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$LiNa_2AlF_6$: a powder structure solution

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Lithium sodium aluminium fluoride was obtained as a white powder by melting a stoichiometric mixture of AlF_3, NaF and LiF at 1223 K, and then cooling to 923 K and sintering at this temperature for 4 h. The *ab initio* crystal structure determination was carried out using X-ray powder diffraction techniques. The monoclinic structure of $LiNa_2AlF_6$ can be related to cubic elpasolite. The Li and Al atoms lie on inversion centres. The main octahedral AlF_6 structural elements are not deformed, but are rotated slightly with respect to the unit-cell axes. The Li atoms have octahedral coordinations, whereas the Na atoms have cubo-octahedral coordinations. The Na coordination polyhedron is distorted in comparison with that of elpasolite.

Comment

Several producers of raw aluminium use an electrolyte with up to 2.5% of an LiF additive to improve the processing characteristics. Maintaining the ideal LiF and other constituent concentrations is an important technological task. Fast monitoring of electrolyte chemical compositions can be achieved using X-ray diffraction to quantify the phases from a cooled electrolyte sample. The procedure needs reliable X-ray diffraction reference data for the crystallized phases. The present study of $LiNa_2AlF_6$ was prompted particularly by the task of lithium regulation in electrolytes and, consequently, the relevant lithium-bearing phases are under consideration.

The Na_3AlF_6–Li_3AlF_6 phase diagram has been examined several times (Holm & Holm, 1970). However, it is not yet completely clear what kind of diffraction data can be applied for phase identification and what are the exact phase compositions. According to the phase diagram of Holm & Holm (1970), there are three lithium-bearing phases, *viz.* Li_3AlF_6, $Li_3Na_3Al_2F_{12}$ and $LiNa_2AlF_6$. The first and second phases have been structurally characterized (Burns *et al.*, 1968; Geller, 1971). Concerning the third, Holm & Holm reported that they had found an orthorhombic cell. However, they were inclined to consider it as monoclinic because this improved the understanding of the phase transformation. It was also reported that the system demonstrates several phase transitions below the solidus temperature and has extensive fields of solid solutions. The current investigation focused on $LiNa_2AlF_6$, since this is the most closely related phase to that which formed during a sample-taking procedure in the course of electrolyte monitoring. X-ray powder diffraction techniques were used because the phase was a product of subsolidus transformations and a single crystal was not accessible.

An almost pure substance was obtained and an *ab initio* crystal structure determination was carried out. X-ray powder indexing without reference to the systematically absent reflections or the crystal structure actually gives an orthorhombic cell, because the deviation of β from 90° is rather small (0.06°). However, the more accurate analysis of overlapped groups of reflections, and especially the total powder diffraction profile-fitting procedure (Le Bail *et al.*, 1988), positively identifies a monoclinic cell. The final structure refinement confirmed this choice completely.

The crystal structure of $LiNa_2AlF_6$ (Fig. 1) is built up from AlF_6 octahedra arranged according to a body-centred cell. The geometry of AlF_6 is almost perfectly regular and the variation in Al—F bond lengths is no more than 0.01 Å. These lengths correspond well with those in Na_3AlF_6 (Hawthorne & Ferguson, 1975). The angles deviate from 90° by slightly more than 1°. This seems acceptable because the average octahedral angle deviation in Na_3AlF_6 (Hawthorne & Ferguson, 1975) is about 0.7°, and that in Li_3AlF_6 is greater than 1° (Burns *et al.*, 1968). The Li atoms are surrounded by distorted fluorine octahedra, with average bond lengths of about 2.048 Å. The Na atom is in a more spacious position, with distorted cubo-octahedral geometry.

According to the geometrical features, the structure may be considered as a cryolite type, which is often referred to the elpasolite family, NaK_2AlF_6 (Morss, 1974). More accurate referring can be achieved by comparing with α- and β-Na_3AlF_6. The β-cryolite is characterized by higher symmetry,

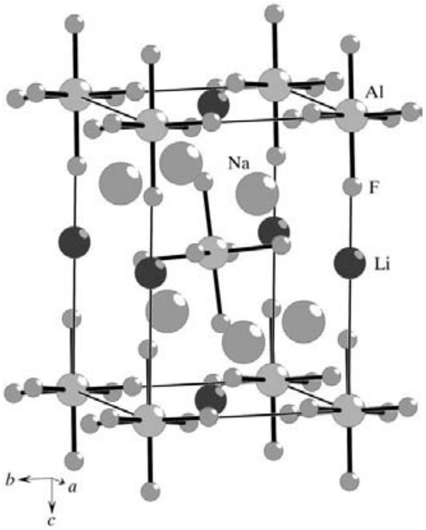

Figure 1
The crystal structure of $LiNa_2AlF_6$.

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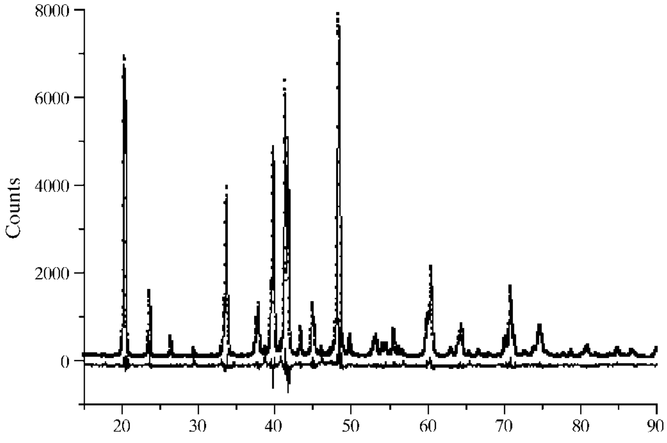

Figure 2
Rietveld plot for $LiNa_2AlF_6$; the difference profile is shown underneath.

space group *Immm* (Yang *et al.*, 1993), with greater differentiation between the cationic positions, whereas α-cryolite is monoclinic, with a smaller variation in Na—F distance (Hawthorne & Ferguson, 1975). It seems that a monoclinic distortion compensates for cationic inequality.

It is also relevant to note the remarkable structural differences between $LiNa_2AlF_6$ and $Li_3Na_3Al_2F_{12}$, with a similar composition. In $Li_3Na_3Al_2F_{12}$, Li has a tetrahedral coordination and Na has an eightfold coordination, whereas in $LiNa_2AlF_6$, Li has an octahedral coordination and Na has a 12-fold coordination. This is the basis for a supposition that $LiNa_2AlF_6$ should evolve preferentially towards the crylolite structure by loss of Li upon heating.

Thus, the structure of $LiNa_2AlF_6$ has commonality with both α- and β-cryolites. It is similar to the α-phase in symmetry, atom arrangement and AlF_6 octahedral orientation, and to the β-phase in the specific differentiation between alkali metal positions.

Experimental

$LiNa_2AlF_6$ was obtained as a white powder by melting a stoichiometric mixture of AlF_3, NaF and LiF at 1223 K, and then cooling to 923 K and sintering at this temperature for 4 h. The initial high-purity AlF_3, NaF and LiF ingredients were used as received (REACHIM). An alternative synthesis route consists of heating a stoichiometric mixture of Na_5AlF_{14}, NaF and LiF at 973 K.

Table 1
Selected geometric parameters (Å, °).

Li—F1	2.044 (7)	Na—F1^{vii}	2.318 (5)
Li—F2^{vi}	2.051 (4)	Na—F2	2.592 (7)
Li—F3^{i}	2.042 (3)	Na—F2^{viii}	2.614 (6)
Al—F1	1.792 (7)	Na^{ii}—F2	2.315 (7)
Al—F2^{iii}	1.803 (4)	Na—F3^{ii}	2.346 (6)
Al—F3^{v}	1.808 (3)	Na^{iv}—F3	2.618 (6)
Na—F1	2.436 (3)	Na^{ix}—F3	2.582 (6)
F1—Al—F2^{iii}	89.7 (2)	F2^{viii}—Al—F3^{v}	91.3 (2)
F1—Al—F2^{viii}	90.3 (2)	F1—Al—F3^{vi}	91.15 (19)
F1—Al—F3^{v}	88.85 (19)	F2^{viii}—Al—F3^{vi}	88.7 (2)

Symmetry codes: (i) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (ii) $-x, 1-y, 1-z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $x, y, 1+z$; (v) $x, y, z-1$; (vi) $-x, -y, 1-z$; (vii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (viii) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (ix) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

Crystal data

$LiNa_2AlF_6$
$M_r = 193.89$
Monoclinic, $P2_1/n$
$a = 5.2863$ (4) Å
$b = 5.3603$ (4) Å
$c = 7.5025$ (6) Å
$\beta = 90.005$ (2)°
$V = 212.59$ Å^3
$Z = 2$
$D_x = 3.03$ Mg m^{-3}
Cu $K\alpha$ radiation
$T = 293$ K
Specimen shape: circular flat plate
20 × 20 × 0.5 mm
Specimen prepared at 1000 kPa
Specimen prepared at 973 K
Particle morphology: thin powder, white

Data collection

DRON-4 powder diffractometer
Specimen mounting: packed powder pellet
Specimen mounted in reflection mode
$2\theta_{min} = 15$, $2\theta_{max} = 118°$
Increment in $2\theta = 0.02°$

Refinement

Refinement on F^2
$R_p = 0.075$
$R_{wp} = 0.108$
$R_{exp} = 0.059$
$R_B = 0.044$
$S = 1.85$
Wavelength of incident radiation: 1.540562–1.544390 Å
Excluded region(s): none
Profile function: Pearson VII
305 reflections
40 parameters
Weighting scheme based on measured s.u.'s
$(\Delta/\sigma)_{max} < 0.1$
Preferred orientation correction: March–Dollase correction (Dollase, 1986)

Experimental data were collected on an automatic diffractometer with Bragg–Brentano geometry under ambient conditions. The sample was prepared using a top-loading standard quartz sample holder. Corundum was used as the external standard. Cell parameters were obtained using the programs described by Kirik *et al.* (1979) and Visser (1969). Analysis of the systematic absences gave space group $P2_1/n$. The errors given in the tables primarily report the precision of the measurements rather than their accuracy.

Data collection: DRON-4 data collection software; cell refinement: modified Rietveld (1969) program *DBWM* (Wiles & Young, 1981); data reduction: *XDIG* (local program); program(s) used to solve structure: Patterson and Fourier syntheses (Altomare *et al.*, 1994, 1995); program(s) used to refine structure: modified Rietveld program *DBWM*; molecular graphics: *XP* (Siemens, 1989).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1026). Services for accessing these data are described at the back of the journal.

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