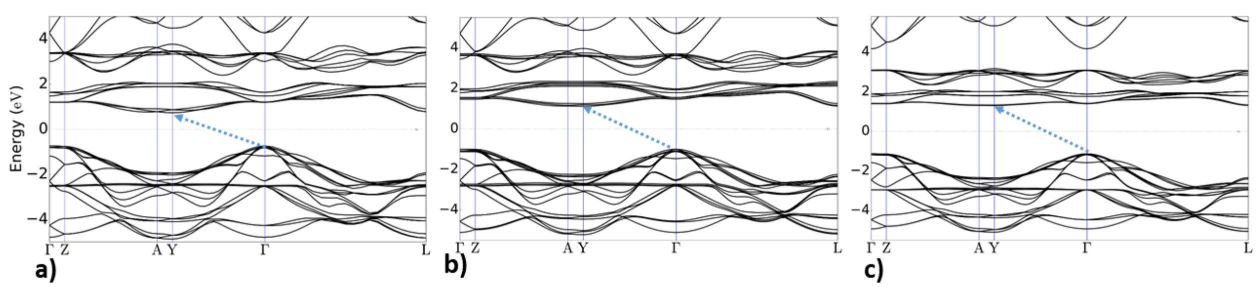

Fig. SI4 The band structure along high symmetry direction in the Brillouin zone for the $NaScSe_2$ structure computed using **a)** GGA **b)** SCAN and **c)** mBJ XC functionals. The high symmetry *k*-points are $\Gamma \equiv (0, 0, 0)$, $Z \equiv \left(0,0,\frac{1}{2}\right)$, $A \equiv \left(0,\frac{1}{2},\frac{1}{2}\right)$, $Y \equiv \left(0,\frac{1}{2},0\right)$, $L \equiv \left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$.

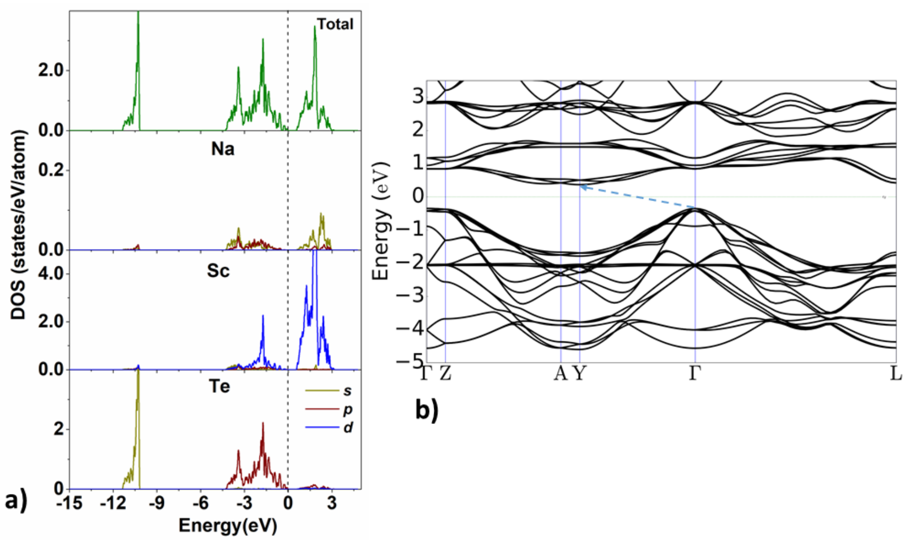

Fig. SI5 (a) The total and projected density of states (DOS) and **(b)** the band structure along high symmetry direction in the Brillouin zone for the $NaScTe_2$ structure. The dotted line in (a) indicates the valence band maximum. The high symmetry *k*-points are $\Gamma \equiv (0, 0, 0)$, $Z \equiv \left(0,0,\frac{1}{2}\right)$, $A \equiv \left(0,\frac{1}{2},\frac{1}{2}\right)$, $Y \equiv \left(0,\frac{1}{2},0\right)$, $L \equiv \left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$.

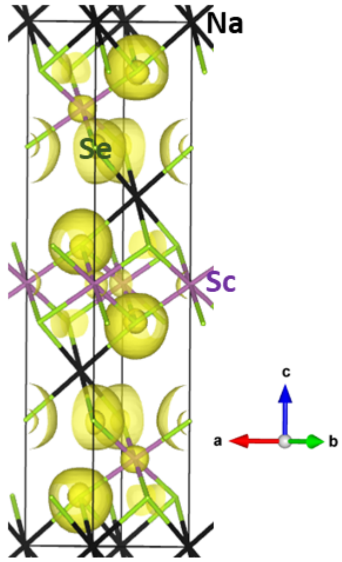

Fig. SI6 The 3D iso-surfaces of the electron localization function (ELF) for the $NaScSe_2$ with $ELF = 0.75$. The yellow cloud indicates the density of transferred charge.

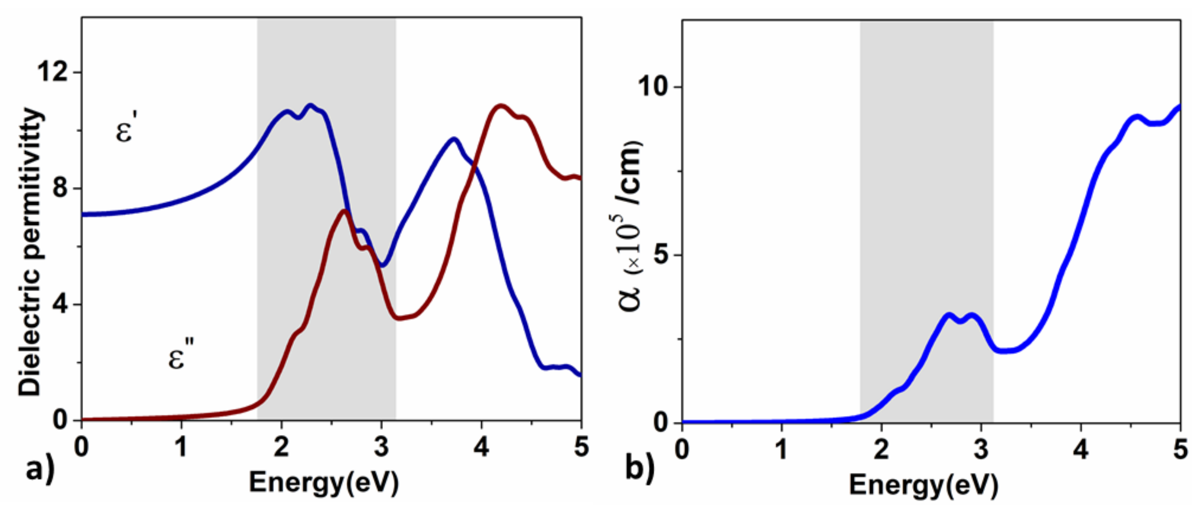

Fig. SI7 (a) The real $(\varepsilon^{'})$ and imaginary $(\varepsilon^{''})$ parts of frequency-dependent dielectric function for the $NaScSe_2$. **(b)** The absorption coefficient (α) values as a function of photon energy.

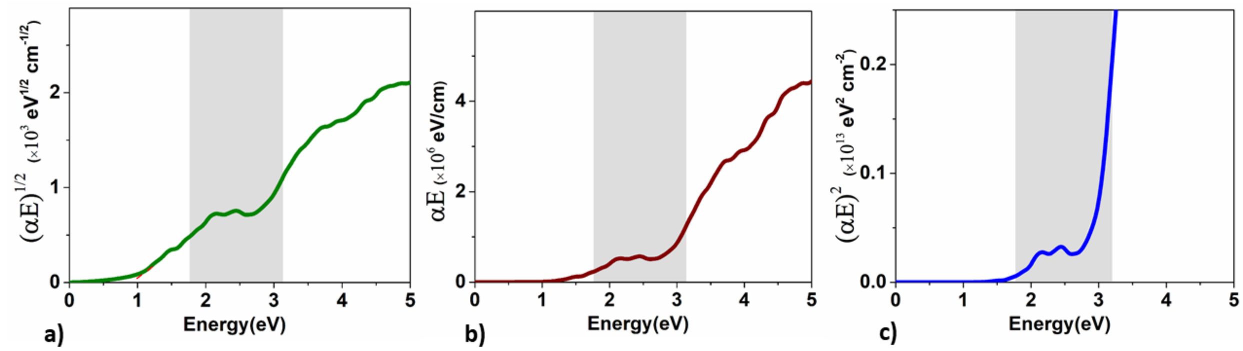

Fig. SI8 (a) The values of the $(\alpha E)^{1/2}$, **(b)** (αE), and **(c)** $(\alpha E)^2$ as a function of energy for the $NaScTe_2$. The symbols α and E represent absorption and energy, respectively.

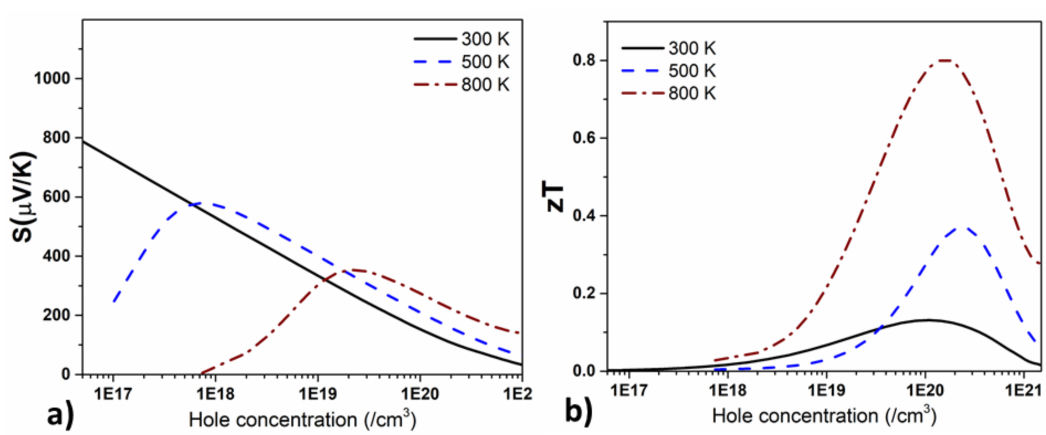

Fig. SI9 (a) The Seebeck coefficient $(\mu V/K)$ and **(b)** the zT values as a function of hole concentration for the $NaScTe_2$ structure.

S1: Optical Properties

The optical parameters are computed from the complex dielectric function $\varepsilon(\omega) = \varepsilon^{'}(\omega) + \varepsilon^{"}(\omega)$ which is in turn is computed from the single-particle energy bands. The imaginary part of the dielectric function $\varepsilon^{"}(\omega)$ is obtained from the expression [7]:

$$\varepsilon^{"}_{ij}(\omega) = \frac{4\pi^2 e^2}{V_c} \lim_{q\to 0} \sum_{c,v,\vec{k}} 2 w_{\vec{k}} \delta(\varepsilon_{c\vec{k}} - \varepsilon_{v\vec{k}} - \omega) \times \langle u_{c\vec{k}+\hat{e}_i q} | u_{v\vec{k}} \rangle \langle u_{c\vec{k}+\hat{e}_j q} | u_{v\vec{k}} \rangle^{*} \tag{S1-1}$$

where V_c is the volume of the unit cell; indices *v* and *c* indicate the valence band (VB) and the conduction band (CB) states, respectively; $u_{c\vec{k}}$ is the cell periodic part of the orbitals at the wave vector $\vec{k}$; $\varepsilon_{c\vec{k}}$ and $\varepsilon_{v\vec{k}}$ are CB and VB single-electron energy at $\vec{k}$; $w_{\vec{k}}$ is the weight of the k-points;

$\hat{e}_i$ and $\hat{e}_j$ are the unit vectors for the three Cartesian directions. The real part of the dielectric function $\varepsilon^{'}(\omega)$ is obtained using the Kramers-Kronig transformation as:

$$\varepsilon_{ij}^{'}(\omega) = 1 + \frac{2}{\pi}P\int_0^\infty \frac{\varepsilon_{ij}^{''}(\omega^{'})\omega^{'}}{\omega^{'2} - \omega^2 + i\eta}d\omega^{'} \tag{S1-2}$$

where η is a small complex shift and P is the principal value. The absorption coefficient $\alpha(\omega)$ is given in terms of $\varepsilon^{'}(\omega)$ and $\varepsilon^{''}(\omega)$ as:

$$\alpha(\omega) = \frac{\sqrt{2}\omega}{c}\left[\sqrt{\varepsilon^{'}(\omega)^2 + \varepsilon^{''}(\omega)^2} - \varepsilon^{'}(\omega)\right]^{1/2} \tag{S1-3}$$

S2: Thermoelectric properties

The first-principles thermoelectric parameters are obtained from the electronic band structure and semi-classical Boltzmann transport theory within the rigid band approach [8]. The carrier concentration (*p*- or *n*-type) in the system is introduced by shifting the chemical potential. The electrical conductivity (σ_{ij}) as a function of temperature (T) and chemical potential (μ) is calculated as:

$$\sigma_{ij}(T;\mu) = \frac{1}{V}\int \sigma_{ij}(\epsilon)\left[-\frac{\partial f_\mu(T;\mu)}{\partial \epsilon}\right]d\epsilon \tag{S2-1}$$

where V is the volume, ϵ is the energy, $f_\mu(T;\mu)$ is the Fermi function. σ_{ij} as function of energy (ϵ) can be expressed as:

$$\sigma_{ij}(\epsilon) = \frac{1}{N}\sum_{n,\vec{k}}\sigma_{ij}(n,\vec{k})\ \delta(\epsilon - \epsilon_{n,\vec{k}}) \tag{S2-2}$$

where $\epsilon_{n,\vec{k}}$ are the band energies and N is the number of $\vec{k}$ points in the Brillouin zone. $\sigma_{ij}(n,\vec{k})$ is given in terms of relaxation time $\tau_{n,\vec{k}}$ and group velocity $\vec{v}(n,\vec{k})$ as:

$$\sigma_{ij}(n,\vec{k}) = e^2\tau_{n,\vec{k}}v_i(n,\vec{k})v_j(n,\vec{k}) \tag{S2-3}$$

The Seebeck coefficient tensor (S_{ij}) as a function of temperature (T) and chemical potential (μ) is given as :

$$S_{ij}(T;\mu) = \frac{1}{eTV\sigma_{ij}(T;\mu)}\int \sigma_{ij}(\epsilon)(\epsilon - \mu)\left[-\frac{\partial f_\mu(T;\mu)}{\partial \epsilon}\right]d\epsilon \tag{S2-4}$$

The total thermal conductivity (k) is given as $k = k_e + k_l$ where k_e is the electronic component and k_l is the lattice (phonon) component of k. The electronic part of thermal conductivity (k_e) is related to electrical conductivity (σ) as $k_e = L_0 \sigma T$ (Wiedemann-Franz relation), where $L_0 = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2$ is the Lorentz number. The quantities σ and k_e are computed with respect to the relaxation time $\tau = \left(T_0 \times n_0^{1/3}\right)/\left(T n^{1/3}\right) \times 10^{-14} s$ where n_0 is the carrier concentration at $T_0 = 300\ K$. The figure of merit (zT) is calculates using $zT = \frac{S^2 \sigma T}{\left(k_e + k_l\right)}$.

Table SI1 The atomic displacement parameters (Å^2) for the $NaScQ_2$ (Q = Se and Te) structures.

		U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
	$NaScSe_2$						
Na01		0.0247(9)	0.0247(9)	0.0234(16)	0.0123(4)	0.000	0.000
Sc01		0.0115(3)	0.0115(3)	0.0174(6)	0.00577(17)	0.000	0.000
Se01		0.01196(19)	0.01196(19)	0.0157(3)	0.00598(10)	0.000	0.000
	$NaScTe_2$						
Na01		0.037(6)	0.037(6)	0.030(8)	0.019(3)	0.000	0.000
Sc01		0.0117(19)	0.0117(19)	0.039(4)	0.0058(10)	0.000	0.000
Te01		0.0146(6)	0.0146(6)	0.0343(10)	0.0073(3)	0.000	0.000

Table SI2 The geometric parameters (Å) for the $NaScSe_2$ structure.

Na01—Se01^{i}	2.9814 (5)	Na01—Na01^{x}	3.9191 (6)
Na01—Se01^{ii}	2.9814 (5)	Na01—Na01^{xi}	3.9191 (6)
Na01—Se01^{iii}	2.9814 (5)	Na01—Na01^{xii}	3.9191 (6)
Na01—Se01^{iv}	2.9814 (5)	Sc01—Se01^{xiii}	2.7203 (4)
Na01—Se01^{v}	2.9814 (5)	Sc01—Se01^{xiv}	2.7203 (4)
Na01—Se01^{vi}	2.9814 (5)	Sc01—Se01^{xv}	2.7203 (4)
Na01—Na01^{vii}	3.9191 (6)	Sc01—Se01^{xvi}	2.7203 (4)
Na01—Na01^{viii}	3.9191 (6)	Sc01—Se01^{xvii}	2.7203 (4)
Na01—Na01^{ix}	3.9191 (6)	Sc01—Se01^{xviii}	2.7203 (4)

Se01^{i}—Na01—Se01^{ii}	180.000 (13)	Se01^{iv}—Na01—Na01^{xi}	90.0
Se01^{i}—Na01—Se01^{iii}	82.182 (16)	Se01^{v}—Na01—Na01^{xi}	48.909 (8)
Se01^{ii}—Na01—Se01^{iii}	97.818 (16)	Se01^{vi}—Na01—Na01^{xi}	131.091 (8)
Se01^{i}—Na01—Se01^{iv}	97.818 (16)	Na01^{vii}—Na01—Na01^{xi}	60.0
Se01^{ii}—Na01—Se01^{iv}	82.182 (16)	Na01^{viii}—Na01—Na01^{xi}	120.0
Se01^{iii}—Na01—Se01^{iv}	180.000 (13)	Na01^{ix}—Na01—Na01^{xi}	120.0
Se01^{i}—Na01—Se01^{v}	82.182 (16)	Na01^{x}—Na01—Na01^{xi}	180.0
Se01^{ii}—Na01—Se01^{v}	97.818 (16)	Se01^{i}—Na01—Na01^{xii}	90.0
Se01^{iii}—Na01—Se01^{v}	82.182 (16)	Se01^{ii}—Na01—Na01^{xii}	90.0
Se01^{iv}—Na01—Se01^{v}	97.818 (16)	Se01^{iii}—Na01—Na01^{xii}	131.091 (8)
Se01^{i}—Na01—Se01^{vi}	97.818 (16)	Se01^{iv}—Na01—Na01^{xii}	48.909 (8)
Se01^{ii}—Na01—Se01^{vi}	82.182 (16)	Se01^{v}—Na01—Na01^{xii}	48.909 (8)
Se01^{iii}—Na01—Se01^{vi}	97.818 (16)	Se01^{vi}—Na01—Na01^{xii}	131.091 (8)
Se01^{iv}—Na01—Se01^{vi}	82.182 (16)	Na01^{vii}—Na01—Na01^{xii}	120.0
Se01^{v}—Na01—Se01^{vi}	180.000 (13)	Na01^{viii}—Na01—Na01^{xii}	60.0
Se01^{i}—Na01—Na01^{vii}	131.091 (8)	Na01^{ix}—Na01—Na01^{xii}	180.0
Se01^{ii}—Na01—Na01^{vii}	48.909 (8)	Na01^{x}—Na01—Na01^{xii}	120.0
Se01^{iii}—Na01—Na01^{vii}	48.909 (8)	Na01^{xi}—Na01—Na01^{xii}	60.0
Se01^{iv}—Na01—Na01^{vii}	131.091 (8)	Se01^{xiii}—Sc01—Se01^{xiv}	180.0
Se01^{v}—Na01—Na01^{vii}	90.0	Se01^{xiii}—Sc01—Se01^{xv}	92.166 (15)
Se01^{vi}—Na01—Na01^{vii}	90.0	Se01^{xiv}—Sc01—Se01^{xv}	87.834 (15)
Se01^{i}—Na01—Na01^{viii}	48.909 (8)	Se01^{xiii}—Sc01—Se01^{xvi}	87.834 (15)
Se01^{ii}—Na01—Na01^{viii}	131.091 (8)	Se01^{xiv}—Sc01—Se01^{xvi}	92.166 (15)
Se01^{iii}—Na01—Na01^{viii}	131.091 (8)	Se01^{xv}—Sc01—Se01^{xvi}	180.0
Se01^{iv}—Na01—Na01^{viii}	48.909 (8)	Se01^{xiii}—Sc01—Se01^{xvii}	87.835 (16)
Se01^{v}—Na01—Na01^{viii}	90.0	Se01^{xiv}—Sc01—Se01^{xvii}	92.165 (15)
Se01^{vi}—Na01—Na01^{viii}	90.0	Se01^{xv}—Sc01—Se01^{xvii}	87.835 (15)
Na01^{vii}—Na01—Na01^{viii}	180.0	Se01^{xvi}—Sc01—Se01^{xvii}	92.165 (15)
Se01^{i}—Na01—Na01^{ix}	90.0	Se01^{xiii}—Sc01—Se01^{xviii}	92.165 (15)
Se01^{ii}—Na01—Na01^{ix}	90.0	Se01^{xiv}—Sc01—Se01^{xviii}	87.835 (16)
Se01^{iii}—Na01—Na01^{ix}	48.909 (8)	Se01^{xv}—Sc01—Se01^{xviii}	92.165 (15)
Se01^{iv}—Na01—Na01^{ix}	131.091 (8)	Se01^{xvi}—Sc01—Se01^{xviii}	87.835 (15)
Se01^{v}—Na01—Na01^{ix}	131.091 (8)	Se01^{xvii}—Sc01—Se01^{xviii}	180.000 (16)

$Se01^{vi}$—Na01—$Na01^{ix}$	48.909 (8)	$Sc01^{ii}$—Se01—$Sc01^{iv}$	92.166 (16)
$Na01^{vii}$—Na01—$Na01^{ix}$	60.0	$Sc01^{ii}$—Se01—$Sc01^{vi}$	92.166 (16)
$Na01^{viii}$—Na01—$Na01^{ix}$	120.0	$Sc01^{iv}$—Se01—$Sc01^{vi}$	92.166 (15)
$Se01^{i}$—Na01—$Na01^{x}$	48.909 (8)	$Sc01^{ii}$—Se01—$Na01^{xiv}$	173.088 (15)
$Se01^{ii}$—Na01—$Na01^{x}$	131.091 (8)	$Sc01^{iv}$—Se01—$Na01^{xiv}$	92.627 (11)
$Se01^{iii}$—Na01—$Na01^{x}$	90.0	$Sc01^{vi}$—Se01—$Na01^{xiv}$	92.627 (11)
$Se01^{iv}$—Na01—$Na01^{x}$	90.0	$Sc01^{ii}$—Se01—$Na01^{xvi}$	92.627 (11)
$Se01^{v}$—Na01—$Na01^{x}$	131.091 (8)	$Sc01^{iv}$—Se01—$Na01^{xvi}$	173.088 (15)
$Se01^{vi}$—Na01—$Na01^{x}$	48.909 (8)	$Sc01^{vi}$—Se01—$Na01^{xvi}$	92.627 (11)
$Na01^{vii}$—Na01—$Na01^{x}$	120.0	$Na01^{xiv}$—Se01—$Na01^{xvi}$	82.182 (16)
$Na01^{viii}$—Na01—$Na01^{x}$	60.0	$Sc01^{ii}$—Se01—$Na01^{xvii}$	92.627 (11)
$Na01^{ix}$—Na01—$Na01^{x}$	60.0	$Sc01^{iv}$—Se01—$Na01^{xvii}$	92.627 (11)
$Se01^{i}$—Na01—$Na01^{xi}$	131.091 (8)	$Sc01^{vi}$—Se01—$Na01^{xvii}$	173.088 (15)
$Se01^{ii}$—Na01—$Na01^{xi}$	48.909 (8)	$Na01^{xiv}$—Se01—$Na01^{xvii}$	82.182 (16)
$Se01^{iii}$—Na01—$Na01^{xi}$	90.0	$Na01^{xvi}$—Se01—$Na01^{xvii}$	82.182 (16)

Symmetry codes: (i) -*x*+2/3, -*y*+1/3, -*z*+1/3; (ii) *x*-2/3, *y*-1/3, *z*-1/3; (iii) -*x*-1/3, -*y*-2/3, -*z*+1/3; (iv) *x*+1/3, *y*+2/3, *z*-1/3; (v) -*x*-1/3, -*y*+1/3, -*z*+1/3; (vi) *x*+1/3, *y*-1/3, *z*-1/3; (vii) *x*-1, *y*-1, *z*; (viii) *x*+1, *y*+1, *z*; (ix) *x*, *y*-1, *z*; (x) *x*+1, *y*, *z*; (xi) *x*-1, *y*, *z*; (xii) *x*, *y*+1, *z*; (xiii) -*x*-2/3, -*y*-1/3, -*z*+2/3; (xiv) *x*+2/3, *y*+1/3, *z*+1/3; (xv) -*x*+1/3, -*y*+2/3, -*z*+2/3; (xvi) *x*-1/3, *y*-2/3, *z*+1/3; (xvii) *x*-1/3, *y*+1/3, *z*+1/3; (xviii) -*x*+1/3, -*y*-1/3, -*z*+2/3.

Table SI3 The geometric parameters (Å) for the $NaScTe_2$ structure.

Na01—$Te01^{i}$	3.2180 (11)	Sc01—$Te01^{vii}$	2.9460 (10)
Na01—$Te01^{ii}$	3.2180 (11)	Sc01—$Te01^{viii}$	2.9460 (10)
Na01—$Te01^{iii}$	3.2180 (11)	Sc01—$Te01^{ix}$	2.9460 (10)
Na01—$Te01^{iv}$	3.2180 (11)	Sc01—$Te01^{x}$	2.9460 (10)
Na01—$Te01^{v}$	3.2180 (11)	Sc01—$Te01^{xi}$	2.9461 (10)
Na01—$Te01^{vi}$	3.2180 (11)	Sc01—$Te01^{xii}$	2.9461 (10)
$Te01^{i}$—Na01—$Te01^{ii}$	180.00 (5)	$Te01^{ix}$—Sc01—$Te01^{xi}$	88.47 (4)
$Te01^{i}$—Na01—$Te01^{iii}$	81.98 (3)	$Te01^{x}$—Sc01—$Te01^{xi}$	91.53 (4)
$Te01^{ii}$—Na01—$Te01^{iii}$	98.02 (3)	$Te01^{vii}$—Sc01—$Te01^{xii}$	91.53 (4)

$Te01^{i}$—Na01—$Te01^{iv}$	98.02 (3)	$Te01^{viii}$—Sc01—$Te01^{xii}$	88.47 (4)
$Te01^{ii}$—Na01—$Te01^{iv}$	81.98 (3)	$Te01^{ix}$—Sc01—$Te01^{xii}$	91.53 (4)
$Te01^{iii}$—Na01—$Te01^{iv}$	180.00 (5)	$Te01^{x}$—Sc01—$Te01^{xii}$	88.47 (4)
$Te01^{i}$—Na01—$Te01^{v}$	98.02 (3)	$Te01^{xi}$—Sc01—$Te01^{xii}$	180.00 (5)
$Te01^{ii}$—Na01—$Te01^{v}$	81.98 (3)	$Sc01^{ii}$—Te01—$Sc01^{iv}$	91.53 (4)
$Te01^{iii}$—Na01—$Te01^{v}$	98.02 (3)	$Sc01^{ii}$—Te01—$Sc01^{v}$	91.53 (4)
$Te01^{iv}$—Na01—$Te01^{v}$	81.98 (3)	$Sc01^{iv}$—Te01—$Sc01^{v}$	91.53 (4)
$Te01^{i}$—Na01—$Te01^{vi}$	81.98 (3)	$Sc01^{ii}$—Te01—$Na01^{viii}$	173.41 (5)
$Te01^{ii}$—Na01—$Te01^{vi}$	98.02 (3)	$Sc01^{iv}$—Te01—$Na01^{viii}$	93.061 (7)
$Te01^{iii}$—Na01—$Te01^{vi}$	81.98 (3)	$Sc01^{v}$—Te01—$Na01^{viii}$	93.062 (8)
$Te01^{iv}$—Na01—$Te01^{vi}$	98.02 (3)	$Sc01^{ii}$—Te01—$Na01^{x}$	93.061 (8)
$Te01^{v}$—Na01—$Te01^{vi}$	180.00 (5)	$Sc01^{iv}$—Te01—$Na01^{x}$	173.41 (5)
$Te01^{vii}$—Sc01—$Te01^{viii}$	180.0	$Sc01^{v}$—Te01—$Na01^{x}$	93.062 (8)
$Te01^{vii}$—Sc01—$Te01^{ix}$	91.53 (4)	$Na01^{viii}$—Te01—$Na01^{x}$	81.98 (3)
$Te01^{viii}$—Sc01—$Te01^{ix}$	88.47 (4)	$Sc01^{ii}$—Te01—$Na01^{xi}$	93.062 (8)
$Te01^{vii}$—Sc01—$Te01^{x}$	88.47 (4)	$Sc01^{iv}$—Te01—$Na01^{xi}$	93.062 (8)
$Te01^{viii}$—Sc01—$Te01^{x}$	91.53 (4)	$Sc01^{v}$—Te01—$Na01^{xi}$	173.41 (5)
$Te01^{ix}$—Sc01—$Te01^{x}$	180.0	$Na01^{viii}$—Te01—$Na01^{xi}$	81.98 (3)
$Te01^{vii}$—Sc01—$Te01^{xi}$	88.47 (4)	$Na01^{x}$—Te01—$Na01^{xi}$	81.98 (3)
$Te01^{viii}$—Sc01—$Te01^{xi}$	91.53 (4)		

Symmetry codes: (i) -*x*+2/3, -*y*+1/3, -*z*+1/3; (ii) *x*-2/3, *y*-1/3, *z*-1/3; (iii) -*x*-1/3, -*y*-2/3, -*z*+1/3; (iv) *x*+1/3, *y*+2/3, *z*-1/3; (v) *x*+1/3, *y*-1/3, *z*-1/3; (vi) -*x*-1/3, -*y*+1/3, -*z*+1/3; (vii) -*x*-2/3, -*y*-1/3, -*z*+2/3; (viii) *x*+2/3, *y*+1/3, *z*+1/3; (ix) -*x*+1/3, -*y*+2/3, -*z*+2/3; (x) *x*-1/3, *y*-2/3, *z*+1/3; (xi) *x*-1/3, *y*+1/3, *z*+1/3; (xii) -*x*+1/3, -*y*-1/3, -*z*+2/3.