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Ultrapurification of ^{76}Ge-Enriched GeH_4 by Distillation

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Abstract—^{76}Ge-enriched germane has been ultrapurified by low-temperature distillation. The nature and concentration of molecular impurities in the germane samples were determined by gas chromatography/mass spectrometry, high-resolution Fourier transform IR spectroscopy, and gas chromatography. The distillate contains no more than 10^{-5} mol % hydrocarbons, 10^{-4} mol % carbon dioxide, 10^{-3} to 10^{-1} mol % digermane and trigermane, and $<3 \times 10^{-5}$ mol % other impurities. A distinctive feature of the impurity composition of the isotopically enriched germane samples is the presence of silicon tetrafluoride and sulfur hexafluoride impurities.

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INTRODUCTION

High-purity germanium is used in the fabrication of IR optical components, high-resolution nuclear detectors, thin-film silicon/germanium structures for photoelectric converters, and other devices. Germanium isotopes possess a number of unique properties. In particular, ^{76}Ge is a potentially attractive detector material for neutrinoless double beta decay experiments [1, 2].

One effective way to produce high-purity germanium is the hydride route, which relies on the thermal decomposition of germane after ultrapurification. There has been considerable effort devoted to the physicochemical principles of the preparation and analysis of high-purity germane and the germanium isolated from it [3, 4]. Fractional distillation has been demonstrated to be effective in the ultrapurification of germane of natural isotopic composition, and analytical techniques with low detection limits have been developed for a wide range of molecular impurities in germane.

The techniques used to determine the impurity composition of germane include gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS), and, occasionally, high-resolution laser diode IR spectroscopy [5–7]. These techniques allow one to detect hydrogen, C_1–C_4 hydrocarbons, their fluorinated and chlorinated derivatives, inorganic hydrides (AsH_3 and PH_3), water, alkyl derivatives of germane, and chlorogermanes with low detection limits, at a level of 10^{-6} to 10^{-5} mol %.

Data on the ultrapurification and impurity composition of isotopically enriched germane, including $^{76}GeH_4$, a substance of practical importance, are not available in the literature. At the same time, the centrifugal isotope enrichment of germane, a process proposed by Aref'ev et al. [8], may be responsible for the specific features of the impurity composition of germane.

In this paper, we report ultrapurification of ^{76}Ge-enriched germane by distillation and its impurity composition.

EXPERIMENTAL

Germane ultrapurification was carried out by batch distillation at a temperature of –85°C and pressure of 0.15 MPa, using a laboratory-scale middle-fed stainless steel column, with rectifying sections 40 and 70 cm in height and 2 cm^2 in cross-sectional area, packed with nichrome prismatic coils 2.5 × 2.5 × 0.2 mm in dimensions. The germane charge weight was ~300 g. The light and heavy fractions, enriched in less and more volatile impurities, respectively, were simultaneously taken from the top and bottom of the distillation column at intervals. After each distillation cycle, the distillate was drawn off from the middle feed tank. The yield of the purified product was 70%.

We studied different germane samples: germane of natural isotopic composition (prepared by reacting germanium tetrachloride with sodium borohydride) purified by distillation (sample 1), germane enriched in ^{76}Ge to 88 at % by centrifugation (sample 2), and the same germane purified by distillation (sample 3). In addition, we isolated and investigated $^{76}GeH_4$ fractions containing molecular impurities more and less volatile than germane (samples 4 and 5, respectively).

The germane samples were analyzed for molecular impurities by GC/MS, GC, and high-resolution (0.05 cm^{-1}) Fourier transform IR spectroscopy as

Impurity compositions of GeH_4 samples as determined by GC/MS, GC, and IR spectroscopy

Impurity	Mole percent				
	sample 1	sample 2	sample 3	sample 4	sample 5
CH_4	–	$<1 \times 10^{-5}$	$<5 \times 10^{-6}$	$<5 \times 10^{-6}$	$(5 \pm 1) \times 10^{-5}$
C_2H_4	–	$<5 \times 10^{-6}$	$<5 \times 10^{-6}$	$<5 \times 10^{-6}$	$(9.5 \pm 0.8) \times 10^{-4}$
C_2H_6	–	$(1.6 \pm 0.2) \times 10^{-4}$	$<1 \times 10^{-5}$	$<1 \times 10^{-5}$	$(1.0 \pm 0.2) \times 10^{-4}$
C_3H_6	–	–	$<1 \times 10^{-6}$	$(6.5 \pm 0.8) \times 10^{-4}$	$<1 \times 10^{-6}$
C_3H_8	$<8 \times 10^{-7}$	$<8 \times 10^{-7}$	$<8 \times 10^{-7}$	$(1.5 \pm 0.2) \times 10^{-4}$	$<8 \times 10^{-7}$
n-C_4H_{10}	$<9 \times 10^{-7}$	$(3 \pm 1) \times 10^{-6}$	$<9 \times 10^{-7}$	$(3.0 \pm 0.5) \times 10^{-5}$	$<9 \times 10^{-7}$
i-C_4H_{10}	$<9 \times 10^{-7}$	$(6 \pm 1) \times 10^{-6}$	$<9 \times 10^{-7}$	$(1.0 \pm 0.2) \times 10^{-4}$	$<9 \times 10^{-7}$
C_5–C_9 hydrocarbons	$<1 \times 10^{-6}$	$(1.5 \pm 0.2) \times 10^{-3}$	$(7 \pm 2) \times 10^{-6}$	$(9 \pm 3) \times 10^{-2}$	$(1.2 \pm 0.3) \times 10^{-6}$
Chlorinated and fluorinated hydrocarbons	$(9 \pm 4) \times 10^{-7}$	$(1.5 \pm 0.2) \times 10^{-3}$	$<2 \times 10^{-7}$	$(7.6 \pm 0.8) \times 10^{-2}$	$(2.4 \pm 0.5) \times 10^{-6}$
Alcohols, ethers	$<2 \times 10^{-6}$	–	$<2 \times 10^{-6}$	$(5 \pm 1) \times 10^{-5}$	$<2 \times 10^{-6}$
Alkylgermanes	$(5 \pm 2) \times 10^{-5}$	$(1.9 \pm 0.6) \times 10^{-4}$	$<2 \times 10^{-6}$	$(7 \pm 2) \times 10^{-3}$	$(3 \pm 1) \times 10^{-6}$
Chlorogermanes	$<1 \times 10^{-6}$	$(3 \pm 1) \times 10^{-1}$	$<1 \times 10^{-6}$	5 ± 2	$(4 \pm 1) \times 10^{-3}$
Polygermanes	$(2.2 \pm 0.9) \times 10^{-3}$	$(4.5 \pm 1.5) \times 10^{-1}$	$(1.6 \pm 0.6) \times 10^{-1}$	12 ± 4	$(4 \pm 2) \times 10^{-3}$
CO_2	$(1.3 \pm 0.2) \times 10^{-3}$	$(1.8 \pm 0.2) \times 10^{-3}$	$(4.0 \pm 0.6) \times 10^{-4}$	$(3.3 \pm 0.4) \times 10^{-3}$	$(2.6 \pm 0.3) \times 10^{-2}$
SiF_4	$<2 \times 10^{-5}$	$(1.3 \pm 0.6) \times 10^{-2}$	$<2 \times 10^{-5}$	$<2 \times 10^{-5}$	$(7.1 \pm 1.7) \times 10^{-1}$
SF_6	$<3 \times 10^{-5}$	$(3.3 \pm 1.6) \times 10^{-3}$	$<3 \times 10^{-5}$	$<3 \times 10^{-5}$	$(4.1 \pm 0.8) \times 10^{-2}$

Note: Sample 1, GeH_4 of natural isotopic composition, purified by distillation; sample 2, $^{76}GeH_4$ enriched by centrifugation; sample 3, $^{76}GeH_4$ purified by distillation; sample 4, the $^{76}GeH_4$ fraction taken from the bottom of the column; sample 5, the $^{76}GeH_4$ fraction taken from the top of the column.

described elsewhere [7, 9]. Samples for analysis were taken from the gas phase. The analysis results for the GeH_4 samples are presented in the table.

RESULTS AND DISCUSSION

The data in the table demonstrates that, as a result of ^{76}Ge enrichment, C_4–C_9 hydrocarbons, chlorinated and fluorinated hydrocarbons, chlorogermanes, alkylgermanes, and polygermanes are concentrated in the germane. The contents of different groups of impurities in the enriched germane range widely, from 10^{-7} to 10^{-1} mol %. Clorogermane and digermane are present in the highest concentrations, at a level of 10^{-1} mol %.

Distillation effectively reduces the contents of all the molecular impurities detected. The contents of 36 impurity species in the distillate are within 1×10^{-5} mol %. The highest contents are those of polygermanes (10^{-1} mol % digermane and 6×10^{-4} mol % trigermane) and carbon dioxide (4×10^{-4} mol %). The content of ethane, the most difficult to remove impurity ($\alpha = 1.21 \pm 0.03$ [3]), in the distillate ($<1 \times 10^{-5}$ mol %) is more than one order of magnitude lower than its initial content (1.6×10^{-4} mol %). The C_1 and C_2 hydrocarbons (methane, ethane, and ethylene) are concentrated in the overhead (light fraction). All of the other impurities detected are concentrated in the bottom fraction: saturated hydrocarbons having more than two carbon atoms, chlorinated and fluorinated hydrocarbons, aromatic hydrocarbons, alcohols and ethers, germane homologues, alkyl derivatives of germane, and chlorogermanes.

The spectroscopically detected SiF_4 and SF_6 are atypical of germane of natural isotopic composition. The presence of these impurities in the isotopically enriched sample is probably associated with the "memory" of the centrifuge cascade, which was previously used to separate silicon and sulfur isotopes. SF_6 and CO_2 are concentrated in the light fraction even though they should be considered low-volatile according to their boiling points. One possible reason for this behavior of CO_2 and SF_6 impurities in germane is that, at the distillation parameters used, they form a solid phase in the condenser of the column. Its sublimation leads to an increased content of these impurities in the overhead fraction.

In all of the samples studied, the $^{76}Ge_2H_6O$ (germanoxane), SiH_4 (silane), and CO (carbon monoxide) contents were below the detection limits of IR spectroscopy for these impurities (1×10^{-4} to 1×10^{-3} mol %).

CONCLUSIONS

High-purity ^{76}Ge-enriched germane has been prepared by distillation. The distillate contains no more than 10^{-5} mol % hydrocarbons, 10^{-4} mol % carbon dioxide, 10^{-3} to 10^{-1} mol % digermane and triger-

mane, and $<3 \times 10^{-5}$ mol % other impurities. A distinctive feature of the impurity composition of the isotopically enriched germane samples is the presence of silicon tetrafluoride and sulfur hexafluoride impurities.

REFERENCES

1. Schoenert, S., The GERmanium Detector Array (GERDA) for the Search of Neutrinoless Beta Beta Decays of Ge-76 at LNGS, *Nucl. Phys. Proc. Suppl.,* 2005, vol. 145, pp. 242–245.
2. Aalseth, C., Anderson, D., Arthur, R., et al., The Proposed Majorana Ge-76 Double-Beta Decay Experiment, *Nucl. Phys. Proc. Suppl.,* 2005, vol. 138, pp. 217–220.
3. Devyatykh, G.G. and Zorin, A.D., *Letuchie neorganicheskie gidridy osoboi chistoty* (Ultrapure Volatile Inorganic Hydrides), Moscow: Nauka, 1974.
4. Devyatykh, G.G, Gusev, A.V., and Vorotyntsev, V.M., Preparation of High-Purity Germanium, *Vysokochist. Veshchestva,* 1988, no. 1, pp. 5–16.
5. Krivtsun, V.M., Kuritsyn, Yu.A., Snegirev, E.P., et al., Measurement of Low PH_3 Concentrations in GeH_4 with a Tunable-Laser-Diode Spectrometer, *Zh. Prikl. Spektrosk.,* 1985, vol. 63, pp. 571–576.
6. Devyatykh, G.G., Zasavitskii, I.I., Il'in, V.M., et al., Tunable-Laser-Diode IR Spectrometer for Molecular Analysis of High-Purity Volatiles, *Vysokochist. Veshchestva,* 1990, no. 6, pp. 106–114.
7. Krylov, V.A., Chernova, O.Yu., Kireev, S.M., et al., Determination of Impurities in High-Purity Germane by Gas Chromatography/Mass Spectrometry, *Perspekt. Mater.,* 2008, no. 6, pp. 227–229.
8. Aref'ev, D.G., Vasin, S.A., Dolgov, S.G., et al., Application of Germane for Germanium Isotope Separation in Gas Centrifuges, *Perspekt. Mater.,* 2010, no. 8, pp. 19–24.
9. Sennikov, P.G., Kotkov, A.P., Adamchik, S.A., et al., Impurities in Monosilanes Synthesized by Different Processes, *Neorg. Mater.,* 2010, vol. 46, no. 4, pp. 415–420 [*Inorg. Mater.* (Engl. Transl.), vol. 46, no. 4, pp. 358–363].