Crystal Chemistry and Layered Structural Description of Oxychalcogenides Involving f-Transition Elements*

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Increasing attention has been focused lately on oxychalcogenides of the lanthanide and actinide elements, either with or without a second metal. A large number of compounds covering a wide range of properties and applications has been synthesized and the need for systematization has therefore become apparent. A few fruitful contributions were recently presented [1, 2], and the fundamentals of an ordering scheme are now proposed as an essay towards a structural classification of this important group of inorganic compounds.

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Two basic structural families disclosing different symmetry trends are represented amongst the layered rare earth oxychalcogenides, the prototypes being the trigonal structure of Ce_2O_2S and the tetragonal arrangements of Nd_2O_2Te and UOSe. These crystal structures are illustrative examples of metrical commensurability and symmetrical coherency in heterogeneous layered arrays [3] and they typify the two fundamental syngonies in the sense of Caro [4].

Essentially, two structural categories [5] may be recognized — sheet structures and atomic or eutactic heterogeneous arrays — depending upon chemical bonding features that may be indirectly assessed through the analysis of the actual values of the free parameters (axial and positional) in the crystal structure. The proposed structural description is based on the layer notation and structure-type symbolism previously developed for the closely related oxyhalide compounds [6]. In fact most oxychalcogenide crystal structures correspond to heterogeneous close-packings resulting from the coherent stacking of oxygen and chalcogen commensurate homogeneous layers with metal atoms occupying suitable interstices according to their stereochemical requirements. These packing layers are usually based on the same plane network (triangular, T; or square, Q) in which case the radius ratio oxygen/chalcogen determines the multiplicities of the metrically coherent plane unit cells. An upper numerical index adjoining the layer symbol is used to express the rank of such cells. More or less distorted Q^1/Q^2 stackings in either closest (f) or simple (s) stacking mode are possible (Fig. 1), the first one being by far the most common. In such arrays, the oxygens are centering tetrahedra of rare earth atoms (R) which have coordination number eight or nine depending on the thickness of the chalcogen 2-D slab. The OR_4 tetrahedra share edges giving rise to extended sheets of composition RO (layer symbol I^{101} according to ref. 5).

The layered Q^1/Q^2 arrangements up to now identified amongst oxychalcogenides are schematically drawn in Fig. 2. The oxygen atoms form the Q^2 layer and the chalcogens may either form a single Q^1 layer or multi-stored planar modules conforming with a cubic close-packing and accommodating the extra metal atoms in octahedral or tetrahedral interstitial sites. However, if a significant decrease of the c/a ratio occurs in the structure, the (nQ_f^1) modules become comparable to a body-centered cubic 2-D slab cut out along (100). In such a case, larger sites are available in a much higher proportion, thus allowing for increased mobility of the extra metal atoms. Body-centered cubic slabs are assigned to the crystal structure-types of the compounds $LaOGaSe_2$, $La_2O_2SnS_3$, $Ce_4O_4Ga_2S_5$ and $La_4O_4Ga_{1.33}S_4$. Furthermore, interaction may occur, resulting in the formation of anionic dimers within the chalcogen layers (e.g., $La_2O_2S_2$).

Layer misfits with corrugation to attain commensurability are found within Q^i/Q^j arrays (e.g., $La_4O_4Se_3$) as well as within Q^i/T^j stackings ($Nd_4O_4Ga_2S_5$). A partial listing of the crystal struc-
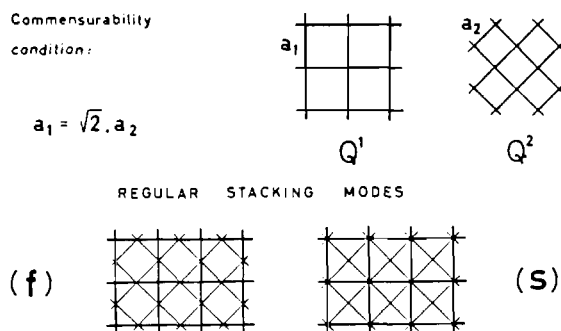
Fig. 1. Metrical commensurability and regular stacking modes for Q^1 and Q^2 layers.

TABLE 1. Representative Structure Types for Oxychalcogenides of the Rare Earth Elements

STP (Structural formula)	Prototype compound	Crystal data scs[a]	Space group	Chemical domain	Layer sequence	References
$\mathrm{Th}^{9}\{[O]|Se]\}^{(Q^{2}\,{}^{t}_{f}-2Q^{t}_{f})_{s}}$	ThOSe	$tP6$	$P4/nmm$	U, Th/S, Se, Te	$(Q^{2}\,{}^{t}_{f}-2Q^{t}_{f})_{s}$	7
$\mathrm{Ce}^{9}\{[As]|[S]\}^{(Q^{2}\,{}^{t}_{f}-2Q^{t}_{f})_{s}}$	CeAsS	$mP12$	$P2_{1}/n$	Ce/As/S	$(Q^{2}\,{}^{t}_{f}-2Q^{t}_{f})_{s}$	8
$\mathrm{Nd}_{2}^{8}\{[O_{2}]|[Te]\}^{(Q^{2}\,{}^{t}_{f}-Q^{t})_{t}}$	$\mathrm{Nd_2O_2Te}$	$tI10$	$I4/mmm$	La, Nd/Te	$(Q^{2}\,{}^{t}_{f}-Q^{t})_{f}$	9
$\mathrm{Bi}_{2}^{8}\{[O_{2}]|[S]\}^{(Q^{2}\,{}^{t}_{f}-Q^{t})_{t}}$	$\mathrm{Bi_2O_2S}$	$oP10$	$Pnnm$	Bi/S	$(Q^{2}-Q^{t})_{f}$	10
$\mathrm{Ce}^{9}\mathrm{Bi}^{o}\{[O]|[S_{2}]\}^{(Q^{2}\,{}^{t}_{f}-4Q^{t}_{f})_{s}}$	$\mathrm{CeBiOS_2}$	$tP10$	$P4/nmm$	La, Ce/Sb, Bi/S	$(Q^{2}\,{}^{t}_{f}-4Q^{t}_{f})_{s}$	11
$\mathrm{La}^{9}\mathrm{Ga}^{t}\{[O]|[Se_{2}]\}^{(Q^{2}\,{}^{t}_{f}-4Q^{t}_{f})_{s}}$	$\mathrm{LaOGaSe_2}$	$oP20$	$P2_{1}ab$	La/Ga, In/S, Se	$(Q^{2}\,{}^{t}_{f}-4Q^{t}_{f})_{s}$	12
$\mathrm{U}_{2}^{9}\mathrm{Er}^{o}\{[O_{2}]|[Se_{3}]\}^{(Q^{2}\,{}^{t}_{f}-3Q^{t}_{f})_{t}}$	$\mathrm{U_2O_2ErSe_3}$	$tI16$	$I4/mmm$	U/Er/S	$(Q^{2}\,{}^{t}_{f}-3Q^{t}_{f})_{f}$	13
$\mathrm{La}_{2}^{9}\mathrm{Sn}^{t}[O_{2}]|[S_{3}]\}^{(Q^{2}\,{}^{t}_{f}-3Q^{t}_{f})_{t}}$	$\mathrm{La_2O_2SnS_3}$	$oP32$	$Pbnm$	La—Nd/Sn/S, Se	$(Q^{2}\,{}^{t}_{f}-3Q^{t}_{f})_{f}$	14
$\{[^{\pi4}\mathrm{La}_{2}\,{}^{t(2Q^{t}_{f})}\mathrm{Te}_{2}]_{\infty}^{101}\}_{\infty}^{1s}[\mathrm{Te}_{2}]\,\tilde{Q}^{2}_{f}\}_{f}^{s}$	$\mathrm{LaTe_2}$	$tP6$	$P4/nmm$	La, Nd, Sm/Te, Se	$(Q^{2}\,{}^{t}_{f}-2Q^{t}_{f})_{s}$	15
$\{[^{\pi4}\mathrm{Sm}_{2}\mathrm{Sb}_{2}^{t(2Q^{t}_{f})}]_{\infty}^{101}\}_{\infty}^{1s}[\mathrm{Sb}_{2}]\,\tilde{Q}^{2}_{f}\}_{f}^{s}$	$\mathrm{SmSb_2}$	$oC24$	$Cmca$	Sm/Sb	$(Q^{2}\,{}^{t}_{f}-2Q^{t}_{f})_{s}$	16
$\{[^{\pi3}\mathrm{La}_{2}\mathrm{O}_{2}^{t(2T_{h})}]_{\infty}^{101}\}_{\infty}^{1s}(\mathrm{T}_{s})\}_{f}^{s}$	$\mathrm{La_2O_2S}$	$hP5$	$P\bar{3}m1$	La—Yb, Y/S, Se	$\sim\mathrm{T_c}$	17
$\{[^{\pi3}\mathrm{Sc}_{2}\mathrm{O}_{2}^{t(2T_{h})}]_{\infty}^{101}\}_{\infty}^{1s}[\mathrm{S}^{t}]\}_{f}^{s}$	$\mathrm{Sc_2O_2S}$	$hP10$	$P6_{3}/mmc$	Sc/S	$\sim\mathrm{T_{cch}}$	18
$\{[^{\pi4}\mathrm{La}_{2}\mathrm{O}_{2}^{t(Q^{t})}]_{\infty}^{101}\mathrm{I}_{f}^{t}\}_{\infty}^{1s}[\mathrm{S}_{2}|_{10}(\mathrm{Q}^{t})]\}_{f}^{t}$	LaOS	$tI16$	$I\bar{4}2m$	La, Pr, Nd/S	$(Q^{2}\,{}^{t}_{f}-2Q^{t}_{f})_{f}$	19
$\{[^{\pi4}\mathrm{La}_{2}\mathrm{S}_{2}^{t(2Q^{t}_{f})}]_{\infty}^{101}\mathrm{I}_{\tilde{s}}^{t}\}_{\infty}^{1s}[\mathrm{IS}_{2}|_{10}(\mathrm{Q}^{2})|_{10}]\mathrm{I}_{\tilde{s}}^{t}\}_{f}^{t}$	$\mathrm{LaS_2}\,(\beta)$	$oP24$	$Pnma$	La/S	$(Q^{2}\,{}^{t}_{f}-2Q^{t}_{f})_{f}$	20
$\{[^{\pi4}\mathrm{La}_{2}\mathrm{Se}_{2}^{t(2Q^{t}_{f})}]_{\infty}^{101}\mathrm{I}_{\tilde{s}}^{t}\}_{\infty}^{1s}[\mathrm{ISe}_{2}|_{10}(\mathrm{Q}^{2})|_{10}]\mathrm{I}_{\tilde{s}}^{t}\}_{f}^{s}$	$\mathrm{LaSe_2}$	$mP12$	$P2_{1}/a$	La, Ce/S, Se	$(Q^{2}\,{}^{t}_{f}-2Q^{t}_{f})_{s}$	21
$\{[^{\pi4}\mathrm{La}_{4}\mathrm{O}_{4}^{t(\tilde{Q}^{4})}\mathrm{I}_{f}^{t}]_{\infty}^{101}[\mathrm{ISe}_{2}|\mathrm{Se}]_{10}(\tilde{Q}^{3})\}_{f}^{b}$	$\mathrm{La_4O_4Se_3}$	$oC22$	$B2mm$	La—Yb/Se	$\tilde{Q}^{3}/\tilde{Q}^{4}$	22
$\{[^{\pi4}\mathrm{La}_{2}\mathrm{O}_{2}^{t(Q^{2})}]_{\infty}^{101}[\mathrm{Ag}_{2}\mathrm{S}_{2}]^{t}\,2\mathrm{Q}^{t}_{f}\}_{s}$	LaAgOS	$tP8$	$P4/nmm$	La/Ag, Cu/S	$(Q^{2}\,{}^{t}_{f}-2Q^{t}_{f})_{s}$	23
$\{[^{\pi4}\mathrm{Nd}_{4}\mathrm{O}_{4}^{t(\tilde{Q}^{8})}][\mathrm{Ga}_{2}\mathrm{S}_{5}^{t}\,\tilde{T}^{11}]\}$	$\mathrm{Nd_4O_4Ga_2S_5}$	$oP96$	$Pbca$	La, Pr—Sm/Ga, Ge/S, Se	$\tilde{Q}^{i}/\tilde{T}^{j}$	24
$\{[^{\pi4}\mathrm{Ce}_{4}\mathrm{O}_{4}^{t(Q^{2})}]_{\infty}^{101}[\mathrm{Ga}_{2}\square_{6}\mathrm{S}_{5}\square]^{3}\mathrm{Q}^{t}_{f}\}_{f}$	$\mathrm{Ce_4O_4Ga_2S_5}$	$tI22$	$I4/mmm$	La, Ce/Ga, As/S	$(Q^{2}\,{}^{t}_{f}-3Q^{t}_{f})_{f}$	25
$\{[^{\pi4}\mathrm{La}_{4}\mathrm{O}_{4}^{t(Q^{2})}]_{\infty}^{101}[\mathrm{Ga}_{1.33}\square_{0.67}\mathrm{S}_{4}\square_{2}]\overbrace{3\mathrm{Q}^{t}_{f}}\}_{s}$	$\mathrm{La_4O_4Ga_{1.33}S_4}$	$tP22$	$P4/nmm$	La, Ce/Ga/S	$(Q^{2}\,{}^{t}_{f}-3Q^{t}_{f})_{s}$	1
$\mathrm{La}_{6}^{8}\mathrm{La}_{4}^{7}\mathrm{In}_{2}^{t}\mathrm{In}_{2}^{10}\mathrm{In}_{2}^{0}\{[O_{6}]|[S_{17}]\}^{T^{i}+Q^{j}}$	$\mathrm{La_{10}O_6In_6S_{17}}$	$oI78$	$Immm$	La/In/S	$T^{i}+Q^{j}$	26

[a] scs = short crystallographic symbol (crystal system, lattice type, total number of filled positions in unit cell).

TABLE II. Complex Structural Arrangements

Compound	scs	Space group	Structural description	References
$Ce_3O_3S_2$	$oP32$	$Pnam$	(010) $\frac{1}{2}$[100] shear/La_2O_2S + extra S layers	27
$Ce_4O_4S_3$	$oP22$	$Pbam$	same as above but unequal slab width	28
$Pr_{10}OS_{14}$	$tI220$	$I4_1/acd$	complex arrangement	29
$LaOCrS_2$	$oP20$	$Pbnm$	mixed layers $Q^1 + Q^2 //(460)$	30
$CeOCrS_2$	$mC20$	$B2/m$	mixed layers $T^i + T^j/R^{ij} //(010)$	31
$LaOGaS_2$	$oP20$	$Pmca$	complex array	1
$LaOAsS_2$	a			2
$Pu_2O_4U_2Se_3$	monoclinic		subst. derivat. $Ce_4O_4S_3$	32
La_3OGaS_5	$oP40$	$Pnam$	complex array (slabs)	33
$La_4O_3As_2S_6$	$oI60$	$Ibam$	complex array (slabs)	34
$La_5O_7V_3S_6$	$oP44$	$Pmnm$	mixed layer $Q^1 + Q^2 //(\bar{8}60)$	35
$La_{3.33}O_2Ga_6S_{12}$	$tP24$	$P42_1m$	melilite type	36

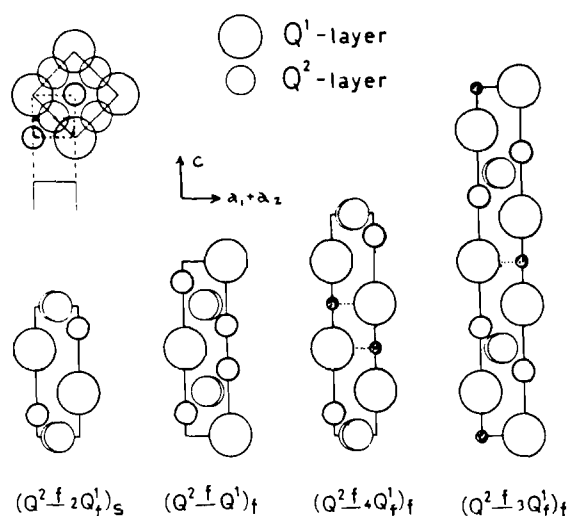^aStructure not determined.

Fig. 2. Packing arrays in Q^1/Q^2 oxychalcogenides. ○, rare earth atoms; ●, extra metal atoms.

ture types assigned to the oxychalcogenides compounds is given in Table I which also includes a few representative layered structure types of the rare earth chalcogenides and pnictides. Table II contains the remaining compounds whose structural complexity hinders the listing of structural formulae.

Final Remarks

A complete report on the structure types of oxyhalide compounds — which partially overlap the structural domain dealt with at present — will be published elsewhere. There, a structural relationship between Q^1/Q^2 arrays and both perovskite and K_2NiF_4 structure types will be fully discussed, along with implications on the crystal chemistry and physical properties of the oxychalcogenides of f-transition elements.

Acknowlegements

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