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Analysis of High-Purity Germanium Dioxide by Atomic Absorption Spectrometry

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Abstract—To ensure analytical support for the growth of bismuth orthogermanate single crystals, we have developed an electrothermal atomic absorption technique for analysis of germanium dioxide with the separation of the host through reactive evaporation in the form of germanium tetrachloride. The technique allows Cd, Co, Cu, Cr, Mn, Ni, and Pb to be determined with detection limits in the range 1×10^{-8} to 1×10^{-7} wt %.

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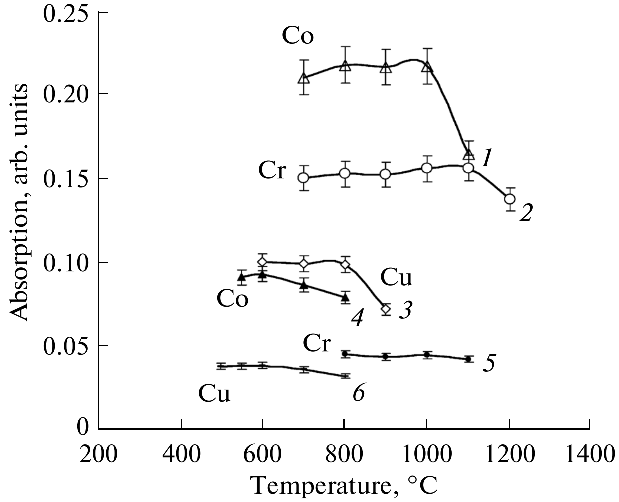
INTRODUCTION

High-purity germanium dioxide (GeO_2) is used in the preparation of bismuth orthogermanate ($Bi_4Ge_3O_{12}$) scintillator single crystals, which are employed as detectors in medical applications and high-energy physics [1]. The impurity composition of $Bi_4Ge_3O_{12}$ single crystals influences their electro-optical properties and radiation resistance [2–5] and depends on the crystal growth process and the purity of the raw materials used. To monitor the quality of germanium dioxide, one should develop analytical techniques that would ensure the determination of technologically important impurities with detection limits (DLs) at a level of 10^{-6} wt % or lower.

Previous reports described atomic emission techniques for the spectral analysis of germanium dioxide with dc arc excitation (dc arc AES) and separation of the host through reactive evaporation in the form of the volatile compound (t_b = 83.1°C [6]) $GeCl_4$ (germanium tetrachloride) during heating (t ~ 70–80°C) on a Teflon plate, by an IR lamp [7, 8] in an open system or autoclave [9, 10]. A combined dc arc AES technique for the analysis of germanium dioxide [7] ensures impurity DLs at a level of 10^{-7} to 10^{-5} wt %. Chanysheva et al. [8] were able to lower the impurity DLs of dc arc AES to a level of 10^{-8} to 10^{-6} wt % by optimizing the excitation and detection conditions and taking advantage of the most sensitive analytical lines. GeO_2 decomposition and concurrent separation of the host via $GeCl_4$ evaporation in an autoclave (closed system) reduce the extent of a control experiment, because chemical transformations of the host are combined with effective purification of the reagent, preconcentration in a closed system, and the reduction in the range of auxiliary materials and the number of steps in the analytical technique. Vapor-phase autoclave preconcentration directly in a graphite electrode at a temperature of 230–240°C ensures a DL of dc arc AES for impurities, including widespread ones, at a level of 10^{-8} to 10^{-6} wt % [9]. With this preconcentration technique, Fe, V, Ga, Al, and Sb impurities fail to enter the analytical concentrate because of the formation of volatile chlorides in the dissolution process, and neither B, not P, nor As are concentrated. Karpov and Orlova [10] added water to a reaction vessel (autoclave liner) and used an aqueous solution of mannitol and ammonium persulfate, which enabled the above elements to be determined by dc arc AES with DLs from 10^{-7} to 10^{-6} wt %.

Germanium evaporation in the form of $GeCl_4$ in an open system and an autoclave was used to analyze GeO_2 for impurities by inductively coupled plasma (ICP) atomic emission and ICP mass spectrometry [11]. The results demonstrate that this mass spectrometric technique, in combination with the evaporation of the host in an autoclave, allows one to determine a number of elements with extremely low DLs, down to 10^{-10} wt %, but the process involves losses of technologically important impurities, such as Cr and Pb.

Previously, Petrova et al. [12] and Korda et al. [13] used flame atomic absorption spectrometry (AAS) to determine the main component (germanium) in crude germanium dioxide. In this study, we have proposed a procedure that employs electrothermal atomic absorption spectrometry (ETAAS) for determining technologically important impurities in germanium dioxide, with germanium separation through reactive evaporation in the form of germanium tetrachloride in an open system. The procedure requires no expensive apparatus and is easy to implement.



Co, Cr, and Cu analytical signals as functions of temperature in the pyrolysis step using atomizers (*1–3*) with and (*4–6*) without pyrolytic coating.

EXPERIMENTAL

Apparatus. We used a Hitachi Z-8000 atomic absorption spectrophotometer with Zeeman background correction. Solutions to be analyzed (20 μL) were placed in an atomizer using a micropipette. Ag, Cd, Co, Cr, Cu, Mn, Ni, and Pb were determined using analytical lines at 328.1, 228.8, 240.7, 357.9, 324.8, 279.6, 232.0, and 283.3 nm, respectively. Graphite atomizers were chosen in order to minimize the DL for the analyte. Ag, Cd, and Pb were determined using polycrystalline graphite atomizers with no pyrolytic coating. Co, Cr, Cu, Mn, and Ni were determined using graphite atomizers with pyrolytic coating, which increased the analytical signal (by a factor of ~2–3) and the temperature in the pyrolysis step (by 100–200°C). The figure shows pyrolysis curves obtained for Co, Cr, and Cu using graphite atomizers with and without pyrolytic coating. Similar pyrolysis curves were obtained for Ni and Mn. The temperature programs of the graphite atomizers were optimized using pyrolysis and atomization curves obtained for all elements of interest using solutions of samples after evaporation of the host (Tables 1, 2). ETAAS determinations of elements were carried out during flash heating of the furnace in the pyrolysis and atomization steps. In the atomization step, the argon flow was turned off (gas stop regime) and the atomic absorption peak area was measured.

Table 1. ETAAS element determination conditions

Step	Drying	Pyrolysis	Atomization	Annealing
Temperature, °C	80–120	See Table 2		
Step duration, s	30	30	5	3
Argon flow rate, mL/min	200	200	0	200

Reagents and labware. We used deionized water with a resistivity of ≥12 MΩ/cm and extrapure-grade HNO_3 and HCl, further purified by subboiling distillation. The HNO_3 and HCl concentrations after double distillation were ~14 and 7 M, respectively. The hydrochloric acid used to decompose germanium dioxide samples was first analyzed by dc arc AES with preconcentration (5 mL of the acid was boiled down on 50 mg of graphite powder) (Table 3).

The samples were decomposed using small Teflon beakers and a large Teflon beaker, ~15 mL and ~0.8 L in volume, respectively. After germanium dioxide decomposition, the solutions were boiled down in conical Teflon dishes. Analyte and reference solutions were placed in disposable polyethylene tubes 1.5 and 15 mL in volume, respectively.

Reference solutions. Working reference solutions (Cd, Co, Cu, Cr, Mn, Ni, Pb) were prepared using state standards containing 1 g/L of an analyte in 1 M HNO_3: GSO 7773-2000, GSO 7784-2000, GSO 7255-96, GSO 7257-86, GSO 7266-96, GSO 7265-96, and GSO 7252-96 (OAO Ural Plant of Chemical Reagents). A solution containing 1 g/L of Ag was prepared by dissolving a weighed amount (100 mg) of the metal in concentrated HNO_3 while heating the mixture. Sequentially diluting (~0.7 M HNO_3) the solutions containing 1 g/L of the analytes, we prepared working reference solutions containing (μg/L) Ag, 1–30; Cd, 0.2–3; Cu, 1–30; Co, 1–30; Cr, 0.5–20; Mn, 0.2–5; Ni, 2–50; and Pb, 2–20.

ETAAS analysis of germanium dioxide. Weighed samples (~0.25 g) of germanium dioxide powder were placed in small Teflon beakers, 3 mL of ~7 M HCl was added, and the beakers were shaken to ensure complete wetting of the sample. Next, the beakers were covered with tightly fitting lids and placed in a large Teflon beaker with a screw lid, which was placed in a thermostat for ~6 h (t = 80 ± 5°C). The solutions obtained after GeO_2 decomposition were transferred to Teflon dishes and boiled down in a box under an IR lamp at a temperature of ≤80°C to give wet salts. The impurity concentrate was then dissolved in 0.1 mL of ~0.7 M HNO_3, the dish was rinsed with 0.1 mL of ~0.7 M HNO_3, the solutions were poured together into polyethylene tubes, and the solution volume was brought to 0.3 mL with ~0.7 M HNO_3 using a micropipette. Next, we took 20 μL of the resultant solution, placed it in the graphite atomizer of the atomic absorption spectrometer, and sequentially determined Ag, Cd, Cu, Co, Cr, Mn, Ni, and Pb under the conditions optimized for each analyte (Tables 1, 2). Control experiments were performed for each determination and at each sample preparation

Table 2. Temperature conditions of ETAAS determination of elemental impurities

Element	Temperature, °C		
	pyrolysis	atomization	annealing
Ag	600	2400	2600
Cd	300	1500	1800
Co*	1000	2200	2400
Cr*	1100	2900	3000
Cu*	800	2200	2400
Mn*	700	2300	2500
Ni*	900	2200	2400
Pb	500	2100	2300

* Graphite atomizers with pyrolytic coating were used.

step. From a calibration plot made using the reference solutions, we determined the content of the target analyte in the solution being analyzed. From the solution volume and sample weight, we determined the weight percentage of the impurity.

RESULTS AND DISCUSSION

The accuracy of the above procedure was checked by the standard addition method. To this end, we first analyzed a high-purity germanium dioxide sample and then added impurities to it. The content of intrinsic impurities in the sample was determined by a combination of ETAAS and dc arc AES [8] using the same procedure as above to separate the host (Table 4). The impurity composition of GeO_2 and comparison of the data obtained by the two independent techniques indicated that the impurity content was as low as 10^{-8} to 10^{-6} wt % and that the proposed ETAAS analysis technique was free of systematic errors. Ni and Pb cannot be determined by a combined dc arc AES technique [8], because the content of these metals in the germanium dioxide sample in question is below the detection limit of this technique. After analysis of the high-purity germanium dioxide sample, Ag, Cd, Co, Cu, Cr, Mn, Ni, and Pb impurities were added to it by dripping nitrate solutions on a weighed amount of germanium dioxide during dissolution. The concentrations of the added elements (10^{-6} to 10^{-5} wt %) exceeded the content of intrinsic impurities by 20–100 times. The analytical data for the sample containing added impurities are presented in Table 5. The confidence intervals indicated for the average mass of the impurities were calculated as $\Delta c = \pm t_{p,n}s/\sqrt{n}$, where

Table 3. DC arc AES analysis data for HCl purified by subboiling distillation

Impurity	Weight percent
Ag, Be, Mn	ND ($<8 \times 10^{-9}$)
Al	3×10^{-7}
As, P	ND ($<8 \times 10^{-6}$)
Au, Pt, W	ND ($<3 \times 10^{-7}$)
B, Co, Cr	ND ($<2 \times 10^{-7}$)
Ba, Ca, Sb	ND ($<8 \times 10^{-7}$)
Bi	5×10^{-7}
Cd	ND ($<4 \times 10^{-8}$)
Cu	ND ($<1 \times 10^{-8}$)
Fe	3×10^{-7}
Ga, In	ND ($<3 \times 10^{-8}$)
Mg	2×10^{-7}
Mo, Pb, Ti, V, Zr	ND ($<8 \times 10^{-8}$)
Si	6×10^{-5}
Sn	2×10^{-7}
Zn	ND ($<1 \times 10^{-7}$)

ND = not detected (with the detection limit specified in parentheses).

Table 4. DC arc AES and ETAAS analysis data for a germanium dioxide sample (G 20-1210 2/13), with the separation of the host in the form of $GeCl_4$ ($P = 0.95$)

Impurity	Weight percent			
	dc arc AES [8] $n = 4–5$	ETAAS	n	s_r
Ag	ND ($<5 \times 10^{-8}$)	ND ($<6 \times 10^{-8}$)	7	–
Cd	ND ($<2 \times 10^{-7}$)	ND ($<1 \times 10^{-8}$)	8	–
Cu	$(1.2 \pm 0.2) \times 10^{-7}$	$(1.4 \pm 0.2) \times 10^{-7}$	7	0.15
Co	ND ($<1 \times 10^{-6}$)	ND ($<6 \times 10^{-8}$)	8	–
Cr	$(1.7 \pm 0.6) \times 10^{-6}$	$(1.7 \pm 0.1) \times 10^{-6}$	9	0.09
Mn	$(1.5 \pm 0.3) \times 10^{-7}$	$(1.4 \pm 0.2) \times 10^{-7}$	7	0.13
Ni	ND ($<2 \times 10^{-6}$)	$(1.1 \pm 0.1) \times 10^{-6}$	8	0.11
Pb	ND ($<5 \times 10^{-7}$)	$(3.1 \pm 0.2) \times 10^{-7}$	9	0.09

Table 5. Evaluation of the accuracy of ETAAS analyses of germanium dioxide by the standard addition method ($P = 0.95$)

Element	Weight percent				
	sample	added	found	n	s_r
Ag	ND ($<6 \times 10^{-8}$)	1.6×10^{-5}	$(1.3 \pm 0.2) \times 10^{-5}$	9	0.18
Cd	ND ($<1 \times 10^{-8}$)	1.6×10^{-6}	$(1.6 \pm 0.1) \times 10^{-6}$	11	0.08
Cu	$(1.4 \pm 0.2) \times 10^{-7}$	1.4×10^{-5}	$(1.4 \pm 0.1) \times 10^{-5}$	10	0.10
Co	ND ($<6 \times 10^{-8}$)	1.2×10^{-5}	$(1.2 \pm 0.1) \times 10^{-5}$	11	0.08
Cr	$(1.7 \pm 0.1) \times 10^{-6}$	3.9×10^{-5}	$(4.0 \pm 0.1) \times 10^{-5}$	12	0.05
Mn	$(1.4 \pm 0.2) \times 10^{-7}$	4.0×10^{-6}	$(4.1 \pm 0.2) \times 10^{-6}$	11	0.07
Ni	$(1.1 \pm 0.1) \times 10^{-6}$	3.6×10^{-5}	$(3.7 \pm 0.2) \times 10^{-5}$	12	0.09
Pb	$(3.1 \pm 0.2) \times 10^{-7}$	1.6×10^{-5}	$(1.6 \pm 0.1) \times 10^{-5}$	12	0.08

Table 6. Comparison of the detection limits of dc arc AES and ETAAS for impurities in germanium dioxide

Impurity	Weight percent	
	ETAAS	dc arc AES [8]
Cd	1×10^{-8}	2×10^{-7}
Co	6×10^{-8}	1×10^{-6}
Cu	6×10^{-8}	1×10^{-7}
Cr	4×10^{-8}	1×10^{-6}
Mn	1×10^{-8}	5×10^{-8}
Ni	1×10^{-7}	1×10^{-6}
Pb	1×10^{-7}	1×10^{-6}

$t_{p,n}$ is Student's coefficient for a given confidence probability P and s parallel determinations (9–12), and s is the standard deviation of convergence. It follows from the results that there were no systematic errors for any element, except for silver, whose content was underestimated. Thus, this element was excluded from the list of detectable impurities. It seems likely that, after GeO_2 dissolution in HCl and subsequent boiling down to wet salts, some of the silver precipitated in the form of AgCl.

Table 6 lists the impurity DLs of ETAAS (calculated using the 3s criterion) and dc arc AES [8]. Note that, even though the dc arc AES analysis technique is more informative as to the number of detectable elements (the total number of concurrently detectable elements is 31), the DLs of ETAAS are an order of magnitude lower. Low DLs were obtained with the proposed technique because, after evaporation of the host, the impurity concentrate can be converted to a small solution volume (0.3 mL) sufficient for subsequent ETAAS analysis. To further lower the DLs (by a factor of 5), one can reduce the volume of the solution to be analyzed (to ~50 μL) and determine only one element in each impurity concentrate. The analysis time will then, however, be considerably longer.

CONCLUSIONS

We have chosen conditions and optimized the temperature and time for ETAAS determinations of Cd, Co, Cu, Cr, Mn, Ni, and Pb in germanium dioxide and developed an ETAAS analysis technique with the separation of the host through reactive evaporation in the form of germanium tetrachloride. The technique allows the above impurities to be determined with detection limits of 1×10^{-8}, 6×10^{-8}, 6×10^{-8}, 4×10^{-8}, 1×10^{-8}, 1×10^{-7}, and 1×10^{-7} wt %, respectively.

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