Refinement of the crystal structure of dilithium zirconium hexafluoride, Li_2ZrF_6, *synthesized at 11 GPa and 1063 K*

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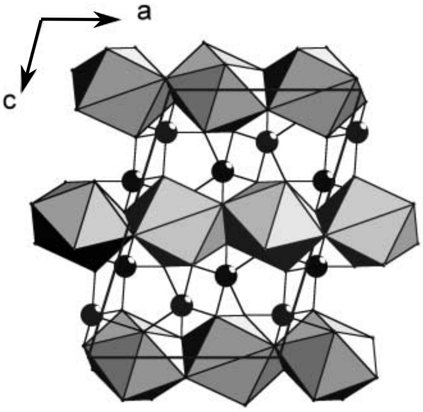

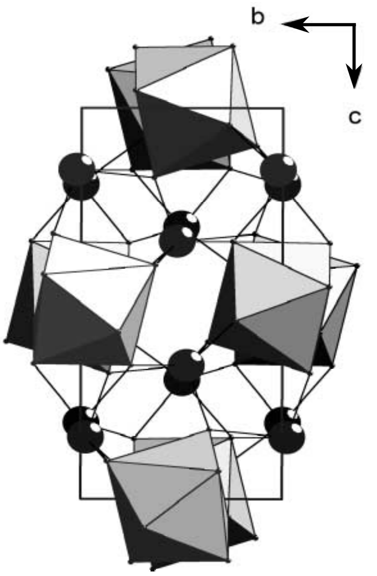

Abstract

F_6Li_2Zr, monoclinic, $P12_1/c1$ (No. 14), $a = 7.4223(1)$ Å, $b = 4.9492(1)$ Å, $c = 10.9691(1)$ Å, $\beta = 106.95(1)°$, $V = 385.4$ Å^3, $Z = 4$, $R(P) = 0.055$, $R(I) = 0.133$, $T = 293$ K.

Source of material

A single crystal of Li_2ZrF_6, grown by the Czochralski method, was ground into a fine powder in ethanol. The high-pressure high-temperature syntheses were performed with a Walker-type multi-anvil apparatus. The pressure medium consisted of a MgO (95 %wt.) / Cr_2O3 (5 %wt.) octahedron with the edge length of 18 mm. Force was applied by eight tungsten carbide cubes with corners truncated to triangular faces. The samples , loaded into Pt ampoules of 2 mm in diameter and of 3.5 mm in height, were pressurized to 11 GPa and then heated at 1063 K for 2 hours. The heating elements, isolated from the ampoules by MgO sleeves, were made of $LaCrO_3$ ceramics. The temperatures at the samples were measured with the W-26%Re / W-5%Re thermocouples. The recovered product was investigated with powder X-ray diffraction at ambient conditions.

Experimental details

The unit cell parameters were refined on 59 reflections ($2\theta < 66.04°$) using the Program CELREF [1]. Silicon (NIST SRM Silicon 640c, $a = 5.431195(9)$ Å) was used as internal standard. Our lattice parameters deviate from those reported earlier [2] ($a = 7.43$ Å, $b = 4.9167$ Å, $c = 10.9792$ Å, $\beta = 106.99°$, $V = 383.5$ Å^3; 21 reflections in a similar 2θ range were used for the refinement) for a sample synthesized at different conditions (7 GPa and 973 K). The Li_2TbF_6 structural model of [3] was used for the Rietveld refinement of the high-pressure high-temperature phase of Li_2ZrF_6.

Discussion

At atmospheric conditions, Li_2ZrF_6 ($P\bar{3}1m$, No. 164, $Z = 1$) has a structure in which all the cations are octahedrally coordinated to fluorine atoms [4,5]. The anions are in a hexagonal-close-packed array. The octahedra around the Li atoms share their edges. The octahedra ZrF_6 share all their corners with the LiF_6 polyhedra. It is a disordered variant of the colquiriite structure ($P31c$, No. 163, $Z = 2$) [6].

Above 7 GPa and 973 K, this compound transforms into a new phase [2] of the Li_2TbF_6 type ($P2_1/c$, No. 14, $Z = 4$) [3,5] with the zirconium atoms in edge-sharing bicapped trigonal prisms along the *a* axis. Lithium atoms are present in two types of coordination polyhedra: octahedra and square pyramids. This structure could be considered a distorted variant of the γ-Na_2UF_6 ordered fluorite (*Immm*, $Z = 2$), in which all the cations are surrounded by fluorines in a cube coordination [3].

Table 1. Data collection and handling.

Powder:	white
Wavelength:	Cu K_α radiation (1.54060 Å)
μ:	138.8 cm^{-1}
Diffractometer, scan mode:	Stoe STADI P, 2θ
$2\theta_{max}$, stepwidth:	99.96°, 0.02°
$N(points)_{measured}$:	4849
$N(hkl)_{measured}$:	394
$N(param)_{refined}$:	33
Programs:	CELLREF [1], GSAS [8], DIAMOND [9]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
Zr	4*e*	0.2520(3)	0.5141(2)	0.0009(2)	0.0167(2)
F(1)	4*e*	0.4537(8)	0.189(1)	0.4299(5)	0.010
F(2)	4*e*	0.1043(8)	0.3578(9)	0.8242(5)	0.010
F(3)	4*e*	0.0466(8)	0.229(1)	0.5468(5)	0.010
F(4)	4*e*	0.3948(8)	0.2163(9)	0.6533(5)	0.010
F(5)	4*e*	0.2450(7)	0.6479(9)	0.3980(4)	0.010
F(6)	4*e*	0.2510(7)	0.746(1)	0.6503(4)	0.010
Li(1)	4*e*	0.407(2)	0.518(4)	0.306(2)	0.020
Li(2)	4*e*	0.038(2)	–0.019(4)	0.172(2)	0.020

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