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Structural, thermal, and IR studies of β -[Nd₂O₂](CrO₄), an unexpected analog of a slag phase [Ba₂F₂](S⁶⁺O₃S²⁻)

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Abstract: A family of Ln_2CrO_6 ($\text{Ln}=\text{Pr}, \text{Nd}, \text{Sm-Tb}$) compounds has been re-investigated using powder X-ray diffraction and IR spectroscopy. The structure of $\beta\text{-Nd}_2\text{CrO}_6 \equiv \beta\text{-[Nd}_2\text{O}_2\text{]}\text{(CrO}_4\text{)}$ is similar to that of the slag compound $[\text{Ba}_2\text{F}_2](\text{S}^{6+}\text{O}_3\text{S}^{2-})$ in that it exhibits a disordered arrangement of $(\text{CrO}_4)^{2-}$ anions between $[\text{Nd}_2\text{O}_2]^{2+}$ litharge-type blocks. Its structural architecture is also related to other layered α - and γ - $[\text{Ln}_2\text{O}_2](\text{AO}_4)$ species ($A=\text{S}, \text{Cr}, \text{Mo}$), showing various orientations of the tetrahedral anions within the interlayer space. Size relationships between the incorporated tetrahedral anions and formation of different structure types (denoted as $M1$ -, $M2$ - and T -type) are reviewed. The possible existence of new compounds which are isostructural with, or structurally related to, $\beta\text{-[Nd}_2\text{O}_2\text{]}\text{(CrO}_4\text{)}$ and bearing other transition metal-centred tetrahedral anions are discussed.

Keywords: chromates; high temperature X-ray diffraction; layered structures; litharge-derivative structures; rare-earth metals.

Introduction

Layered structural motifs are common among the structures of rare-earth oxide compounds containing additional tetrahedral anions [1, 2]. The structures of oxide sulfates and phosphates, $[\text{Ln}_2\text{O}_2](\text{SO}_4)$ and $[\text{Ln}_3\text{O}_3](\text{PO}_4)$, are characterized by the alternation of positively charged $[\text{Ln}_n\text{O}_n]^{n+}$ litharge-type slabs and various anions in the interlayer space [3–5]. More complex oxyhalide derivatives such as $[\text{LnO}]_4(\text{MO}_4)(X)$ ($M=\text{P}$ or As ; $X=\text{Cl}$ or Br) are also known [6–8]. The $[\text{Ln}_2\text{O}_2](\text{SO}_4)/[\text{Ln}_2\text{O}_2]\text{S}$ systems have been demonstrated to exhibit high capacity for oxygen storage [9]. Similar oxysulfates were also used as precursors for $\text{Ln}_2\text{O}_2\text{S}$ -based luminescent materials [10]. Fluoride analogs of the oxide compounds were also reported, viz. $[\text{Pb}_2\text{F}_2](\text{MO}_4)$ ($M=\text{S}, \text{Se}$ [11, 12]) and, notably, a unique thiosulfate bearing slag phase of composition $[\text{Ba}_2\text{F}_2](\text{S}^{6+}\text{O}_3\text{S}^{2-})$ [13].

Most of these structures contain tetrahedral anions centered by p -block elements (P, S, As, Se), whereas analogs involving d -block elements are rare as yet. Only several layered $[\text{Ln}_2\text{O}_2](\text{MoO}_4)$ compounds with the earliest rare-earths have been synthesized [14, 15]. Balestracci and Mareschal [16] reported a series of $[\text{Ln}_2\text{O}_2](\text{CrO}_4)$ oxide chromates obtained via the decomposition of nitrate mixtures. Their X-ray diffraction patterns were reported to differ from those of oxysulfates, but the diffractograms were not provided. Later [17], a series of $[\text{Ln}_2\text{O}_2](\text{CrO}_4)$ compounds ($\text{Ln}=\text{La-Dy}$, except Ce and Pm) were prepared via a solid-state metathesis route. The structure of $[\text{La}_2\text{O}_2](\text{CrO}_4)$ proved to be analogous with that of $[\text{La}_2\text{O}_2](\text{SO}_4)$, but not so those of the $[\text{Ln}_2\text{O}_2](\text{CrO}_4)$ species ($\text{Ln}=\text{Pr}, \text{Nd}, \text{Sm-Tb}$) which are different and isostructural. Note, their XRD patterns differed significantly from that of the $[\text{La}_2\text{O}_2](\text{CrO}_4)$. Their XRD patterns could be indexed using a monoclinic unit cell with $a=15.5\text{--}15.7\text{ \AA}$, $b=7.76\text{--}8.02\text{ \AA}$, $c=4.00\text{--}4.07\text{ \AA}$ and $\beta=92\text{--}93^\circ$ [17], but the crystal structures could not be determined despite numerous attempts. Our recent investigations have shown that the structure determination of such compounds may be severely hampered by the observation that several sets of unit cell

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parameters may yield fairly similar indexing FOMs [12]. Therefore, the unit cell used initially for the structural determination of Nd₂CrO₆ might be not the right one. This assumption is corroborated by the fact that the calculated unit cell volume of Pr₂CrO₆ was slightly larger than that of La₂CrO₆ thus contradicting the expectation of a volume reduction due to the lanthanide contraction. In this paper we describe the results of the successful crystal structure determination of β -Nd₂CrO₆ $\equiv$ β -[Nd₂O₂](CrO₄), completed by IR spectroscopy and a study of its high-temperature X-ray behavior.

Experimental

Synthesis

The Ln₂CrO₆ (Ln = Pr, Nd, Sm, Eu, Gd, Tb) compounds were prepared via solid-state exchange reactions at 600–700 °C between LnOCl (Vekton, Russia) and K₂CrO₄ (Vekton, Russia) in a 2:1 molar ratio. The KCl by-product was dissolved in distilled water and the insoluble residues were dried under ambient conditions. Their PXRD patterns were in good agreement with those observed earlier [16]. The relative amounts of by-products, viz. KLn(CrO₄)₂ [18], and LnCrO₃ [19], increases with the increasing atomic number of the rare-earth cations.

Structure determination of Nd₂CrO₆

Powder diffraction data for the structure determination of Nd₂CrO₆ were collected on a Rigaku Ultima IV diffractometer utilizing CuK α _{1,2} radiation. The PXRD pattern was indexed in the monoclinic unit cell: C2/m, $a = 15.6322(1)$ Å, $b = 4.0176(1)$ Å, $c = 4.0696(1)$ Å, $\beta = 92.126(1)^\circ$, $V = 255.41(1)$ Å³. Note that the b parameter value is halved with respect to the previous reported one [17]. Several remaining unindexed weak reflections correspond to the trace admixtures (~1%) of NdCrO₃ [19] and KNd(CrO₄)₂ [18]. Their presence seems to be the reason for the earlier incorrect determination of a twice as large unit cell since the strongest reflections of NdCrO₃ mimic the doubling of the b parameter of the true Nd₂CrO₆ unit cell. Space group assignment and Rietveld refinement were done in the JANA2006 software [20]. The structure solution prior to the Rietveld refinement (Lorentz profile function, Legendre polynomials) was done using the SUPERFLIP algorithm [21] implemented in JANA2006. In order to account for preferred orientation, the modified March-Dollase approach was applied [22]. The localization of atoms in the [Nd₂O₂]²⁺ slab was straightforward, whereas all Fourier maxima in the interlayer space were only half as strong as would be expected for chromium and oxygen atoms. Consequently, the chromate group was resolved as a disordered arrangement of two equally possible interpenetrating orientations (Figure 1). Constraints were applied on the geometry of the CrO₄ moiety. Several attempts to resolve the disorder in the doubled unit cells as reported in [4, 11] remained unsuccessful. The methods and software utilized were the same [21] as used previously for the structure determination of related layered lead compounds [12, 23].

Fig. 1: Disordered CrO₄ tetrahedra in the structure of β -[Nd₂O₂](CrO₄). All of the oxygen atoms (O_c) and Cr atoms are half-occupied.

Unit cell parameters of the obtained isostructural Ln₂CrO₆ compounds are listed in Table 1. Further details of the data collection and refinement are given in Table 2, atomic coordinates are provided in Table 3, and selected bond lengths in Table 4. The Rietveld refinement plot is shown in Figure 2.

Upon closer inspection of the compounds with similar unit cell metrics and atomic arrangements it was found, surprisingly, that the atomic arrangement in Nd₂CrO₆ corresponds closely to that of the [Ba₂F₂](S⁶⁺O₃S²⁻) structure [13]. In particular, the character of the disorder in [Ba₂F₂](S⁶⁺O₃S²⁻) is very similar to that one observed in Nd₂CrO₆. The structural model obtained by single-crystal X-ray analysis and provided in [13] was successfully refined for PXRD data of Nd₂CrO₆ and confirmed the general agreement of both structures with only one exception: The oxygen atom originating from S2 (see the designations in [13]) was too far from Cr, so that it was blurred by the refinement, while a distinct Fourier maximum was observed at about 1.6 Å from Cr and assigned to oxygen. The correspondence between atoms in the published [Ba₂F₂](S⁶⁺O₃S²⁻) and in the crystal structure of Nd₂CrO₆ described herein is as follows: Ba $\leftrightarrow$ Nd1, S1 $\leftrightarrow$ Cr1, S2 $\leftrightarrow$ O4, O1 $\leftrightarrow$ O3, O2 $\leftrightarrow$ O2, F $\leftrightarrow$ O1.

IR spectra

The IR spectra (Figure 3) were acquired on a Bruker Vertex 70 FTIR spectrometer for two representatives, Nd₂CrO₆ and Gd₂CrO₆, which is the latest rare-earth member obtained with acceptably low amount (~5%) of by-phases.

Thermal behavior

The thermal behavior of Nd₂CrO₆ was studied in air by means of a Rigaku Ultima X-ray diffractometer (CuK α radiation) with a high-temperature camera Rigaku HTA 1600. The sample was prepared from a heptane suspension on a Pt-Rh plate. Temperature steps of 20 °C were used in the range 25–800 °C. Unit-cell parameters at different temperatures were refined by least-squares methods. The main coefficients of the thermal expansion tensor were determined using a linear approximation of the temperature dependence by the *ThetaToTensor* program [24]. The evolution of the powder diffraction patterns with increasing temperature is shown

Tab. 1: Unit-cell parameters (monoclinic, $C2/m$) of β -[Ln₂O₂](CrO₄) series determined from Le Bail PXRD pattern decomposition.

Compound	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (deg)	<i>V</i> (Å ³)	<i>R_p</i> / <i>R_{wp}</i>
Pr ₂ CrO ₆	15.6319(9)	4.0368(2)	4.0794(2)	92.019(4)	257.27(4)	5.17/8.17
Nd ₂ CrO ₆	15.6321(5)	4.0176(1)	4.0696(1)	92.126(1)	255.41(2)	6.49/8.47
Sm ₂ CrO ₆	15.476(1)	3.9641(3)	4.0230(4)	91.784(5)	246.69(6)	2.64/3.90
Eu ₂ CrO ₆	15.444(2)	3.9409(5)	4.0024(6)	91.56(1)	243.52(8)	2.19/3.51
Gd ₂ CrO ₆	15.407(2)	3.9197(5)	3.9982(6)	92.02(1)	241.30(8)	2.30/3.53
Tb ₂ CrO ₆	15.297(6)	3.898(1)	3.982(1)	92.06(2)	237.3(2)	2.75/4.57

Tab. 2: Crystallographic data and refinement parameters for β -[Nd₂O₂](CrO₄).

Phase composition	Target phase + 1.03(5)% NdCrO ₃ + 0.98(6)% KNd(CrO ₄) ₂
Space group	$C2/m$
<i>Z</i>	2
<i>a</i> (Å)	15.6322(1)
<i>b</i> (Å)	4.0176(1)
<i>c</i> (Å)	4.0696(1)
β (deg)	92.126(1)
<i>V</i> (Å ³)	255.41(1)
Density (g/cm ³)	5.675
Radiation	CuK $\alpha_{1,2}$
2 θ range (deg)	8–125
Number of points	5691
Number of reflections	239
Overall parameters	63
Structural parameters	20
Restraints	1 (CrO ₄ ²⁻ moiety)
<i>R_f</i>	0.035
<i>R_p</i>	0.065
<i>R_{wp}</i>	0.084
χ^2	1.71

Tab. 3: Atomic coordinates and isotropic displacement parameters (in Å²) in β -[Nd₂O₂](CrO₄).

Atom	Site	<i>s.o.f.</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U_{iso}</i>
Nd1	4 <i>i</i>	1	0.82700(5)	0	0.2591(2)	0.0117(3)
Cr1	4 <i>i</i>	1/2	0.9700(3)	0	0.932(1)	0.026(2)
O1	4 <i>i</i>	1	0.7509(5)	0	0.746(2)	0.016(3) ^a
O2	4 <i>i</i>	1/2	0.0733(4)	0	0.061(4)	0.016(3) ^a
O3	8 <i>j</i>	1/2	0.9309(7)	0.818(2)	0.731(2)	0.016(3) ^a
O4	4 <i>i</i>	1/2	0.9287(8)	0	0.288(3)	0.016(3) ^a

^aRefined with the same *U_{iso}*.

in Figure 4a. No decomposition of Nd₂CrO₆ occurs up to 800 °C. Refined unit-cell parameters for Nd₂CrO₆ at different temperatures demonstrate linear behavior and increase with the temperature rise (Figure 1S). Thermal expansion coefficients for Nd₂CrO₆ are as follows: $\alpha_{11} = -4.7 \times 10^{-6}$, $\alpha_{22} = 11.9 \times 10^{-6}$, $\alpha_{33} = 27.3 \times 10^{-6} \text{ °C}^{-1}$, $\alpha_v = 34.5 \times 10^{-6} \text{ °C}^{-1}$ at 800 °C.

Tab. 4: Selected interatomic distances (Å) and bond angles (deg) in the structure of β -[Nd₂O₂](CrO₄).

Litharge slab	<i>d</i> (Nd1–O1)	2.382(7)
		2.330(7)
		2.350(4) × 2
CrO ₄ anion	< <i>d</i> (Nd–O)>	2.353(6)
	<i>d</i> (Cr1–O2)	1.613(7)
	<i>d</i> (Cr1–O3)	1.624(9) × 2
	<i>d</i> (Cr1–O4)	1.612(13)
	< <i>d</i> (Cr–O)>	1.615(9)
	α (O2–Cr1–O3)	111.6(3) × 2
	α (O2–Cr1–O4)	114.6(6)
	α (O3–Cr1–O3)	103.7(4)
	α (O3–Cr1–O4)	107.4(3) × 2
Interlayer distances	<i>d</i> (Nd1–O2)	2.685(6) × 2
	<i>d</i> (Nd1–O3)	2.572(9) × 2
		2.840(9) × 2
	<i>d</i> (Nd1–O4)	2.562(8) × 2
	< <i>d</i> (Nd–O)>	2.665(8)

Fig. 2: Final Rietveld refinement plot for β -[Nd₂O₂](CrO₄). Admixtures [II – KNd(CrO₄)₂, III – NdCrO₃] were included in the refinement.

Discussion

The present study confirms the earlier suggestion [17] that the Ln₂CrO₆ (*Ln* = Pr, Nd, Sm, Eu, Gd, Tb) compounds may form layered structures (Figure 5a). The present work has shown that the studied Ln₂CrO₆ representatives can be considered to adopt the same structure type as [Ba₂F₂]

Fig. 3: IR spectra of the β -[Nd₂O₂](CrO₄) and β -[Gd₂O₂](CrO₄).

(S⁶⁺O₃S²⁻) [13] (Figure 5b), thus demonstrating the crystal chemical similarity between oxide compounds of trivalent rare earths cations (and Bi) on one side, and fluoride compounds of divalent alkaline earths cations (and Pb) on the other side. The less symmetrical S⁶⁺O₃S²⁻ anion behaves in similarly as the highly symmetrical CrO₄²⁻.

The crystal structure of Nd₂CrO₆ is based on [Nd₂O₂]²⁺ litharge-type slabs (Figure 6) analogous to those found in the structure of the NdOCl precursor. The “additional” oxygen (O_a) atoms (not bonded to Cr⁶⁺ cation in CrO₄²⁻) form short and strong O_a-Nd bonds thus forming ONd₄ oxocentered tetrahedra [2], which share common edges

to form [Nd₂O₂]²⁺ layers. The Nd-O_{Cr} bonds to the oxygen atoms (O_{Cr}) of the CrO₄ tetrahedral group are longer and relatively weak (Table 4). Thus the structural formula of Nd₂CrO₆ can be written in two parts as β -[Nd₂O₂](CrO₄). The structural architecture of β -[Nd₂O₂](CrO₄) is similar to the previously reported structure of [Nd₃O₃](PO₄) [3]. Instead of PO₄³⁻ the disordered CrO₄²⁻ tetrahedra (Figures 1 and 5) are sandwiched between the layers in β -[Nd₂O₂](CrO₄).

The thermal expansion of β -[Nd₂O₂](CrO₄) is strongly anisotropic (Figure 4b) and is strongest in the direction inclined ~45° relative to the plane of the [Nd₂O₂]²⁺ layer. The observed character of the thermal expansion is generally typical for layered structures. As described above, the Nd-O_l bonds are relatively weak, thus allowing for more intensive expansion along this direction.

The IR spectrum (Figure 3) shows relatively small shifts and split of the fundamental frequencies of the chromate anion. In [25], the latter are given as $\nu_1(A_1) = 846 \text{ cm}^{-1}$, $\nu_2(E) = 347 \text{ cm}^{-1}$, $\nu_3(T_2) = 890 \text{ cm}^{-1}$, and $\nu_4(T_2) = 375 \text{ cm}^{-1}$. The bands which can be attributed to the CrO₄²⁻ moiety in the spectrum of the β -[Nd₂O₂](CrO₄) are 845, 870, 880, and 930 cm⁻¹. The strong band in the low-frequency range is likely to contain contributions from both (CrO₄)²⁻ anions and [Nd₂O₂]²⁺ bands (originating from the A_{2u} band observed at 360–380 cm⁻¹ in structurally related NdOX (X = Cl or Br) oxyhalides [26]). The split E_u band of [Nd₂O₂]²⁺ is most likely located at ~500 cm⁻¹ (530–535 cm⁻¹ for NdOX [27]). It shifts blue in the spectrum of the β -[Gd₂O₂](CrO₄). The positions of the bands assigned to the chromate anion are similar to those observed for KNd(CrO₄)₂ (ν_1 : 880 cm⁻¹, ν_2 : 325–360 cm⁻¹; ν_3 : two bands at 810–840 and

Fig. 4: Evolution of the PXRD pattern of β -[Nd₂O₂](CrO₄) as a function of temperature (a) and pole figures of the thermal expansion coefficients (b).

Fig. 5: General projections of the crystal structures of β -[Nd₂O₂](CrO₄) (a), [Ba₂F₂](S⁶⁺O₃S²⁻) [13] (b), α -[La₂O₂](CrO₄) [17] (c) and [La₂O₂](MoO₄) [15] (d) along the b axis. Litharge-type [Nd₂O₂]²⁺, [Ba₂F₂]²⁺ and [La₂O₂]²⁺ slabs are marked.

915–960 cm⁻¹; ν_4 : 355–475 cm⁻¹ [25]). The latter structure is also monoclinic [18] and features two crystallographically different CrO₄²⁻ anions; therein, the distortions of the

CrO₄²⁻ tetrahedra are not very strong [$d(\text{Cr}-\text{O}) = 1.61\text{--}1.71$ Å; $\alpha(\text{O}-\text{Cr}-\text{O}) = 101\text{--}112^\circ$]. Therefore, we assume that the distortions of the CrO₄²⁻ group in the structure of β -[Nd₂O₂]

Fig. 6: General projection of the [Nd₂O₂]²⁺ slab along the *a* axis. Additional oxygen atoms (O_a) are the centres of ONd₄ tetrahedra. See the text for details.

(CrO₄) are not stronger than those in KNd(CrO₄)₂. Based on relative IR intensities of the vibrational modes given in [25], we tentatively attribute the weak band at 845 cm⁻¹ to ν_1 mode while the two strong and one medium bands at 870, 880, and 930 cm⁻¹, respectively, to the more intense ν_3 mode. The region above 1500 cm⁻¹ is almost featureless suggesting that the β -[Nd₂O₂](CrO₄) is anhydrous and does not absorb water when the KCl by-product is washed away after the synthesis. The bands assigned to the CrO₄²⁻ moiety retain their position in the spectrum of β -[Gd₂O₂](CrO₄) (Figure 3).

To finish the discussion of the structural part, we want to stress that the choice of the correct unit cell during the indexing of powder data is essential for these compounds and requires careful evaluation until a plausible solution

is obtained. Note the small deviation of the *b/c* ratio in β -[Nd₂O₂](CrO₄) from unity (0.987) and of the β angle from 90°. In the structure of [Ba₂F₂](S⁶⁺O₃S²⁻), the *b/c* ratio is almost the same (0.991), but β deviates significantly from 90° (101.5°). A similar phenomenon has been observed for [Pb₂F₂](SO₄) and [La₂O₂](SO₄), where *a*/*2b* = 0.976 and *c*/*2b* = 0.979, respectively [4, 11].

Some trends in the structural chemistry of layered [Ln₂O₂](AO₄) compounds (Table 5) can be established. Ce³⁺ compounds are unknown to date due to the strong reducing behavior of trivalent cerium [17]. With the relatively small (SO₄)²⁻ anion, a complete isostructural series (except Ce and Pm) is formed from α -[La₂O₂](SO₄) to α -[Lu₂O₂](SO₄) [16]. All of these sulfates adopt a monoclinic structure (which we denote as *M1*-type) (Figure 5c), first established for [Pb₂F₂](SO₄) [11]. Oxide sulfates of some trivalent actinides are also known to crystallize in this structure type [28, 29]. With the larger (SeO₄)²⁻, the *M1*-type structure is observed only for *Ln* = La and Nd [30]. Among the chromates, the *M1*-type is known for the La compound only.

β -[Nd₂O₂](CrO₄) and the corresponding chromates of Pr–Tb adopt the [Ba₂F₂](S⁶⁺O₃S²⁻) structure type, which we denote as *M2*-type. With the larger MoO₄²⁻, a tetragonal structure (*T*-type) (Figure 5d) is observed for *Ln* = La, and probably Pr and Nd [14, 15]. Isostructural tungstates are unknown to date which can be tentatively explained by the tendency of the (WO₄)²⁻ anion to polymerize with increase of the tungsten coordination number. The largest anion in this series, (S₂O₃)²⁻, can reside only between the [Ba₂F₂]²⁺ slabs which show the largest inter-layer space in the *M2*-type structures. The space between the litharge-type blocks is restricted by their dimensions

Tab. 5: Crystallographic data of [Ln₂O₂](TO₄) and related layered compounds with litharge-derived blocks.

Formula	<i>a</i> (Å)	<i>b</i> (Å) β (°)	<i>c</i> (Å)	<i>V</i> (Å ³)	Ref.
Type <i>M1</i> (monoclinic, <i>C2/c</i> , <i>Z</i> = 4)					
[Pb ₂ F ₂](SO ₄) ^a	14.242(2)	4.4419(6) 107.418(2)	8.667(1)	523.15(1)	[11]
[Pb ₂ F ₂](SeO ₄)	14.0784(2)	4.6267(1) 108.98(1)	8.8628(2)	545.93(1)	[12]
α -[Ln ₂ O ₂](TO ₄)					
[La ₂ O ₂](SO ₄)	14.349(1)	4.2852(5) 107.00(1)	8.386(1)	492.54(1)	[4]
[Eu ₂ O ₂](SO ₄)	13.6702(9)	4.1931(3) 107.456(7)	8.1394(6)	445.07(1)	[5]
[La ₂ O ₂](CrO ₄)	14.4001(2)	4.4095(1) 107.362(1)	8.4719(1)	513.43(1)	[17]
Type <i>M2</i> (monoclinic, <i>C2/m</i> , <i>Z</i> = 2)					
[Ba ₂ F ₂](S ⁶⁺ O ₃ S ²⁻)	15.3172(5)	4.5898(1) 101.449(1)	4.6320(2)	319.17(2)	[12]
β -[Ln ₂ O ₂](TO ₄)					
[Nd ₂ O ₂](CrO ₄) ^b	15.6322(1)	4.0176(1) 92.126(1)	4.0696(1)	255.41(1)	This work
Type <i>T</i> (tetragonal, <i>I4₁/acd</i> , <i>Z</i> = 2)					
γ -[Ln ₂ O ₂](TO ₄)					
[La ₂ O ₂](MoO ₄)	5.7970(1)		32.0353(3)	1076.95(1)	[14, 15]
[Nd ₂ O ₂](MoO ₄)	5.658(1)		31.586(8)	1011.16(1)	[15]

^aReported in *A2/a*; ^bOther members are listed in Table 1.

in the ab plane [dictated by the size and relative rigidity of the F(Pb,Ba)₄ or OLn₄ tetrahedra towards stretching or compression in the layer plane], and the probability of forming layered structures is low for larger anions. With increasing relative size of the AO₄ vs. OLn₄ (FBa₄) tetrahedra, the M1-type structure becomes less favourable compared to the M2-type, and even less so to the T-type. An interesting chemical selectivity is observed for the fluoride litharge-type slabs which do not accommodate transition metal-based anions, contrary to the oxidic [Ln₂O₂]²⁺. This observation suggests that some other anions incorporating d -block elements could possibly be introduced into the M1-, M2- or T-type structures. As the ionic radii of later An³⁺ are close to those of early Ln³⁺, hypothetical actinide oxysulfates similar to [An₂O₂](SO₄) (An = Am and successors [28, 29]) might exist under proper conditions. Taking into account that K₂AO₄ compounds with A = Cr [31], Mn [32], Fe [33], and Ru [34] are isostructural, one can expect the formation of transition metal bearing M1-type Ln₂AO₆ compounds, at least for Ln = La and A = Mn and Fe. Though (MnO₄)²⁻ and (FeO₄)²⁻ are smaller compared to (CrO₄)²⁻, existence of the corresponding Pr and Tb compounds seems to be less probable due to the possible transition into the higher oxidation state Ln^{IV} (which probably occurs, to a small extent, already in Pr₂CrO₆ and Tb₂CrO₆ [16]). For the proposed La₂RuO₆, the M2-type seems to be more probable due to the larger size of (RuO₄)²⁻. However, synthetic approaches to obtain these compounds are yet obscure as the suggested K₂AO₄ (A = Mn, Fe, Ru) precursors are essentially less stable compared to K₂CrO₄ used for the preparation of β -[Ln₂O₂](CrO₄) series reported in this contribution. Ionothermal or low-temperature melt techniques might be the most promising candidates for the preparation of these evidently metastable compounds.

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References

- [1] M. S. Wickleder, Inorganic lanthanide compounds with complex anions. *Chem. Rev.* **2002**, *102*, 2011.
- [2] S. V. Krivovichev, O. Mentré, O. I. Siidra, M. Colmont, S. K. Filatov, Anion-centered tetrahedra in inorganic compounds. *Chem. Rev.* **2013**, *113*, 6459.
- [3] K. K. Palkina, N. E. Kuz'mina, B. F. Dzhurinskii, E. G. Tselebrovskaya, Neodymium oxyphosphate Nd₃PO₇. *Dokl. Akad. Nauk SSSR* **1995**, *341*, 644.
- [4] S. G. Zhukov, A. Yatsenko, V. V. Chernyshev, V. Trunov, E. Tserkovnaya, O. Antson, J. Hölsä, J. Baules, H. Schenk, Structural study of lanthanum oxysulfate (LaO)₂SO₄. *Mater. Res. Bull.* **1997**, *32*, 43.
- [5] I. Hartenbach, T. Schleid, Serendipitous formation of single-crystalline Eu₂O₂(SO₄). *Z. Anorg. Allg. Chem.* **2002**, *628*, 2171.
- [6] H. Ben Yahia, U. C. Rodewald, K. Boulahya, J. M. Gonzalez-Calbert, R. Pöttgen, HRTEM, SAED and XRD investigations of La₄O₄[AsO₄]Br and Pr₄O₄[AsO₄]Br. *Solid State Sci.* **2011**, *13*, 239.
- [7] H. Ben Yahia, U. C. Rodewald, K. Boulahya, R. Pöttgen, HRTEM, SAED and XRD investigations of RE₄O₄[AsO₄]Cl (RE = La, Pr, Nd, Sm, Eu, Gd). *Mater. Res. Bull.* **2014**, *53*, 257.
- [8] H. Ben Yahia, U. C. Rodewald, C. Feldmann, M. Roming, F. Weill, R. Pöttgen, X-ray diffraction and SAED characterizations of RE₄O₄(PO₄)Cl (RE = La, Pr, and Nd) and photoluminescence properties of Eu³⁺-doped La₄O₄(PO₄)Cl. *J. Mater. Chem.* **2014**, *C2*, 1131.
- [9] M. Machida, K. Kawamura, K. Ito, K. Ikeue, Large-capacity oxygen storage by lanthanide oxysulfate/oxysulfide systems. *Chem. Mater.* **2005**, *17*, 1487.
- [10] X. Wang, J.-G. Li, M. S. Molokeev, X. Wang, W. Liu, Q. Zhu, H. Tanaka, K. Suzuta, B. N. Kim, Y. Sakka, Hydrothermal crystallization of a Ln₂(OH)₄SO₄ · nH₂O layered compound for a wide range of Ln (Ln = La–Dy), thermolysis, and facile transformation into oxysulfate and oxysulfide phosphors. *RSC Adv.* **2017**, *7*, 13331.
- [11] A. R. Kampf, Grandreefite, Pb₂F₂SO₄: crystal structure and relationship to the lanthanide oxide sulfates, Ln₂O₂SO₄. *Am. Miner.* **1991**, *76*, 278.
- [12] D. O. Charkin, I. V. Plokhikh, A. I. Zadoya, S. M. Kazakov, A. N. Zaloga, M. Kozin, W. Depmeier, O. I. Siidra, [Pb₂F₂](SeO₄): a heavier analogue of grandreefite, the first layered fluoride selenate. *Phys. Chem. Miner.* **2018**, *45*, 69.
- [13] A. R. Kampf, The crystal structure of Ba₂F₂(S⁶⁺O₃S²⁻), a natural thiosulphate weathering product of old smelting slags at the Surrender Mill, Yorkshire, UK. *Miner. Mag.* **2009**, *73*, 251.
- [14] J. S. Xue, M. R. Antonio, L. Soderholm, Polymorphs of Ln₂MoO₆: a neutron diffraction investigation of the crystal structures of La₂MoO₆ and Tb₂MoO₆. *Chem. Mater.* **1995**, *7*, 333.
- [15] V. A. Efremov, A. V. Tyulin, V. K. Trunov, Actual structure of tetragonal Ln₂O₂MoO₄ and factors determining the forming structure of the coordination polyhedra. *Koord. Khim.* **1987**, *13*, 1276.
- [16] R. Balestracci, J. Mareschal, Etude structurale des sulfates basiques des terres rares et d'yttrium. *Mater. Res. Bull.* **1967**, *2*, 993.
- [17] D. O. Charkin, R. O. Grischenko, A. A. Sadybekov, R. J. Goff, P. Lightfoot, A new approach to synthesis of layered fluorites containing molecular anions: synthesis of Ln₂O₂CO₃, K(LnO)CO₃, and Ln₂O₂CrO₄ via metathesis reactions. *Inorg. Chem.* **2008**, *47*, 3065.
- [18] I. Bueno, C. Parada, O. Garcia, E. G. Puebla, A. Monge, C. R. Valero, Crystal growth, structure, and properties of KLa(CrO₄)₂. *Dalton Trans.* **1988**, *7*, 1911.
- [19] M. W. Lufaso, S. J. Mugavero, W. R. Gemmill, Y. J. Lee, T. Vogt, H. C. zur Loye, Pressure- and temperature-dependent X-ray diffraction studies of NdCrO₃. *J. Alloys Compd.* **2007**, *433*, 91.

- [20] V. Petříček, M. Dušek, L. Palatinus, Crystallographic computing system JANA2006: general features. *Z. Kristallogr. – Cryst. Mat.* **2014**, 229, 345.
- [21] L. Palatinus, G. Chapuis, Superflip – a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. *J. Appl. Crystallogr.* **2007**, 40, 786.
- [22] S. V. Burakov, A. N. Zaloga, E. S. Semkin, I. S. Yakimov, Research on convergence of multipopulation binary- and real-coded genetic algorithms for solution of crystal structure from X-ray powder diffraction data. *Cryst. Res. Tech.* **2015**, 50, 724.
- [23] D. O. Charkin, I. V. Plokhikh, A. N. Zaloga, M. V. Lobanov, S. M. Kazakov, One disorder out of two orders: synthesis and crystal structures of cation-ordered PbNaF₂NO₃, anion-ordered Pb₂O₂FNO₃, and continuous disordered (Pb,Na)₂(O,F)₂₋₈NO₃ solid solution with Sillén-derived structures. *Solid State Sci.* **2017**, 71, 111.
- [24] R. S. Bubnova, V. A. Firsova, S. K. Filatov, Software for determining the thermal expansion tensor and the graphic representation of its characteristic surface (theta to tensor-TTT). *Glass Phys. Chem.* **2013**, 39, 347.
- [25] E. J. Baran, E. G. Ferrer, I. Bueno, C. Parada, Vibrational spectra of some double chromates of the type LnK(CrO₄)₂. *J. Raman Spectr.* **1990**, 21, 27.
- [26] G. Meyer, T. Schleid, Oxidchloride unter reduzierten Bedingungen: Einkristalle von NdOCl und GdOCl. *Z. Anorg. Allg. Chem.* **1986**, 533, 181.
- [27] L. J. Basile, J. R. Ferraro, D. Gronert, IR spectra of several lanthanide oxyhalides. *J. Inorg. Nucl. Chem.* **1971**, 33, 1047.
- [28] R. D. Baybarz, J. A. Fahey, R. G. Haire, The preparation, crystal structures, and some properties of californium oxysulfate and oxysulfide. *J. Inorg. Nucl. Chem.* **1974**, 36, 2023.
- [29] W. H. Jr. Hale, W. C. Mosley, Preparation of curium oxysulfate and curium oxide by resin calcinations. *J. Inorg. Nucl. Chem.* **1973**, 35, 165.
- [30] S. Karvinen, K. Lumme, L. Niinistö, Thermal decomposition of lanthanum selenate pentahydrate in air and nitrogen. *J. Thermal Anal. Calorim.* **1987**, 32, 919.
- [31] K. Toriumi, Y. Saito, Electron density distribution in crystals of α -K₂CrO₄. *Acta Crystallogr.* **1978**, B34, 3149.
- [32] G. J. Palenik, Crystal structure of potassium manganate. *Inorg. Chem.* **1967**, 6, 507.
- [33] M. L. Hoppe, E. O. Schlemper, R. K. Murmann, Structure of dipotassium ferrate(VI). *Acta Crystallogr.* **1982**, B38, 2237.
- [34] D. Fischer, R. Hoppe, K. M. Mogare, M. Jansen, Syntheses, crystal structures and magnetic properties of Rb₂RuO₄ and K₂RuO₄. *Z. Naturforsch.* **2005**, B60, 1113.

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