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BaLn_2Se$_4$ (Ln = Er, Tm and Yb)

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The compounds BaLn_2Se$_4$ (Ln = rare-earth metal = lanthanide = Er, Tm and Yb), namely barium di(erbium/thulium/ytterbium) tetraselenide, crystallize in the orthorhombic space group *Pnma* in the CaFe$_2$O$_4$ structure type. In this structure type, all atoms possess *m* symmetry. The Ln atoms are octahedrally coordinated by six Se atoms. A three-dimensional channel structure is formed by the corner- and edge-sharing of these LnSe$_6$ octahedra. The Ba atoms are coordinated to eight Se atoms in a bicapped trigonal–prismatic arrangement, and they occupy the channels of the three-dimensional framework.

Comment

Ternary compounds of the family ALn_2Q_4 (A = alkaline earth, Ln = lanthanide, and Q = S, Se and Te) have been extensively studied because of their magnetic and optical properties. Additionally, these compounds present intriguing structural variations. Members of this family crystallize in four structure types, namely MgAl$_2$O$_4$ (Passerini, 1930), Th$_3$P$_4$ (Meisel, 1939), Yb$_3$S$_4$ (Chevalier *et al.*, 1967) and CaFe$_2$O$_4$ (Decker & Kasper, 1957). The ALn_2Q_4 compounds in the MgAl$_2$O$_4$ structure type have A replacing Mg and Ln replacing Al. Those in the Th$_3$P$_4$ structure type have the A and Ln cations disordered over the Th site in a 1:2 ratio. Those in the Yb$_3$S$_4$ structure type have the A cation replacing the one Yb^{2+} site and the Ln cations replacing the two Yb^{3+} sites. The ALn_2Q_4 compounds in the CaFe$_2$O$_4$ structure type have A replacing Ca and Ln replacing Fe.

The members of the BaLn_2Q_4 (Q = S, Se and Te) subfamily whose structures are known adopt either the Th$_3$P$_4$ or the CaFe$_2$O$_4$ structure type. The present compounds, *viz.* BaLn_2Se$_4$ (Ln = Er, Tm and Yb), crystallize in the orthorhombic space group *Pnma* in the CaFe$_2$O$_4$ structure type. Fig. 1 shows the unit cell of these BaLn_2Se$_4$ compounds. The formal oxidation states may be assigned as Ba^{2+}, Ln^{3+} and Se^{2-}. The two crystallographically unique Ln atoms are six-coordinated, bonded to an octahedral arrangement of Se atoms. The Ba atom is surrounded by eight Se atoms in a bicapped trigonal–prismatic geometry. Each LnSe$_6$ octahedron shares edges with a neighboring octahedron to form two types of dimers, namely $Ln(1)_2$Se$_{10}$ and $Ln(2)_2$Se$_{10}$. These dimers share edges in the [010] direction to form infinite chains. Additionally, in the (010) plane each $Ln(1)_2$Se$_{10}$ dimer shares four corners with $Ln(2)_2$Se$_{10}$ dimers, and *vice versa*, to form extended sheets. The combination of chains in the [010] direction and sheets in the (010) plane forms a three-dimen-

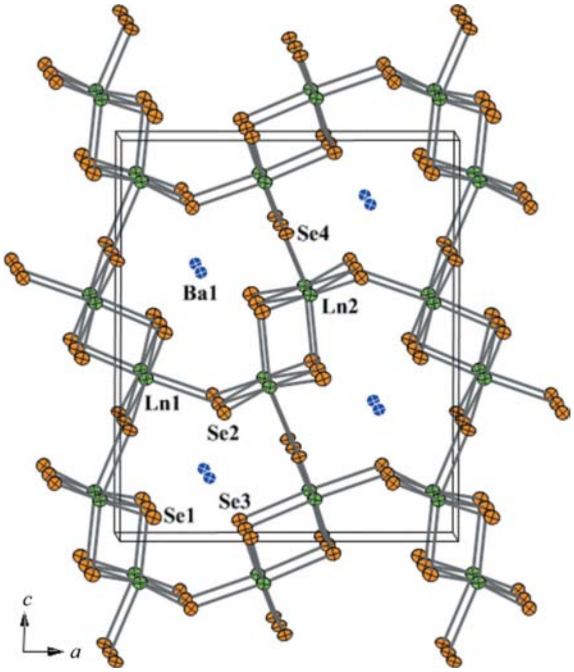

Figure 1
A view down [010] of the unit cell of BaLn_2Se$_4$ (Ln = Er, Tm and Yb), with displacement ellipsoids at the 95% probability level.

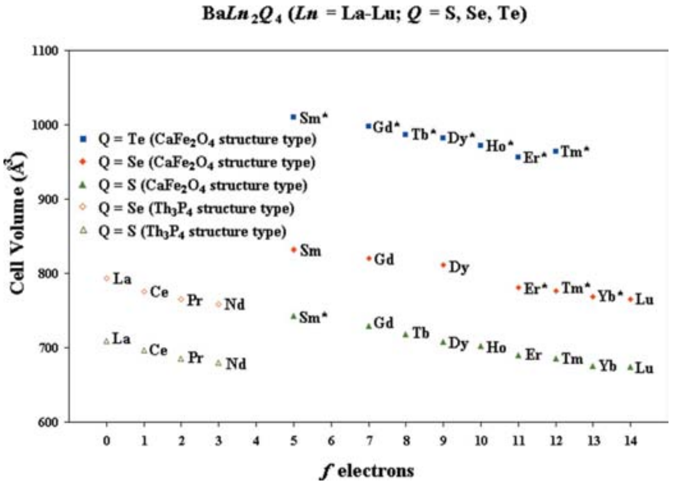

Figure 2
A plot of cell volume *versus* the number of *f* electrons for the BaLn_2Q_4 subfamily. An asterisk indicates a result from single-crystal X-ray diffraction data; otherwise, the result is from powder X-ray diffraction data.

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sional channel structure, with Ba^{2+} cations residing in the channels.

Fig. 2 shows the relation between the cell volume and lanthanide element (number of *f* electrons) for the present and previously known members of the $BaLn_2Q_4$ subfamily (Patrie *et al.*, 1964; Flahaut *et al.*, 1965; Carpenter & Hwu, 1992*a*; Narducci *et al.*, 2000). The trend in cell volume *versus* number of *f* electrons approximately follows the lanthanide contraction. The earlier lanthanides of Te could not be synthesized (Narducci *et al.*, 2000). The later lanthanides of all three chalcogens crystallize in the $CaFe_2O_4$ structure type, whereas the earlier lanthanides of Se and S crystallize in the Th_3P_4 structure type. It is not clear why there is this change from the lower-density $CaFe_2O_4$ structure type to the higher-density Th_3P_4 structure type between Nd^{3+} and Sm^{3+}.

Nonstoichiometry has been claimed in some of the ALn_2Q_4 compounds on the basis of single-crystal X-ray diffraction data. For example, $Ba_{1-x}Sm_2S_{4-x}$ ($x = 0.10$; Carpenter & Hwu, 1992*a*) is said to exhibit deficiencies on both the alkaline-earth and the chalcogen atoms. Additionally, $Ca_{1-x}Yb_{2+x}S_4$ ($x = 0.04$; Carpenter & Hwu, 1992*b*) of the Yb_3S_4 structure type is said to show a slight deficiency of Ca, which is compensated for by a mixing of Yb^{2+} on the Ca^{2+} site. Such mixing is possible because the ionic radii for seven-coordinate Ca^{2+} and Yb^{2+} are approximately equal (1.06 and 1.08 Å, respectively; Shannon, 1976). Refinement of the present $BaLn_2Se_4$ compounds in which the occupancy factors were allowed to vary revealed no evidence either of alkaline-earth or chalcogen deficiencies or of Ba^{2+} and Yb^{2+} disorder. Mixing of Ba^{2+} and Yb^{2+} on the eight-coordinate alkaline-earth site is disfavored because of the mismatch in ionic radii (1.42 and 1.14 Å, respectively; Shannon, 1976). In the absence of support from other physical measurements, such claims, including the present one, based solely on X-ray diffraction data, must be viewed as provisional.

Experimental

The $BaLn_2Se_4$ compounds were synthesized by high-temperature solid-state reactions. The following reagents were used as obtained: Er (Alfa Aesar, 99.5%), Tm (Strem Chemicals, 99.9%), Yb (Alfa Aesar, 99.99%), filings from a Ba rod (Johnson Matthey, 99.5%), Se (Cerac, 99.999%) and Sb (Aldrich, 99.5%). The $BaLn_2Se_4$ compounds were synthesized from *Ln* (0.13 mmol), Ba (0.12 mmol) and Se (0.76 mmol). Sb (0.12 mmol) was added as a flux to aid in crystallization of the final product. The reactants were loaded into fused-silica tubes under an argon atmosphere in a glove-box. The tubes were evacuated to 10^{-4} Torr, flame sealed and then placed in a computer-controlled furnace. The tubes were heated to 1123 K over a period of 17 h, held at 1123 K for 6 d, cooled at a rate of 3 K h^{-1} to 673 K and annealed at 673 K for one week, and finally the furnace was turned off. The resulting thin orange (Er and Tm) and red (Yb) needles were manually extracted from the product. The yield was approximately 30% based on *Ln*. The product also contained a gray metallic melt, as well as a black powder. Analysis of the crystals with an EDX-equipped (energy-dispersive X-ray spectroscopy) Hitachi S-3400 scanning electron microscope showed the presence of Ba, *Ln* and Se, but not of Sb.

Compound (I)

Crystal data

$BaEr_2Se_4$
$M_r = 787.70$
Orthorhombic, *Pnma*
$a = 12.628$ (3) Å
$b = 4.1398$ (8) Å
$c = 14.953$ (3) Å
$V = 781.7$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 44.77$ mm^{-1}
$T = 100$ K
0.30 × 0.05 × 0.05 mm

Data collection

Bruker APEXII diffractometer
Absorption correction: numerical (*SADABS*; Sheldrick, 2008*b*)
$T_{min} = 0.025$, $T_{max} = 0.196$
8227 measured reflections
1036 independent reflections
987 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.066$
$S = 1.54$
1036 reflections
44 parameters
$\Delta\rho_{max} = 1.59$ e Å^{-3}
$\Delta\rho_{min} = -2.68$ e Å^{-3}

Compound (II)

Crystal data

$BaTm_2Se_4$
$M_r = 791.04$
Orthorhombic, *Pnma*
$a = 12.605$ (3) Å
$b = 4.1311$ (8) Å
$c = 14.919$ (3) Å
$V = 776.9$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 46.28$ mm^{-1}
$T = 110$ K
0.22 × 0.06 × 0.05 mm

Data collection

Bruker APEXII diffractometer
Absorption correction: numerical (*SADABS*; Sheldrick, 2008*b*)
$T_{min} = 0.021$, $T_{max} = 0.178$
8761 measured reflections
1070 independent reflections
1041 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.042$
$S = 1.27$
1070 reflections
44 parameters
$\Delta\rho_{max} = 1.69$ e Å^{-3}
$\Delta\rho_{min} = -1.36$ e Å^{-3}

Compound (III)

Crystal data

$BaYb_2Se_4$
$M_r = 799.26$
Orthorhombic, *Pnma*
$a = 12.580$ (3) Å
$b = 4.1150$ (8) Å
$c = 14.860$ (3) Å
$V = 769.2$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 47.99$ mm^{-1}
$T = 100$ K
0.17 × 0.02 × 0.02 mm

Data collection

Bruker APEXII diffractometer
Absorption correction: numerical (*SADABS*; Sheldrick, 2008*b*)
$T_{min} = 0.113$, $T_{max} = 0.429$
8818 measured reflections
1056 independent reflections
1012 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.042$
$S = 1.22$
1056 reflections
44 parameters
$\Delta\rho_{max} = 1.35$ e Å^{-3}
$\Delta\rho_{min} = -1.90$ e Å^{-3}

The structures were standardized by means of the program *STRUCTURE TIDY* (Gelato & Parthé, 1987).

For all compounds, data collection: *APEX2* (Bruker, 2008); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008*a*); program(s) used to refine structure: *SHELXL* (Sheldrick, 2008*a*); molecular graphics: *CrystalMaker* (Palmer, 2009); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008*a*).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3208). Services for accessing these data are described at the back of the journal.

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