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DOI: **Th(VO₃)₂(SeO₃) and Ln(VO₃)₂(IO₃) (Ln = Ce, Pr, Nd, Sm, and Eu): Unusual Cases of Aliovalent Substitution**

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Th(VO₃)₂(SeO₃) and Ln(VO₃)₂(IO₃) (Ln = Ce, Pr, Nd, Sm, and Eu) have been prepared and characterized. Surprisingly, these compounds are isotypic and rather extreme examples of aliovalent substitution (Th^{IV} vs. Ln^{III}; Se^{IV}O₃²⁻ vs. I^{VO₃}) are possible in this structure type.

There are a variety of structure types that are surprisingly permissive in their ability to not just allow for replacement of ions with new ions of identical charge and similar size, but rather allow for aliovalent substitution of dramatically different ions and sometimes even entire complex moieties without changing the overall topology.¹ Examples of this include the rock-salt, perovskite, glasserite, and ZrSiS types to name a few.² This allows for fine-tuning of physico-chemical properties that are critical for the optimization of key emergent phenomena. One of the best examples where structural chemistry and the resultant properties can be exquisitely controlled is in the *f*-block because in both the 4*f* and 5*f* series the decrease in ionic radii is extraordinarily systematic, and at least in the 4*f* series, redox chemistry seldom complicates analysis.

Comparisons of the chemistry of early lanthanides with actinides in the trivalent oxidation state stems from their similarities in ionic radii and coordination geometries, which typically results in them forming isotypic series.³ Lanthanide and actinide ions with same oxidation state and coordination number can possess nearly identical ionic radii.^{3b} As a result, Ce^{IV} has long been used as a surrogate for Pu^{IV}, and Nd^{III} as a replacement for Am^{III}.⁴ As aptly stated by Neidig and co-workers, distinguishing with 4*f* and 5*f* chemistry is not simply an academic exercise, but rather has profound impact on the ability to create closed nuclear fuel cycles.⁵ In oxoanion compounds, both lanthanides and actinides can be coordinated with six to twelve oxygen atoms, yielding a vast range of coordination geometries.⁶ Numerous lanthanide and actinide-containing analogues with most of the common oxoanions have been discovered, e.g. [RE^{IV}₂Te₇O₁₇]Cl₂ (RE = Ce and Pu), RE^{III}₂(HPO₃)₃(H₂O) (RE = Ce, Pr, Nd, Pu, and Am), and RE^{III}[B₄O₆(OH)₂Cl] (RE = La, Ce, and Pu).^{6a,7}

In attempt to prepare lanthanide and actinide-containing materials that allow for comparisons in bonding and physical properties, using

vanadate-iodate or vanadate-selenite systems, Th(VO₃)₂(SeO₃) and Ln(VO₃)₂(IO₃) (Ln = Ce, Pr, Nd, Sm, and Eu) were discovered.⁸ Surprisingly, these compounds feature aliovalent replacement of not just the *f*-elements, but rather the oxoanions as well, and yet a single structure type is retained. This indicates that the M(VO₃)₂(EO₃) system may well be an example of one that tolerates massive variations in composition that can be exploited in the fine-tuning of electronic features. What differentiates this family from many others is that it is surprisingly complex. Most systems that allow for this much variability are easily-described, high-symmetry topologies and probably represent deep thermodynamic sinks.

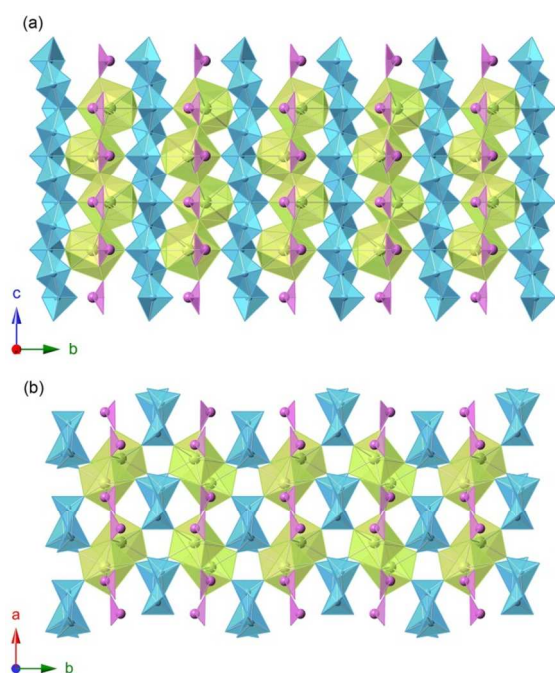


FIGURE 1. (a) A view of the three-dimensional framework of Th(VO₃)₂(SeO₃) and Ln(VO₃)₂(IO₃) extending along the *a* axis. (b) A view of the three-dimensional framework of Th(VO₃)₂(SeO₃) and Ln(VO₃)₂(IO₃) extending down the *c* axis. ThO₅ or LnO₅ polyhedra are shown yellow, IO₃ or SeO₃ in magenta, and VO₅ in light blue.

Single crystal X-ray diffraction studies reveal that $\text{Th}(\text{VO}_3)_2(\text{SeO}_3)$ and $\text{Ln}(\text{VO}_3)_2(\text{IO}_3)$ are isotypic, and crystallize in the orthorhombic space group, *Pbcm*. It is important to note that despite the fact that all of the building units in these compounds lack inversion centers that the overall structure is still centrosymmetric.^{8a,9} $\text{La}(\text{VO}_3)_2(\text{IO}_3)$ has been previously reported, but all others are new.¹⁰ As shown in Figure 1, $\text{Th}(\text{VO}_3)_2(\text{SeO}_3)$ and $\text{Ln}(\text{VO}_3)_2(\text{IO}_3)$ exhibit a three-dimensional framework composed of one $\text{Th}^{\text{IV}}/\text{Ln}^{\text{III}}$ ion, one $\text{SeO}_3^{2-}/\text{IO}_3^-$ anion, and two crystallographically independent vanadium centers. In order to better understand the 3D framework, it can be divided into two components: the $\text{Th}(\text{SeO}_3)^{2+}/\text{Ln}(\text{IO}_3)^{2+}$ layer and $\text{V}_2\text{O}_6^{2-}$ chains (cf. Figure S1). The $\text{Th}(\text{SeO}_3)^{2+}/\text{Ln}(\text{IO}_3)^{2+}$ layer is constructed from edge-sharing Th/Ln chains bridged by $\text{SeO}_3^{2-}/\text{IO}_3^-$ polyhedra along the *a* axis. Both Th and Ln ions are coordinated by nine O atoms, forming a tricapped trigonal prismatic geometry (Figure 2). The SeO_3^{2-} and IO_3^- oxoanions adopt the standard trigonal pyramidal geometry, and are bound by three O atoms with an average Se–O length of 1.72(3) Å, and I–O length of 1.81(3) Å, respectively. $\text{V}(1)\text{O}_5$ and $\text{V}(2)\text{O}_5$ polyhedra edge-share alternatively to form a zigzagging $\text{V}_2\text{O}_6^{2-}$ chain along the *c* axis (cf. Figure S1b). The $\text{V}(1)\text{O}_5$ polyhedra display a distorted trigonal bipyramidal geometry with two short cis V=O bonds of 1.642(4) and 1.662(3) Å, and three long V–O bonds ranging from 1.908(2) to 1.947(6) Å. The $\text{V}(2)\text{O}_5$ units, however, exhibit a distorted square pyramidal coordination environment. Similarly, there are two short cis V=O bonds and three long V–O bonds.

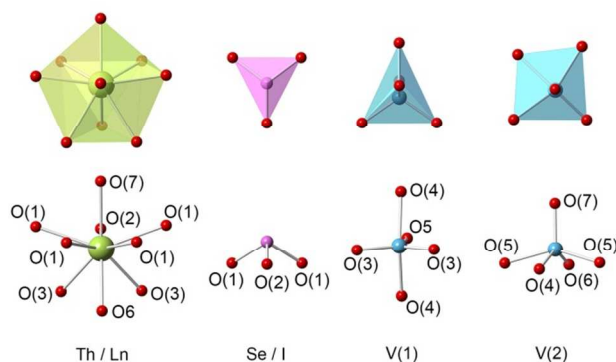


FIGURE 2. Top and side views of the coordination geometries of Th/Ln , Se/I , and V in $\text{Th}(\text{VO}_3)_2(\text{SeO}_3)$ and $\text{Ln}(\text{VO}_3)_2(\text{IO}_3)$. ThO_9 or LnO_9 polyhedra is shown yellow, IO_3^- or SeO_3^- in purple, VO_5 in light blue, and the oxygen atoms are red spheres.

Bond-valence sums (BVS) were calculated for the heavy atom sites and yielded values consistent with +3 for all of the lanthanide ions, including cerium, i.e. the cerium example is not Ce^{IV} . The valence states for all of the others atoms are what should be expected (i.e. Th^{IV} , I^{V} , and Se^{IV}). Both $\text{V}(1)$ and $\text{V}(2)$ cations in all analogues are pentavalent based on the BVS. Despite the aliovalent nature of Th^{IV} vs. Ln^{III} and SeO_3^{2-} vs. IO_3^- , $\text{Th}(\text{VO}_3)_2(\text{SeO}_3)$ and $\text{Ln}(\text{VO}_3)_2(\text{IO}_3)$ exhibit the same topologies. This is really co-substitution, because the combinations of $\text{Th}^{\text{IV}}/\text{IO}_3^-$ versus $\text{Ln}^{\text{III}}/\text{SeO}_3^{2-}$ with the vanadium units allows for charge neutrality to be maintained. This is nevertheless unexpected because: 1) the complexity of the building units, 2) the dramatically different bond distances between these units, and 3) the intricacy of the overall connectivity of the framework. It occurs nevertheless presumably because both types of *f*-element cations allow

for the same coordination chemistry, and both oxoanions form trigonal pyramids.

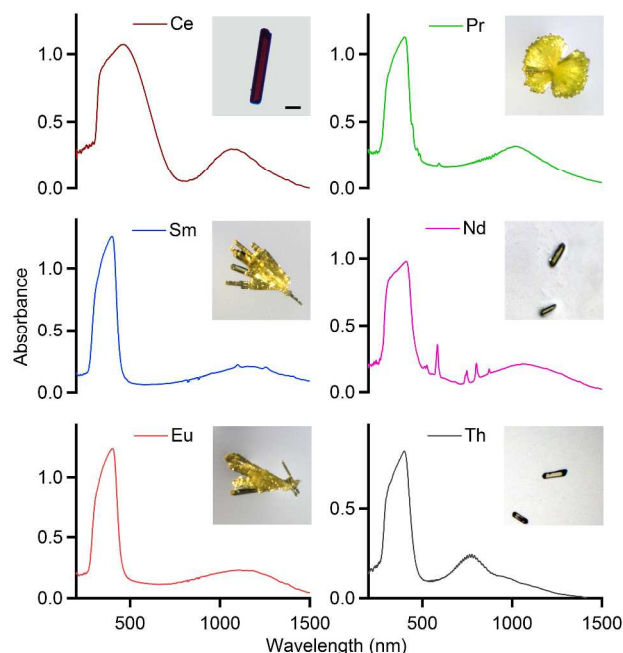


FIGURE 3. UV-vis-NIR absorption spectra and photographs of $\text{Th}(\text{VO}_3)_2(\text{SeO}_3)$ and $\text{Ln}(\text{VO}_3)_2(\text{IO}_3)$.

The absorption spectra of $\text{Th}(\text{VO}_3)_2(\text{SeO}_3)$ and $\text{Ln}(\text{VO}_3)_2(\text{IO}_3)$ were acquired from single crystals using a microspectrophotometer and are shown in Figure 3. The characteristic *f-f* transitions anticipated for these compounds are only clearly resolved in the Pr and Nd compounds because large CT features from the vanadium units dominate the visible/NIR regions of the spectra.^{8b,11} The only member of this family that has atypical optical properties is $\text{Ce}(\text{VO}_3)_2(\text{IO}_3)$, which exhibits a dark-red color, whereas the others are yellow. Absorption in the high energy region by $\text{Ce}(\text{VO}_3)_2(\text{IO}_3)$ is much broader than in the other compounds. A definitive explanation for this coloration is unwarranted at this stage because there are numerous factors that may be affecting it. First, for Ce^{III} the transition is not *f-f* but rather *f-d*, and is therefore allowed by the selection rules, and is much more intense.¹² Second, MLCT from the Ce^{III} to iodate and/or vanadate may be occurring. Third, the cerium compound could be a semiconductor. While the second suggestion is intriguing, many investigators have been led astray by the coloration of cerium compounds, and in at least one case the explanation was sadly mundane and was simply the result of oxygen defects in the structure.¹³

If one assumes that $\text{Ce}(\text{VO}_3)_2(\text{IO}_3)$ is a semiconductor, the absorbance data can be converted to optical energy plots as shown in Figure 4. This reveals a bandgap of 1.64 eV as estimated by constructing a least squares fit of the decrease in absorption and extrapolating to the x-intercept.

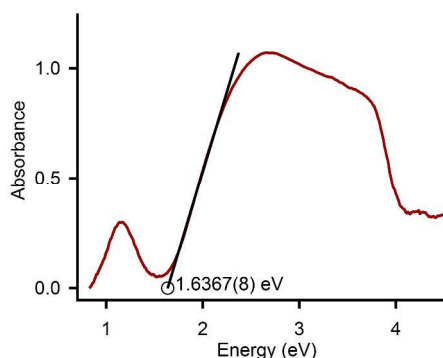


FIGURE 4. Optical energy spectrum of $\text{Ce}(\text{VO}_3)_2(\text{IO}_3)$ used to determine the approximate band gap. The least-squares fit is shown along with the x intercept which is the calculated band gap.

Conclusions

This study indicates that the $\text{M}(\text{VO}_3)_2(\text{EO}_3)$ structure type may be a surprising complex example of a topology with unusual stability that allows for wide variations in composition without architectural alterations. As discussed in our opening statements, the goal with such systems is optimize desirable properties with compositional tuning. The Ce member of this series is displaying electronic features that are worthy of further investigation. One might also ask if it is possible to prepare $\text{Th}_{1-x}\text{Ln}_x(\text{VO}_3)_2(\text{SeO}_3)_{1-y}(\text{IO}_3)_y$, and what properties would such a system exhibit? These, and other related studies, are underway.

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Notes and references

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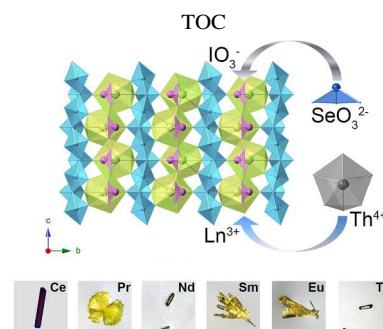
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‡ Electronic Supplementary Information (ESI) available: [CIF files, experimental section, Figure S1, SEM-EDS data, Powder X-Ray Diffraction data, table of crystallographic data, table for selected bond distances, and table for BVS are provided]. See DOI: 10.1039/c000000x/

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Six isotopic compounds with rather extreme examples of aliovalent substitution (Th^{IV} vs. Ln^{III} , SeO_3^{2-} vs. IO_3^-) have been synthesized.