Aminoguanidinium Fluorozirconates: Improved Synthesis and Thermal Decomposition of $CN_4H_8ZrF_6$, $CN_4H_8ZrF_6{\cdot}{}^1/_2H_2O$, $CN_4H_8ZrF_6{\cdot}H_2O$, $(CN_4H_7)_2ZrF_6$, and $CN_4H_7ZrF_5$

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Introduction

The family of fluorozirconate compounds X_mZrF_n ($m = 1, 2, 3$; $n = 5, 6, 7$; $X =$ monovalent, divalent, or trivalent metal ion or inorganic/organic cation) constitutes a large group of materials for which several members have found a broad range of applications. These include the formation of high impact absorbing foams,[1] fabrication of infrared transmitting glasses,[2] protective coatings for magnesium alloys,[3] production of fiber-optic communication lines,[4] textile flame retardants,[5] and tooth enamel protectants.[6] In addition, $CN_4H_8ZrF_6$ has recently been shown to be ferroelectric (possessing such associated properties as piezoelectricity, pyroelectricity, and second-order harmonic generation),[7] which could make it potentially useful for applications such as the new binary code-based nonvolatile ferroelectric random-access memory,[8] among many other uses.[9]

The fluorozirconates also exhibit a wide and fascinating assortment of molecular structure. The relatively large Zr^{4+} ion has no occupied d-orbitals, hence lacks geometrical preference in forming compounds. Small variations in intermolecular interaction can therefore lead to a wide diversity of molecular structure for compounds of similar molecular composition. This is especially true for the aminoguanidinium fluorozirconates, for which extensive hydrogen-bonding interactions have profound influence on molecular structure. Figure 1 shows the variations observed in fluorozirconate polyhedra in $CN_4H_8ZrF_6$,[10] $CN_4H_8ZrF_6{\cdot}H_2O$,[11] $CN_4H_8ZrF_6{\cdot}{}^1/_2H_2O$,[12] $(CN_4H_7)_2ZrF_6$,[10] and $CN_4H_7ZrF_5$.[13]

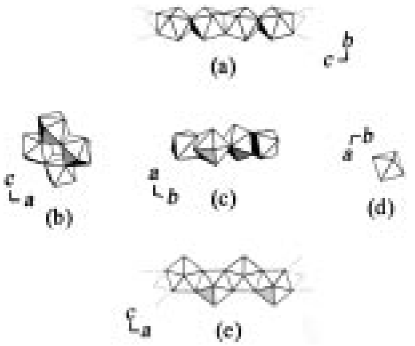

Figure 1. $Zr_xF_y{}^{n-}$ polyhedra as oriented in the unit cell of (a) anhydrous $CN_4H_8ZrF_6$, with infinite chains of edge-sharing ZrF_8 antiprisms, (b) $CN_4H_8ZrF_6{\cdot}H_2O$, with four ZrF_8 antiprisms sharing square-face edges to form $Zr_4F_{24}{}^{8-}$ rings, (c) $CN_4H_8ZrF_6{\cdot}{}^1/_2H_2O$, with edge-sharing pairs of ZrF_7 and ZrF_8 polyhedra, (d) $(CN_4H_7)_2ZrF_6$, with isolated ZrF_6 octahedra, and (e) $CN_4H_7ZrF_5$, with infinite chains of edge-sharing ZrF_7 pentagonal bipyramids.

The current literature procedures for preparing aminoguanidinium fluorozirconates produce a complex mixture of compounds.[10] Although separation may be possible on the basis of minor variations in crystal morphology, this is highly laborious, and the amount of pure material obtained is limited to small quantities. Our interest in ferroelectric $CN_4H_8ZrF_6$ prompted us to develop preparation methods that eliminate these problems. We report here procedures that produce gram quantities of pure $CN_4H_8ZrF_6$, $CN_4H_8ZrF_6{\cdot}{}^1/_2H_2O$, $CN_4H_8ZrF_6{\cdot}H_2O$, $(CN_4H_7)_2ZrF_6$, and $CN_4H_7ZrF_5$. We also report the results of thermal decomposition studies of the materials.

Experimental Section

Material identification was made by comparing the experimental powder X-ray diffraction (PXRD) patterns to those generated from known single-crystal data by means of the software package Lazy-Pulverix.[14] Room-temperature PXRD data were collected with a General Electric XRD-5 powder diffractometer using Cu Kα radiation. Differential scanning calorimetry measurements were performed using a Perkin-Elmer DSC 7. Thermogravimetric analysis measurements were made with a Fisher Series 200A TGA.

Water solubility data were obtained at room temperature by adding sufficient known mass of compound to a known volume of water that left some material undissolved in the saturated solution. Small portions of water were then slowly titrated, with thorough mixing, into the

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mixture until all solid dissolved. All compounds except $CN_4H_7ZrF_5$ were soluble in water but insoluble in less polar solvents such as acetone, benzene, and ethanol; $CN_4H_7ZrF_5$ requires ~0.3 M HF in order to dissolve in water.

The starting materials aminoguanidine bicarbonate (98.5%), zirconium(IV) fluoride hydrate (97%), and 48% hydrofluoric acid (reagent grade) were from Aldrich. To avoid the formation of stable SiF_6^{2-} compounds,[15] all preparation procedures were performed in polypropylene apparatus.

Preparation of Aminoguanidinium(2+) Hexafluorozirconate, $CN_4H_8ZrF_6$, and Aminoguanidinium(2+) Hexafluorozirconate Monohydrate, $CN_4H_8ZrF_6 \cdot H_2O$.[16] An aqueous solution of $CN_4H_8F_2$ and HF was produced by cautiously adding 10 mL (310 mmol) of HF to a beaker containing 1.36 g (9.99 mmol) of $CN_4H_6 \cdot H_2CO_3$. In a second beaker, a solution of H_2ZrF_6 and HF was made by mixing 1.67 g (9.99 mmol) of $ZrF_4 \cdot 3H_2O$ and 23 mL (720 mmol) of HF. Both solutions required heating in a hot water bath to completely dissolve all solids. The two solutions were combined and diluted with distilled water to a total volume of 60 mL. The solution was slowly evaporated to ~10 mL in an 80 °C oven for approximately 24 h, after which colorless, transparent crystals of $CN_4H_8ZrF_6$ were harvested. Solubility in water is 0.19(1) g/mL.

Crystallization at room temperature over a 7 day period, rather than at 80 °C for a shorter time, results in pure $CN_4H_8ZrF_6 \cdot H_2O$. Solubility of the monohydrate in water is 0.20(1) g/mL. Unlike the other materials investigated in this report, an opaque white coating forms on $CN_4H_8ZrF_6 \cdot H_2O$ crystals within 24−48 h of exposure to air.

Preparation of Aminoguanidinium(2+) Hexafluorozirconate Semihydrate, $CN_4H_8ZrF_6 \cdot {}^1/_2H_2O$, and Aminoguanidinium(1+) Hexafluorozirconate, $(CN_4H_7)_2ZrF_6$. $ZrF_4 \cdot 3H_2O$ (1.67 g, 9.99 mmol) was mixed in 40 mL of hot water while stirring ~5 min in a boiling water bath. To this hot mixture 2.6 mL (81 mmol) of HF was added and the solution stirred. $CN_4H_6 \cdot H_2CO_3$ (2.08 g, 15.3 mmol) was added to the hot mixture and stirred until all solids dissolved; the reaction mixture was cooled to room temperature and allowed to sit for several days until the volume was ~15 mL. $CN_4H_8ZrF_6 \cdot {}^1/_2H_2O$ crystallized as colorless, transparent crystals. Solubility in water is 0.21(2) g/mL.

Aminoguanidinium(1+) hexafluorozirconate, $(CN_4H_7)_2ZrF_6$, was prepared in a similar manner except 4.08 g of $CN_4H_6 \cdot H_2CO_3$ (30.0 mmol) was added to the hot mixture of $ZrF_4 \cdot 3H_2O$ and HF. The resulting colorless, transparent crystals had a solubility in water of 0.43(1) g/mL

Preparation of Aminoguanidinium(1+) Pentafluorozirconate, $CN_4H_7ZrF_5$. $CN_4H_6 \cdot H_2CO_3$ (1.36 g, 9.99 mmol), 1.67 g (9.99 mmol) of $ZrF_4 \cdot 3H_2O$, 0.76 mL (23.7 mmol) of HF, and 40 mL of water were placed in a digestion bomb and heated to 150 °C for 3−5 h. The bomb was thoroughly shaken at regular intervals during the last hour of heating. After allowing the bomb to cool to room temperature, the solution was transferred to a beaker and allowed to evaporate slowly at room temperature. The resulting transparent, colorless crystals of $CN_4H_7ZrF_5$ were harvested when the solution volume decreased to ~10 mL. The solubility in 0.28 M HF is 0.12(1) g/mL.

Results and Discussion

Synthesis of aminoguanidinium fluorozirconates from CN_4H_6 and ZrF_4 depends strongly upon the concentration of HF. As the following equilibria show, formation of $CN_4H_8ZrF_6 \cdot nH_2O$ ($n = 0, {}^1/_2, 1$) requires excess HF in order to shift equilibria sufficiently toward formation of the doubly charged $CN_4H_8^{2+}$ and ZrF_6^{2-} ions, whereas progressively smaller concentrations of HF are needed to form the $CN_4H_7^+$ cation in $(CN_4H_7)_2ZrF_6$ and in $CN_4H_7ZrF_5$:

$$ZrF_4 + HF \rightleftharpoons ZrF_5^- + H^+$$

$$ZrF_5^- + HF \rightleftharpoons ZrF_6^{2-} + H^+$$

$$CN_4H_6 + HF \rightleftharpoons CN_4H_7^+ + F^-$$

$$CN_4H_7^+ + HF \rightleftharpoons CN_4H_8^{2+} + F^-$$

The relative stability constants for the above equilibria are unknown but, under the reaction conditions reported here, the stability of ZrF_6^{2-} is greater than ZrF_5^-, as evidenced by the fact that ZrF_5^-, in the absence of ZrF_6^{2-}, could be produced only if a stoichiometric quantity of HF and ZrF_4 was used. For the aminoguanidium cations, $CN_4H_8^{2+}$ was exclusively formed if a large excess of HF was added to the solution, whereas $CN_4H_7^+$ was produced at lower HF concentrations.

Uncontrolled crystallization of products from solutions containing excess HF results in mixtures of $CN_4H_8ZrF_6 \cdot nH_2O$ ($n = 0, {}^1/_2, 1$). The identical solubilities of these materials at room temperature prevent them from being separated by fractional crystallization methods. The factors involved in formation of $CN_4H_8ZrF_6$, $CN_4H_8ZrF_6 \cdot {}^1/_2H_2O$, and $CN_4H_8ZrF_6 \cdot H_2O$ are complex, but small variations in hydrogen-bonding interaction due to changes in solvent, solute, and temperature, together with a narrow range in the depth of the potential minima in internal energy corresponding to the structures in Figure 1, have a profound influence on structure formation. Minor variations in reaction conditions are therefore expected to have large influences on the material formed.

For $CN_4H_8ZrF_6$, crystallization at temperatures between 40 and 80 °C was sufficient to form only the desired compound. The need for elevated temperatures in producing $CN_4H_8ZrF_6$, to the exclusion of $CN_4H_8ZrF_6 \cdot {}^1/_2H_2O$ and $CN_4H_8ZrF_6 \cdot H_2O$, is most likely a consequence of the entropy change associated with its formation. Considering the number of reactant species required, the entropy change for formation of $CN_4H_8ZrF_6 \cdot {}^1/_2H_2O$ and $CN_4H_8ZrF_6 \cdot H_2O$ is more negative, hence less favorable, than for $CN_4H_8ZrF_6$. Increasing temperature results in an increasingly unfavorable $T\Delta S$ contribution to ΔG for formation of the monohydrate and semihydrate, thus favoring $CN_4H_8ZrF_6$. At room temperature, the increase in stability from formation of additional hydrogen bonding with H_2O molecules favors formation of the two hydrates.

The selective preparation of $(CN_4H_7)_2ZrF_6$ and $CN_4H_7ZrF_5$ is readily achieved by control of reactant stoichiometry and solubility. The formation of $CN_4H_7ZrF_5$ requires digestion in order to solubilize all starting materials.

Crystals of all five compounds with dimensions > 1 mm are stable in capped plastic containers for several weeks at room temperature; finely ground powders decompose within days. Storage of crystals in glass results in decomposition to white powders and etching of the container surface. Decomposition products could not be identified, powder patterns of the decomposed samples not matching those of known fluorozirconates or ZrF_4.

As first reported by Davidovich,[17] aminoguanidinium hexafluorozirconates decompose upon heating. On the basis of the amount of mass lost, TGA and DSC experiments conducted under a nitrogen flow indicate that the materials decompose stepwise: first with loss of water (if present), then by loss of

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(16) The molar ratios of the starting materials and reaction conditions are not unique nor necessarily optimum for forming the compounds. However these conditions give pure products consistently and reproducibly. Variations of the given ratios also produced the desired materials, but not reproducibly and rarely in the absence of other members of the family.

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HF, and finally by decomposition to ZrF_4. The hydrates $CN_4H_8ZrF_6 \cdot {}^1/_2H_2O$ and $CN_4H_8ZrF_6 \cdot H_2O$ lose water between 100 and 110 °C to form anhydrous $CN_4H_8ZrF_6$. At temperatures between 190 and 240 °C, all title compounds except $CN_4H_7ZrF_5$ and $(CN_4H_7)_2ZrF_6$ lose HF, giving $CN_4H_7ZrF_5$. All title compounds except $(CN_4H_7)_2ZrF_6$ decompose to ZrF_4 between 360 and 375 °C, whereas $(CN_4H_7)_2ZrF_6$ decomposes to ZrF_4 at 200 °C.[18]

It should be noted that a fully reversible and reproducible endothermic phase transition is observed at ∼109 °C in $CN_4H_8ZrF_6$; this is a ferroelectric−paraelectric phase transition.[19] $CN_4H_8ZrF_6$ is the only ferroelectric member of the family. None of the other materials exhibit a phase transition.

Conclusion

The preparation procedures described represent a vastly improved method for obtaining gram quantities of five closely related and potentially useful aminoguanidinium fluorozirconates. One, $CN_4H_8ZrF_6$, is a new ferroelectric. All have been fully characterized in terms of their PXRD patterns, solubility, and decomposition products.

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(18) The decomposition temperatures were found to be scan-rate dependent. Slow scan rates of 5 °C/min generally resulted in decomposition temperatures up to 40 °C lower than for more rapid scan rates of 40 °C/min.

(19) As described in ref 7, the ferroelectric/paraelectric phase transition temperature is dependent upon heating rate. The temperature reported here is an extrapolation to zero heating rate.