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Methods of Purification of Zirconium Tetrafluoride for Fluorozirconate Glass

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High-purity zirconium tetrafluoride (ZrF_4) has been produced using sublimation and distillation techniques. The transitionmetal impurities have been determined in these purified samples, and it has been found that distillation is the preferred method of purification using a number of criteria. A detailed description of the apparatus used to produce this material is also given.

I. Introduction

 \mathbf{I} Is now well established that, to produce transparent, crystal-free fluoride glass, special attention has to be paid to decreasing the level of optically absorbent impurities (e.g., transition-metal cations) and to decreasing the level of impurities that can cause extrinsic losses, (e.g., scattering from crystallites). In addition, we have discovered that stable, crystal-free fluoride glasses containing very high levels of lanthanide fluorides (required for microchip laser applications) can be prepared only using extremely low oxide-containing zirconium tetrafluoride (ZrF_4) .^{1–3} Commercially available ZrF₄ frequently contains sufficient oxide/water contamination to limit the incorporation of high levels of, for instance, ErF₃ in a fluorozirconate glass. Therefore, further purification of commercially available ZrF_4 is necessary if these glasses are to become useful in applications such as optically pumped singlelongitudinal-mode rare-earth-doped laser systems operating in the eye-safe region. This communication describes in detail the methods we have adopted to prepare such starting materials for glass synthesis.

Ewing and Sommers⁴ have published a comprehensive review on the purification and analysis of metal fluorides. Sublimation of ZrF_4 is the most-cited method in the literature. It is a simple method that decreases transition elements and improves the anhydrous and oxide quality of ZrF4. However, another less-cited technique involves distillation of ZrF4 from a ZrF4-BaF2 melt. This procedure was first reported by Robinson⁵⁻⁷ and was concerned with purifying highly contaminated ZrF₄. Robinson lowered the level of iron from 320 to 4 ppm, whereas simple sublimation lowered the iron to ~ 30 ppm. This communication describes the purification of ZrF₄ using sublimation and distillation techniques but starting here with a much purer commercial product as a feed stock. Therefore, the question is whether either or both of these techniques reach their thermodynamic limit around the ppm level or can continue to offer a route to purification into the 100 ppb range.

II. Experimental Procedure

(1) Apparatus

All purification steps were conducted in a specially built drybox. This had the considerable advantage that purified material was never exposed to the atmosphere. The drybox atmosphere was constantly purged with dry nitrogen obtained from liquid-nitrogen boil-off. Purification was conducted in a quartz reactor fitted with a glass lid (Fig. 1). Two aluminum rings, bolted together, held the glass lid to the flange of the reactor. A Viton® (DuPont, Wilmington, DE) O-ring between the two glass surfaces acted as a seal between them. Viton was chosen because of its superior heat resistance. All operations were conducted in a flowing atmosphere of purified helium. Helium was chosen because the level of water and oxygen could be decreased to ppb levels.8 This was accomplished by first passing the gas through a U-tube filled with molecular sieves (4 A) at 77 K and then passing the gas through a column filled with activated manganese oxide (IOT-2-HP, Agilent Technologies, Palo Alto, CA). A 0.5 µm filter was used to remove any particulate matter from the gas stream.

Vitreous carbon (Sigridur type G, Hochtemperatur-Werkstoffe GmbH, Andermach, Germany) crucibles were used for all experiments. Vitreous carbon was chosen because it is nonreactive toward fluoride melts, and it couples very effectively with the field generated by an induction furnace. Initial experiments on a small scale were conducted using a pair of GAK3 crucibles (the volume of each crucible was 67 mL) held mouth-to-mouth using a special quartz assembly (Fig. 1). In latter experiments, it was possible to scale up the purification (see below), and, in this case, the lower vessel was a GAK10 crucible (volume of 116 mL). The top vessel was a GAZ13 crucible (volume of 150 mL). To hold these two crucibles together, a special grooved ring was fabricated from vitreous carbon.

In both cases, the lower crucible was heated using induction heating. The busbars of a 7 kW induction furnace (Radyne, Milwaukee, WI) operating at 450 kHz were sealed through the back of the drybox, and the jacket was positioned in place such that the single coil of the induction furnace surrounded the lower crucible. This arrangement ensured that only the lower crucible was heated and that a temperature gradient was automatically established. To combat high temperatures occurring in the drybox during processing, a water-cooled copper heat shield surrounded the quartz reactor, and a refrigeration unit was installed in the drybox.

(2) Reagents

A single 1 kg batch of ZrF_4 (Batch No. 28039, Morita Kakagu, Osaka, Japan) was used for all studies. Other chemicals used were BaF₂ (Fluorotran grade, BDH Chemicals, Pty., Ltd., Poole, U.K.), NaF (Fluorotran grade, BDH), and zirconium metal (99.99%, Cerac, Inc., Milwaukee, WI).

(3) Sublimation of ZrF_{4}

Initially, 20 g of ZrF_4 was placed in the lower crucible. The apparatus was assembled, and the atmosphere inside the reactor

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Fig. 1. Quartz reactor complete with GAZ6 vitreous carbon crucibles. Coil of the induction furnace is not shown for clarity.

replaced with dry helium. A flow (50 mL/min) of helium was maintained at all times during the purification. The ZrF_4 was first dried at low temperature (to remove any volatiles), and then the temperature was increased to $850^{\circ}-875^{\circ}C$ for 1 h. The yield was 10 g. This method was subsequently scaled up using the larger crucibles, and as much as 100 g of ZrF_4 was sublimed to give ~50 g of purified material in 3 h.

(4) Distillation of ZrF_4 -BaF₂ Melts

A similar procedure to that described above was used to distill ZrF_4 -BaF₂ melts. A mixture of 100 g of ZrF_4 and 25 g of BaF₂ (81:19 mol% ZrF_4 :BaF₂) was placed in the lower GAK10 vitreous carbon crucible. This mixture was first dried at low temperature, and then the temperature was increased to 850° - $875^{\circ}C$ and held at this temperature for 3 h. A distillation rate of 15 g/h was achieved. In some experiments, the distillation was allowed to proceed for another 1 or 2 h. However, the production rate decreased to <10 g/h in the 4th and 5th hour. In some experiments, pure zirconium metal (2wt%) was added to the melt before distillation.

(5) Analysis

Trace-metal analysis was performed using graphite-furnace atomic absorption spectroscopy (AAS; Model SpectrAA 400 and Model GTA 96 graphite tube atomizer, Varian, Palo Alto, CA).⁹ Oxygen and carbon were measured using secondary ion mass spectroscopy (SIMS; by Charles Evans and Associates, Sunnyvale, CA). Diffuse reflectance FTIR spectra (DRIFTS) were measured (Telstra Research Laboratories, Melbourne, Australia), as previously described.¹⁰ Spectra were recorded in transmission mode. Powder X-ray diffractometry (XRD; Scintag, Santa Clara, CA) studies were conducted.

III. Results

Purified ZrF_4 was prepared either by sublimation or by distillation from a ZrF_4 -BaF₂ melt using the apparatus described above. Correct placement of the bottom crucible in the coil of the induction furnace consistently resulted in an easily removed dendritic polycrystalline material depositing in the upper crucible. Yields for either sublimation or distillation were similar.

To compare the cationic purity of these products, the transitionmetal impurities were monitored. This involved the development of a complex methodology of dissolution of ZrF_4 , complexation of the transition metals, and then extraction and analysis using graphite-furnace AAS techniques.⁸ We concentrated on measuring the levels of iron, nickel, and copper. Table I gives the values of these elements in two samples of unprocessed ZrF_4 , two different samples of sublimed ZrF_4 , and five different samples of distilled ZrF_4 .

In addition to transition-metal analysis, a number of other physicochemical measurements were made on the distilled ZrF_4 to further ascertain the degree of purity of this material compared with commercially available material. The distilled product was subjected to XRD, FTIR, and SIMS analysis.

(1) Samples of ZrF_4 were analyzed using powder XRD, and the pattern compared with a library pattern.¹¹ There was found to be a very good match with Powder Diffraction File 33–1480, which is for the β form of ZrF_4 . Commercial samples showed additional small peaks.

(2) Using SIMS, Charles Evans and Associates found the levels of oxygen and carbon in the distilled ZrF_4 to be at or below the instrumental background, i.e., carbon <0.18 ppm and oxygen <0.47 ppm. This is a substantial improvement over the results for the commercial ZrF_4 , which showed carbon between 0.8 and 2.0 ppm and oxygen between 5 and 15 ppm. Special precautions were taken to seal all samples from atmospheric moisture before dispatch to the United States for SIMS evaluation so that valid comparisons could be made.

(3) DRIFTS is a sensitive probe for OH contamination.¹⁰ Figure 2 illustrates the DRIFTS spectra of the Morita ZrF_4 starting material and distilled ZrF_4 . Figure 2 shows that the peaks at 3400 and 1600 cm⁻¹ due to OH are very much diminished in the purified sample.

Because the distillation method was adopted as the superior technique, it was then possible to examine another refinement of this method. This is the electromotive series displacement (ESD) procedure described by Pastor and Robinson.¹² ESD relies on the plating out of reducible transition-metal impurities on a finely dispersed electropositive material, e.g., zirconium particles. However, when finely divided zirconium metal was added to a ZrF_4 -BaF₂ melt and then distilled, a material was obtained that was quite different from previously purified ZrF_4 samples. The polycrystalline solid in the upper crucible varied in color from brown to gray, and the crucibles were not recorded by Robinson,⁷ and this method was abandoned.

One problem encountered concerned the substantial mass of melt left after the distillation was complete (\sim 55 g ZrF₄ and 25 g

 Table I.
 Transition-Metal Impurities in ZrF₄ Samples

ZrF ₄ sample		Impurity (ppm)		
	No.	Iron (±0.04)	Nickel (±0.02)	Copper (±0.02)
Commercial	1 2	1.06 1.20	0.53 0.46	0.18 0.22
Sublimation	$\frac{1}{2}$	0.53 0.44	0.25 0.20	$\begin{array}{c} 0.10\\ 0.06 \end{array}$
Distillation	1 2 3 4 5	0.18 0.26 0.12 0.14 0.24	0.21 0.27 0.21 0.20 0.21	$\begin{array}{c} 0.10 \\ 0.11 \\ 0.12 \\ 0.10 \\ 0.12 \end{array}$



Fig. 2. DRIFTS spectra of Morita ZrF_4 (upper curve) and distilled ZrF_4 (lower curve). (Spectra are offset with respect to each other for clarity).

BaF₂). To maximize the yield of purified ZrF₄, we investigated the effect of adding further aliquots of impure ZrF_4 to the melt remaining after distillation and then redistilling this mixture. This procedure was repeated three times and a sample of ZrF₄ was analyzed from each distillation. Although the impurity level of the melt increased with each addition of ZrF4, no increase in transition-metal impurities was found in any of the samples of purified ZrF₄; i.e., all four samples returned similar levels of iron, nickel, and copper.

IV. Discussion

This research program has established that distillation is the method of choice for purification of ZrF_4 for several reasons.

(1) The analytical values given in Table I show that sublimation decreases the iron, nickel, and copper impurities by a factor of 2, while distillation decreases the iron by a factor of 8-10. The substantial decrease in the iron impurity resulting from distillation is due to two factors. First, the melt decreases the sublimation tendency of Fe³⁺ and Fe²⁺ because of a vapor pressure decrease of their fluorides as a consequence of Raoult's law. Second, there is a tendency of FeF₃ to fluorinate ZrO_2 (Eq. (1)) to form Fe₂O₃. ZrO_2 is produced by the reaction of water with ZrF_4 (Eq. (2)) or by the reaction of BaO with ZrF_4 (Eq. (4)).¹³ (BaO is the hydrolysis product of BaF_2 and water (Eq. (3))). The advantage of this reaction scheme is that Fe_2O_3 is far less volatile than FeF_3 . This scheme is analogous to the decrease of iron in sublimation by the deliberate addition of oxides, first reported by Tatsuno.14

$$\operatorname{ZrO}_2 + \frac{4}{2}\operatorname{FeF}_3 \to \operatorname{ZrF}_4 + \frac{2}{2}\operatorname{Fe}_2\operatorname{O}_3 \tag{1}$$

$$ZrF_4 + 2H_2O \rightarrow ZrO_2 + 4HF$$
(2)

$$BaF_2 + H_2O \rightarrow BaO + 2HF \tag{3}$$

$$ZrF_4 + 2BaO \rightarrow ZrO_2 + 2BaF_2 \tag{4}$$

One important consequence of this reaction scheme is that multiple distillations are therefore possible, with no increase in impurity level. This is advantageous for producing large amounts of material with little waste.

(2) The presence of a liquid is much more favorable for chemical homogeneity and heat transfer. In sublimation, thermal contact between the solid and the crucible may be variable. Whereas the yields for both processes were comparable, the yield for the distillation process did decrease during the 4th and 5th hours. The reason for this was that, as the distillation proceeded, the melt became barium-rich and higher temperatures were required to continue distilling ZrF₄ from the melt.

(3) The melt functions to physically wet oxide particles, preventing them from contaminating the final product. In sublimation, an impurity-rich oxide residue results, and it is possible for this oxide impurity to become entrained in the vapor.

(4) Because a melt is produced, it is possible to use ESD. This is not possible using simple sublimation techniques. However, our results show that ESD using zirconium metal produces a variable material that is not suitable for glass synthesis.

V. Conclusion

Purification of ZrF₄ by distillation of ZrF₄-BaF₂ melts was achieved. The purified material was extremely dry and had low levels of carbon, oxygen, and transition metals. These results showed that distillation was an effective method and was superior to the frequently reported method of sublimation in the literature. Using this material, we were able to report the highest level of Er(III) doping in fluorozirconate glasses.^{1–3}

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