Crystal structure of europium lithium gallium, $\text{EuLi}_{0.24}\text{Ga}_{1.76}$

A. Fedorchuk^{I,II}, Yu. Prots^{*II}, W. Schnelle^{II} and Yu. Grin^{II}^I Ivan Franko National University of Lviv, Inorganic Chemistry Department, Kyrylo and Mefodia Str. 6, 79005 Lviv, Ukraine^{II} Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, Germany

Received July 12, 2005, accepted and available on-line September 3, 2005; CSD no. 409841

Abstract

$\text{EuGa}_{1.76}\text{Li}_{0.24}$, orthorhombic, *Imma* (no. 74), $a = 4.6433(4)$ Å, $b = 7.6322(6)$ Å, $c = 7.7341(7)$ Å, $V = 274.1$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.037$, $wR_{\text{ref}}(F) = 0.098$, $T = 293$ K.

Source of material

A set of bulk samples around the composition $\text{EuLi}_x\text{Ga}_{2-x}$ was prepared from the elements. Lithium (99.9 mass %, Alfa) and gallium (99.99 mass %, ChemPur) were used as delivered, whereas europium (99.9 mass %, ChemPur) was re-distilled before use. Mixtures of elements with total mass of approximately 1.5 g were welded in niobium tubes and placed in the evacuated and sealed quartz ampoules. To prevent reaction of europium and lithium with air and moisture, all manipulations of educts and products were performed inside an argon-filled glove box ($p(\text{O}_2, \text{H}_2\text{O}) < 1$ ppm, purification by molecular sieve and copper catalyst). At the first step of the synthesis, the ampoules were slowly heated to 900 °C within 24 h and held at this temperature for 2 h. After that, the temperature was decreased within one day to 300 °C. Subsequently, the samples were annealed at this temperature for 30 d and then quenched in cold water. A single crystal with irregular shape suitable for data collection was mechanically extracted from the sample with nominal composition $\text{Eu}_{30}\text{Li}_{30}\text{Ga}_{40}$ and encapsulated into a glass capillary.

Experimental details

For calculation of interatomic distances, the lattice parameters were used as obtained from X-ray powder diffraction data (Image Plate Guinier Camera HUBER G670, $\text{Co K}\alpha_1$ radiation, $\lambda = 1.788965$ Å, silicon as internal standard, $a = 5.43102$ Å).

Discussion

Europium digallide [1–3] dissolves up to 12 at. % Li. The unit cell parameters of EuGa_2 ($a = 4.644(2)$ Å, $b = 7.626(2)$ Å, $c = 7.638(2)$ Å; $d(\text{Ga}—\text{Ga}) = 2.654(2)$ Å, $2.692(2)$ Å ($2\times$), $2.812(2)$ Å [3]) change differently with increasing lithium content in the homogeneity range: whereas the a parameter is not affected by the composition, the b and, especially the c parameter, increase with increasing lithium content. Despite the expected cationic behavior, Li species replace gallium in the polyanion. In the crystal structure of the title compound, gallium and lithium species (occupation of the M position $0.880(6)$ Ga + 0.120 Li) form slightly puckered hexagonal nets with shorter $M—M$ distances of $2.6882(7)$ Å or $2.689(1)$ Å ($2\times$), which are stacked along $[010]$. The shortest distance between the nets is slightly longer ($2.857(2)$ Å). Distances inside the lithium-gallium polyanion are larger in comparison with the according separations in the binary compound. Since EuGa_2 is an electronically balanced system with covalently bonded atoms within the polyanion [3], a reduced number of bonding electrons due to the gallium-to-lithium substitution leads consequently to an elongation of the bonds within the polyanion and larger unit cell volume in comparison with binary EuGa_2 . From measurements of the magnetic susceptibility on $\text{EuLi}_x\text{Ga}_{2-x}$ ($\mu_{\text{eff}} = 7.98 \mu_{\text{B}}$ for $x = 0.12$ and $\mu_{\text{eff}} = 7.90 \mu_{\text{B}}$ for $x = 0.24$), europium is, as it was found also for EuGa_2 [3], in the ground state $^8S_{7/2}$ of the $4f^7$ (Eu^{2+}) and cannot compensate lack of electrons necessary for the bonding in the polyanion.

Table 1. Data collection and handling.

Crystal:	gray platelet, size $0.070 \times 0.050 \times 0.020$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	319.44 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7, ω/ϕ
$2\theta_{\text{max}}$:	66.9°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	1613, 286
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 262
$N(\text{param})_{\text{refined}}$:	14
Program:	WinCSD [4]

* Correspondence author (e-mail: prots@cpfs.mpg.de)

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Eu	4e	¼	½	0.29799(8)	0.0104(2)	0.0096(3)	0.0137(3)	0	0	0
M	8i	¼	0.68720(1)	0.91239(1)	0.0096(5)	0.0146(7)	0.0095(5)	0	0	-0.0007(4)

$M = \text{Ga}_{0.880(6)}\text{Li}_{0.120}$

Acknowledgment. A. F. is thankful to the Max-Planck Society for a research fellowship.

References

1. Markiv, V. Ya.; Beljavina, N. N.; Zhunkovska, T. I.: X-ray investigation of the alloys in the system Y-Cu-Ga and of the sections RECu₂-REGa₂. *Dopov. Akad. Nauk Ukr. RSR, Ser. A: Fiz.-Mat. Tekhn. Nauki* (1982) 84-88.
2. Buschow, K. H. J.; de Mooij, D. B.: Note on the crystal structure of EuGa₂. *J. Less-Common Met.* **97** (1984) L5-L9.
3. Sichevych, O.; Ramlau, R.; Giedigkeit, R.; Schmidt, M.; Niewa, R.; Grin, Yu.: EuGa₂ and some related compounds: structure and bonding. 13th Int. Conf. on Solid Compounds of Transition Elements. Stresa, Italy 2000, p. 13.
4. Akselrud, L. G.; Zavali, P. Yu.; Grin, Yu.; Pecharsky, V. K.; Baumgartner, B.; Wölfel, E.: Use of the CSD program package for structure determination from powder data. *Mater. Sci. Forum* **133-136** (1993) 335-340.