Crystal structure of lithium potassium yttrium pentafluoride $LiKYF_5$ prepared from high-temperature melt, $F_{10}K_2Li_2Y_2$

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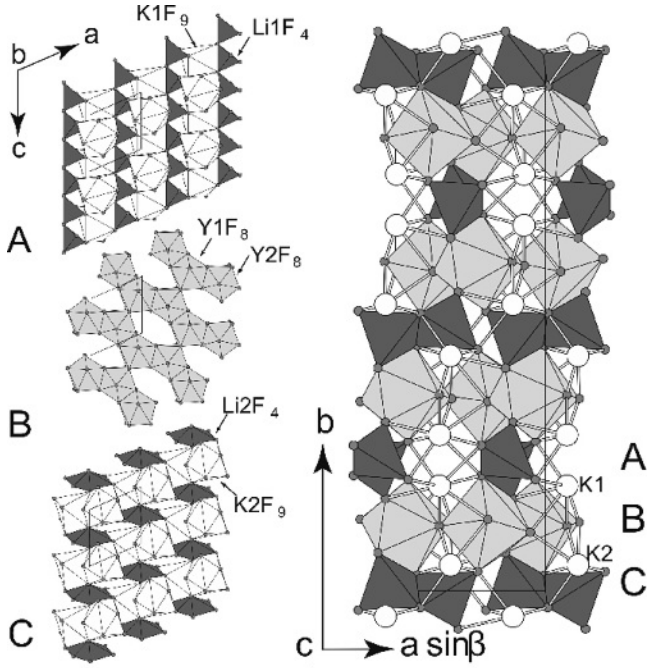

Abstract

$F_{10}K_2Li_2Y_2$, monoclinic, $P2_1/c$ (no. 14), a = 6.3683(4) Å, b = 23.888(1) Å, c = 6.4310(4) Å, β = 113.545(2)°, V = 896.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.0312, $wR_{ref}(F^2)$ = 0.0784, T = 293 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.13×0.15×0.20 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	139.24 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID, ω
$2\theta_{max}$:	61°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7581, 2677
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2172
$N(param)_{refined}$:	146
Programs:	SIR97 [10], SHELX [11], ATOMS [12], ABSCOR [13], PROCESS-AUTO [14]

Source of material

Single crystals were grown by the micro-pulling-down method (μ-PD method) [9]. The starting materials, LiF, KF, and YF_3 powders (>4 *N* purity), were mixed in the ratio LiF:KF:YF_3 = 1.1:1.1:1.0 and then placed in a carbon crucible having a hole with a diameter of 2 mm at the bottom. The crucible was positioned at the center of a high-frequency induction coil in a vacuum-tight chamber. After baking at 300 °C under high vacuum (under 10^{-2} Pa) to remove the adsorbed water and oxygen from the starting material, crystal growth was performed in a high-purity CF_4/Ar mixture at a growth speed of approximately 6 mm/h using Pt wire as a seed. The obtained crystal specimens were cylindrical, with a length and diameter of about 40 mm and 2 mm, respectively.

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Discussion

A study on Nd:$LiKYF_5$ for low-threshold laser applications was reported by a Russian group [1,2]. Photoluminescence spectroscopy and single-crystal X-ray diffraction measurements revealed that a single site for Nd was created in the host structure prepared by the hydrothermal method (H-type). However, the optical properties of the crystal sample prepared by the Czochralski (CZ) method suggested that there was equal probability of Nd occupying two different sites [3-6]. A relevant study demonstrated the local structural features around the Y sites in order to clear the controversy around these findings [7]. More recently, our group developed Nd:$LiKYF_5$ crystal to be used as a possible scintillator material showing 5*d*-4*f* luminescence in the ultraviolet region [8]. The $LiKYF_5$ crystal prepared from the high-temperature melt by the micro-pulling-down method (μ-PD) [9] was isotypic to that prepared by the CZ method. This paper reports the structure of $LiKYF_5$ prepared from the high-temperature melt (M-type). Local structural units of KF_9, YF_8, and LiF_4 are formed in the M-type structure. As shown in Fig. 1, the structure is composed of a layer of YF_8 polyhedra linked by [LiF_4] tetrahedra. [$Li1F_4$] produce a chain structure similar to that in the H-type structure. The Li1–F distances and F–Li1–F angles range from 1.842(6) to 2.043(6) Å and from 85.2(3)° to 123.0(2)°, respectively. The smallest F2–Li1–F10 angle corresponds to edge sharing between [$Li1F_4$] and [$Y1F_8$]. On the other hand, the [$Li2F_4$] pair forms a butterfly-like block by edge sharing. The first and second longest Li2–F2 distances of 1.868(6) and 1.986(6) Å, respectively, are attributed to this unique geometry, and the smallest angle of F5–Li2–F8 = 89.1(3)° again corresponds to edge sharing between [$Li2F_4$] and [$Y2F_8$]. These geometrical features agree well with the significant distortion of the [LiF_4] tetrahedra in the title compound. The structure could be described by the stuck of three types of layers A, B, and C. A and B are equivalent to those in the H-type structure, where these two layers are alternatingly arranged. Layer B is composed of [YF_8], and the average distances for [$Y1F_8$] and [$Y2F_8$] are 2.290 Å and 2.283 Å, respectively. This feature supports the almost equivalent role of the Y sites for Nd substitution. The variations in the [LiF_4] linkage in the M-type structure and the direction of the linear coordination blocks of [KF_9] cause the difference between layers A and C.

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}
Li(1)	4*e*	0.657(1)	0.2494(3)	0.036(1)	0.025(3)	0.019(3)	0.023(3)	0.001(2)	0.009(3)	–0.001(2)
Li(2)	4*e*	0.221(1)	–0.0019(3)	–0.450(1)	0.023(3)	0.019(3)	0.023(3)	–0.002(2)	0.008(3)	–0.001(2)
Y(1)	4*e*	0.53373(5)	0.12581(1)	–0.31648(5)	0.0101(2)	0.0120(2)	0.0110(2)	–0.0002(1)	0.0041(1)	–0.0002(1)
Y(2)	4*e*	–0.10151(5)	0.12594(1)	–0.68041(5)	0.0102(2)	0.0117(2)	0.0112(2)	0.0004(1)	0.0043(1)	0.0002(1)
K(1)	4*e*	0.1684(1)	0.20100(3)	–0.0333(1)	0.0215(4)	0.0193(4)	0.0225(4)	0.0009(3)	0.0116(3)	0.0015(3)
K(2)	4*e*	0.2551(1)	0.04922(3)	0.0407(1)	0.0219(4)	0.0219(4)	0.0239(4)	0.0027(3)	0.0126(3)	0.0004(3)
F(1)	4*e*	0.8811(3)	0.11232(8)	–0.0465(4)	0.0119(9)	0.027(1)	0.0138(9)	0.0027(8)	0.0042(8)	0.0000(8)
F(2)	4*e*	0.4948(4)	0.22108(8)	–0.2689(4)	0.020(1)	0.0139(9)	0.020(1)	0.0017(7)	0.0077(9)	0.0000(8)
F(3)	4*e*	0.5470(3)	0.13686(9)	0.0495(4)	0.0115(9)	0.036(1)	0.0129(9)	0.0027(8)	0.0038(8)	–0.0014(8)
F(4)	4*e*	0.4673(4)	0.03692(8)	–0.2556(4)	0.020(1)	0.0146(9)	0.027(1)	–0.0028(8)	0.0100(9)	0.0016(8)
F(5)	4*e*	0.6854(3)	0.07296(8)	–0.5313(4)	0.024(1)	0.0136(9)	0.027(1)	0.0000(7)	0.0172(9)	–0.0007(8)
F(6)	4*e*	0.2631(3)	0.13147(8)	–0.6704(3)	0.0118(9)	0.028(1)	0.0139(9)	–0.0001(7)	0.0056(8)	0.0003(8)
F(7)	4*e*	0.1677(4)	0.12398(8)	–0.3265(4)	0.0125(9)	0.031(1)	0.014(1)	0.0003(7)	0.0050(8)	–0.0016(8)
F(8)	4*e*	–0.0177(3)	0.03204(8)	–0.6908(4)	0.0185(9)	0.0150(9)	0.022(1)	0.0038(7)	0.0098(9)	0.0015(8)
F(9)	4*e*	–0.0776(3)	0.21352(8)	–0.7794(4)	0.018(1)	0.016(1)	0.025(1)	0.0017(7)	0.0089(9)	0.0029(8)
F(10)	4*e*	–0.2550(3)	0.17720(8)	–0.4696(3)	0.024(1)	0.0127(9)	0.024(1)	–0.0009(7)	0.0154(9)	–0.0023(8)

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