Crystal structures of europium magnesium gallium, $EuMg_xGa_{4-x}$, and europium lithium gallium, $EuLi_xGa_{4-x}$ (x 0.5)

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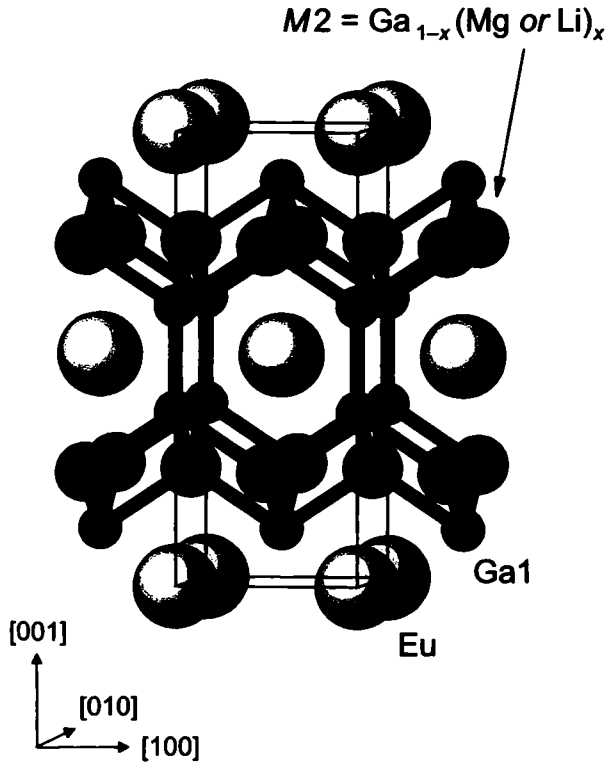

Abstract

$EuGa_{3.45}Mg_{0.55}$, tetragonal, *I4/mmm* (no. 139), $a = 4.3831(1)$ Å, $c = 11.0632(4)$ Å, $V = 212.5$ Å^3, $Z = 2$, $R_{gt}(F) = 0.021$, $wR_{ref}(F) = 0.025$, $T = 295$ K.

$EuGa_{3.46}Li_{0.54}$, tetragonal, *I4/mmm* (no. 139), $a = 4.3456(1)$ Å, $c = 10.8453(5)$ Å, $V = 204.8$ Å^3, $Z = 2$, $R(I) = 0.079$, $R(P) = 0.096$, $T = 295$ K.

Source of material

A set of samples around the composition EuM_xGa_{4-x} (M = Mg, Li) was prepared from the elements. Magnesium (99.98 mass %, Alfa), 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 with the educts and products were performed inside an argon-filled glove box ($p(O_2, H_2O) < 1$ ppm). 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 400 °C. The samples were annealed at this temperature for ten months and subsequently quenched in cold water. A single-crystal fragment with irregular shape suitable for intensity collection was extracted from the sample with nominal composition $Eu_{17}Mg_{17}Ga_{66}$ and mounted 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, $CoK_{\alpha 1}$ (λ = 1.788965 Å) and $CuK_{\alpha 1}$ (λ = 1.540598 Å) radiation, silicon as internal standard, $a = 5.43102$ Å). The crystal structure of $EuLi_xGa_{4-x}$ was refined from the powder diffraction data.

Discussion

Europium tetragallide is an unique tetragallide of the rare earth metals with the $BaAl_4$ type of the crystal structure [1-3]. Ytterbium forms a tetragallide with a monoclinically distorted variant of this structure type [4,5]. Other rare earth metals do not form tetragallides at all. Electronic stability limits for $EuGa_4$ were investigated by replacing gallium with the electron-poorer elements as lithium and magnesium.

Chemical bonding in $EuGa_4$ is described as gallium polyanion with two- and three-centre bonds with Eu^{2+} cations embedded into the cavities of the 3D anionic network. Gallium is represented in two bonding forms: five-bonded (Ga1 position) and four-bonded (Ga2 or *M*2) [3]. Considering the cationic character of lithium and magnesium, one would expect them to replace europium in the crystal structure of $EuGa_4$. De facto, both metals replace gallium atoms in the polyanion on the *M*2 position: 0.72(3) Ga + 0.28 Mg and 0.73(5) Ga + 0.27 Li for magnesium and lithium compounds, respectively. This replacement influences mostly the Ga1—Ga1 contact, which increases from 2.485(3) Å in $EuGa_4$ to 2.536(6) Å or 2.533(1) Å in magnesium and lithium substituents, respectively. In addition, the Ga1—*M*2 contact does not change significanty from 2.623(1) Å in the binary compound to 2.655(3) Å in $EuMg_{0.55}Ga_{3.45}$ and 2.608(1) Å for $EuLi_{0.54}Ga_{3.46}$.

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1. Europium magnesium gallium, $EuMg_{0.55}Ga_{3.45}$

Table 1. Data collection and handling.

Crystal:	gray metallic lustre platelet, size 0.070 × 0.060 × 0.050 mm
Wavelength:	Ag K_α radiation (0.56087 Å)
μ:	197.8 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS I, φ
$2\theta_{max}$:	47.4°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1188, 123
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 122
$N(param)_{refined}$:	9
Program:	WinCSD [6]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Eu	2*a*	0	0	0	0.008(1)	U_{11}	0.016(1)	0	0	0
Ga(1)	4*e*	0	0	0.3854(4)	0.013(1)	U_{11}	0.015(2)	0	0	0
M(2)	4*d*	½	0	¼	0.012(2)	U_{11}	0.012(2)	0	0	0

M(2) = $Ga_{0.72(3)}Mg_{0.28}$

2. Europium lithium gallium, $EuLi_{0.54}Ga_{3.46}$

Table 3. Data collection and handling.

Powder:	gray, size 5 – 20 μm
Wavelength:	Co $K_{\alpha 1}$ radiation (1.78897 Å)
μ:	831.3 cm^{-1}
Diffractometer:	Stoe STADI P
$2\theta_{max}$, stepwidth:	99.99°, 0.005°
$N(points)_{measured}$:	18691
$N(hkl)_{measured}$:	32
$N(param)_{refined}$:	11
Program:	WinCSD [6]

Table 4. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Eu	2*a*	0	0	0	0.0169(6)	U_{11}	0.0128(9)	0	0	0
Ga(1)	4*e*	0	0	0.38321(9)	0.0067(6)	U_{11}	0.021(1)	0	0	0
M(2)	4*d*	½	0	¼	0.0141(8)	U_{11}	0.020(1)	0	0	0

M(2) = $Ga_{0.73(5)}Li_{0.27}$

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