ChemistryEurope
Excellence in Chemistry Research Worldwide

Research Article
doi.org/10.1002/ceur.202500275

www.journal.chemistry-europe.org

On The Existence of Highly Condensed Sulfatotungstates and Sulfatomolybdates

Vivien Wessels, Fabian Kraus, Lkhamsuren Bayarjargal, Hans-Albrecht Krug von Nidda, Georg Eickerling, and Henning A. Höppe*

Dedicated to the memory of Prof. Dr. Rüdiger Kniep

The first alkaline earth sulfatotungstate $Ca[WO(SO_4)_3]$ is also the first one featuring a condensed anionic host structure. A solvothermal approach by using tungstic acid, $CaSO_4$ and oleum led to $Ca[WO(SO_4)_3]$ comprising corrugated two-dimensional (2D) layers in the *a-b* plane. It crystallises in a new structure type in space group *Pnma* (no. 62). Blue α-$K_2[MoO_2(SO_4)_2]$ marks the first highly condensed structure for sulfatomolybdates, synthesized via melting MoO_3 and $K_2S_2O_7$. It crystallises in a new structure type in the non-centrosymmetric space group *Cc* (no. 9), yielding a doubled SHG response compared with potassium dihydrogen phosphate. Electron spin resonance spectroscopy proves the presence of Mo^{5+} ions causing the blue color. High condensation of the sulfate, tungstate and molybdate moieties seems to be remarkable considering the highly charged centres S^{6+}, W^{6+}, and Mo^{6+}. Moreover, the electrostatic, optical, and thermal properties of the title compounds are elucidated. UV–vis measurements show a pronounced ligand-to-metal-charge–transfer of the tungstate and molybdate moieties dominating the absorption edge. Thermal gravimetric analysis reveals a rather high thermal stability for both compounds.

1. Introduction

Most chemists would doubt the existence of highly condensed structures composed of oxide polyhedra centred around sixfold positively charged atoms such as sulfur, tungsten, or molybdenum. Indeed, this represents a synthetic challenge in itself—obtaining phase-pure samples poses an even greater one. Sulfatotungstates and sulfatomolybdates constitute rather new material classes featuring TM-O-S bridges (TM = Mo, W). Both can further be classified as silicate-analogous like borosulfates and borophosphates because they comprise sulfate moieties, that is, tetrahedral building units lacking inversion symmetry.[1] This often fosters promising optical properties due to partial mixing of orbitals and thereby, enhancing their luminescence probabilities; in case that the whole structure lacks inversion symmetry, nonlinear-optical properties are of interest. Adding tungstate or molybdate moieties may enhance the luminescence properties of doped-rare-earth ions due to the so-called antenna effect, which enables the energy transfer of a parity allowed ligand-to-metal-charge-transfer (LMCT) as in tungstates and molybdates onto an activator normally featuring parity forbidden transitions, such as f-f transitions in rare-earth ions.[2] A further important parameter is the dimensionality of such possible host structures; with increasing dimensionality the stiffness of the anion is increased reducing vibrational loss of luminescence intensity. Thus, higher dimensional sulfatotungstates and sulfatomolybdates should be even better suited material classes by providing tetrahedral building units condensed to tungstate or

V. Wessels, F. Kraus, H. A. Höppe
Professur für Festkörperchemie und Materialwissenschaften
Institute of Physics
Universität Augsburg
Universitätsstraße 1
86159 Augsburg, Germany
E-mail: henning@ak-hoeppe.de

L. Bayarjargal
Institut für Geowissenschaften
Universität Frankfurt
Altenhöferallee 1, 60438 Frankfurt, Germany

H.-A. Krug von Nidda
Experimental Physics V
Center for Electronic Correlations and Magnetism
Institute of Physics
Universität Augsburg
Universitätsstraße 1
86159 Augsburg, Germany

G. Eickerling
CPM
Institute of Physics
Universität Augsburg
Universitätsstraße 1
86159 Augsburg, Germany

Supporting information for this article is available on the WWW under https://doi.org/10.1002/ceur.202500275

Research Article
doi.org/10.1002/ceur.202500275

molybdate moieties. In our contribution, we present the successful phase-pure synthesis and structural characterization of the most highly condensed sulfatomolybdate and sulfatotungstate reported to date, inherently reducing vibrational quenching; moreover, the sulfatomolybdate is non-centrosymmetric, which will be addressed also.

For sulfatotungstates, only two different structure types are known yet, namely $A_8[W_2O_4(SO_4)_6]$ ($A = K^+$, Rb^+) and $M_2[W_2O_3(SO_4)_6]$ ($M = Y^{3+}$, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Ho^{3+}, Lu^{3+}, Bi^{3+}).[3,4] Both comprise non-condensed fundamental building units and are therefore classified after Liebau analogously to silicates as zero dimensional (0D) materials.[5] In the field of sulfatomolybdates the compounds $A_4[MoO_2(SO_4)_3]$ ($A = Na^+$, K^+), the now β polymorph $K_2[MoO_2(SO_4)_2]$ and $Rb_2[Mo_3O_6(SO_4)]$ are known featuring 0D and 1D anions, respectively.[6,7] Low dimensionalities do not seem surprising due to the highly charged centres S^{6+}, W^{6+}, and Mo^{6+}. The highest condensation known so far for oligosulfates $[S_nO_{3n+1}]^{2-}$ is $n = 6$ as in $Rb_2[S_6O_{19}]$.[8] Hence, we are pleased to report on our quest to explore such compounds with higher dimensionality, which may be suited as antenna materials.

2. Results and Discussion

$Ca[WO(SO_4)_3]$ crystallises in a new structure type in the orthorhombic space group *Pnma* (no. 62) with four formula units per unit cell. The fundamental building unit $[WO_3(SO_4)_3]^{6-}$ consists of a tungstate octahedron and three sulfate tetrahedra, connected via common edges to give W-O-S bridges (**Figure 1**). These units condense further to layers perpendicular to the *c*-axis, yielding the first 2D sulfatotungstate. The layers follow a zig–zag arrangement along the *a*-axis (Figure S1, Supporting Information). All atoms are located on Wyckoff position 4*c*, only O12, O21 and O33 are assigned to 8*d*. The calcium atoms are coordinated by seven terminal oxygen atoms of sulfate tetrahedra to form a capped trigonal prism. Tungsten is surrounded by five bridging and one terminal oxygen atom, that is, O1, featuring the shortest W—O bond length of the compound with 169.0(3) pm (sum of Shannon radii:[9] 184 pm). This is due to the repulsion between the highly charged central atoms W^{6+} and S^{6+}, causing a relatively large polyhedron deviation of −3.98% for the tungstate octahedra, calculated by the method of Balić-Žunić and Makovicky.[10,11] The adjacent sulfate tetrahedra exhibit minor deviations of −0.04 (S1), −0.39 (S2), and −0.03% (S3). Longer S—O bonds are found in the W—O—S bridges for the same reason as for the W—O1 bond length. Further, the average Ca—O bond length amounts to 238 pm, which is slightly shorter than the expected length of 241 pm according to Shannon[9] considering a seven-fold coordination.

α-$K_2[MoO_2(SO_4)_2]$, the new second phase of this composition, adopts the monoclinic non-centrosymmetric space group *Cc* (no. 9) with four formula units per unit cell. It therefore differs from the known β-$K_2[MoO_2(SO_4)_2]$, here denoted as β-phase due to its lower density (α-$K_2[MoO_2(SO_4)_2]$: 2.917 g cm^{-3}, β-$K_2[MoO_2(SO_4)_2]$: 2.863 g cm^{-3}).[7] All atoms are situated on Wyckoff position 4*a*. The fundamental building unit consists of a molybdate octahedron condensed to two sulfate tetrahedra (**Figure 2**). Molybdenum is coordinated by four bridging and two terminal oxygen atoms. These $[MoO_2(SO_4)_2]^{2-}$ units are further connected yielding the first 3D anion for sulfatomolybdates (Figure S2, Supporting Information). While the sulfate tetrahedra with −0.07 (S1) and −0.11% (S2) show only slight polyhedron deviations,[10,11] the molybdate octahedra show a larger deviation of −5.99%, similarly to the tungstate octahedron in $Ca[WO(SO_4)_3]$ for the same reason. Here, the Mo–O bond lengths toward O1 and O2 of 169.0(3) and 168.6(4) pm are thus shorter than the sum of Shannon radii[9] of 197 pm, alike in β-$K_2[MoO_2(SO_4)_2]$.[7] The potassium atoms are coordinated by eleven (K1) and eight oxygen atoms (K2), respectively, as confirmed by MAPLE calculations (MAPLE = MAdelung Part of Lattice Energy[12,13]).

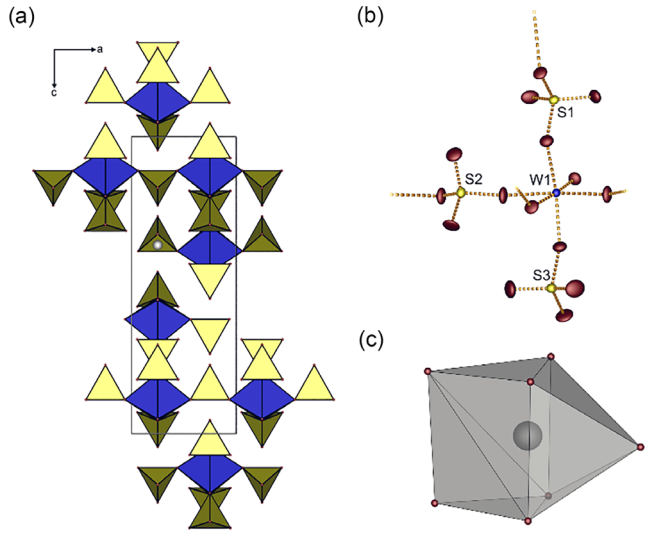

Figure 1. Unit cell of $Ca[WO(SO_4)_3]$ a), fundamental building unit b) and coordination environment of the calcium cations c); tungstate octahedra blue, sulfate tetrahedra yellow, calcium atoms grey; ellipsoids are set to a probability level of 50%.

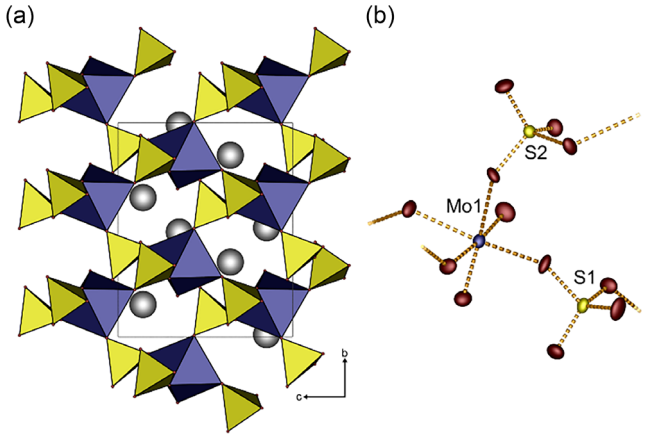

Figure 2. Unit cell of α-$K_2[MoO_2(SO_4)_2]$ a) and fundamental building unit b); molybdate octahedra violet, sulfate tetrahedra yellow, potassium grey; ellipsoids are set to a probability level of 50%.

Research Article
doi.org/10.1002/ceur.202500275

The average K—O distances match with the estimated bond lengths after Shannon. K1 exhibits average bond lengths of 296 pm (estimated 297 pm), K2 of 288 pm (estimated 286 pm).[9] The fundamental building units of α-$K_2[MoO_2(SO_4)_2]$ and β-$K_2[MoO_2(SO_4)_2]$ (Figure S3, Supporting Information) look quite similar, but the further connection of these units yields a 1D chain in β-$K_2[MoO_2(SO_4)_2]$ and a 3D framework in α-$K_2[MoO_2(SO_4)_2]$. While in the latter the sulfate units connect to different $[MoO_6]^{6-}$ octahedra, $[S1O_4]^{2-}$ and $[S2O_4]^{2-}$ in β-$K_2[MoO_2(SO_4)_2]$ condense with a further $[MoO_6]^{6-}$ octahedron to a vierer ring, preventing the formation of a higher dimensional structure.

Phase-pure, crystalline powders of $Ca[WO(SO_4)_3]$ and α-$K_2[MoO_2(SO_4)_2]$ were obtained in acid–base reactions according to the Lux-Flood concept via a solvothermal process and a reaction melt, respectively. The X-ray diffraction patterns are depicted in **Figure 3**; the structure models were confirmed by a Rietveld refinement (Tables S6 and S7, Supporting Information). Astonishingly, $Ca[WO(SO_4)_3]$ seems to be more stable against humidity than the aforementioned $M_2[W_2O_3(SO_4)_6]$ ($M = Y^{3+}$, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Ho^{3+}, Lu^{3+}, Bi^{3+}). While the latter decomposes within seconds, $Ca[WO(SO_4)_3]$ is stable for several minutes to hours, probably because of the lower hydration enthalpy of Ca^{2+} compared with M^{3+}.[14] In contrast, α-$K_2[MoO_2(SO_4)_2]$ is stable in air, apparently.

Electrostatic consistency of both structure models was proven by calculations based on the MAPLE concept.[13] Hereby, the single crystal data was used to calculate the MAPLE value, which is compared to the sum of the MAPLE values of corresponding binary or tertiary compounds (**Table 1**). The deviations remain below 1%, indicating an electrostatic consistency of the structure models.

Furthermore, the title compounds were investigated by UV–vis (Figures S6–S9, Supporting Information), FT-IR and Raman spectroscopy (Figures S4 and S12, Supporting Information). The former reveals a high reflectance throughout the visible region, predicting an almost colorless appearance for $Ca[WO(SO_4)_3]$ as observed. The absorption edge occurs around 390 nm due to a O^{2-}-W^{6+} LMCT with a maximum around 290•nm, which is in accordance with reported octahedral tungstates.[15] The UV–vis spectrum of α-$K_2[MoO_2(SO_4)_2]$ shows two broad absorption bands with a high reflection in the bluish region. Electron spin resonance spectroscopy proofs the presence of Mo^{5+} ions in α-$K_2[MoO_2(SO_4)_2]$ (Figure S13, Supporting Information). Therefore, *d–d* transitions are responsible for the blue hue of the powder. For both new compounds Tauc plots indicated indirect bandgaps of 3.3 and 3.5•eV; the fit of the potassium compound is ominous, though, as the two broad absorption bands yield an anormal reflection spectrum. Therefore, this band gap was also calculated to be indirect with an underestimated value around 2.7 eV (Figure S14, Supporting Information). Furthermore, α-$K_2[MoO_2(SO_4)_2]$ shows a weak blue luminescence due to the O^{2-}-Mo^{6+} LMCT emission (Figure S10, Supporting Information). For $Ca[WO(SO_4)_3]$ no luminescence was detected alike the observation in $M_2[W_2O_3(SO_4)_6]$,[4] probably due to further quenching processes. Even at liquid nitrogen temperature no luminescence was observed. The reason is yet speculative. Possible explanations might be the quenching of the luminescence by neighbouring sulfate tetrahedra, the relative disadvantageous orientation of the dipoles within the structure or anion defects.

The vibrational spectra of $Ca[WO(SO_4)_3]$ and α-$K_2[MoO_2(SO_4)_2]$ show bands in the same region as in $M_2[W_2O_3(SO_4)_6]$. Bands between 1400 and 950 cm^{-1} can be assigned to symmetric ν_{sym}(S—O) and antisymmetric ν_{asym}(S—O) stretching vibrations in

Table 1. Results of the MAPLE calculations for Ca[WO(SO4)3] and α-K2[MoO2(SO4)2] compared to MAPLE values of the binary compounds.

$Ca[WO(SO_4)_3]$ (SC-XRD)	CaO[16] + WO_3[21] + 3 SO_3[22]
MAPLE = 120,225 kJ mol^{-1}	MAPLE = 119,784 kJ mol^{-1}
(Δ = 0.37%)	
α-$K_2[MoO_2(SO_4)_2]$ (SC-XRD)	K_2SO_4[23] + MoO_3[24] + SO_3[22]
MAPLE = 88,673 kJ mol^{-1}	MAPLE = 88,382 kJ mol^{-1}
(Δ = 0.33%)	

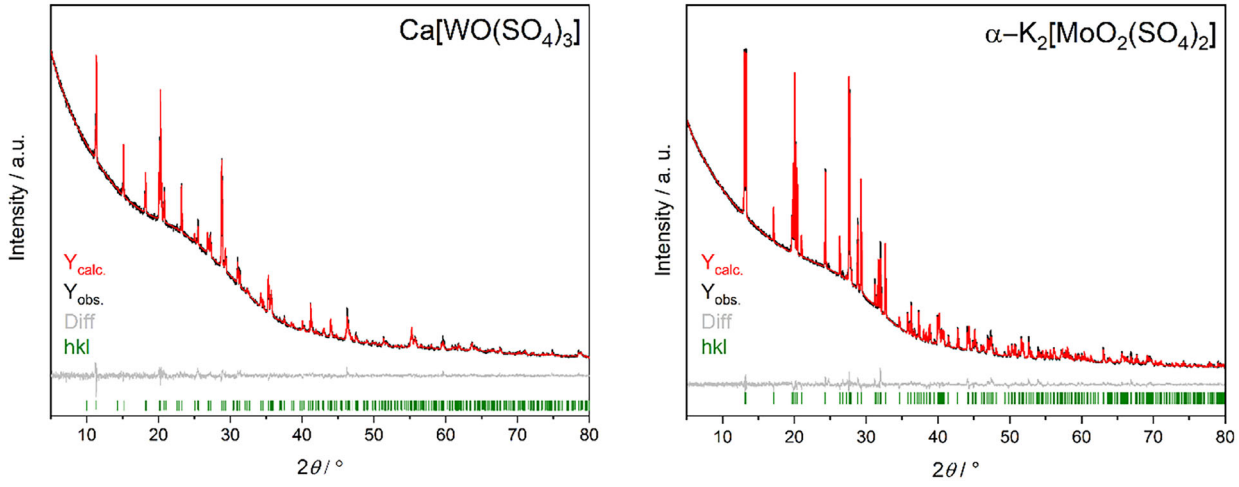

Figure 3. Experimental X-ray diffraction pattern and Rietveld refinement of $Ca[WO(SO_4)_3]$ (left) and X-ray diffraction pattern of α-$K_2[MoO_2(SO_4)_2]$ (right).

Research Article
doi.org/10.1002/ceur.202500275

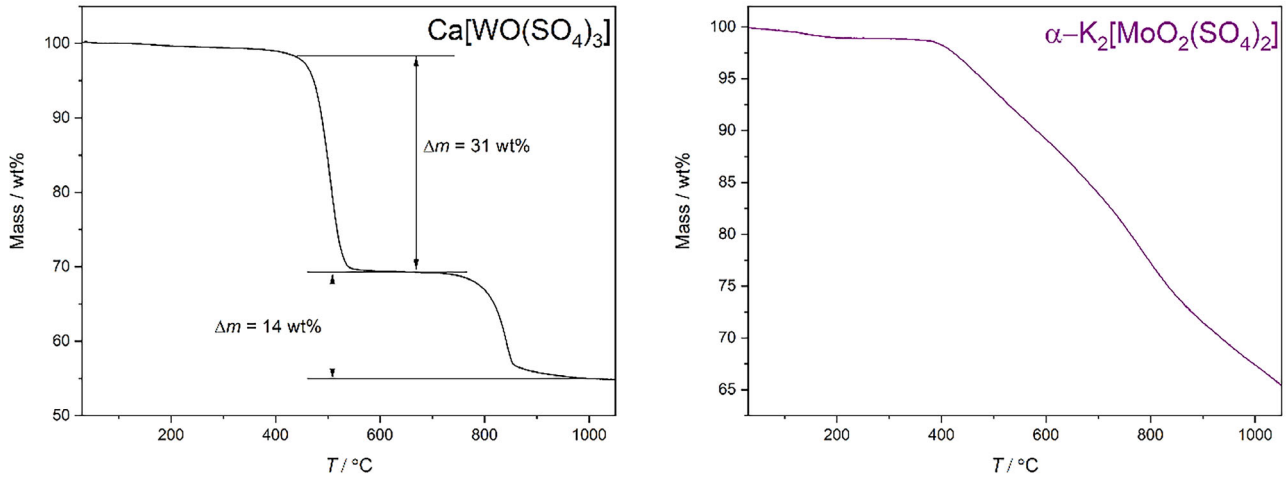

Figure 4. Thermogravimetric analysis of $Ca[WO(SO_4)_3]$ (left) and α-$K_2[MoO_2(SO_4)_2]$ (right).

sulfate tetrahedra, while bending vibrations δ(S—O) are located between 650 and 400 cm^{-1}.[16,17] Stretching vibrations ν_{sym} (W—O) and ν_{asym} (W—O) in the tungstate moieties are found between 960 and 600 cm^{-1}, bending vibrations δ (W—O) are located below 500 cm^{-1}.[18] The same holds for the molybdate vibrations; stretching vibrations ν_{sym} (Mo–O) and ν_{asym} (Mo–O) occur between 990 and 600 cm^{-1}, bending vibrations δ (Mo–O) could not be detected due to their occurrence below 400 cm^{-1}.[19] Comparable vibrational bands are observed in β-$K_2[MoO_2(SO_4)_2]$ as well with no significant shifts (Figure S5, Supporting Information).[7] Minor deviations occur between 990 and 630 cm^{-1} with a more pronounced band for α-$K_2[MoO_2(SO_4)_2]$ around 870 cm^{-1}, probably due to different Mo–O—S vibrations in the fundamental building unit. Furthermore, the second harmonic generation properties (SHG) of α-$K_2[MoO_2(SO_4)_2]$, unequivocally crystallising in the non-centrosymmetric space group *Cc*, were investigated. Considering the grain size, the SHG intensity (Table S9, Supporting Information) is ≈8 times higher then in quartz and ≈2 times higher than in the reference material potassium dihydrogen phosphate.

The thermal stability of the title compounds was assessed via a Thermogravimetric Analysis (TGA) under nitrogen atmosphere, with a thermal treatment up to 1050°C. Both compounds show a remarkably high thermal stability (**Figure 4**). $Ca[WO(SO_4)_3]$ decomposes by releasing SO_3 in two steps. Reasonable reaction equations are the following, whereas the product of the last step was proven by powder X-ray diffraction (Figure S11, Supporting Information).

$$2Ca[WO(SO_4)_3] \rightarrow 2Ca[WO_3(SO_4)] + 4SO_3(g) \quad (1)$$

$$2Ca[WO_3(SO_4)] \rightarrow 2CaWO_4 + 2SO_3(g) \quad (2)$$

The expected mass losses of the several steps agree well with the observed values (Table S8, Supporting Information). Compared to known sulfatotungstates, the relative thermal stability of 500 °C seems to be similar (e.g. $Eu_2[W_2O_3(SO_4)_6]$: 430 °C. $Lu_2[W_2O_3(SO_4)_6]$: 510°C).[4] α-$K_2[MoO_2(SO_4)_2]$ is stable up to 390 °C. It decomposes in one large step, presumably by releasing SO_3. Contrarily, β-$K_2[MoO_2(SO_4)_2]$ featuring 1D chains shows a thermal stability up to 405 °C,[7] which is slightly higher than in the 3D compound in this work. This trend seems to be in accordance with the behavior of borosulfates, where the thermal stability decreases with increasing dimensionality of the host structure as well.[20]

Further investigations including a comparison of further optical properties are in train and will be presented elsewhere.

Acknowledgements

L.B. thanks the Deutsche Forschungsgemeinschaft for generous support under the project BA4020.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Vivien Wessels: investigation (lead); visualization (lead); writing—original draft (equal); writing—review and editing (equal). **Fabian Kraus**: investigation (supporting). **Lkhamsuren Bayarjargal**: funding acquisition (supporting); investigation (supporting). **Hans-Albrecht Krug von Nidda**: investigation (supporting). **Georg Eickerling**: investigation (supporting). **Henning A. Höppe**: conceptualization (lead); investigation (equal); project administration (lead); resources (lead); supervision (lead); validation (lead); writing original draft (equal); writing—review and editing (equal).

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Research Article
doi.org/10.1002/ceur.202500275

Keywords: calcium · potassium · silicate-analogous · sulfatomolybdate · sulfatotungstate

[1] a) P. Netzsch, P. Gross, H. Takahashi, H. A. Höppe, *Inorg. Chem.* **2018**, *57*, 8530. b) J. Bruns, H. A. Höppe, M. Daub, H. Hillebrecht, H. Huppertz, *Chem. Eur. J.* **2020**, *26*, 7966. c) M. Daub, A. J. Lehner, H. A. Höppe, *Dalton Trans.* **2012**, *41*, 12121. d) H. A. Höppe, S. J. Sedlmaier, *Inorg. Chem.* **2007**, *46*, 3467. e) P. Netzsch, M. Hämmer, P. Gross, H. Bariss, T. Block, L. Heletta, R. Pöttgen, J. Bruns, H. Huppertz, H. A. Höppe, *Dalton Trans.* **2019**, *48*, 4387.
[2] a) G. Blasse, A. Bril, *J. Chem. Phys.* **1966**, *45*, 2350. b) D. L. Dexter, *J. Chem. Phys.* **1953**, *21*, 836. c) H. Höppe, *Rare-Earth Elements. Solid State Materials: Chemical, Optical and Magnetic Properties*, Walter de Gruyter GmbH & Co KG, Berlin/Boston **2024**.
[3] a) U. Betke, M. S. Wickleder, *Eur. J. Inorg. Chem.* **2011**, *2011*, 4400. b) K. Ståhl, R. W. Berg, *Acta Cryst. E* **2009**, *65*, i88. c) S. Schäffer, R. W. Berg, *Acta Cryst. E* **2005**, *61*, i49.
[4] V. Wessels, S. Kügle, H. A. Höppe, *Dalton Trans.* **2024**, *53*, 15703.
[5] F. Liebau, *Mineral. Mag.* **1987**, *51*, 471.
[6] a) S. J. C. Schäffer, R. W. Berg, *Acta Cryst. E* **2008**, *64*, i20. b) S. J. C. Schäffer, R. W. Berg, *Acta Cryst. E* **2008**, *64*, i73. c) J. Fuchs, H.-U. Kreusler, A. Förster, *Z. Naturforsch.* **1979**, *34*, 1683.
[7] T. Noerbygaard, *Proc.* **1998**, *1998*, 553.
[8] L. V. Schindler, A. Becker, M. Wieckhusen, T. Klüner, M. S. Wickleder, *Angew. Chem. Int. Ed.* **2016**, *55*, 16165.
[9] R. D. Shannon, *Acta Cryst. A* **1976**, *32*, 751.
[10] T. B.ć Žunić, E. Makovicky, *Acta Cryst. B* **1996**, *52*, 78.
[11] E. Makovicky, T. Balić-Žunić, *Acta Cryst. B* **1998**, *54*, 766.
[12] a) R. Hoppe, *Z. Naturforsch.* **1995**, *50*, 555. b) R. Hoppe, *Angew. Chem. Int. Ed.* **1966**, *5*, 95.
[13] R. Hübenthal, MAPLE, in *Program for the Calculation of the Madelung Part of Lattice Energy*, University of Gießen, Germany **1993**.
[14] D. W. Smith, *J. Chem. Educ.* **1977**, *54*, 540.
[15] a) Z. Zhang, W. Wang, W. Yin, M. Shang, L. Wang, S. Sun, *Appl. Catal. B: Environ.* **2010**, *101*, 68. b) E. I. Ross-Medgaarden, I. E. Wachs, *J. Phys. Chem. C* **2007**, *111*, 15089. c) S. G. Jantz, F. Pielnhofer, M. Dialer, H. A. Höppe, *Z. Anorg. Allg. Chem.* **2017**, *643*, 2024.
[16] C. Ablitt, H. McCay, S. Craddock, L. Cooper, E. Reynolds, A. A. Mostofi, N. C. Bristowe, C. A. Murray, M. S. Senn, *Chem. Mater.* **2020**, *32*, 605.
[17] a) V. Ramakrishnan, V. U. Nayar, G. Aruldhas, *Infrared Phys.* **1985**, *25*, 607. b) M. V. Barashkov, A. I. Komyak, S. N. Shashkov, *J. Appl. Spectrosc.* **1999**, *1*, 100. c) Y. Denisenko, A. S. Aleksandrovsky, V. V. Atuchin, A. S. Krylov, M. S. Molokeev, A. S. Oreshonkov, N. P. Shestakov, O. V. Andreev, *J. Ind. Eng. Chem.* **2018**, *68*, 109.
[18] a) C. Guery, C. Choquet, F. Dujeancourt, J. M. Tarascon, J. C. Lassegues, *J. Solid State Electrochem.* **1997**, *1*, 199. b) M. F. Daniel, B. Desbat, J. C. Lassegues, B. Gerand, M. Figlarz, *J. Solid State Chem.* **1987**, *67*, 235.
[19] a) G.-A. Nazri, C. Julien, *Solid State Ion.* **1992**, *53*, 376. b) L. Seguin, M. Figlarz, R. Cavagnat, J. C. Lassegues, *Spectrochim. Acta A* **1995**, *51*, 1323.
[20] E. Turgunbajew, H. A. Höppe, *Angew. Chem. Int. Ed.* **2025**, *64*, e202424952.
[21] A. Aird, M. C. Domeneghetti, F. Mazzi, V. Tazzoli, E. K. H. Salje, *J. Condens. Matter Phys.* **1998**, *10*, L569.
[22] R. Pascard, C. Pascard-Billy, *Acta Cryst.* **1965**, *18*, 830.
[23] N. V. Zubkova, I. V. Pekov, D. A. Ksenofontov, V. O. Yapaskurt, D. Y. Pushcharovsky, E. G. Sidorov, *Dokl. Earth Sci.* **2018**, *479*, 339.
[24] L. Kihlborg, *Arkiv Foer Kemi*, **1963**, *21*, 357.

Manuscript received: July 21, 2025
Version of record online: