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The Short Series of the Oxygen-Poor Lanthanide Oxide Selenides $M_{10}OSe_{14}$ with M = La–Nd

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Abstract: Single crystals and phase pure samples of oxygen-poor ternary lanthanide oxide selenides with the composition $M_{10}OSe_{14}$ (M = La–Nd; tetragonal, $I4_1/acd$; a = 1592.0–1559.8 pm, c = 2106.5–2062.9 pm) could be obtained by reacting the corresponding metals, selenium and selenium dioxide as oxygen source. Their crystal structures are isotypic with $Pr_{10}OS_{14}$ and thus contain isolated $[OM_4]^{10+}$ tetrahedra ($d(O^{2-}-M^{3+})$ = 243–248 pm) embedded in a complex anionic $^3_\infty\{[M_6Se_{14}]^{10-}\}$ lanthanide selenide matrix ($d(M^{3+}-Se^{2-})$ = 288–358 pm). All three crystallographically independent M^{3+} cations exhibit eight contacts to chalcogenide anions (O^{2-} and/or Se^{2-}) resulting in the formation of bicapped trigonal prismatic coordination polyhedra. The optical band gaps of the oxide selenides $M_{10}OSe_{14}$ amount to values between 1.89 and 2.04 eV indicating wide band-gap semiconductors.

Keywords: lanthanides; oxide selenides; crystal structures; band gaps; synthesis

1. Introduction

Up to now many oxide selenides of the trivalent lanthanides with four different compositions, but five structure types, are known to literature: $M_{10}OSe_{14}$ (M = La, Pr) [1–3], M_2OSe_2-I (M = Gd) [4], M_2OSe_2-II (M = Pr) [1,2], M_2O_2Se (M = La, Pr, Nd, Sm, Gd, Er, Ho, Yb, Lu) [1,2,5] and $M_4O_4Se_3$

(M = La–Nd, Sm) [1,2,6,7]. Oxide centered metal tetrahedra $[OM_4]^{10+}$ represent the dominating structural feature of all, but occurs as isolated entities just in the $M_{10}OSe_{14}$-type compounds. While the M_2OSe_2-I-type representatives exhibit their condensation to a chain via common *cis*-oriented edges, the remaining three examples show different kinds of layers built up of these $[OM_4]^{10+}$ tetrahedra also by vertex- and edge-condensation. Furthermore, selenide and diselenide anions coexist in the crystal structure of the $M_4O_4Se_3$-type compounds according to $M_4O_4Se[Se_2]$. The title compounds $M_{10}OSe_{14}$ (M = La–Nd) follow up and suffer from the same kind of problem as the homologous oxide sulfides $M_{10}OS_{14}$ [8,9]: Both were formerly addressed as B-type modifications of the corresponding lanthanide sesquichalcogenides M_2Ch_3 (Ch = S and Se) [10,11]. *Besançon* and coworkers [12,13] have refined $Pr_{10}OS_{14}$ as first example of this structure type. More recently, *Meerschaut et al.* [14] refined a structure model for $La_{10}O_{0.945}Se_{14.055}$ with a mixed occupation of O^{2-} and Se^{2-} anions at a common *Wyckoff* position ($8a$), which raises some questions. We are now presenting the crystal structures of the complete short $M_{10}OSe_{14}$ series with M = La–Nd here. A comment on $La_{10}O_{0.945}Se_{14.055}$ is given as well as a detailed comparison between the title compounds and the isostructural lanthanide oxide sulfides $M_{10}OS_{14}$ (M = La–Nd, Sm, Gd) [8,9]. Furthermore, we compare the optical band gaps of the title compounds with those of the C-type sesquiselenides of the lanthanides M_2Se_3 and the oxide selenide diselenides $M_4O_4Se[Se_2]$.

2. Results and Discussion

2.1. Structure Description

The oxygen-poor ternary lanthanide oxide selenides $M_{10}OSe_{14}$ crystallize with the $Pr_{10}OS_{14}$-type structure [12,13] in the tetragonal system with the space group $I4_1/acd$ (no. 142) and eight formula units per unit cell (M = La: a = 1592.04(9) pm, c = 2106.48(14) pm; M = Ce: a = 1578.96(9) pm, c = 2086.59(14) pm; M = Pr: a = 1568.74(8) pm, c = 2073.42(13) pm; M = Nd: a = 1559.83(8) pm, c = 2062.91(12) pm). Compared to the lattice constants of $La_{10}OSe_{14}$ at 153 K (a = 1588.8(2), c = 2101.4(3) pm) [3] and within all expectations, the lattice parameters presented here show slightly larger values than those subjected to the X-ray experiments at room temperature (298 K).

Eight crystallographically independent atoms (see Table 1) reside at four different *Wyckoff* positions: O at $8a$ (site symmetry: $\bar{4}$..), Se4 at $16e$ (.2.), M3 at $16f$ (..2) along with M1, M2, Se1, Se2 and Se3 all at the general $32g$ site with symmetry 1. The coordination spheres of the trivalent lanthanide cations M^{3+} exhibit a trigonal prismatic shape with two caps each (see Figure 1). From these, just $(M2)^{3+}$ binds the light O^{2-} anion apart from seven contacts to Se^{2-}, while $(M1)^{3+}$ and $(M3)^{3+}$ show eight bonds to only Se^{2-} anions.

Figure 1. View of the coordination spheres of the trivalent lanthanide cations (**a**) $(M1)^{3+}$; (**b**) $(M2)^{3+}$; and (**c**) $(M3)^{3+}$ in the crystal structure of the $M_{10}OSe_{14}$ representatives (M = La–Nd).
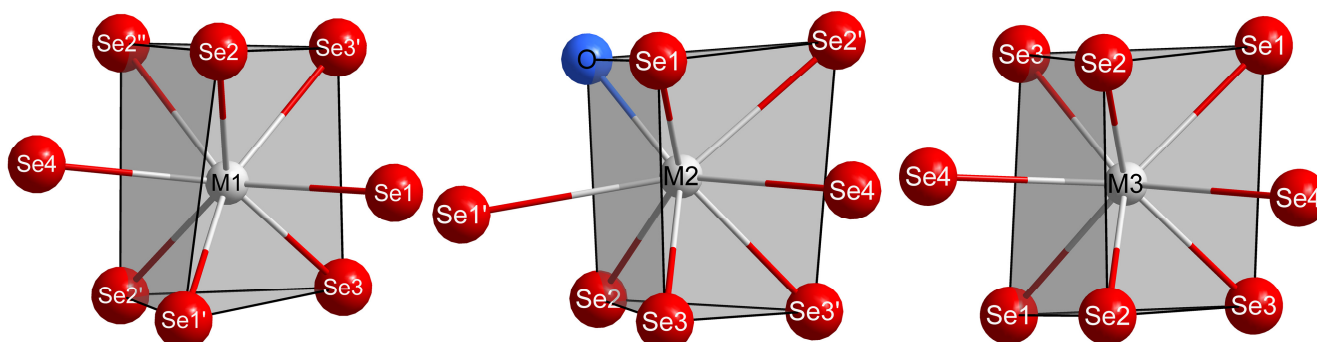
Table 1. Fractional atomic coordinates for the four $M_{10}OSe_{14}$ representatives with M = La–Nd.

Atom		x/a	y/b	z/c	Atom		x/a	y/b	z/c
$La_{10}OSe_{14}$					$Pr_{10}OSe_{14}$				
La1	32g	0.13003(4)	0.02695(4)	0.04721(2)	Pr1	32g	0.12991(3)	0.02686(3)	0.04742(2)
La2	32g	0.37036(4)	0.25434(4)	0.05965(2)	Pr2	32g	0.37071(3)	0.25436(3)	0.05951(2)
La3	16f	0.13330(4)	$x + 1/4$	$1/8$	Pr3	16f	0.13364(4)	$x + 1/4$	$1/8$
O	8a	0	$1/4$	$3/8$	O	8a	0	$1/4$	$3/8$
Se1	32g	0.02192(6)	0.38134(7)	0.00124(4)	Se1	32g	0.02218(5)	0.38111(5)	0.00199(4)
Se2	32g	0.34224(7)	0.07046(7)	0.09270(4)	Se2	32g	0.34290(5)	0.07081(5)	0.09262(4)
Se3	32g	0.03914(6)	0.07100(7)	0.17174(4)	Se3	32g	0.03885(5)	0.07057(5)	0.17167(4)
Se4	16e	0.35523(9)	0	$1/4$	Se4	16e	0.35463(7)	0	$1/4$
$Ce_{10}OSe_{14}$					$Nd_{10}OSe_{14}$				
Ce1	32g	0.13000(3)	0.02686(3)	0.04741(2)	Nd1	32g	0.12963(3)	0.02694(3)	0.04743(2)
Ce2	32g	0.37049(3)	0.25428(3)	0.05949(2)	Nd2	32g	0.37075(3)	0.25459(3)	0.05933(2)
Ce3	16f	0.13347(3)	$x + 1/4$	$1/8$	Nd3	16f	0.13381(3)	$x + 1/4$	$1/8$
O	8a	0	$1/4$	$3/8$	O	8a	0	$1/4$	$3/8$
Se1	32g	0.02201(4)	0.38106(5)	0.00168(3)	Se1	32g	0.02249(5)	0.38122(5)	0.00236(4)
Se2	32g	0.34256(5)	0.07063(5)	0.09262(3)	Se2	32g	0.34298(5)	0.07106(5)	0.09269(4)
Se3	32g	0.03891(5)	0.07076(5)	0.17178(3)	Se3	32g	0.03876(5)	0.07060(5)	0.17159(4)
Se4	16e	0.35487(6)	0	$1/4$	Se4	16e	0.35395(7)	0	$1/4$

All important interatomic distances (Table 2) are very similar to those found in other well-investigated compounds (Table 3). According to the oxygen implementation, the Se^{2-}–M^{3+} distance ranges expands largely from the C-type M_2Se_3 to the $M_{10}OSe_{14}$ compounds (Tables 2 and 3). Regarding the significantly different distances between O^{2-}/Se^{2-} and $(M2)^{3+}$ (243–248 pm *vs.* 288–348 pm) the refinement of a mixed site occupation of O^{2-} and Se^{2-} at the *Wyckoff* position 8a just like in $La_{10}O_{0.945}Se_{14.055}$ [14] is certainly not appropriate.

Table 2. Important internuclear distances (d/pm) for the four $M_{10}OSe_{14}$ representatives (M = La–Nd).

| $M_{10}OSe_{14}$			M = **La**	M = **Ce**	M = **Pr**	M = **Nd**
	–Se1	(1×)	298.7(1)	296.4(1)	294.4(1)	292.4(1)
	–Se4	(1×)	301.1(1)	298.2(1)	296.2(1)	294.1(1)
	–Se2	(1×)	306.0(1)	303.4(1)	301.5(1)	300.2(1)
M1	–Se1'	(1×)	306.2(1)	304.2(1)	302.2(1)	300.2(1)
	–Se3	(1×)	307.7(1)	304.7(1)	302.5(1)	300.6(1)
	–Se2'	(1×)	309.8(1)	307.1(1)	305.4(1)	303.8(1)
	–Se3'	(1×)	310.0(1)	307.9(1)	306.1(1)	304.6(1)
	–Se2"	(1×)	357.9(1)	355.4(1)	353.8(1)	352.4(1)
	–O	(1×)	248.2(1)	246.1(1)	244.2(1)	243.0(1)
	–Se1	(1×)	294.5(1)	291.9(1)	289.9(1)	288.0(1)
	–Se2	(1×)	304.2(1)	301.4(1)	299.2(1)	297.6(1)
M2	–Se3	(1×)	308.8(1)	305.6(1)	304.1(1)	302.4(1)
	–Se3'	(1×)	314.9(1)	312.0(1)	310.1(1)	308.6(1)
	–Se4	(1×)	320.1(1)	317.9(1)	316.3(1)	314.9(1)
	– Se2'	(1×)	329.1(1)	326.2(1)	323.6(1)	321.6(1)
	–Se1'	(1×)	348.3(1)	345.3(1)	343.3(1)	342.2(1)
	–Se3	(2×)	300.6(1)	298.1(1)	296.2(1)	294.5(1)
M3	–Se2	(2×)	308.1(1)	305.6(1)	303.4(1)	301.8(1)
	– Se1	(2×)	315.3(1)	311.8(1)	309.3(1)	306.9(1)
	– Se4	(2×)	322.8(1)	319.7(1)	317.5(1)	315.8(1)

Table 3. Selected internuclear distances (d/pm) and angles ($\sphericalangle$/deg) for the $M_{10}OSe_{14}$ representatives (M = La–Nd) in comparison to those for known related compounds (*in italics*).

Distances/angles/examples		$La_{10}OSe_{14}$	$Ce_{10}OSe_{14}$	$Pr_{10}OSe_{14}$	$Nd_{10}OSe_{14}$
$d(Se^{2-}–M^{3+})$		295–358	292–355	290–354	288–352
example 1		*C-La$_2$Se$_3$* [15]	*C-Ce$_2$Se$_3$* [16]	*C-Pr$_2$Se$_3$* [15]	*C-Nd$_2$Se$_3$* [17]
		304–323	*302–320*	*299–318*	*297–317*
example 2		*La$_5$NSe$_6$* [18]	*Ce$_3$ONSe$_2$* [19]	*Pr$_2$OSe$_2$* [1]	*Nd$_3$ONSe$_2$* [19]
		289–355	*293–355*	*293–331*	*289–347*
$d(O^{2-}–M^{3+})$	(4×)	248.2	246.1	244.2	243.0
example		*La$_{10}OS_{14}$* [8]	*Ce$_{10}OS_{14}$* [8]	*Pr$_{10}OS_{14}$* [8]	*Nd$_{10}OS_{14}$* [8]
		245.4	*243.0*	*242.1*	*240.8*
$\sphericalangle M$2-O-M2	(4×)	107.9	108.0	108.0	108.1
$\sphericalangle M$2-O-M2'	(2×)	112.6	112.5	112.4	112.2
example		*La$_{10}OS_{14}$* [8]	*Ce$_{10}OS_{14}$* [8]	*Pr$_{10}OS_{14}$* [8]	*Nd$_{10}OS_{14}$* [8]
$\sphericalangle M$2-O-M2	*(4×)*	*108.1*	*108.2*	*108.2*	*108.3*
$\sphericalangle M$2-O-M2'	*(2×)*	*112.3*	*112.1*	*112.1*	*111.9*

Isolated oxide-anion centered metal tetrahedra $[O(M2)_4]^{10+}$ (Figure 2b) embedded in a complex anionic lanthanide selenide matrix $^3_\infty\{[(M1)_3(M3)_3Se_{14}]^{10-}\}$ dominate the crystal structure of the title compounds (Figure 2a). The distances between O^{2-} and $(M2)^{3+}$ in these oxide selenides $M_{10}OSe_{14}$ decrease from 248 pm for M = La to 243 pm for M = Nd caused by the lanthanide contraction, but they

also amount to values slightly higher than in the corresponding lanthanide oxide sulfides $M_{10}OS_{14}$ (Table 3, M = La–Nd). Although most trends remain the same in the oxide chalcogenides $M_{10}OCh_{14}$ from M = La to M = Nd, the angles $M2$-O-$M2$ exhibit lower values in the selenide compounds, while the angles $M2$-O-$M2'$ show higher values as compared to the sulfide representatives. These effects certainly originate from the different sizes of the chalcogenide anions within the complex anionic lanthanide chalcogenide matrix $_\infty^3\{[(M1)_3(M3)_3Ch_{14}]^{10-}\}$ (S^{2-} *vs.* Se^{2-}). Similar to the $M_{10}OS_{14}$-type compounds (M = La–Nd, Sm and Gd) [8,9], most of the oxygen-free part in this crystal structure of the $M_{10}OSe_{14}$ series ($M_{10}Se_{14} \equiv M_2Se_{2.8}$, M = La–Nd) can be interpreted as closely related to the cation-defective Th_3P_4-type structure [20] of the corresponding lanthanide sesquiselenides M_2Se_3 known as their C-type modification [15–17]. Hence the internuclear distances between Se^{2-} and M^{3+} do not differ significantly, with the exception of the contacts $M1$-Se2″ and $M2$-Se1′ in the title compounds (compare Table 2 and Table 3).

Figure 2. View at (**a**) the unit-cell representation; and (**b**) the isolated $[O(M2)_4]^{10+}$ tetrahedra with their full Se^{2-} surrounding in the crystal structure of the $M_{10}OSe_4$ representatives (M = La–Nd).


    (**a**)   (**b**)
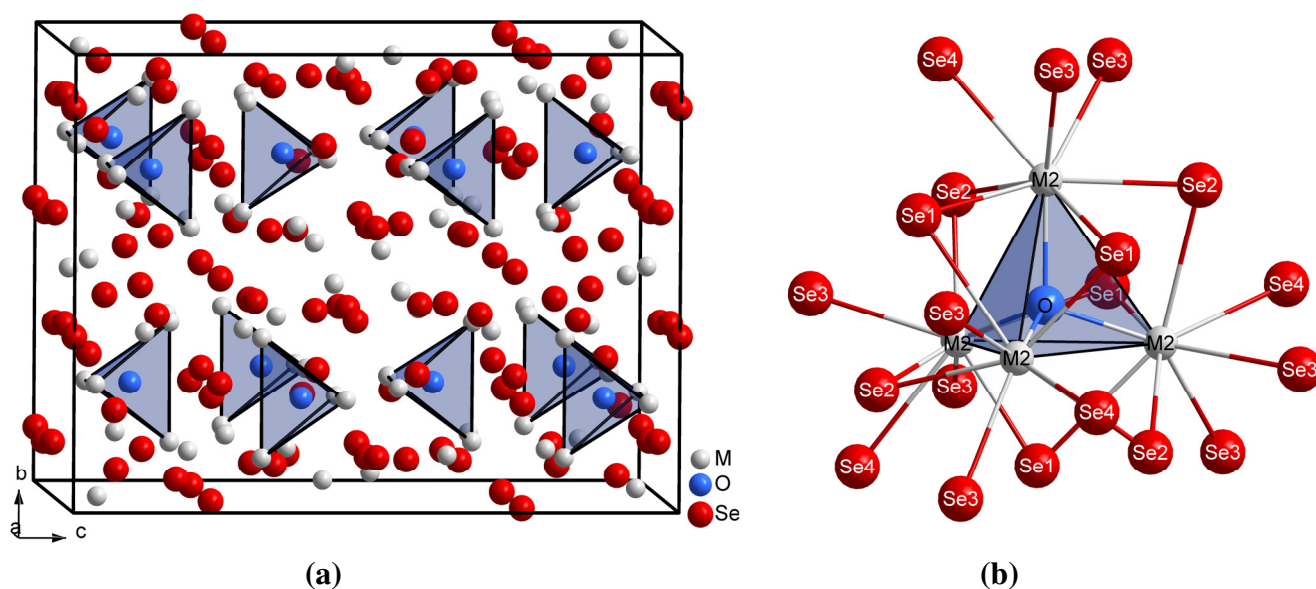
2.2. Optical Band Gaps

The optical band gaps of the oxide selenides $M_{10}OSe_{14}$ amount to values between 1.89 eV and 2.04 eV (see Table 4 and Figure 3), so they should represent typical semiconducting materials. In comparison with the oxygen-richer oxide selenide diselenides $M_4O_4Se[Se_2]$ the band gaps are exhibiting lower values than those of the title compounds. Similar to the $M_4O_4Se[Se_2]$ series the transitions of electrons from the $4f$ to the $5d$ orbitals or within the $4f$ shell of the lanthanides in the related $M_{10}OSe_{14}$ representatives can be detected below the actual band gap for the corresponding cerium (mainly $4f$–$5d$), praseodymium and neodymium compounds (mainly intra $4f$).

Table 4. Comparison of the optical band gaps of the $M_{10}OSe_{14}$, $M_4O_4Se[Se_2]$ and C-M_2Se_3 representatives (M = La–Nd).

General formula	Reference	M = La	M = Ce	M = Pr	M = Nd
$M_{10}OSe_{14}$	this work	2.04 eV	1.97 eV	1.89 eV	1.98 eV
$M_4O_4Se[Se_2]$	[7]	1.89 eV	1.69 eV	1.87 eV	1.87 eV
M_2Se_3	[21]	2.3 eV	1.85 eV	2.0 eV	2.0 eV

Figure 3. Diffuse reflectance spectra (DRS) of the $M_{10}OSe_{14}$ representatives (M = La–Nd) after applying a *Kubelka-Munk* transformation.
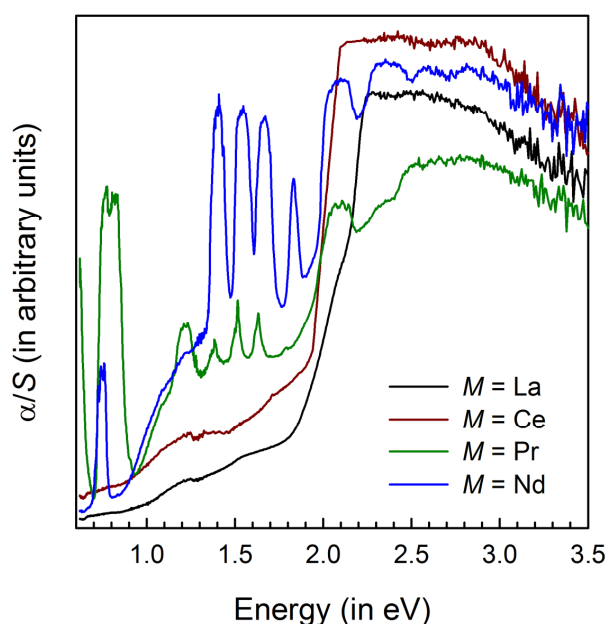
Strobel et al. [7] interpret the conduction band (CB) as predominately an attribute of the 4p states of Se and the valence band (VB) as the main attribute of the empty 5d orbitals of the respective lanthanides. This should be also true for the oxide selenides $M_{10}OSe_{14}$. But the differences in the crystal structures (tetragonal for $M_{10}OSe_{14}$ *vs.* orthorhombic for $M_4O_4Se_3$) and the different kinds of selenide units (Se^{2-} in $M_{10}OSe_{14}$ *vs.* Se^{2-} and [Se$_2$]$^{2-}$ in $M_4O_4Se_3$) cause some variations in the optical band gaps. While for the title compounds just the eightfold coordination is realized for the trivalent lanthanide cations, the $M_4O_4Se_3$ representatives exhibit eight- as well as sixfold coordination spheres for these cations. More importantly, the diselenide units [Se$_2$]$^{2-}$ in the $M_4O_4Se_3$ cases probably shift the band gaps to significantly smaller values as the bonding situation and therefore the energy levels of VB should be quite different from those examples with just Se^{2-} anions (M_2Se_3 and $M_{10}OSe_{14}$). All these band gaps are somewhat lower than those of the C-type lanthanide sesquiselenides M_2Se_3 with M = La–Nd investigated by *Prokofiev et al.* [21] (1.85–2.30 eV), but they clearly support a strong similarity between all these selenide representatives (M_2Se_3, $M_{10}OSe_{14}$ and $M_4O_4Se[Se_2]$). Furthermore, it opens not only for the oxide selenides with the general formula $M_{10}OSe_{14}$ (M = La–Nd) but a new scientific field for their applications as red pigments without toxic metals like cadmium [22].

3. Experimental Section

Single crystals and phase pure samples of the $M_{10}OSe_{14}$ representatives with M = La–Nd were obtained after heating mixtures of the respective lanthanide metal (ChemPur: 99.9%), selenium (Merck: 99.9%) and selenium dioxide (SeO$_2$, ChemPur: 99.999%) in molar ratios of 20:27 : 1 along with an excess of caesium chloride (CsCl, ChemPur: 99.9%) as flux at 800 °C for four days in evacuated silica ampoules according to:

$$20\,M + 27\,Se + SeO_2 \longrightarrow 2\,M_{10}OSe_{14} \qquad (1)$$

For crystals of high quality, these mixtures had to be cooled within four days from 800 to 500 °C followed by a subsequent slow cooling process down to room temperature within ten hours.

All four water- and air-stable products were characterized by single-crystal X-ray diffraction (IPDS-I, Stoe, Mo-Kα radiation with graphite monochromator: λ = 71.01 pm) at room temperature. Essential information for the structure solutions and refinements for the representatives of the $M_{10}OSe_{14}$ series (M = La–Nd) using the program packages SHELXS-97 and SHELX-97 [23] as well as X-RED (within X-SHAPE) for correction of absorption [24] and scattering factors from the International Tables (Volume C) [25] is available from Table 5. Further details can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-424095 (La$_{10}$OSe$_{14}$), CSD-424094 (Ce$_{10}$OSe$_{14}$), CSD-94413 (Pr$_{10}$OSe$_{14}$), and CSD-424093 (Nd$_{10}$OSe$_{14}$).

Table 5. Crystallographic data for the four $M_{10}OSe_{14}$ representatives (M = La–Nd).

$M_{10}OSe_{14}$	M = La	M = Ce	M = Pr	M = Nd
Colour	red	ruby red	ruby red	ruby red
Crystal system	tetragonal	tetragonal	tetragonal	tetragonal
Space group/Formula units	$I4_1/acd/Z$ = 8	$I4_1/acd/Z$ = 8	$I4_1/acd/Z$ = 8	$I4_1/acd/Z$ = 8
a (pm)	1592.04(9)	1578.96(9)	1568.74(8)	1559.83(8)
c (pm)	2106.48(14)	2086.59(14)	2073.42(13)	2062.91(12)
c/a	1.323	1.321	1.322	1.322
V_m (cm^3/mol)/D_x (g/cm^3)	401.91/6.247	391.60/6.442	384.11/6.588	377.83/6.786
F(000)/ θ_{max}	8432/30.2	8512/31.6	8592/30.4	8672/31.6
±h/±k/±l	22/22/29	23/23/30	22/22/29	22/22/30
Reflections (all/independent)	36621/1999	52742/2178	43025/1926	39083/2117
μ/mm^{-1}	34.70	36.69	38.66	40.58
R_{int}/R_σ	0.118/0.051	0.127/0.047	0.101/0.034	0.087/0.026
R_1/wR_2	0.069/0.078	0.066/0.057	0.052/0.067	0.059/0.096
GooF	0.986	0.973	0.986	1.037

Diffuse reflectance spectra (DRS) were recorded on a TIDAS UV-VIS-spectrometer (J&M) equipped with optic fibers. As reference, a Ba[SO$_4$] standard found application. For converting the reflectance into absorbance and obtaining the band gap information, the *Kubelka-Munk* function was applied. This approximation relates the absorbance coefficient (α) and the diffusion coefficient (S) of the compounds. The absorption-edge energies (E_g) were derived by the intersection points of the particular baseline along the energy axis and the extrapolated line of the linear part of the threshold.

4. Conclusions

The crystal structures of all four representatives of the oxide selenides $M_{10}OSe_{14}$ with M = La–Nd exhibit the $Pr_{10}OS_{14}$-type arrangement. Hence, the lanthanide selenide matrix ${}^{3}_{\infty}\{[(M1)_3(M3)_3Se_{14}]^{10-}\}$ embed isolated $[O(M2)_4]^{10+}$ tetrahedra. It should be noted that no hint of the existence of representatives with heavier lanthanides (M = Sm–Lu) could be obtained so far, but we are still busy trying to synthesize them. The optical band gaps amount to values between 1.89 and 2.04 eV encouraging investigations in their ability to be used for application as red pigments. Based on the interplay of the light anions O^{2-} and N^{3-} in the *perovskite*-type compounds $Ca_{(1-x)}La_xTaO_{(2-x)}N_{(1+x)}$ [26], we are also actively investigating the band-gap changes in correlation with nitride incorporation in this structure type represented by the recently published compound $La_{10.25}O_{0.25}N_{0.75}Se_{14}$ [27,28].

Acknowledgments

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