Supporting information

Phase identification and structure determination from multiphasic crystalline powder samples by rotation electron diffraction

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Table S1 EDS results for all the four phases in the NiSeOCl sample. The EDS was not calibrated and the results cannot be used for quantitative analysis.

/Element	**Phase 1**/ at%	**Phase 2** at%	**Phase 3**/ at%	**Phase 4** at%
O	52	44	43	44
Cl	-	7	11	8
Ni	18	18	19	21
Se	30	31	26	27

S1. *Ab initio* structure solution of Phase 1 ($NiSeO_3$)

3D RED data was collected from a crystallite of **Phase 1**(~ 500 nm in size), as shown in Figure S1 and Table 1. From the reciprocal space reconstructed from RED data, two reciprocal lattices from **Phase 1** were observed, as marked by different colours in Figure S1a. The orientations of the two crystals are slightly different from each other so that the reciprocal lattices could be separated manually using the *RED* data processing software. The two reciprocal lattices gave similar *C*-centred monoclinic unit cell, with a = 15.58 Å, b = 9.96Å, c = 14.82 Å, β = 110.2 ° (marked in white in Figure S1a) and a = 15.60 Å, b = 9.98 Å, c = 14.79 Å, β = 109.8 ° (marked in green in Figure S1a), respectively. The possible space groups were deduced from the 2D main zone diffraction patterns cuts from the reconstructed 3D RED data, see Figures S1b-d. In the ($h0l$) slice (Figure S1c), reflections with odd l are much weaker than the ones with even l. This means that there might be a *c*-glide perpendicular to the *b*-axis. This was also confirmed using the statistics of the reflections from *RED* for the symmetry determination. Therefore, the possible space groups are *Cc* and *C*2/*c*. Reflections with $d \geq 0.52$ Å were used for structure solution by direct methods. A reasonable solution could be obtained with the higher space-group symmetry *C*2/*c*. All 20 symmetry-independent atoms (four Se, four Ni and twelve O atoms) were located directly. The structure model was refined against the RED data, with *R*1 = 0.295 for 1142 independent reflections obtained from white reciprocal lattice in Figure S1a. Comparing the corresponding atomic coordinates from RED and the ICSD database (Miljak et al., 2007), the maximum atomic deviation is 0.05 Å for Ni, 0.05 Å for Se and 0.13 Å for O. That means that the structure model from RED dataset was correct in spite of the high *R*1 value. Such a high *R*1 value is typical for electron diffraction data, which is mainly due to multiple scattering and the lack of absorption correction. The RED data for **Phase 1** were collected from one crystallite and two reciprocal lattices were observed and separated. The RED dataset from each of the reciprocal lattices were used for the structure solution, which gave the same structure model (Table 1).

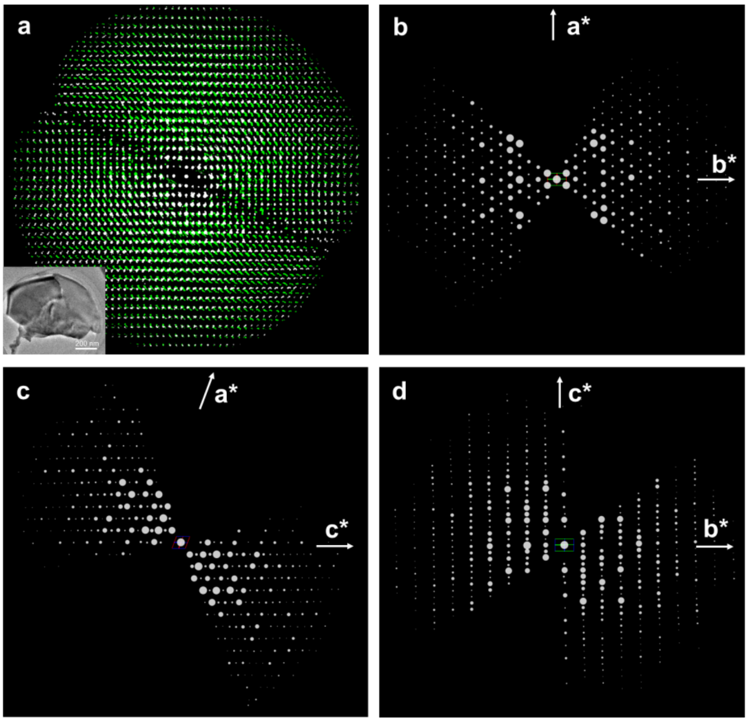

Figure S1 (a) Two 3D reciprocal lattices of **Phase 1** reconstructed from one RED data, marked in white and green, respectively. These lattices can be separated using the *RED* data processing software. The lattice marked as white is further analysed in (b-d). Inset is the crystallite from which the RED data was collected. (b-d) 2D cuts of the (b) (*hk*0), (c) (*h*0*l*) and (d) (0*kl*) slice from the white 3D reciprocal lattice in (a). The systemic absences are *hkl*: *h* + *k* = 2n + 1; *hk*0: *h* + *k* = 2n + 1; *h*0*l*: *h* = 2n + 1; 0*kl*: *k* = 2n + 1; 0*k*0: *k* = 2n + 1. After careful checking of the diffraction intensities in the (*h*0*l*) plane in (c), there is an indication that reflections with *l* = 2n+1 might be absent because reflections with odd *l* are much weaker than those with even *l*. The non-zero intensities of the odd reflections may be due to dynamical effects. The possible space groups are *Cc* and *C*2/*c*.

S2. *Ab initio* structure solution and structure description of Phase 3 ($Ni_5Se_6O_{14}(OH)_2Cl_4$)

3D RED data was collected from a particle of **Phase 3** (~ 600 nm × 350 nm × 30 nm in size), as shown in Figure S2a. It has a *C*-centred monoclinic cell with a = 21.94 Å, b = 8.38 Å, c = 12.68 Å and β = 118.1°. The possible space groups are *Cc* and *C*2/*c*, as deduced from the systematic absences observed from the *hk*0, *h*0*l* and 0*kl* planes cut from the reconstructed reciprocal lattice (Figures S2b-d). Violations of the reflection conditions in the (*h*0*l*) slice are due to dynamical effects. As seen in Figure S2a, the crystal of **Phase 3** has a sheet-like morphology and is very thin in one of the dimensions. This causes elongation of diffraction spots perpendicular to the thin sheet and makes the intensity extraction from RED difficult. Because the elongations are weak, the intensity of each elongated reflection was extracted at the centre of the reflection and used for structure solution. A reasonable solution was obtained with the higher space-group symmetry *C*2/*c*. All 16 symmetry-independent non-hydrogen atoms, including three Se, three Ni, two Cl and eight O, were directly located by direct methods. One hydrogen atom was added to an oxygen atom to balance the charge. The structure model of **Phase 3** was then refined to $R1$ = 0.303 for 351 independent reflections. The high $R1$ value might be due to dynamical effects and diffuse scattering. **Phase 3** has a chemical formula of $Ni_5Se_6O_{14}(OH)_2Cl_4$ and is a new compound in the Ni-Se-O-Cl system. The RED method is powerful for structure solution of very thin and layered structures.

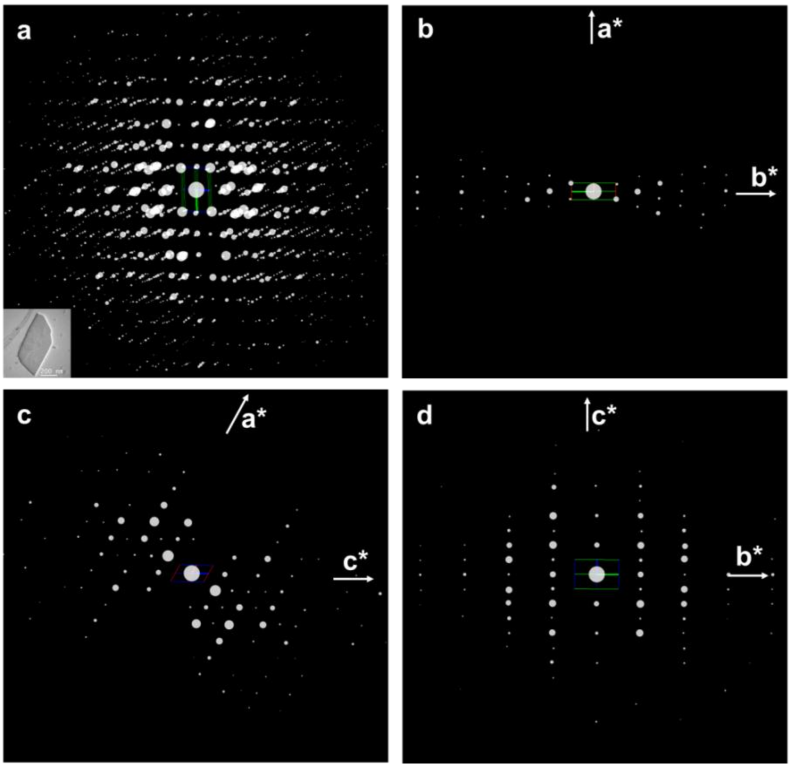

Figure S2 (a) 3D reciprocal lattice of **Phase 3** reconstructed from the RED dataset. Inset is the crystal used for RED data collection. (b-d) 2D cuts of the (b) ($hk0$), (c) ($h0l$) and (d) ($0kl$) slices from the 3D reciprocal lattice in (a). The systemic absences are deduced as hkl: $h + k = 2n + 1$; $hk0$: $h + k = 2n + 1$; $h0l$: $h = 2n + 1$and $l = 2n+ 1$; $0kl$: $k = 2n + 1$; $0k0$: $k = 2n + 1$; $00l$: $l = 2n + 1$. The non-zero intensities of reflections with $l = 2n +1$ in (c) are due to dynamical effects. The possible space groups are *Cc* and *C*2*/c*.

Phase 3 crystallizes in the monoclinic space group *C*2/*c*. It comprises three symmetry-independent Ni^{2+} ions and three independent Se^{4+} cations. All Ni^{2+} cations have distorted octahedral coordinations; Ni(2)O_5Cl, Ni(1)O_4Cl_2 and Ni(3)O_4Cl_2, the latter two have the Cl atoms in *cis* and *trans* positions respectively. The Ni – O bond distances are in the range 1.97(4) – 2.18(5) Å and the Ni – Cl distances are in the range 2.27(3) – 2.45(2) Å. The Ni-octahedra share edges to build a framework with channels running along [010] and [001]. All three Se^{4+} ions have SeO_3 trigonal pyramidal coordination. One of the oxygen atoms around Se(3) is actually a hydroxyl group so that the coordination polyhedron becomes Se(3)O_2(OH). The Se – O bond distances are in the range 1.60(5) to 1.81(5) Å. The coordination polyhedra around Se(1) and Se(2) are connected to form [Se_2O_5] groups while Se(3)O_2(OH) polyhedral do not polymerize. The Se-groups connect to the Ni-octahedra by corner and edge sharing so that they are facing the channels in the crystal structure. The stereochemically active lone pairs on Se^{4+} and the hydroxyl groups are residing in those voids.

S3. *Ab initio* structure solution and structure description of Phase 4 ($Ni_5Se_4O_{12}Cl_2$)

3D RED data was collected from a particle of **Phase 4**, as shown in Figure S3a. A triclinic unit cell with a = 9.44 Å, b = 9.44 Å, c = 8.14 Å, α = 105.1°, β = 91.6°, γ = 101.6° was found. The possible space groups are $P1$ and $P\text{-}1$. A reasonable solution could be obtained with the higher space group symmetry $P\text{-}1$. All 23 symmetry-independent atoms, including four Se, five Ni, two Cl and twelve O, were directly located by direct methods. The structure model of **Phase 4** was then refined to $R1$ = 0.405 for 1464 independent reflections. The high $R1$ value might be due to dynamical effects. **Phase 4** has a chemical formula of $Ni_5Se_4O_{12}Cl_2$ and is a new compound in the Ni-Se-O-Cl system.

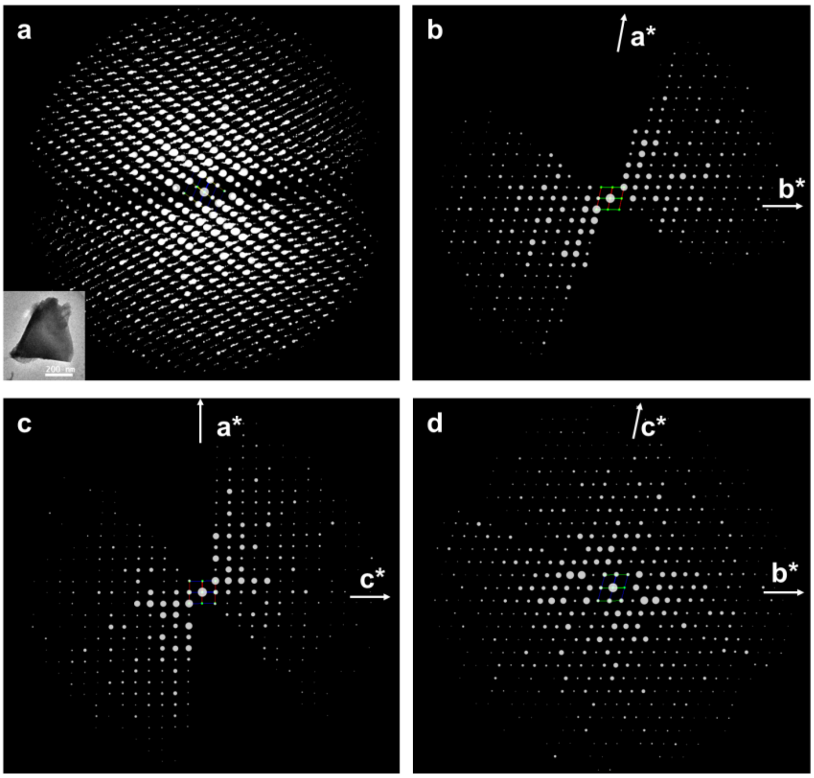

Figure S3 (a) 3D reciprocal lattice of **Phase 4** reconstructed from the RED dataset. Inset is the crystal from which the RED data was collected. (b-d) 2D cuts of the (b) ($hk0$), (c) ($h0l$) and (d) ($0kl$) slices from the 3D reciprocal lattice in (a). The possible space groups are $P1$ and $P\text{-}1$.

Phase 4 ($Ni_5Se_4O_{12}Cl_2$) crystallizes in the triclinic space group $P\text{-}1$. However, it is neither iso-structural with $Ni_5Se_4O_{12}Br_2$ (Jiang & Mao, 2006) nor with the Co-analogue $Co_5Se_4O_{12}Cl_2$ (Becker et al., 2007a). All these three compounds crystallize in the same space group but have different structures. The corresponding tellurium compounds $Ni_5Te_4O_{12}X_2$ (X=Cl, Br) (Johnsson et al., 2003) and $Co_5Te_4O_{12}X_2$ (Becker et al., 2007b) are monoclinic and thus also show different crystal structures. In **Phase 4** ($Ni_5Se_4O_{12}Cl_2$), there are five symmetry-independent Ni^{2+} ions that all have distorted octahedral coordination with 4-6 oxygen and 2-0 Cl; NiO_4Cl_2, NiO_5Cl, NiO_6. The Ni – O bond distances are in the range of 1.87(2) – 2.18(2) Å and the Ni – Cl distances are in the range of 2.33(2) – 2.42(2) Å. The Ni-octahedra share corners and edges to build a framework with channels running along [011] where the Se^{4+} ions reside. The three symmetry-independent Se^{4+} ions have SeO_3 trigonal pyramidal coordination. The Se – O bond distances are in the range of 1.62(2) – 1.98(2) Å. The SeO_3 groups do not polymerise and connect to the Ni-octahedra by corner and edge sharing so that the stereochemically active lone pairs on Se^{4+} are residing in the channels in the crystal structure.

S4. Rietveld Refinement

In order to further confirm the structures, Rietveld refinement was performed against the PXRD data on the structure models of the four phases obtained from RED, using the software *TOPAS* Academic version 4.1(Young, 1995). Background was fitted with a 12th order Chebychev polynomial. The refinement was conducted using a Pearson VII type peak profile function, followed by refinement of the unit cells and zero-shift. After initial check of the PXRD data, we found that **Phase 1** and **Phase 4** are the major phases, while **Phase 2** and **Phase 3** are the minor ones. The atomic coordinates for **Phase 1** and **Phase 4** were refined with the soft restraints of Ni-O, Ni-Cl and Se-O bond distances. Due to their low contents, the atomic coordinates for **Phase 2** and **Phase 3** could not be refined properly and were thus fixed based during the refinement. Finally, the refinement converged with R_{wp} = 0.0670 and R_{exp} = 0.0273 (Table S2 and Figure S4). Comparing the atomic coordinates obtained from RED and after Rietveld refinement, the average deviation for **Phase 1** ($NiSeO_3$) is 0.05 Å for Ni, 0.06 Å for Se and 0.15 Å for O atoms, and that for **Phase 4** is 0.10 Å for Ni, 0.09 Å for Se, 0.20 Å for Cl and 0.23 Å for O atoms. These means that the structure models for the four phases are correct. The refined weight percentage is 48% for **Phase 1**, 14% for **Phase 2**, 4% for **Phase 3**, 34% for **Phase 4**.

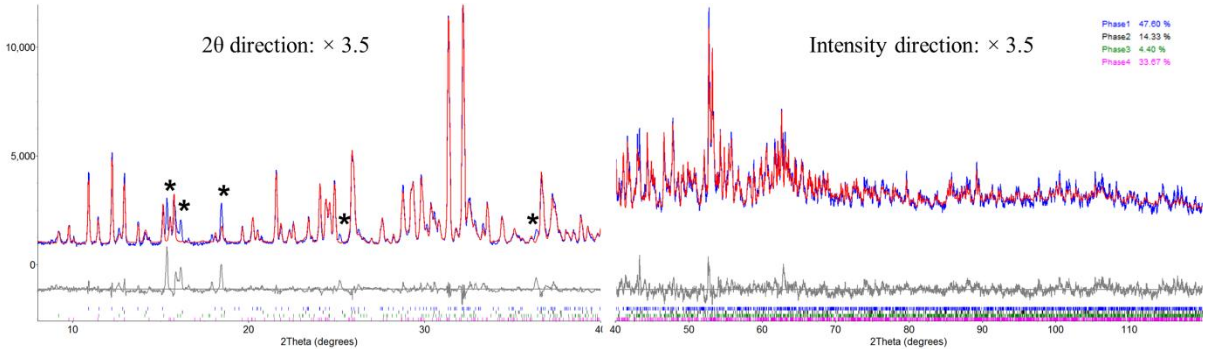

Figure S4 Observed (blue) and calculated (red) PXRD profiles, as well as the difference between observed and calculated profile (gray), for the Rietveld refinement of the Ni-Se-O-Cl sample (λ = 1.5418 Å). The unindexed peaks are marked by asterisk (*). In order to show the fit between the observed and calculated patterns, the low-angle data have been scaled up by 3.5 times along 2θ direction while the high-angle data have been scaled up by 3.5 along intensity direction.

Table S2 Crystallographic data for Rietveld refinement of the Ni-Se-O-Cl sample.

No. of phases		4
Wavelength		Cu Kα, 1.5418 Å
No. of reflections	**Phase 1**	1566
	Phase 2	440
	Phase 3	1534
	Phase 4	1977
No. of parameters		203
No. of restraints	**Phase 1**	36 bond distances for Ni-O and Se-O
	Phase 2	-
	Phase 3	-
	Phase 4	42 bond distances for Ni-O, Ni-Cl and Se-O
R_p		0.0427
R_{wp}		0.0670
R_{exp}		0.0273
GOF		2.46
R_B	**Phase 1**	0.0279
	Phase 2	0.0196
	Phase 3	0.0338
	Phase 4	0.0219

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