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ONE STEP SYNTHESIS OF NF_4BiF_6

WILLIAM W. WILSON AND KARL O. CHRISTE*
Rocketdyne, Division of Rockwell International, Canoga Park, California 91303 (USA)

SUMMARY

A simple one-step synthesis of NF_4BiF_6 in quantitative yield from NF_3, F_2 and BiF_3 is reported.

RESULTS

The existence of NF_4BiF_6 was first reported in 1977, and three methods were given for its synthesis [1]. The first method involved the following two steps.

$$NF_3 + F_2 + (1+n)BiF_5 \xrightarrow[167\ atm\ NF_3 + F_2]{250°C,\ 30\ hr} NF_4BiF_6 \cdot nBiF_5$$

$$NF_4BiF_6 \cdot nBiF_5 \xrightarrow[vacuum\ pyrolysis]{280°C,\ 1.5\ hr} NF_4BiF_6 + nBiF_5$$

The second and third methods were based upon the displacement reaction between NF_4BF_4 and BiF_5 using either heat or a solvent such as HF:

$$NF_4BF_4 + BiF_5 \xrightarrow{180°C} NF_4BiF_6 + BF_3$$

$$NF_4BF_4 + BiF_5 \xrightarrow[HF]{25°C} NF_4BiF_6 + BF_3$$

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These methods exhibit the following drawbacks. All three methods require the use of BiF_5 which is commercially not readily available and which is relatively expensive. Also, the first method involves two steps with a final yield of only 83%. The second and third methods both require high purity NF_4BF_4 which must be prepared by a cumbersome method, such as UV-photolysis [2]. In view of our renewed interest in NF_4BiF_6, it was desirable to find an improved synthesis for this material.

A simple one-step synthesis of NF_4BiF_6 was discovered which produces pure NF_4BiF_6 in quantitative yield:

$$NF_3 + 2\ F_2 + BiF_3 \xrightarrow[200\ atm\ NF_3 + F_2]{235°C,\ 9\ days} NF_4BiF_6$$

This new method eliminates the need for BiF_5 which is replaced by the relatively inexpensive and commercially readily available BiF_3. At the lowered reaction temperature of 235°C, a reaction time of 9 days was necessary to avoid the formation of perfluoropolybismuthate(V) salts. It was found in another analogous reaction that after only 4.5 days the product composition was just $NF_4BiF_6 \cdot 0.47BiF_5$. Continuous rotation of the reactor or other mixing of the reagents is expected to shorten the reaction time, but further attempts to maximize the reaction conditions were beyond the scope of this study.

EXPERIMENTAL

Into a 100-ml Monel cylinder equipped with a Monel valve, which had been prepassivated with ClF_3, was loaded BiF_3 (9.960g, 37.45mmol) inside the dry N_2 atmosphere of a glove box. After the cylinder was connected to the stainless-steal Teflon-FEP vacuum line, it was evacuated and cooled to -196°C. First the NF_3 (255mmol) and then the F_2 (255mmol) were added to the cylinder in vacuo. The cylinder was warmed to room temperature and then placed into an oven at 235°C for 9 days. The cylinder was rotated 11/2 times after the second day and again after the sixth day to expose fresh surface of the molten

mass to the NF_3 and F_2. Finally, the cylinder was cooled to room temperature and the excess NF_3 and F_2 were removed in vacuo. Remaining inside the cylinder was a white solid mass (15.322g vs. 15.464g expected for 37.45mmol NF_4BiF_6), the Raman and infrared spectra of which showed no detectable perfluoropolybismuthate(V) impurities.

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