## FLUORINE COMPOUNDS, INORGANIC, LITHIUM

## 1. Lithium Fluoride

**1.1. Properties.** Lithium fluoride [7789-24-4], LiF, is a white nonhygroscopic crystalline material that does not form a hydrate. The properties of lithium fluoride are similar to the alkaline-earth fluorides. The solubility in water is quite low and chemical reactivity is low, similar to that of calcium fluoride and magnesium fluoride. Several chemical and physical properties of lithium fluoride are listed in Table 1. At high temperatures, lithium fluoride hydrolyzes to hydrogen fluoride when heated in the presence of moisture. A bifluoride [12159-92-1], LiF·HF, which forms on reaction of LiF with hydrofluoric acid, is unstable to loss of HF in the solid form.

**1.2. Manufacture.** Lithium fluoride is manufactured by the reaction of lithium carbonate or lithium hydroxide with dilute hydrofluoric acid. If the lithium carbonate is converted to the soluble bicarbonate, insolubles can be removed by filtration and a purer lithium fluoride can be made on addition of hydrofluoric acid (12). High purity material can also be made from other soluble lithium salts such as the chloride or nitrate with hydrofluoric acid or ammonium bifluoride (13).

Optical crystals of high purity lithium fluoride are grown by use of the Stockbarger process (10) in sizes to 25 cm dia  $\times$  25 cm high (14). Typical commercial material contains 99.2% LiF; typical impurities include Li<sub>2</sub>CO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> at < 0.1% levels, and SO<sup>2-</sup><sub>4</sub>, PO<sup>3-</sup><sub>4</sub>, and heavy metals as Pb at < 0.01% levels. The price during 1991 was \$10.91/kg in truckload quantities. Annual production is probably less than 100 metric tons. Lithium fluoride toxicity relative to use in thermoluminescent dosimetry is discussed in Reference 15; 10 mg/d is proposed as the maximum permissible daily intake for the average human body. Ingestion of 200 mg/kg of body weight is lethal to guinea pigs (16).

**1.3.** Uses. Lithium fluoride is used primarily in the ceramic industry to reduce firing temperatures and improve resistance to thermal shock, abrasion, and acid attack (see CERAMICS). Another use of LiF is in flux compositions with other fluorides, chlorides, and borates for metal joining (17) (see SOLDERS).

Lithium fluoride is an essential component of the fluorine cell electrolyte; 1% LiF in the KF·2HF electrolyte improves the wettability of the carbon anodes and lowers the tendency of the cells to depolarize (18). Thermoluminescent radiation dosimeters used in personnel and environmental monitoring and in radiation therapy contain lithium fluoride powder, extruded ribbons, or rods (19).

Molten lithium fluoride is used in salt mixtures for an electrolyte in high temperature batteries (qv) (FLINAK) (20), and as a carrier in breeder reactors (FLIBE) (21) (see NUCLEAR REACTORS).

Large high purity crystals are cut into windows and refracting components for use in x-ray monochromators (14), and in the vacuum uv, uv, visible, and ir ranges.

## BIBLIOGRAPHY

"Lithium Fluoride" in *ECT* 1st ed., under "Fluorine Compounds, Inorganic," Vol. 6, pp. 709–710, by F. D. Loomis, Pennsylvania Salt Manufacturing Co.; in *ECT* 2nd ed., Vol. 9, p. 627, by G. C. Whitaker, The Harshaw Chemical Co.; "Lithium" under "Fluorine Compounds, Inorganic," in *ECT* 3rd ed., Vol. 10, pp. 757–759, by H. S. Halbedel and T. E. Nappier, The Harshaw Chemical Co.

## CITED PUBLICATIONS

- 1. JANAF Thermochemical Tables, Clearinghouse for Federal Scientific and Technical Information, U.S. Dept. of Commerce, Springfield, Va., Dec. 1963.
- 2. C. B. Stubblefield and R. O. Bach, J. Chem. Eng. Data 17, 491 (1972).
- 3. J. Emsley, J. Chem. Soc. A, 2511 (1971).
- 4. A. W. Jache and G. W. Cady, J. Phys. Chem. 56, 1106 (1952).
- 5. Brit. Pat. 787,771 (Dec. 18, 1957), (to Metropolitan Vickers Electric Co.).
- 6. C. A. Hutchison and H. L. Johnson, J. Am. Chem. Soc. 62, 3165 (1940).
- 7. D. F. C. Morris, Acta Crystallogr. 9, 197 (1956).
- M. C. Ball and A. A. Norbury, *Physical Data for Inorganic Chemists*, Longman, Inc., New York, 1974.
- 9. W. W. Scales, Phys. Rev. 112, 49 (1958).
- Gmelins Handbuch der Anorganischen Chemie, 8th ed., Deutsche Vol. 6, Verlag-Chemie, Weinheim/Bergstrasse, 1960, 305–327.
- J. W. Mellor, Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 2, Suppl. 2, Longman, Green and Co., New York, 1961, 174–178.
- 12. D. C. Stockbarger, Rev. Sci. Instrum. 7, 133 (1936).
- 13. U.S. Pat. 3,132,922 (May 12, 1954), R. D. Goodenough and T. G. Cook (to Dow Chemical Co.).
- 14. Harshaw Optical Crystals, Harshaw Chemical Co., Solon, Ohio, 1967, 32-33.
- 15. N. C. Spoor, Ann. Occup. Hyg. 11(1), 23 (1968).
- H. C. Hodge and F. N. Smith, in J. H. Simon, ed., *Fluorine Chemistry*, Vol. 4, Academic Press, New York, 1965, p. 199.
- 17. U.S. Pat. 3,958,979 (May 25, 1976), A. R. Valdo (to Ethyl Corp.).
- 18. J. T. Pinkston, Ind. Eng. Chem. 39, 255 (1947).
- F. M. Cox, Proc. 2nd Int. Conf. on Luminescence Dosimetry, Oak Ridge National Laboratory, CONF 680920, Oak Ridge, Tenn., Sept. 1968; F. M. Cox, A. C. Lucas, and B. M. Kaspar, Health Phys. 30, 135 (1976); J. F. Valley, C. Pache, and P. Lerch, Helv. Phys. Acta 49(2), 171 (1976).
- 20. G. L. Green, J. B. Hunt, and R. A. Sutula, U.S. Nat. Tech. Inform. Serv., A.D. Rep. 1973, No. 758001.
- C. D. Scott and W. L. Carter, AEC Accession No. 43422, Rept. No. ORNL-3791, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1966.

JOHN R. PAPCUN Atotech

Property	Value	$\operatorname{Reference}^{a}$
melting point, °C	848	1
boiling point, °C	1681	1
solubility, g/100 g solvent		
water, $25.4^{\circ}\mathrm{C}$	0.133	2
water, 81.8°C	0.150	2
acetic acid, $25^{\circ}\mathrm{C}$	0.084	3 3
acetic acid, $50^{\circ}\mathrm{C}$	0.152	3
liquid HF, 12°C	10.3	$\frac{4}{5}$
tetrahydrofuran, 25°C	0.6	5
crystalline form	cubic (NaCl)	6
$a_0, nm$	0.401736	
density at 20°C, g/cm <sup>3</sup>	2.635	6
index of refraction	1.3915	6
lattice energy, kJ/mol <sup>b</sup>	$1020\pm10$	7
standard heat of formation, $kJ/mol^b$	-613.0	1
standard entropy, $J/(mol \cdot K)_{r}^{b}$	35.9	1
heat capacity, $C_p$ , $J/(\text{mol} \cdot \text{K})^b$	42.01	1
heat of fusion, $kJ/mol^b$	27.09	1
heat of vaporization, $kJ/mol^b$	213	8
heat of hydration, kJ/mol <sup>b</sup>	1.023	8
debye temperature, $^{\circ}\mathrm{C}$	449	9

Table 1. Properties of Lithium Fluoride

<sup>a</sup> Properties listed in this table can be supplemented by the comprehensive collections in References 10 and 11. <sup>b</sup> To convert kJ to kcal, divide by 4.184.