Crystal structure of β -lithium hexafluorogallate, Li_3GaF_6

J. Köhler

Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany

and A. K. Tyagi

Bhabha Atomic Research Centre, Applied Chemistry Division, Trombay, Bombay (400085), India

Received September 9, 1998, transferred to 1st update of database ICSD in 1999, CSD-No. 409384

Abstract

F_6GaLi_3 , monoclinic, $C12/c1$ (No. 15), $a = 14.367(3)$ Å, $b = 8.571(2)$ Å, $c = 9.994(2)$ Å, $\beta = 94.78(3)^\circ$, $V = 1226.4$ Å³, $Z = 12$, $R_{\text{gt}}(F) = 0.026$, $R_w(F^2) = 0.062$, $T = 293$ K.

Source of material

Powder samples and single crystals of the title compound were obtained by heating intimate mixtures of appropriate amounts of LiF (Merck, 99.9%) and GaF₃ (Merck, 99.9%) at 1100 K for 30 hours in a sealed platinum boat under HF atmosphere. In order to obtain the low temperature modification, β -Li₃GaF₆, slow cooling of the sample to room temperature (50 K/h) is necessary.

Discussion

Compounds of the type Li_3MF_6 ($M = \text{Ti, Al, Ga, V, Cr}$ and Fe) exist in two modifications [1]. The monoclinic low temperature form of lithium hexafluorogallate, β -Li₃GaF₆ crystallizes, like β -Li₃AlF₆ and β -Li₃TiF₆ [2, 3], in the β -Li₃VF₆ type structure [4]. Characteristic building units are distorted octahedra $[\text{GaF}_6]^{3-}$: $d(\text{Ga}-\text{F}) = 187$ pm – 193 pm. The Li atoms are octahedrally or tetrahedrally coordinated by F.

Table 1. Data collection and handling.

Crystal:	white, transparent plate, size 0.01 x 0.03 x 0.03 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	67.67 cm ⁻¹
Diffractometer, scan mode:	Enraf-Nonius CAD4, ω
$2\theta_{\text{max}}$:	57.98°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	6927, 1628
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_0 > 2 \sigma(I_{\text{obs}})$, 1058
$N(\text{param})_{\text{refined}}$:	139
Program:	SHELXL-97 [5]

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}
Ga(1)	4a	0	0	0	0.0033(2)	0.0020(2)	0.0047(2)	-0.0004(2)	0.0023(1)	-0.0001(2)
Ga(2)	8f	0.33809(2)	0.00276(5)	0.70527(3)	0.0035(2)	0.0021(2)	0.0041(2)	0.0001(1)	0.00231(9)	-0.0002(2)
F(1)	8f	0.0936(1)	0.3407(2)	0.1960(2)	0.0050(8)	0.0041(7)	0.0073(9)	-0.0019(6)	0.0033(7)	-0.0017(7)
F(2)	8f	0.2306(1)	0.3408(2)	0.8881(2)	0.0052(8)	0.0059(8)	0.008(1)	0.0002(7)	0.0020(7)	0.0018(7)
F(3)	8f	0.1004(1)	0.3425(2)	0.6933(2)	0.0080(8)	0.0036(8)	0.0072(9)	-0.0002(6)	0.0000(7)	-0.0012(7)
F(4)	8f	0.2487(1)	0.0205(2)	0.8372(2)	0.0055(7)	0.0044(8)	0.0073(7)	0.0002(6)	0.0036(5)	0.0005(7)
F(5)	8f	0.0763(1)	0.1616(2)	-0.0629(2)	0.0073(8)	0.0043(8)	0.007(1)	-0.0020(7)	0.0035(7)	0.0005(7)
F(6)	8f	-0.0732(1)	0.1634(2)	0.0658(2)	0.0054(8)	0.0039(8)	0.007(1)	0.0011(7)	0.0027(7)	-0.0015(7)
F(7)	8f	0.4209(1)	-0.0071(2)	0.5681(2)	0.0066(6)	0.0064(7)	0.0076(7)	-0.0004(8)	0.0047(5)	0.0009(8)
F(8)	8f	0.2622(1)	0.1538(2)	0.6080(2)	0.0059(8)	0.0048(8)	0.008(1)	0.0024(7)	0.0006(7)	0.0002(7)
F(9)	8f	0.0721(1)	0.0051(2)	0.1652(2)	0.0067(6)	0.0050(7)	0.0064(6)	0.0012(7)	0.0011(5)	-0.0002(8)
Li(1)	8f	0.0221(4)	0.3500(6)	0.5373(6)	0.009(2)	0.006(2)	0.010(2)	0.003(2)	0.001(2)	0.001(2)
Li(2)	8f	0.2028(4)	-0.1410(6)	0.9317(6)	0.011(2)	0.003(2)	0.012(3)	-0.001(2)	0.002(2)	0.002(2)
Li(3)	4e	0	0.1885(9)	1/4	0.010(3)	0.011(3)	0.011(4)	0	0.005(3)	0
Li(4)	8f	0.1408(4)	-0.1477(7)	0.2681(6)	0.011(2)	0.005(2)	0.019(3)	-0.001(2)	0.003(2)	-0.001(2)
Li(5)	8f	0.3321(4)	0.2101(6)	0.9481(6)	0.009(2)	0.010(2)	0.012(3)	0.001(2)	0.002(2)	-0.002(2)

Acknowledgment. We thank Prof. Dr. A. Simon for support of this work.

References

1. Massa, W.; Rüdorff, W.: Über α - und β - Li_3MeF_6 -Verbindungen. Z. Naturforsch. **26b** (1971) 1216.
2. Tyagi, A. K.; Köhler, J.: Preparation and Rietveld Refinement of the Structure of β - Li_3AlF_6 . Mat. Res. Bull. **32** (1997) 1683.
3. Tyagi, A. K.; Pöttgen, R.; Köhler, J.: Preparation, Crystal Structure and Magnetic Properties of β - Li_3TiF_6 . β - $\text{Li}_3\text{TiF}_6 = \text{Li}[\text{4}_2\text{Li}[\text{6}]_7(\text{TiF}_6)_2(\text{TiF}_6)]$ - a Double Fluoride? Z. Anorg. Allg. Chem. **622** (1996) 1329.
4. Massa, W.: Die Kristallstruktur von β - Li_3VF_6 . Z. Kristallogr. **153** (1980) 201-210.
5. Sheldrick, G. M.: SHELXL-97, a program for refining crystal structures. University of Göttingen, Germany 1997.