

BaLn₂Se₄ (Ln = Er, Tm and Yb)

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The compounds BaLn₂Se₄ (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 CaFe₂O₄ 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 LnSe₆ 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 ALn₂Q₄ (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 MgAl₂O₄ (Passerini, 1930), Th₃P₄ (Meisel, 1939), Yb₃S₄ (Chevalier *et al.*, 1967) and CaFe₂O₄ (Decker & Kasper, 1957). The ALn₂Q₄ compounds in the MgAl₂O₄ structure type have A replacing Mg and Ln replacing Al. Those in the Th₃P₄ structure type have the A and Ln cations disordered over the Th site in a 1:2 ratio. Those in the Yb₃S₄ structure type have the A cation replacing the one Yb²⁺ site and the Ln cations replacing the two Yb³⁺ sites. The ALn₂Q₄ compounds in the CaFe₂O₄ structure type have A replacing Ca and Ln replacing Fe.

The members of the BaLn₂Q₄ (Q = S, Se and Te) subfamily whose structures are known adopt either the Th₃P₄ or the CaFe₂O₄ structure type. The present compounds, *viz.* BaLn₂Se₄ (Ln = Er, Tm and Yb), crystallize in the orthorhombic space group *Pnma* in the CaFe₂O₄ structure type. Fig. 1 shows the unit cell of these BaLn₂Se₄ compounds. The formal oxidation states may be assigned as Ba²⁺, Ln³⁺ and Se²⁻. 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 LnSe₆ octahedron shares edges with a neighboring octahedron to form two types of dimers, namely Ln(1)₂Se₁₀ and Ln(2)₂Se₁₀. These dimers share edges in the [010] direction to form infinite chains. Additionally, in the (010) plane each Ln(1)₂Se₁₀ dimer shares four corners with Ln(2)₂Se₁₀ 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-

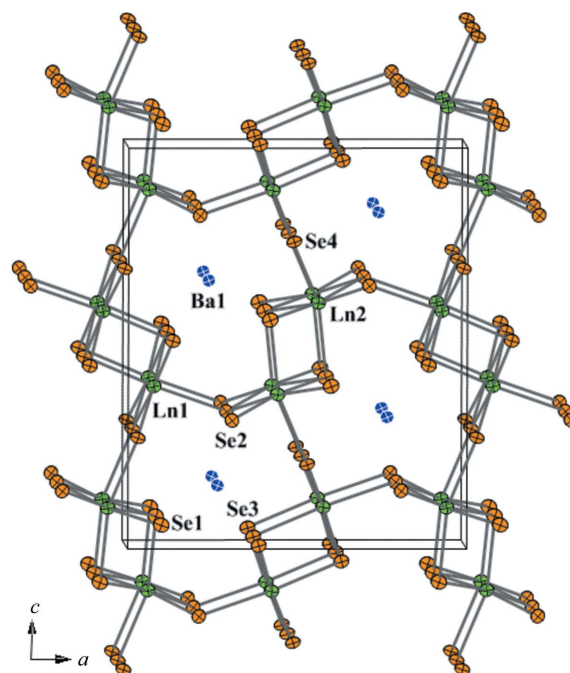


Figure 1
A view down [010] of the unit cell of BaLn₂Se₄ (Ln = Er, Tm and Yb), with displacement ellipsoids at the 95% probability level.

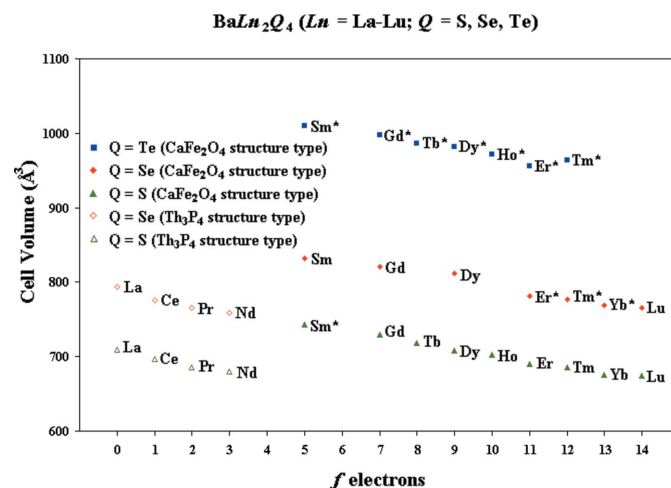


Figure 2
A plot of cell volume *versus* the number of *f* electrons for the BaLn₂Q₄ subfamily. An asterisk indicates a result from single-crystal X-ray diffraction data; otherwise, the result is from powder X-ray diffraction data.

sional channel structure, with Ba²⁺ 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 BaLn₂Q₄ subfamily (Patrie *et al.*, 1964; Flahaut *et al.*, 1965; Carpenter & Hwu, 1992a; 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 CaFe₂O₄ structure type, whereas the earlier lanthanides of Se and S crystallize in the Th₃P₄ structure type. It is not clear why there is this change from the lower-density CaFe₂O₄ structure type to the higher-density Th₃P₄ structure type between Nd³⁺ and Sm³⁺.

Nonstoichiometry has been claimed in some of the ALn₂Q₄ compounds on the basis of single-crystal X-ray diffraction data. For example, Ba_{1-x}Sm₂S_{4-x} (*x* = 0.10; Carpenter & Hwu, 1992a) is said to exhibit deficiencies on both the alkaline-earth and the chalcogen atoms. Additionally, Ca_{1-x}Yb_{2+x}S₄ (*x* = 0.04; Carpenter & Hwu, 1992b) of the Yb₃S₄ structure type is said to show a slight deficiency of Ca, which is compensated for by a mixing of Yb²⁺ on the Ca²⁺ site. Such mixing is possible because the ionic radii for seven-coordinate Ca²⁺ and Yb²⁺ are approximately equal (1.06 and 1.08 Å, respectively; Shannon, 1976). Refinement of the present BaLn₂Se₄ compounds in which the occupancy factors were allowed to vary revealed no evidence either of alkaline-earth or chalcogen deficiencies or of Ba²⁺ and Yb²⁺ disorder. Mixing of Ba²⁺ and Yb²⁺ 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 BaLn₂Se₄ 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 BaLn₂Se₄ 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 ₂ Se ₄	<i>V</i> = 781.7 (3) Å ³
<i>M_r</i> = 787.70	<i>Z</i> = 4
Orthorhombic, <i>Pnma</i>	Mo <i>K</i> α radiation
<i>a</i> = 12.628 (3) Å	<i>μ</i> = 44.77 mm ⁻¹
<i>b</i> = 4.1398 (8) Å	<i>T</i> = 100 K
<i>c</i> = 14.953 (3) Å	0.30 × 0.05 × 0.05 mm

Data collection

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

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.025	44 parameters
<i>wR</i> (<i>F</i> ²) = 0.066	Δ <i>ρ</i> _{max} = 1.59 e Å ⁻³
<i>S</i> = 1.54	Δ <i>ρ</i> _{min} = -2.68 e Å ⁻³
1036 reflections	

Compound (II)

Crystal data

BaTm ₂ Se ₄	<i>V</i> = 776.9 (3) Å ³
<i>M_r</i> = 791.04	<i>Z</i> = 4
Orthorhombic, <i>Pnma</i>	Mo <i>K</i> α radiation
<i>a</i> = 12.605 (3) Å	<i>μ</i> = 46.28 mm ⁻¹
<i>b</i> = 4.1311 (8) Å	<i>T</i> = 110 K
<i>c</i> = 14.919 (3) Å	0.22 × 0.06 × 0.05 mm

Data collection

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

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.018	44 parameters
<i>wR</i> (<i>F</i> ²) = 0.042	Δ <i>ρ</i> _{max} = 1.69 e Å ⁻³
<i>S</i> = 1.27	Δ <i>ρ</i> _{min} = -1.36 e Å ⁻³
1070 reflections	

Compound (III)

Crystal data

BaYb ₂ Se ₄	<i>V</i> = 769.2 (3) Å ³
<i>M_r</i> = 799.26	<i>Z</i> = 4
Orthorhombic, <i>Pnma</i>	Mo <i>K</i> α radiation
<i>a</i> = 12.580 (3) Å	<i>μ</i> = 47.99 mm ⁻¹
<i>b</i> = 4.1150 (8) Å	<i>T</i> = 100 K
<i>c</i> = 14.860 (3) Å	0.17 × 0.02 × 0.02 mm

Data collection

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

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.018	44 parameters
<i>wR</i> (<i>F</i> ²) = 0.042	Δ <i>ρ</i> _{max} = 1.35 e Å ⁻³
<i>S</i> = 1.22	Δ <i>ρ</i> _{min} = -1.90 e Å ⁻³
1056 reflections	

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, 2008a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2008a); molecular graphics: *CrystalMaker* (Palmer, 2009); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008a).

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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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