

FLUORINE COMPOUNDS, INORGANIC, ZINC

1. Zinc Fluoride

Anhydrous zinc fluoride [7783-49-5], ZnF_2 , melts at 872–910°C, has a solubility of only 0.024 g/100 g anhydrous HF at 14.2°C (1), and can be prepared by slowly drying zinc fluoride tetrahydrate [13986-18-0], $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$, in a current of anhydrous hydrogen fluoride to minimize hydrolysis and formation of the oxide. There is x-ray evidence for dihydrate formation during dehydration of the tetrahydrate (2). Anhydrous zinc fluoride can also be prepared from the reaction of Zn metal powder and pyridinium poly(hydrogen fluoride) at ambient temperature (3); by treating zinc hydroxycarbonate with NH_4F followed by thermal decomposition (4); by the reaction of NF_3O (5) or NH_4F and ZnO (6, 7); by the thermal decomposition of $(\text{NH}_4)_2\text{ZnF}_4$ (8); by the reaction of SOF_2 and Zn (9); by the reaction of Zn and HF in the presence of acetonitrile (10); by the reaction of SF_6 and Zn (11); by the reaction of PF_3 and ZnO (12); and by the reaction of ZnO and hydrogen fluoride (13). Zinc fluoride of ca 96% purity is commercially produced for use as a flux in metallurgy (qv). Production is only on a small scale.

Zinc fluoride has been used as a mild fluorinating reagent in replacement of chlorine in halogenated hydrocarbons (14, 15). It is also used as a catalyst in several applications including cyclization processes (15). High purity ZnF_2 is used in the synthesis of fluorophosphate glass (16, 17), fluoride glass (18, 19), high conducting oxyfluoride glass (20), as fluoride glass films (21), in the manufacture of fluoride glass optical fibers (22), and in the preparation of optical transmitting glass (23) (see Glass; Fiber optics).

The only reported toxicity data on zinc fluoride in the NIOSH RTECS file is a LD_{50} of 280 mg/kg for subcutaneous administration in frogs. OSHA has a standard time-weighted average (TWA) of 2.5 mg/m³ based on fluoride. NIOSH has issued a criteria document (24) on occupational exposure to inorganic fluorides.

1.1. Zinc Fluoride Tetrahydrate

Zinc fluoride tetrahydrate [13986-18-0] is prepared by reaction of ZnO and aqueous HF. $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$ has a water solubility of about 1.6 g/100 mL solution at 25°C. Addition of HF increases the solubility to 11.8 g/100 mL in a 29% HF solution. The tetrahydrate loses water at temperatures above 75°C.

1.2. Fluorozincates

Fluorozincates of the formula MZnF_3 , where M = Na [18251-84-8], K [13827-02-6], Rb [29987-38-0], Cs [29507-53-7], NH_4 [14972-88-4], Ag [28667-89-2], N_2H_5 [63439-12-3], and Li [106207-44-7] (25–28); as well as M_2ZnF_4 where M = K [37732-22-2], Rb [35944-46-8], Cs [72161-48-9], and Li [155007-51-9]; Ba [13825-40-6], Sr [15154-47-9], and Ca [15246-41-0] (25–31), have been reported. Potassium fluoro-zincate [13827-02-6], KZnF_3 , and sodium fluoro-zincate [18251-84-8], NaZnF_3 , are used as catalysts in alginate dental impression materials (see Dental materials) (32).

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BIBLIOGRAPHY

"Zinc Fluoride" under "Fluorine Compounds, Inorganic," in *ECT* 1st ed., Vol. 6, p. 738, by F. D. Loomis, Pennsylvania Salt Manufacturing Co.; "Zinc" under "Fluorine Compounds, Inorganic," in *ECT* 2nd ed., Vol. 9, pp. 684–685, by W. E. White, Ozark-Mahoning Co.; in *ECT* 3rd ed., Vol. 10, p. 826, by C. B. Lindahl, Elf Atochem North America, Inc.

Cited Publications

1. A. W. Jache and G. H. Cady, *J. Phys. Chem.* **56**, 1106 (1952).
2. E. A. Secco and R. R. Martin, *Can. J. Chem.* **43**, 175 (1965).
3. K. R. Muddukrishna, R. N. Singh, and D. K. Padma, *J. Fluorine Chem.* **57**(1–3), 155–158 (1992).
4. USSR Pat. 1,590,433 (Sept. 7, 1990), R. Okhunov, N. N. Levina, and D. D. Ikrami.
5. O. D. Gupta, R. L. Kirchmeier, and J. M. Shreeve, *Inorg. Chem.* **29**(3), 573–574 (1990).
6. G. Pourroy, and P. Poix, *J. Fluorine Chem.* **42**(2), 257–263 (1989).
7. G. A. Lopatkina and co-workers, *Khim. Prom-st. (Moscow)*, (11), 846–847 (1978).
8. Eur. Pat. 156,617 A2 (Oct. 2, 1985), M. Watanabe and S. Nishimura.
9. D. K. Padma and co-workers, *J. Inorg. Nucl. Chem.* **43**(12), 3099–3101 (1981).
10. U.S. Pat. 597,546 (July 21, 1975), J. A. Wojtowicz and D. F. Gavin.
11. A. A. Opalovskii and co-workers, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk.*, (6), 83–86 (1974).
12. M. Chaigneau and M. Santarromana, *C. R. Acad. Sci., Ser. C* **278**(25), 1453–1455 (1974).
13. USSR Pat. 265,091 (Mar. 9, 1970), G. A. Lopatkina, T. N. Kolosova, and O. S. Suslova.
14. A. Sekiya and N. Ishikawa, *Bull. Chem. Soc. Jpn.* **51**, 1267 (1978).
15. U.S. Pat. 3,728,405 (Sept. 14, 1970), J. Allan (to E. I. du Pont de Nemours & Co., Inc.).
16. J. Leissner and co-workers, *Mater. Sci. Forum*, 67–68, 137–142 (1991).
17. M. Matecki and M. Poulain, *J. Non-Cryst. Solids* **56**(1–3) (1983).
18. Y. Wang, *J. Non-Cryst. Solids* **142**(1–2), 185–188 (1992).
19. K. Zhang, *J. Chem.*, (2), 136–140 (1990).
20. K. Hirao, A. Tsujimura, and N. Soga, *Zairyo* **39**(438), 283–286 (1990).
21. B. Boulard and C. Jacoboni, *Mater. Res. Bull.* **25**(5), 671–677 (1990).
22. Eur. Pat. 331,483 (Sept. 6, 1989), K. Fujiura and co-workers.
23. M. Poulain and Y. Messaddeq, *Mater. Sci. Forum*, 32–33, 131–136 (1988).
24. *Criteria for a Recommended Standard-Occupational Exposure to Inorganic Fluorides*, PB 246 692, NIOSH 76-103, U.S. Dept. of Health, Education, and Welfare, Washington, D.C., 1975.
25. O. Schmitz-Dumont and A. Bornefeld, *Z. Anorg. Allg. Chem.* **287**, 120 (1956).
26. J. Portier, A. Tressaud, and J. L. Dupin, *C. R. Acad. Sci., Ser. C* **270**(2), 216–218 (1970).
27. J. Slivnik and co-workers, *Vestn. Slov. Kem. Drus.* **26**(1), 19–26 (1979).
28. S. H. Pulcinelli and co-workers, *Rev. Chem. Miner* **23**(2), 238–249 (1986).
29. P. A. Rodnyi, M. A. Terekhin, and E. N. Melchakov, *J. Lumin.* **47**(6), 281–284 (1991).
30. H. G. Von Schnering, D. Vu, and K. Peters, *Z. Kristallogr.* **165**(1–4), 305–308 (1983).
31. Yu. Wan-Lun, and Z. Min-Guang, *J. Phys. Chem.* **17**(20), L525–L527 (1984).
32. U.S. Pat. 2,769,717 (Nov. 6, 1956), J. Cresson (to L. D. Caulk Co.).

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Related Articles

Fluorine Compounds, Inorganic, Introduction; Fluorine Compounds, Inorganic, Aluminum; Fluorine Compounds, Inorganic, Ammonium; Fluorine Compounds, Inorganic, Antimony; Fluorine Compounds, Inorganic,

Arsenic; Fluorine Compounds, Inorganic, Barium; Fluorine Compounds, Inorganic, Calcium; Fluorine Compounds, Inorganic, Cobalt; Fluorine Compounds, Inorganic, Copper; Fluorine Compounds, Inorganic, Germanium; Fluorine Compounds, Inorganic, Halogens; Fluorine Compounds, Inorganic, Hydrogen; Fluorine Compounds, Inorganic, Iron; Fluorine Compounds, Inorganic, Lead; Fluorine Compounds, Inorganic, Lithium; Fluorine Compounds, Inorganic, Magnesium; Fluorine Compounds, Inorganic, Mercury; Fluorine Compounds, Inorganic, Molybdenum; Fluorine Compounds, Inorganic, Nickel; Fluorine Compounds, Inorganic, Nitrogen; Fluorine Compounds, Inorganic, Oxygen; Fluorine Compounds, Inorganic, Phosphorus; Fluorine Compounds, Inorganic, Potassium; Fluorine Compounds, Inorganic, Rhenium; Fluorine Compounds, Inorganic, Silver; Fluorine Compounds, Inorganic, Sodium; Fluorine Compounds, Inorganic, Tantalum; Fluorine Compounds, Inorganic, Tin; Fluorine Compounds, Inorganic, Titanium; Fluorine Compounds, Inorganic, Tungsten; Fluorine Compounds, Inorganic, Zirconium