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# The Concentration Measurements of Tellurium Donor Impurity in Lamellar Bismuth Samples by the Time-of-Flight Mass Spectrometry Method

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The possibility of determining in-depth distribution of tellurium donor impurity in lamellar bismuth samples using the time-of-flight mass spectrometry and electron microscopy methods in the concentration range of 0.005-0.150 at. % Te is studied in the present paper. To measure the amount of tellurium in lamellar bismuth samples, we used a LUMAS-30 time-of-flight mass spectrometer with a pulsed low-pressure glow gas discharge in a combined hollow cathode and a Zeiss Evo-40 scanning electron microscope. The samples for measurements were cut from the middle of the ingots of the Bi-Te alloy with the required impurity concentration. The samples presented a thin plate of a size of 10 × 10 mm$^2$ and 1 mm thickness. The samples were thoroughly washed in distilled water and then etched in a 65 % solution of nitric acid to remove the surface layer with traces of external contaminants. The samples were strengthened as the bottom of the hollow cathode in the gas-discharge cell, where the impulse ionization of the sample atoms in a glow discharge plasma occurred. The relative error in the in-depth distribution of impurities did not exceed 6 %, while the error in determining the concentration of impurities by a mass spectrometer, according to the passport data, did not exceed 5 %. The sensitivity limit in determining the concentration of impurities in the device LUMAS-30, according to the passport data, was $10^{-6}$ at. %. As a result of research, we set that the time-of-flight mass spectrometry method gives a very accurate determination of the tellurium impurity concentration, and also allows to establish a uniform distribution of tellurium over the volume of a doped bismuth lamellar sample. The electron microscopy method using a Zeiss Evo-40 microscope does not give a uniform distribution of tellurium over the sample volume.

**Keywords**: Bismuth, Tellurium, Thin films, Mass spectrometry, Donor impurity.

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## 1. INTRODUCTION

The physical properties of a substance in a massive or film state strongly depend on its structure. For example, in [1] the authors, by studying the influence of particle and grain size on the structural parameters of ceramic samples of a substituted polycrystalline system of iron-yttrium garnet $Y_{3-c}Ca_cFe_5O_{12}$, identified decrease in the specific saturation magnetization with decreasing grains.

However, the structural properties of the ferrogarnets depend not only on the synthesis conditions, but also on doping with a divalent calcium impurity [1]. Therefore, another way to change the properties of a substance is its alloying.

In work [2], the influence of the doping degree on the structural characteristics of bismuth films doped with tellurium in the concentration range of 0.005-0.15 at. % Te and thickness range of 0.3-0.7 μm is investigated. Therein, Demidov E.V. and Matveev D.Yu. established that an increase in the doping degree with tellurium in bismuth films leads to a significant decrease in growth figures. The weak influence of annealing on the crystallite size of bismuth films doped with tellurium indicates high temporal stability of the structure. The average crystallite size varies slightly logarithmically with increasing thickness and concentration of tellurium, as shown by Dilner and Schnelle on the basis of the Mayadas-Shackes model [3, 4]. The influence of the tellurium concentration on the electrical and galvanomagnetic properties of bismuth films is considered in detail in works [5-8].

In all the works mentioned above [1-8], the question about measuring the concentration of impurities by modern methods remains open. For example, for the preparation of Bi-Te films, the concentration of tellurium impurity in bismuth was determined from the weight of the sample of the substance being evaporated, and it was believed that the concentration of tellurium does not change upon transition from a single crystal to a film [6].

In the present work, the results of an experimental study of the quantity of tellurium impurity in bismuth films by the time-of-flight mass spectrometry and scanning electron microscopy methods are presented for the first time.

## 2. METHODS OF THE EXPERIMENT

The initial materials for the production of bismuth films doped with tellurium in this study were bismuth crystals with a tellurium content of 0.005 at. %, 0.010 at. %, 0.050 at. %, 0.075 at. % and 0.150 at. % obtained by the method described in the paper [9].

For the preparation of Bi-Te alloys, Bi-000 bismuth with a purity of 99.9999 % and Te with a purity of 99.999 % were used.

Pure bismuth was preliminarily degassed and purified from oxides by distillation through a capillary at a temperature of 380 °C in a vacuum to $10^{-2}$ mm Hg in an ampoule made of molybdenum glass.

The amount of bismuth and tellurium required for

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the preparation of the alloy was weighed on the ADV-200 damper scales and on the stationary jewelry scales WAGA TORSYJNA-WT, respectively.

At first, the Te sample calculated for approximately 50 g of the alloy was weighed. Calculation of a tellurium sample with given concentration was performed with taking into account output factor $\eta$ of tellurium atoms in bismuth ($\eta = 0.7$). This sample was selected in the form of a single piece, which reduced the probability of a partial loss of it when we are working with it. Then, according to the actual mass of tellurium, the mass of bismuth was calculated. The ampoule with the components of the alloy was pumped to a pressure of $10^{-2}$ mm Hg, after which it was soldered. After that, the ampoule was placed in an oven, where it was kept at a temperature of 380 °C for 24 hours, while the oven was continuously rocked, which ensured good mixing of the alloy. After this, the ampoule was removed from the oven and placed horizontally, and it was allowed to quickly solidified.

Obtained alloys in the ampoules were subjected to zone equalization by two passes of the zone in opposite directions. Zone melting was conducted at a rate of 3 cm/h [9]. As a result of melting, a large-block bismuth crystal doped with tellurium with a given concentration was grown. Thus, alloys with an impurity content of 0.005 at. % Te up to 0.150 at. % Te were prepared.

Quantity of tellurium in the film was set by using bismuth crystals with a previously known tellurium concentration for spraying.

The concentration of tellurium impurity in bismuth was measured by means of a time-of-flight LUMAS-30 mass spectrometer with a pulsed glow discharge gas of low-pressure in a combined hollow cathode and with Zeiss Evo-40 scanning electron microscope (SEM) [10].

The experimental equipment (Fig. 1) consisted of an ionization block for solid samples in a pulsed discharge gas in a hollow cathode and a time-of-flight mass spectrometer Lumas-30 with an orthogonal location of the drift zone, which included a mass-reflectron, which was used as the registering system of the formed ions. Ion optics of the mass-spectrometer was calculated and preliminarily optimized by the collaborators of the Department of Analytical Chemistry of the St. Petersburg State University [10, 11].

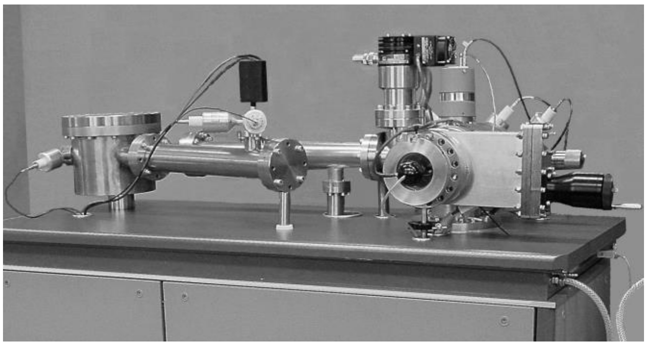

**Fig. 1** – View of the time-of-flight mass spectrometer

Using the electroerosive method by wire cutting, samples for the measurements were cut from the middle of the ingots of the Bi-Te alloy with necessary impurity concentration. The samples were thin plates of a size of 10 × 10 mm² in size and 1 mm thickness. The samples were thoroughly washed in distilled water and then etched in a 65 % solution of nitric acid to remove the surface layer with traces of external contaminants. The samples were strengthened as the bottom of the hollow cathode in the gas-discharge cell, where the impulse ionization of the sample atoms in a glow discharge plasma occurred.

Table 1 shows the conditions that were applied in the analysis of a solid sample.

**Table 1** – Control voltages and some parameters of the time-of-flight mass spectrometer, at which the Bi-Te samples were analyzed

| | |
|---|---|
| Cathode Material | Al (99.999 %) |
| Discharge gas | Ar-He-$H_2$<br>(69.70 %-30 %-0.30 %) |
| Discharge cell pressure | 1.6 Torr |
| Duration of the discharge pulse | 1.7 μs |
| Duration of the pushing pulse | 1.0 μs |
| Pushing pulse delay time | 140 μs |
| Pulse repetition period | 0.3 ms |
| Cathode voltage | – 1500 V |
| Time-of-flight tube voltage | – 2000 V |
| Spraying time | 11 min |
| Number of spectra | 1000 packages of 2000 spectra |

## 3. RESULTS AND DISCUSSION

Several sputterings were made for the impurity distribution depth profile (Table 2). Fig. 2 shows the corresponding mass spectrum for one sputtering on an example of the Bi sample (0.150 at. % Te).

The tellurium concentration in bismuth was determined from the sizes of square areas of the radioactive isotope peaks of tellurium with a main mass of 130 and bismuth 209. The $^{130}$Te isotope was selected considering that his peak, as seen from Fig. 2, had the greatest

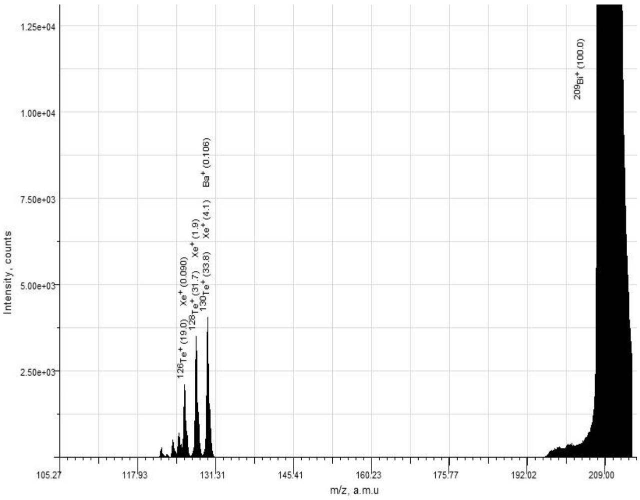

**Fig. 2** – Mass spectrum of Bi (0.150 at. % Te). Combined cathode. The material of cathode wall is Al. Pressure 1.6 Torr. Gas mixture composition: Ar – 69.70 %, He – 30 %, $H_2$ – 0.30 %

**Table 2** – Depth distribution of tellurium impurity in the sample

| Measurement number | *I*, Bi | *I*, Te | at. % Te |
|---|---|---|---|
| 1221 | 8691 | 12.51 | 0.144 |
| 1223 | 8487 | 11.85 | 0.140 |
| 1227 | 8897 | 12.81 | 0.144 |
| 1229 | 7637 | 11.37 | 0.149 |
| 1239 | 10060 | 14.66 | 0.146 |

intensity and was most clearly separated from the remaining (stable) isotopes of tellurium. It is interesting to note, that the calculation was conducted on the assumption that the content of tellurium isotopes in the sample, issued on the mass spectrum, corresponds to the content of isotopes in the natural element.

Investigations of the distribution depth profile of tellurium impurities of the sample (Table 2) indicate the uniformity of their distribution. In addition, the results of concentration measurements by mass spectrometry are perfectly combined with the method for determining the concentration by weight of a tellurium sample calculated for 50 gram of the alloy. As can be seen from the mass spectrum, extraneous chemical elements in the samples are absent.

The measurement of the tellurium concentration by scanning electron microscopy method was conducted on the same samples using a Zeiss Evo-40 microscope.

Fig. 3 and Fig. 4 show the raster electronic spectrum for the sample with a tellurium concentration of 0.15 at. % and its electronic image indicating the location of sounding, respectively.

An electron beam probed the surface of each sample repeatedly at different points (Fig. 4).

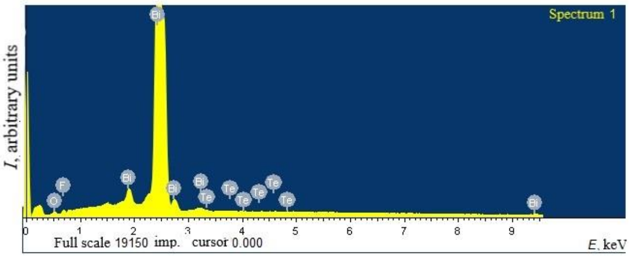

**Fig. 3** – The electronic spectrum of Bi (0.150 at. % Te)

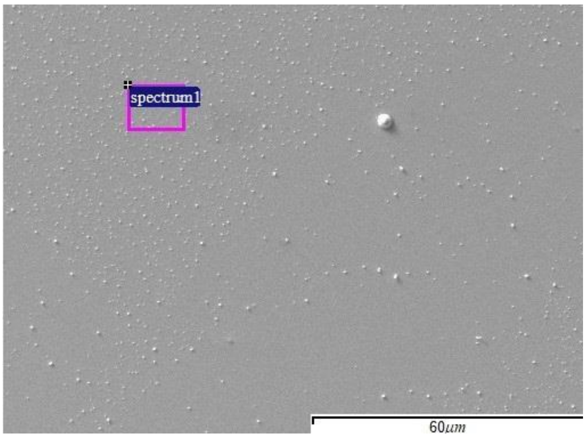

**Fig. 4** – Electronic image of the surface of the Bi sample (0.150 at. % Te)

As can be seen from Fig. 3, besides the peaks of bismuth and tellurium, oxygen and fluorine are present in the samples. In measurements in other areas of the surface, carbon and sodium can be detected.

Table 3 shows the concentration values in weight and atomic percent (at. %) of all elements including in the Bi sample (0.15 at. % Te) for different probing regions. It can be seen from Table 3 that the tellurium concentration assumes unequal values in the investigated areas of surface scanning, which indicates the uneven distribution of the impurity in the sample. So, the measurement of the concentration by the method of scanning electron microscopy does not completely correspond to the concentration calculated by the weight of the sample of doping substance.

**Table 3** – Elemental composition of the Bi sample (0.150 at. % Te) obtained with a Zeiss Evo-40 microscope

| Measurement number | Element | Weight, % | Atomic, % |
|---|---|---|---|
| 1 | O K | 2.09 | 18.95 |
| | F K | 1.89 | 14.41 |
| | Te L | 0.09 | 0.10 |
| | Bi M | 95.93 | 66.53 |
| 2 | O K | 2.14 | 19.19 |
| | F K | 1.96 | 14.85 |
| | Te L | 0.01 | 0.01 |
| | Bi M | 95.89 | 65.94 |
| 3 | C K | 18.39 | 63.53 |
| | O K | 7.45 | 19.33 |
| | F K | 0.74 | 1.62 |
| | Na K | 0.50 | 0.90 |
| | Te L | 1.13 | 0.37 |
| | Bi M | 71.78 | 14.25 |

The present result can be due to incorrect adjustment of the main characteristics of the electron microscope system (low values of accelerating voltages), and as a consequence weak excitation of the *L* series of tellurium, since in the second dimension Te is practically not detected. Perhaps, significant errors in determining the quantitative composition of the samples are due to the imposition of the characteristic lines of one element on the other spectrum.

In the work, the relative error in the impurity depth distribution determined by the time-of-flight mass spectrometry method did not exceed 6 %. The relative error in determining the impurity concentration by a mass spectrometer, according to the passport data, did not exceed 5 %.

Limit sensitivity in determining the concentration of impurities on the device "LYUMAS-30", according to the passport data, is $10^{-6}$ at. %. Absolute errors in the determination of the tellurium concentration in the initial sample for the production of bismuth films with different degrees of doping are: (0.0050 ± 0.0005) at. % Te, (0.010 ± 0.001) at. % Te, (0.050 ± 0.002) at. % Te, (0.075 ± 0.004) at. % Te and (0.150 ± 0.008) at. % Te, respectively.

It should be noted that the difference in the determination of the amount of tellurium impurity in the samples by mass spectrometry was no more than 6-7 % compared to the initial loaded amount of tellurium.

## 4. CONCLUSIONS

The method of time-of-flight mass spectrometry in a pulsed gas discharge in a hollow cathode makes it possible to determine with a high degree of accuracy the tellurium concentration in bismuth samples.

The time-of-flight mass spectrometry method makes it possible to verify and confirm the uniformity of the tellurium volume distribution in the samples.

The presence of these facts can help correctly interpret the experimental results obtained on bismuth films doped with tellurium, since the concentration in the film and the sample is assumed to be unchanged, as evidenced by numerous studies on the electrical and galvanomagnetic properties of thin films and bismuth crystals doped with tellurium.

Attempts to use the scanning electron microscopy method with the Zeiss Evo-40 microscope, as well as X-ray fluorescence analysis with the BRA-18 analyzer did not give the required determination accuracy.

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# Вимірювання концентрації донорної домішки телуру в пластинчастих зразках вісмуту методом час-пролітної масової спектрометрії

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У роботі вивчається можливість визначення глибинного розподілу донорної домішки телуру в пластинчатих зразках вісмуту з використанням методів мас-спектрометрії та електронної мікроскопії в діапазоні концентрацій 0.005-0.150 ат. % Te. Для вимірювання кількості телуру в пластинчатих зразках вісмуту використовувався часопролітний мас-спектрометр LUMAS-30 з імпульсним газовим розрядом низького тиску в комбінованому порожнистому катоді та скануючий електронний мікроскоп Zeiss Evo-40. Зразки для вимірювань вирізали з середини злитків сплаву Bi-Te з необхідною концентрацією домішок. Зразки представляли собою тонку пластину розміром 10 × 10 мм$^2$ і товщиною 1 мм. Їх ретельно промивали дистильованою водою, а потім травили у 65 % розчині азотної кислоти для видалення поверхневого шару зі слідами зовнішніх забруднень. Зразки зміцнювали як дно порожнистого катода в газорозрядній комірці, де відбувалася імпульсна іонізація атомів зразка у плазмі тліючого розряду. Відносна похибка глибинного розподілу домішок не перевищувала 6 %, а похибка визначення концентрації домішок мас-спектрометром, за паспортними даними, не перевищувала 5 %. Межа чутливості при визначенні концентрації домішок у приладі LUMAS-30, за паспортними даними, становила $10^{-6}$ ат. %. В результаті проведених досліджень встановлено, що метод часопролітної масової спектрометрії дає дуже точне визначення концентрації домішок телуру, а також дозволяє встановити рівномірний розподіл телуру у об'ємі легованого пластинчастого зразка вісмуту. Метод електронної мікроскопії з використанням мікроскопа Zeiss Evo-40 не дає рівномірного розподілу телуру у об'ємі зразка.

**Ключові слова:** Вісмут, Телур, Тонкі плівки, Мас-спектрометрія, Донорна домішка.