U.S. DEPARTMENT OF ENERGY

PNNL-20368

Germanium-76 Sample Analysis

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April 2011

Pacific Northwest NATIONAL LABORATORY

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Executive Summary

The MAJORANA DEMONSTRATOR is a large array of ultra-low background high-purity germanium detectors, enriched in ^{76}Ge, designed to search for zero-neutrino double-beta decay ($0\nu\beta\beta$). The DEMONSTRATOR will utilize ^{76}Ge from Russia, and the first one gram sample was received from the supplier for analysis on April 24, 2011. The Environmental Molecular Sciences facility, a DOE user facility at PNNL, was used to make the required isotopic and chemical purity measurements that are essential to the quality assurance for the MAJORANA DEMONSTRATOR. The results of this first analysis are reported here.

Acronyms and Abbreviations

BE	Binding Energy
EMSL	Environmental Molecular Sciences Laboratory
FWHM	Full width at half maximum
PNNL	Pacific Northwest National Laboratory

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1 Purpose

With the results from Super-Kamiokande, SNO, KamLAND, and other neutrino experiments, it has been demonstrated that neutrinos are massive, change flavor, and play an important role in the universe. Measuring the absolute mass of neutrinos and determining their Majorana nature are two of the most important goals of the physics community today. The standard double-beta decay process results in emission of two beta particles and two neutrinos, a process that was first reliably observed in ^{76}Ge by the PNNL-University of South Carolina collaboration in 1990. The much rarer, and yet unconfirmed, $0\nu\beta\beta$ process results in emission of only the two beta particles. Observation of this process would provide direct evidence that neutrinos are Majorana particles and that lepton number is not conserved.

The MAJORANA Collaboration was initiated in 1999 in order to carry out a $0\nu\beta\beta$ experiment in ^{76}Ge. MAJORANA is a collaboration of about 100 scientists at 20 institutions worldwide supported by DOE Office of Science Office of Nuclear Physics, the National Science Foundation, and other international funding agencies. The current plan calls for the MAJORANA DEMONSTRATOR to be constructed and operated over the next several years in parallel with the European ^{76}Ge experiment (GERDA). This is proposed to be followed by a single, merged, Tonne-Scale, international experiment for $0\nu\beta\beta$ in ^{76}Ge.

The MAJORANA DEMONSTRATOR experiment is now constructing an essentially background-free measurement of $0\nu\beta\beta$ in 30 kg of natural Ge plus 30 kg of ^{76}Ge with the goal of determining lepton number conservation and the neutrino mass. The MAJORANA DEMONSTRATOR requires 30 kg of isotopically enriched ^{76}Ge. Currently, the only source of enriched ^{76}Ge is from Russia, at a cost of ~$85/g. This material will be delivered to the MAJORANA DEMONSTRATOR experiment in FY11-FY12, with quality assurance (QA) samples arriving on a periodic basis during this time. These QA samples will require precision isotopic evaluation. One such measurement was performed in 2009 under an EMSL rapid proposal on a single sample using SIMS instruments [Elliott 2009]. Further measurements will take place during FY11-FY12 at EMSL.

Reported here are the results of the first measurements of isotopic composition and chemical purity of a sample of ^{76}Ge delivered by Isoflex, the representative of ECP in Russia. The one-gram sample of $^{76}GeO_2$ was delivered to PNNL on April 25, 2011 for analysis, which was completed on April 27, 2011. The measurements were made in the Environmental Molecular Sciences Laboratory at PNNL under EMSL user proposal #43992.

2 Isotopic Composition

A time-of-flight secondary ion mass spectrometry (ToF-SIMS) system, of the type shown in Figure 2.1, at EMSL was used for the isotopic analysis of the Russian ^{76}Ge sample. Table 2.1 provides the results of the isotopic analysis, where the value in parenthesis is the uncertainty in the last digit.

Figure 2.1. ToF-SIMS Mass Spectrometer Model Used for Isotopic Measurements

Table 2.1. Isotopic Composition of Sample

Isotope	Fractional Composition
^{70}Ge	0.00006(1)
^{72}Ge	0.00011(1)
^{73}Ge	0.00033(3)
^{74}Ge	0.086(5)
^{76}Ge	0.914(5)

3 Chemical Analysis

X-ray photoelectron spectroscopy (XPS) was used to perform the chemical purity analysis. XPS is more surface sensitive and provides relative concentration and chemical state information.

XPS measurements were performed with a Physical Electronics Quantera Scanning X-ray Microprobe. This system uses a focused monochromatic Al Kα X-ray (1486.7 eV) source for excitation and a spherical section analyzer. The instrument has a 32-element multichannel detection system. A 100 W X-ray beam focused to 100 μm diameter was rastered over a 1.4 mm x 0.1 mm rectangle on the sample. The X-ray beam is incident normal to the sample and the photoelectron detector is at 45° off normal. High energy resolution spectra were collected using a pass-energy of 69.0 eV with a step size of 0.125 eV. For the Ag 3d5/2 line, these conditions produced a full width at half maximum (FWHM) of 0.91 eV. The sample experienced variable degrees of charging. Low energy electrons at ~1 eV, 20μA and low energy Ar^+ ions were used to minimize this charging. The binding energy (BE) of adventitious carbon line was set at 284.8 eV to compensate for any surface-charging effects.

The GeO_2 powder samples were pressed onto clean double sided Nichiban tape supported by 1 cm x 3 cm flat Si wafers. The sample holder was then placed into the XPS vacuum introduction system and pumped to less than $1x10^{-6}$ Torr using a turbomolecular pumping system prior to introduction into the main ultra high vacuum system. The main vacuum system pressure is maintained at less than $5x10^{-9}$ Torr during analysis and pumped using a series of sputter ion pumps.

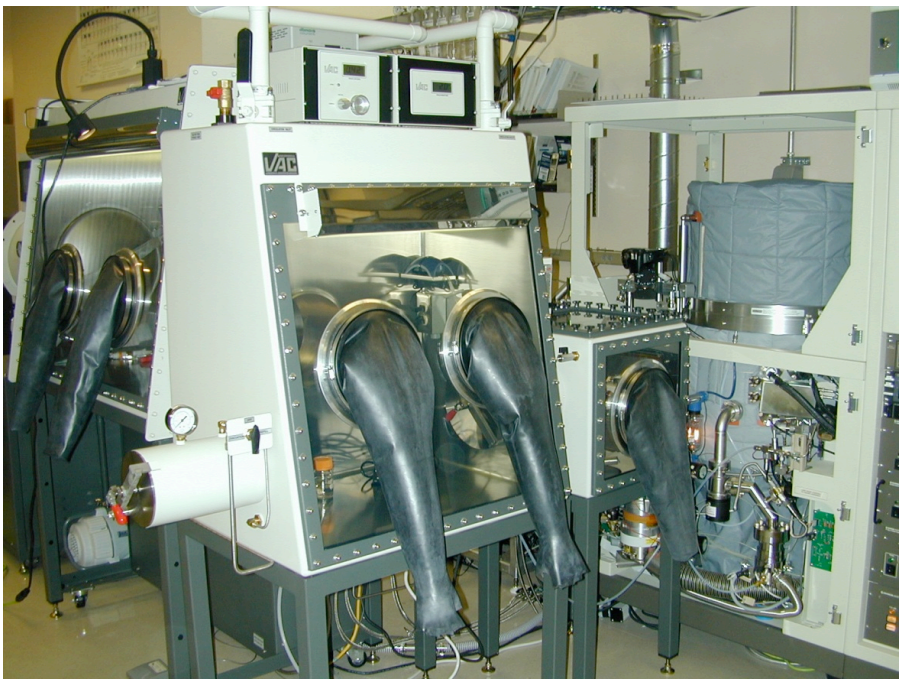

Figure 3.1. PHI Quantera XPS with inert atmosphere glove box for inert sample transfer. XPS is on the right wrapped in the blue blanket.

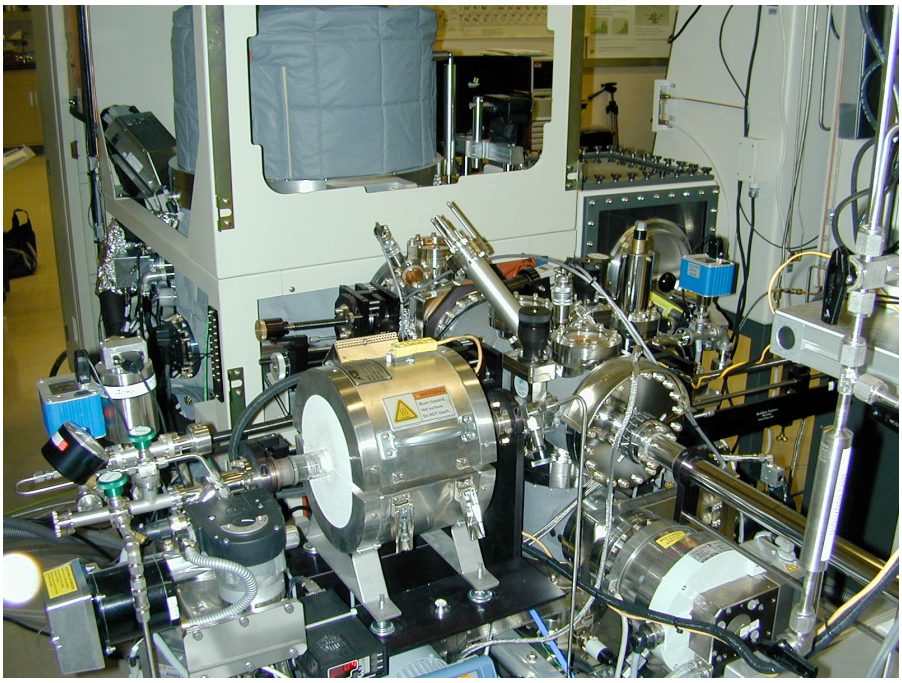

Figure 3.2. PHI Quantera XPS and connecting catalytic side chamber for in-situ controlled pressure and temperature sample processing.

Figures 3.1 and 3.2 show two views of the XPS system in EMSL.

XPS Results

Calculated atomic concentrations for sample number 1-A $^{76}GeO_2$ from the high-energy resolution narrow scan (spectral output file 02261.103). Figure 3.3 shows the broad energy range spectrum obtained. Figures 3.4 – 3.7 show high resolution scans of specific peaks.

Table 3.1 shows the measurement results for the three observed elements: Ge, O, and C. The Relative sensitivity factor (RSF) is corrected for specific instrument effects and is used to derive the atomic percentages shown. From these values, the XPS quantified ratio of Ge/O is 0.52, compared to the expected Ge/O ratio of 0.50.

Table 3.1. Isotopic Composition of Sample

Element:	**C1s**	**O1s**	**Ge3d**
Relative sensitivity factor (RSF)	0.314	0.733	0.535
RSF corrected for specific instrument	21.075	49.679	41.210
Atomic Percent	5.4	62.3	32.3

Contamination

Approximately 5.4 atomic percent carbon was detected on the surface of the sample, which is consistent with adventitious hydrocarbons typically detected on surfaces exposed to atmosphere. No other contaminants were observed above the background level of 0.5 atomic percent.

Chemical States (Measured Binding Energies And Reference Energies)
Both the Ge 2p3 and O 1s photoemission line energies of 1220.8 and 532.1 eV, respectively, are consistent within ±0.2 eV of reference line energies published in the NIST Standard Reference Database 20, Version 3.5. The Ge 2p3 reference line energy for GeO (Ge^{+2}) is 1221.5 eV, whereas it would be 1217.4 eV for Ge metal (Ge^{0}), verifying that the observed material is GeO_2.

The germanium (IV) dioxide (GeO_2) XPS binding energy references are: Wagner [1975] for Ge2p3 (1220.6 eV), Wagner et al. [1980] for O 1s (531.9 eV), and Nefedov et al. [1975] for O1s (532.2 eV).

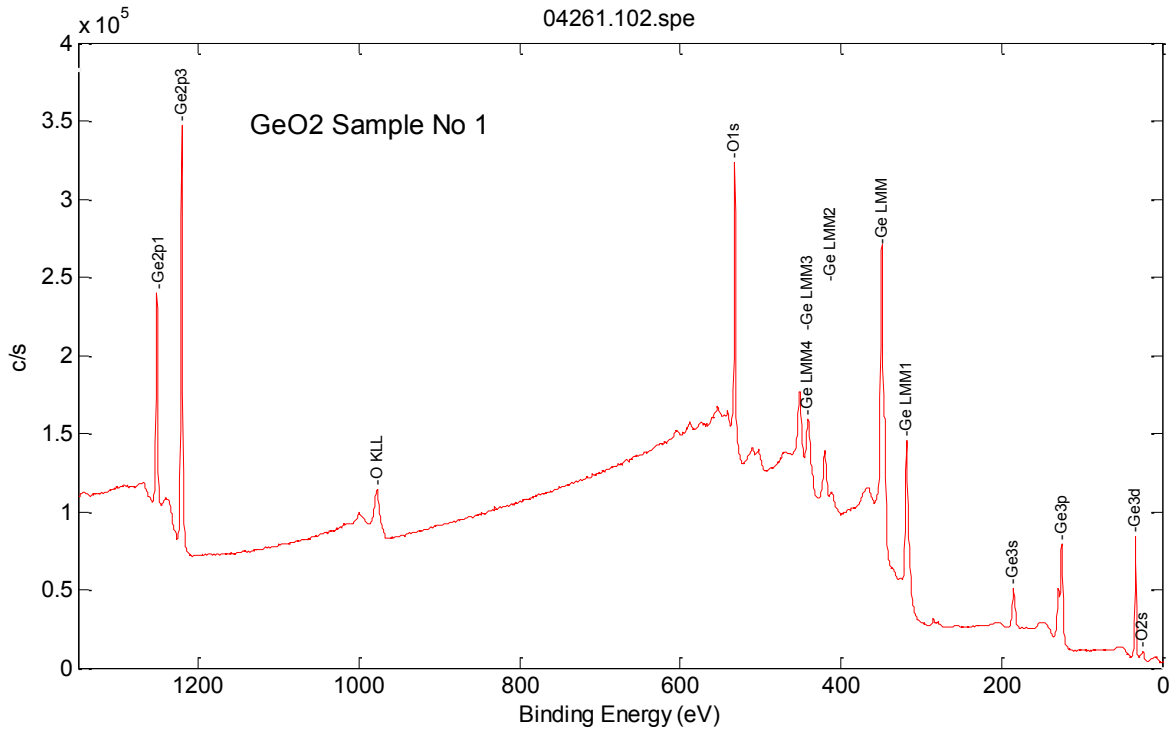

Figure 3.3. XPS wide scan spectrum (low energy resolution).

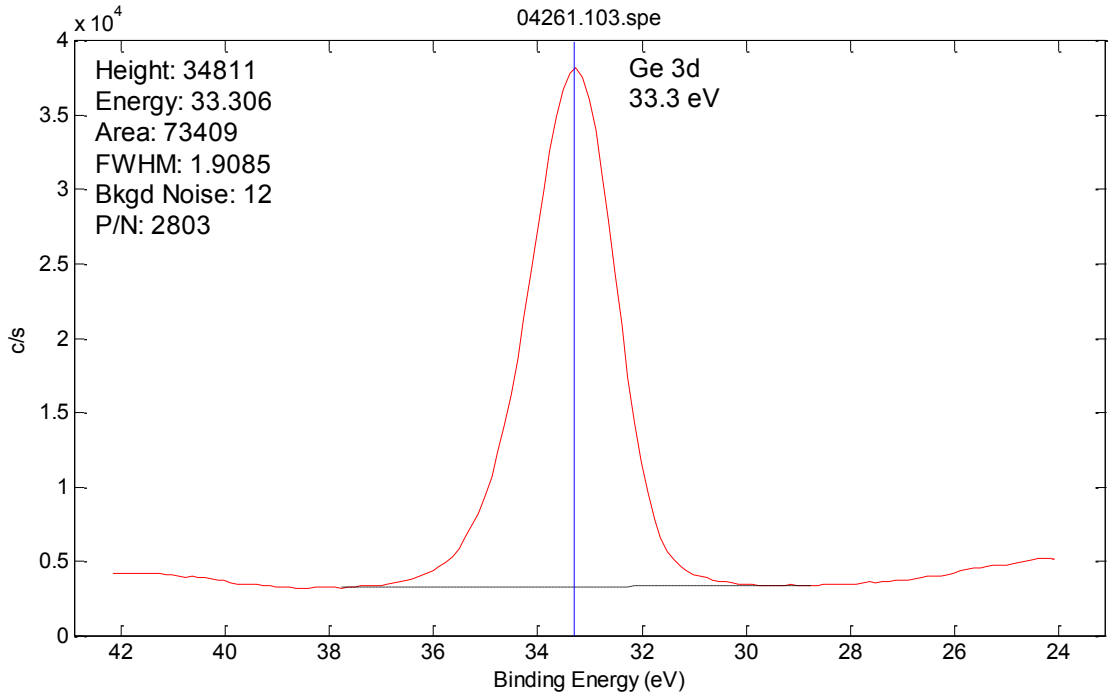

Figure 3.4. XPS narrow scan spectra (high energy resolution) for Ge 3d region.

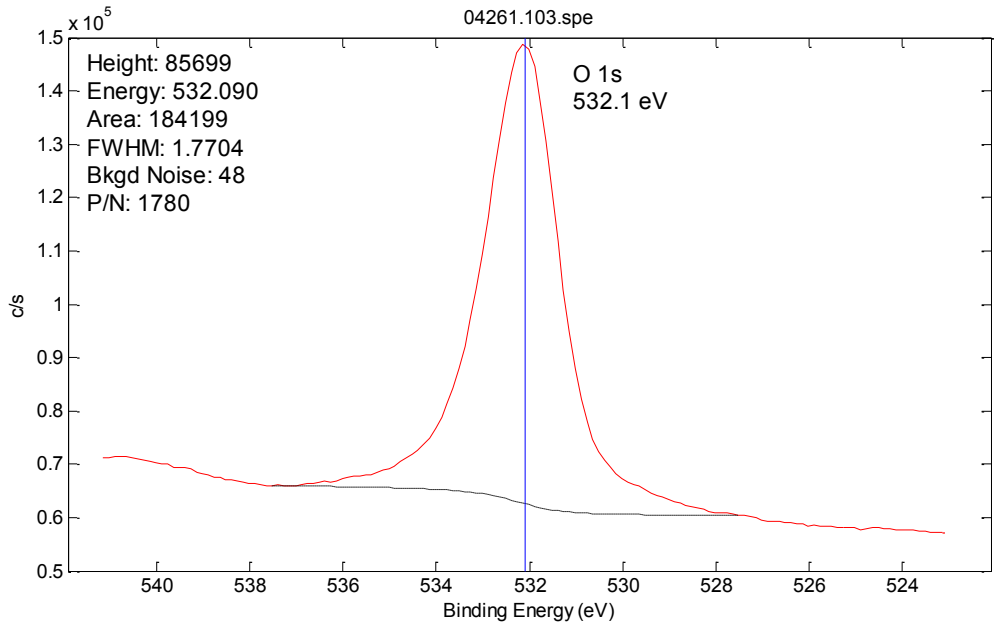

Figure 3.5. XPS narrow scan spectra (high energy resolution) for O 1s region.

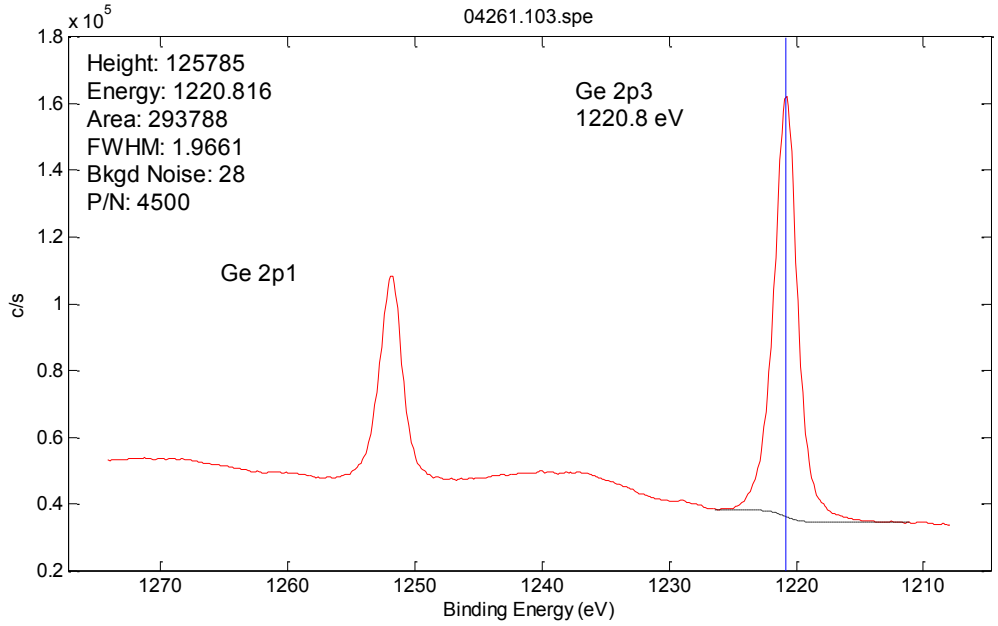

Figure 3.6. XPS narrow scan spectra (high energy resolution) for Ge 2p region.

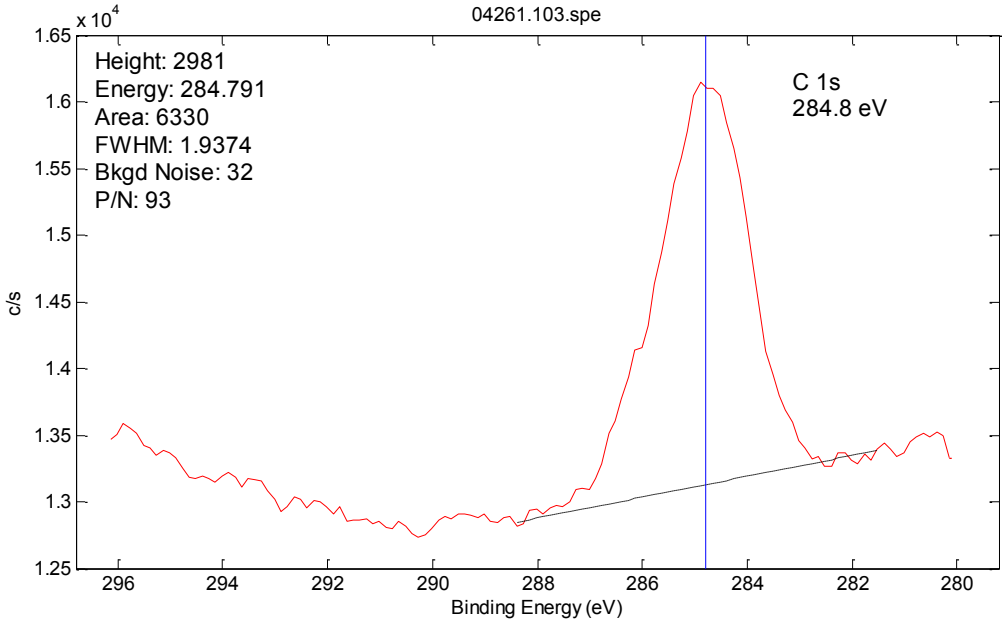

Figure 3.7. XPS narrow scan spectra (high energy resolution) for C 1s region.

4 Conclusions

The results of the isotopic composition of the $^{76}GeO_2$ sample from Russia showed higher than expected enrichment. The chemical purity of the sample is consistent with a GeO2 sample and shows no contamination above background at 0.5 atomic percent.

5 References

Elliott S.R., V.E. Guiseppe, B.H. LaRoque, R.A. Johnson, S.G. Mashnik, *Fast-Neutron Activation of Long-Lived Isotopes in Enriched Ge*, submitted for publication December 2009.

Nefedov V.I., Gati D., Dzhurinskii, B.F., Sergushin N.P., Salyn Y.V. Zh. Neorg. Khimii 20, 2307 (1975)

Wagner C.D., Discuss. Faraday Soc. 60, 291 (1975)

Wagner C.D., Zatko D.A., Raymond R.H. Anal. Chem. 52, 1445 (1980)

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