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Synthesis and crystal structure of $Nd_3Ti_3O_8Se_2$

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Abstract

Black crystals of $Nd_3Ti_3O_8Se_2$ have been synthesized by the reaction of neodymium sesquioxide and titanium sesquiselenide (Nd_2O_3:Ti_2Se_3=1:1) with a small amount of iodine at 1000°C. The compound crystallizes in the monoclinic space group $P2_1/m$ (Z=2) with the cell parameters a=982.69(17) pm, b=391.78(4) pm, c=1349.9(2) pm, β=111.370(19)°.

Keywords: Chemical synthesis; Crystal structure and symmetry; X-ray and X-ray spectroscopies; Neodymium

1. Introduction

Recently we reported on the synthesis and crystal structure of $Pr_{30}Ti_{24}I_8O_{25}Se_{58}$ [1]. The attempt to prepare an isotypic compound with neodymium in the same way failed. Instead, we obtained black single crystals of $Nd_3Ti_3O_8Se_2$, the structure of which we describe in the following.

2. Experimental

$Nd_3Ti_3O_8Se_2$ was synthesized from a mixture of Nd_2O_3 (Strem Chem., 99.9%), Ti_2Se_3 and iodine (Heraeus, 99.999%), handled under inert atmosphere. Ti_2Se_3 was prepared by heating a mixture of titanium (ChemPur, 99.5%) and selenium (ChemPur, 99.999%) at 700°C for 3 days. The starting materials (ratio Nd:Ti=1:1) were placed in a quartz glass tube evacuated to 10^{-3} mbar, sealed and heated at 1000°C for 2 weeks and then quenched to room temperature. The product was obtained as air-stable needles of about 0.2 mm in length with an estimated yield of 20%.

The composition of several crystals was determined by microprobe analysis (Cameca Cambax MB, WDX, relative error: 1% (Nd, Ti, Se). The amount of oxygen cannot be determined). The measured relation Nd:Ti:Se=3:2.85:1.98 is in satisfactory agreement with the composition.

X-ray data were collected by a Stoe imaging plate diffractometer. Data analysis indicated space group $P2_1/m$. The crystal data and the details of the data acquisition are summarized in Table 1. Final values of the atomic coordinates and displacement parameters are given in Table 2.

Further details of the crystal structure investigation may

Table 1
Crystallographic data, data collection and structure refinement for $Nd_3Ti_3O_8Se_2$

Formula	$Nd_3Ti_3O_8Se_2$
Colour	black
Crystal size	$0.2\times0.01\times0.01$ mm^3
System	monoclinic
Space group	$P2_1/m$ (No. 11)
Cell parameters	a=982.69(17) pm α=90°
	b=391.78(4) pm β=111.370(19)°
	c=1349.9(2) pm γ=90°
	V=483.97(12)$\times10^6$ pm^3
	Z=2
Calculated density	5.918 g/cm^3
Absorption coefficient	μ=25.688 mm^{-1}
Temperature	300 K
Diffractometer	STOE IPDS
Radiation	Mo Kα (λ=71.073 pm)
Angular range 2θ	3.19° to 28.06°
hkl range	$-12\le h\le13$; $-4\le k\le4$; $-17\le l\le17$
Total recorded reflections	5699
Independent reflections	1283
Observed reflections ($F>2\sigma$)	1130
R_{int}	0.0330
Programs used	SHELXS-97, SHELXL-97 [4,5], Diamond [6]
Parameters refined	98
Refinement results[a]	R_1=0.0200; wR_2=0.0468
	R_1=0.0241; wR_2=0.0475 (all data)
	g.o.f.=0.970
Residual electronic density	-2.058×10^{-6} e·pm^{-3}/1.599×10^{-6} e·pm^{-3}

[a] Definitions given in Refs. [4,5].

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be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-411400.

3. Results and discussion

The crystal structure consists of infinite chains along the *b*-axis built up from edge- and corner-connected TiX_6 polyhedra (X=O, Se) (cf. Fig. 2) that are separated by Nd^{3+} and Se^{2-} ions. A view along the *b*-axis is shown in Fig. 1.

The TiX_6 polyhedra represent more or less distorted octahedra with distances given in Table 3.

The three crystallographically different neodymium ions have the following anionic environments: Nd1 is surrounded by seven O^{2-} and Se^{2-} ions in form of a capped trigonal prism, the nine anions around Nd2 build up a tricapped trigonal prism and the eight anions around Nd3 form a quadratic antiprism. The corresponding distances are summarized in Table 3. Fig. 3 displays the connections among the polyhedra around the Nd^{3+} ions.

As can be seen from Fig. 2 the Ti1–Ti3 distance is remarkably short (287.3 pm, cf. Table 3). The similar compound $Nd_2Ta_3O_8Se_2$ consists of edge- and corner-connected TaO_6 octahedra leading to an oxidation state <5 for tantalum [2,3]. Here the short Ta–Ta distances are referred to occupied Ta–Ta bonding electronic states. An

Table 2
Fractional coordinates and equivalent isotropic atomic displacement parameters of $Nd_3Ti_3O_8Se_2$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq} (pm^2)
Nd1	0.9508(1)	1/4	0.3368(1)	55(1)
Nd2	0.4101(1)	−1/4	0.0907(1)	38(1)
Nd3	0.5874(1)	−1/4	0.4165(1)	41(1)
Ti1	0.3167(1)	1/4	0.2693(1)	44(2)
Ti2	0.8124(1)	−1/4	0.0994(1)	41(2)
Ti3	0.0465(1)	1/4	0.0893(1)	69(3)
Se1	0.6101(1)	1/4	0.2468(1)	52(2)
Se2	0.8390(1)	1/4	0.5184(1)	59(2)
O1	0.3592(5)	−1/4	0.2631(3)	49(10)
O2	0.2538(5)	1/4	0.1095(3)	71(10)
O3	−0.0008(5)	−1/4	0.0722(3)	42(9)
O4	0.8271(5)	1/4	0.0760(4)	59(10)
O5	0.4418(5)	1/4	0.4156(3)	53(10)
O6	0.6136(5)	−1/4	0.0314(3)	51(10)
O7	0.8772(5)	−1/4	0.2412(3)	74(10)
O8	0.1262(5)	1/4	0.2504(3)	68(10)

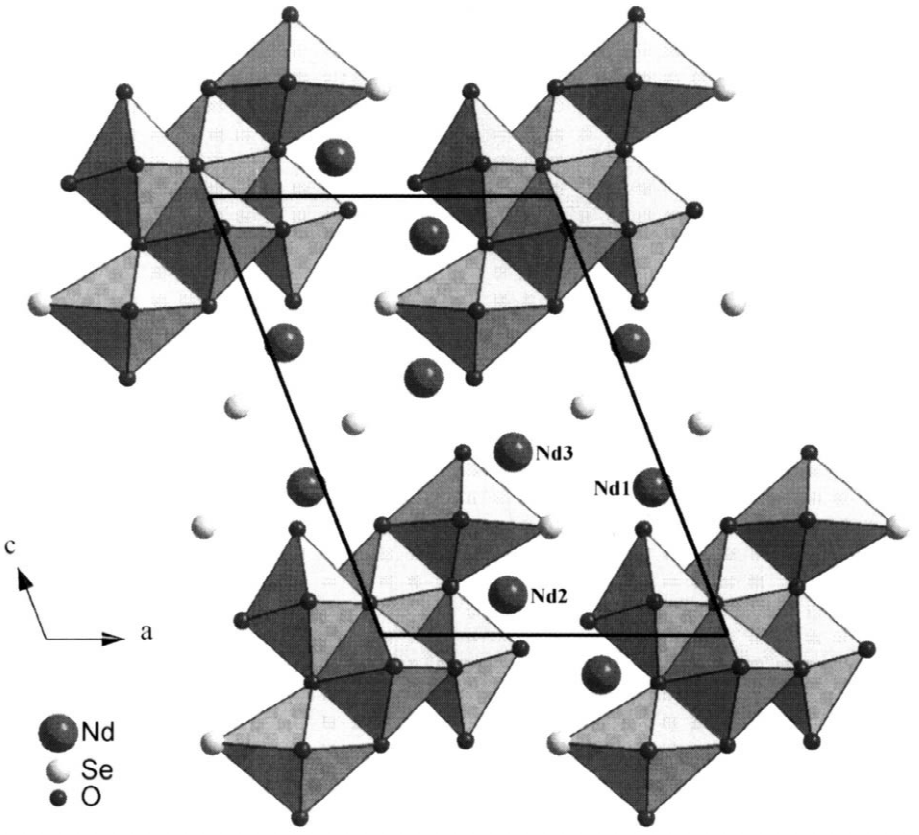

Fig. 1. View of $Nd_3Ti_3O_8Se_2$ along the *b*-axis. The titanium ions are located in the middle of the octahedra.

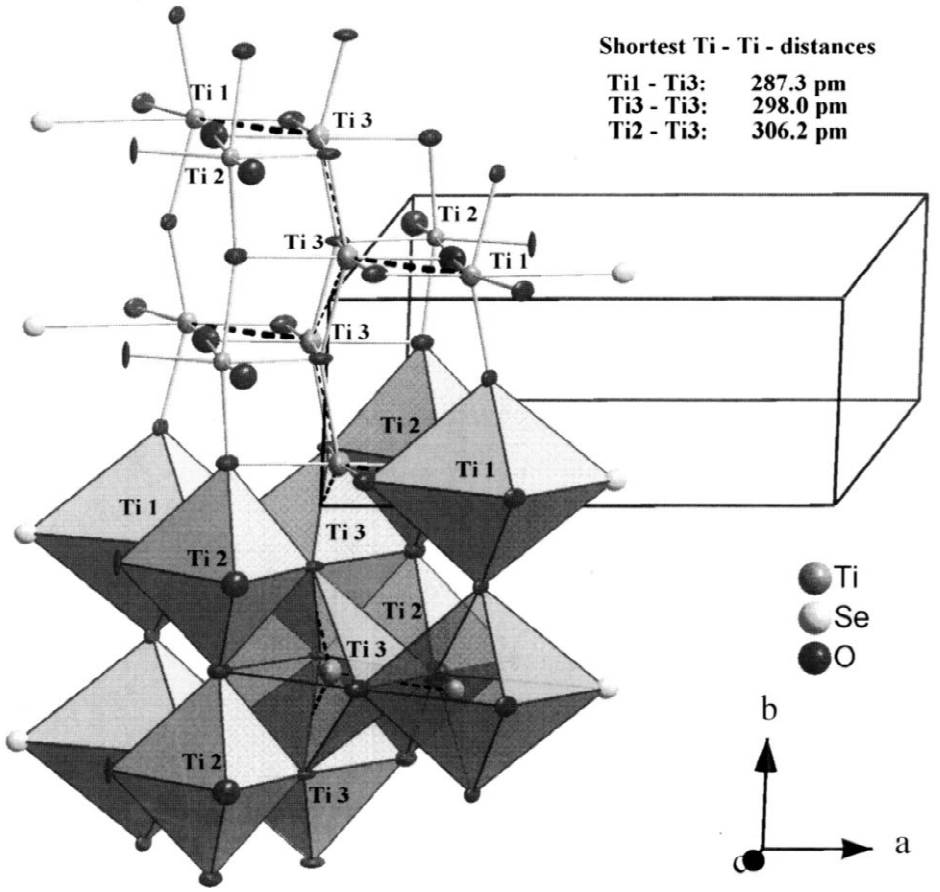

Fig. 2. Chain of edge- and corner-connected TiX_6 octahedra for $Nd_3Ti_3O_8Se_2$.

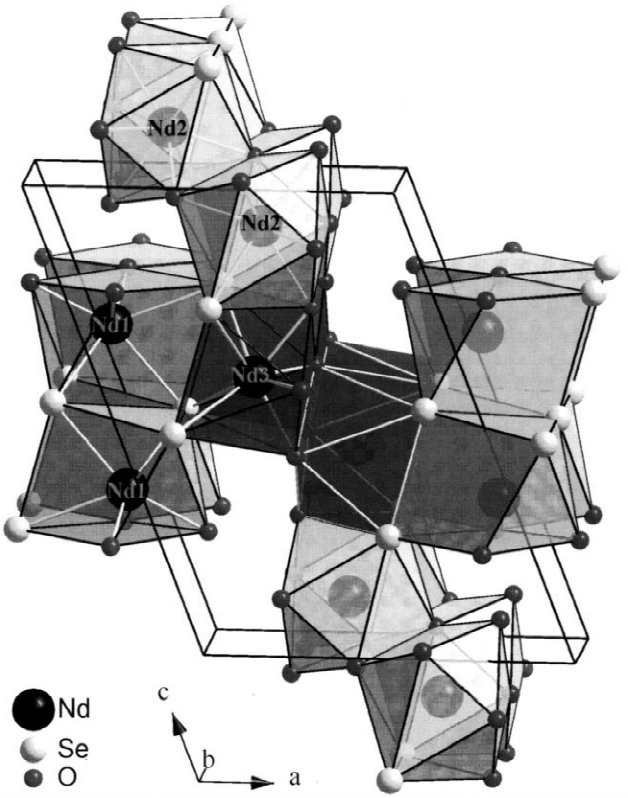

Fig. 3. Connections among the polyhedra around the three crystallographically different Nd^{3+} ions.

analogous electronic situation for titanium is found in $Nd_3Ti_3O_8Se_2$ (oxidation state Ti <4). This may also be explained by covalent interactions between titanium ions. For clarification band structure calculations are planned.

Table 3
Selected bond distances (pm) for $Nd_3Ti_3O_8Se_2$

Nd1–O7	2×	231.2(2)	Nd3–Se2	2×	306.0(1)
Nd1–O8		240.7(5)	Nd3–Se1	2×	308.3(1)
Nd1–Se2	2×	299.7(1)	Nd3–Nd3	2×	383.2(18)
Nd1–Se2		302.9(1)	Nd3–Nd3	2×	391.78(4)
Nd1–Se1		311.8(1)	Ti1–O8		179.5(5)
Nd1–Nd1	2×	391.78(4)	Ti1–O5		190.8(4)
Nd1–Nd1		459.1(16)	Ti1–O1	2×	201.1(1)
Nd1–Nd3	2×	453.4(15)	Ti1–O2		201.6(5)
Nd1–Nd3		454.7(59)	Ti1–Se1		300.7(1)
Nd2–O6		240.9(4)	Ti1–Ti3		287.3(2)
Nd2–O6	2×	251.5(3)	Ti2–O7		178.3(4)
Nd2–O1		255.3(4)	Ti2–O6		183.2(5)
Nd2–O2	2×	255.9(3)	Ti2–O4	2×	199.8(1)
Nd2–O4		258.3(5)	Ti2–O3		199.9(5)
Nd2–Se1	2×	302.1(1)	Ti3–O2		195.5(5)
Nd2–Nd2	2×	391.78(4)	Ti3–O3	2×	200.7(1)
Nd2–Nd2	2×	401.2(19)	Ti3–O8		202.6(5)
Nd2–Nd3		409.8(33)	Ti3–O3		206.0(4)
Nd3–O5		238.6(4)	Ti3–O4		209.7(5)
Nd3–O5	2×	242.3(3)	Ti3–Ti3	2×	298.0(2)
Nd3–O1		243.5(5)	Ti3–Ti2	2×	306.2(1)

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