

Comparison of Bi_2O_3 -targets produced by thermal evaporation and RF magnetron sputtering

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Abstract. For the nuclear chemistry and for the nuclear physics of the heavy elements, bismuth is one of the key target materials, as it is the heaviest stable element. As discussed earlier, compound targets were developed to withstand higher intensive heavy ion beams. In the past, Bi_2O_3 was evaporated from the tantalum crucible and deposited on carbon backings. As the melting temperature of Bi_2O_3 is high (817° C), the process is at the limit of the cooling features of the evaporation set-up. Therefore, we decided to test RF magnetron sputtering as an alternative production method. We will present results of the different behavior of the targets produced via alternative processes.

1 Introduction

Bismuth is an important target material, especially in heavy and super-heavy element (SHE) experiments since it is the heaviest stable nuclei for the synthesis of odd compound nuclei with cold fusion reactions. In heavy ion beam experiments, the low melting temperature of the metal with 271 °C is a problem for high-intensity beams; therefore, it was necessary to investigate higher melting compounds as an alternative, as already done for lead compounds [1].

At first, the bismuth compounds were produced by thermal evaporation, which is a well-established method with a high yield. In addition, it is the method of choice for most of the targets for the super-heavy element program for decades. As bismuth is monoisotopic, this opened the possibility to test radio frequency (RF) magnetron sputtering as an alternative method, as will be described below.

2 Bismuth compounds

As alternative for metallic bismuth, we searched for simple binary compounds with higher melting temperatures. We could buy all compounds readily and deposited them by thermal evaporation on carbon backings on a rotating evaporation wheel, as described in [1]. As a standard, 350 - 450 $\mu\text{g}/\text{cm}^2$ of the target material was evaporated from a tantalum crucible on a carbon backing of 35 - 45 $\mu\text{g}/\text{cm}^2$, which is produced in our laboratory by resistance heating [2]. The following compounds were tested.

Bismuth sulfide (Bi_2S_3) has a melting temperature of ~ 685 °C. The compound already decomposed during thermal evaporation, so Bi_2S_3 was discarded right away. Bismuth fluoride (BiF_3) has a melting temperature of 727 °C. The fluoride could be evaporated successfully

on carbon backing though the as prepared foils showed some stress. A stress relief by heating the foils from the backing side during evaporation, which often improves the quality and stability of foils, in this case only led to decomposition of the material. Bismuth oxide (Bi_2O_3) has a melting temperature of ~ 817°C. Since the melt is very corrosive, a platinum crucible had to be used for evaporation in this case. The bismuth oxide on carbon backing could be evaporated successfully with heating of the backings as well as without heating. Targets from both production routes were prepared

2.1 Final choice of Bi_2O_3 as Targets

In 2003, test experiments at the heavy-ion separator SHIP (Separator for Heavy Ion Particles) were performed with the described compound targets [3]. All compound targets showed cross-sections comparable to that of the metal, but the oxide targets exhibited a much higher durability. Oxide targets formed on heated backings were the most durable. In addition, the melting temperature of the oxide is higher than that of the fluoride. Therefore, the oxide was the alternative of choice. Such targets were applied since as standard bismuth in several beam times. Bismuth oxide is now the target of choice. Some of the stored targets, however, showed peculiar degradation during storage for an unknown reason. Therefore, alternative methods were sought for achieving better properties of Bi_2O_3 -targets.

3 Properties of bismuth oxide

Bi_2O_3 is a polymorphic system with four known different crystallographic phase were the α - and the δ -phase are stable, and the β - and γ -phase are metastable phases only formed upon cooling [4]. Since the high-

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temperature δ -phase has a very high ion conductivity, it is a good candidate as a solid electrolyte for fuel cells or in sensors [5]. Therefore, over the last decades there were intensive investigations on the phase transitions in this binary system with various methods; see e.g. the paper of Schröder et al. [6] and citations therein. Depending on the cooling rate, the atmosphere, the pressure and other parameters, different crystallographic structures occur and are probably frozen. Klinkova et al. [7] also reported oxygen deficiency of a varying extent for the different phases.

With thermal evaporation, there is no possibility to control the cooling and condensation of Bi_2O_3 target material on the backing. Quenching of metastable phases could be possible explanations for the stress within the deposited layers responsible for instability for some targets.

To avoid degradation of the metastable Bi_2O_3 and the restructuring of carbon backings during the production or storage, an alternative production method was sought in which the metastable phases could be avoided. This could lead to better-defined phase homogeneity in the deposited Bi_2O_3 layers. Unfortunately, we could not detect different phases with the methods available.

4 RF Magnetron sputtering

Since magnetron sputtering is a ballistic coating process, the liquid phase and the undesired β - and γ -phase can be avoided. Bismuth is monoisotopic, thus easy and relatively inexpensive to buy as a sputter target. The higher losses compared to thermal evaporation are not a crucial point, as it would be for isotopically enriched target material. Bismuth oxide is a poor electric conductor, so radiofrequency sputtering (RF) magnetron sputtering allows for a stable plasma process.

With RF magnetron sputtering, Bi_2O_3 targets were produced on carbon backings without major problems, though the foils in some batches were heavily stressed and broke already during production. While it is not yet understood, why this sometimes happens, the surviving foils are stable during storage and show no degradation with time. The method and set up used for magnetron sputtering is described in detail in [8, 9].

5 Investigations

To find differences between targets produced with the different techniques, selected targets were analysed. We investigated targets produced with both methods that were not irradiated and that showed no obvious degradation; targets produced with both methods that were irradiated with ^{48}Ca -ions during a SHIP beam time; targets that were not irradiated but showed peculiarities nevertheless.

For this paper, as a first step, only tools and methods were applied that were available in our laboratory to investigate the selected samples. From each target investigated, a photograph of the whole target on the frame was taken to see any phenomenological differences or peculiarities. In addition, a quantitative analysis with an Energy Dispersive X-ray detector

(EDX) was performed, evaluating the ratio of bismuth to oxygen in units of atomic percentage for each sample. We report this ratio for each sample picture in a green box. This value is the calculated mean value of four different point measurements in the region of the target, which is indicated by the red arrow. For non-irradiated targets, only the centre region was investigated. For targets irradiated with an ion beam, the centre region was measured representing the irradiated area and the peripheral area where the beam intensity was minimum for comparison. We only had targets at our disposal that were non-irradiated leftover reserves from beam time campaigns or irradiated targets that survived the ion beam bombardment. Therefore, the number of available specimen was largely restricted. The measured ratios show a rather wide scatter so that only trends are observed and no systematic reliable information.

As a reference, a tablet of the starting material of Bi_2O_3 was analysed by EDX in the same way as the foils, giving a ratio of Bi/O of 0.9. All targets investigated had a thickness between 400 and 500 $\mu\text{g}/\text{cm}^2$ referring to the bismuth content and carbon backings with a thickness between 40 and 60 $\mu\text{g}/\text{cm}^2$ for those prepared with thermal evaporation and between 40 and 50 $\mu\text{g}/\text{cm}^2$ for those prepared by magnetron sputtering.

5.1 Targets prepared by thermal evaporation

All targets shown in figures 1 – 5 were prepared by thermal evaporation. The targets in figure 1 and 2 were not irradiated in a beam time.

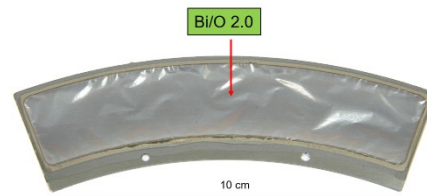


Fig. 1. #7- Bi_2O_3 on C-backing by thermal evaporation on SHIP-frame, not irradiated. Green box indicates ratio of atomic % evaluated by EDX.

In the target shown in figure 2, the carbon backing partly restructured during the evaporation from a smooth layer to a corrugated structure. This effect is a well-known effect for carbon layers. It happens spontaneously upon heating and cannot be influenced by the operator. However, the restructuring seems not to influence the performance during beam time experiments. The Bi/O-ratios here vary between 2.0 and 2.7.

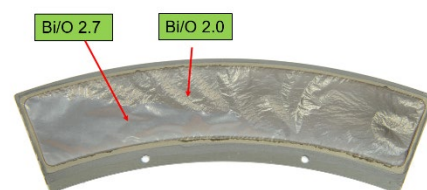


Fig. 2. #5- Bi_2O_3 on C-backing by thermal evaporation on SHIP-frame. Carbon backing partly restructured during evaporation, not irradiated. Green box indicates ratios of atomic % evaluated by EDX.

The target shown in figure 3 was also not irradiated but was stored for 3 years in air. The whole batch of targets that were prepared in that one run disintegrated with time. Nevertheless, this did not happen for other batches that were stored even for longer times. The Bi/O-ratio of 0.9 in this case is noticeable lower than for the intact targets.

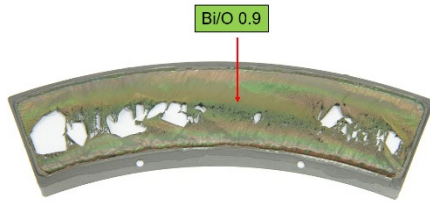


Fig. 3. #79-Bi₂O₃ on C-backing prepared by thermal evaporation on SHIP-frame in 2018 and stored in air for 3 years. Green box indicates ratio of atomic % evaluated by EDX.

The targets shown in figures 4 and 5 were irradiated in a SHIP beam time with ⁴⁸Ca-ions. The intensity distribution of the beam profile during the irradiation is clearly visible. For the target in figure 4, the profile was not well distributed resulting in distinct colour changes and corrugations in a small strip along the centre of the target were the intensity and consequently the temperature was highest. The Bi/O-ratio at the less-irradiated periphery in both cases are 0.9, which is the ratio in the reference material.

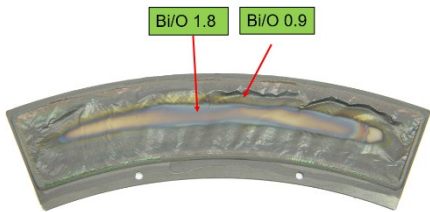


Fig. 4. #15-Bi₂O₃ on C-backing prepared by thermal evaporation on SHIP-frame and irradiated with a ⁴⁸Ca-beam ($\sim 2 \cdot 10^{17}$ particles). Green box indicates ratios of atomic % evaluated by EDX.

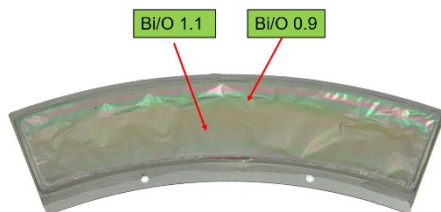


Fig. 5. #29-Bi₂O₃ on C-backing prepared by thermal evaporation on SHIP-frame and irradiated with a ⁴⁸Ca-beam ($\sim 4 \cdot 10^{17}$ particles). Green box indicates ratios of atomic % evaluated by EDX.

5.2 Targets prepared by magnetron sputtering

The targets shown in figures 6 – 8 were prepared by RF magnetron sputtering; those in figure 6 and 7 were not irradiated.

Sometimes, all targets of one batch show strong tensions so that the layers tear or even burst away during

production, as can be seen in figure 7. We cannot influence or predict this effect. The Bi/O-ratios seems to be overall lower comparable to those observed in the targets prepared with thermal evaporation but this is not significant.

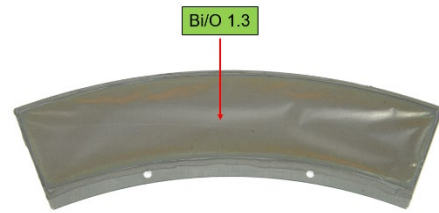


Fig. 6. #15SP-Bi₂O₃ on C-backing prepared by magnetron sputtering. Green box indicates ratio of atomic % evaluated by EDX.

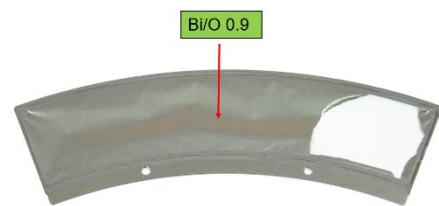


Fig. 7. #21-Bi₂O₃ on C-backing prepared by magnetron sputtering - foils show high tensions. Green box indicates ratio of atomic % evaluated by EDX.

The target shown in figure 8 was irradiated with a ⁴⁸Ca-beam. In addition, here we can observe a clear difference in the Bi/O-ratio between the periphery of the target and the centre, where the beam intensity was highest.

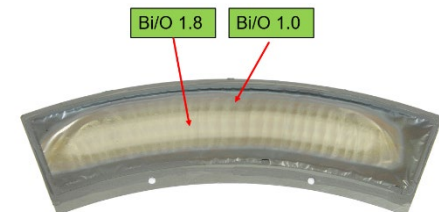


Fig. 8. #50-Bi₂O₃ on C-backing prepared by magnetron sputtering and irradiated with ⁴⁸Ca ($2 \cdot 10^{18}$ particles). Green box indicates ratios of atomic % evaluated by EDX.

5.3 Targets on titanium backing

In figure 9, targets are shown that were produced very recently for a special experiment where a titanium backing was required. To find the most appropriate production process for this experiment, we prepared targets of the same thickness with the different processes for a direct comparison. The titanium backing had a thickness of about 2.1 μm in all cases. The two targets on the left in figure 9 were prepared by thermal evaporation; the target on the far left was prepared without heating of the backing during evaporation (figure 9a) and for the target in the middle (figure 9b), the backing was heated during evaporation. The target in figure 9 on the right was prepared with RF magnetron sputtering (figure 9c).

Here, we see significant differences already in the appearance of the three foils. Rather striking are the Bi/O ratios here. Whereas the Bi/O-ratio of the sputtered target of 1.4 lies well within the range observed for all the targets prepared on carbon backing, the ratio of 4.5 for both targets prepared by thermal evaporation are significantly higher.

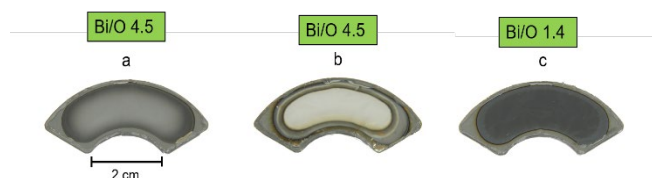


Fig. 9. Bi₂O₃ on titanium backing prepared by
a: Thermal evaporation without heating of the backing,
b: Thermal evaporation with heating of the backing
c: Magnetron Sputtering
Green box indicates ratios of atomic % evaluated by EDX.

6 Discussion and interpretation

The Bi/O-ratios for all targets with carbon backing vary in the range from 0.9 to 2.7. We could neither observe any systematic difference between the foils prepared by thermal evaporation and magnetron sputtering nor between original and irradiated foils. Compared to the Bi/O-ratio of the starting material Bi₂O₃ of 0.92, most layers are largely oxygen deficient. The performance in beam time experiments was comparable though there is some evidence that sputtered targets might show a longer durability.

Though there is evidence from the evaluated Bi/O ratios that bismuth is lost in the beam spot region during irradiation, there was no drop in reaction cross sections reported from the experiment and the targets did not lose weight during irradiation.

For layers deposited on Ti-backing, we see significant differences in the Bi/O-ratio between the two methods.

Already the appearance of the foils is quite different. The measured Bi/O ratios are interesting. For the targets produced with thermal evaporation, the Bi/O ratio is significantly higher than those observed for targets on C-backing: 4.5 compared to max. 2.7. This is not observed for targets prepared by magnetron sputtering.

Because of the complicated phase transformations of Bi₂O₃ upon cooling the structure of evaporated layers is not controllable with our techniques. Presumably, this should happen less in sputtered foils where no liquid phase is involved, but this is not obvious for the investigated samples. However, the large amount of the observed oxygen loss cannot be explained solely with a phase mixing. Such a significant loss of oxygen in preparation could have a stoichiometric background or could be due to different sticking coefficients of oxygen and bismuth on the substrate. Different sticking behaviour probably is the major factor for the differences observed between layers deposited on carbon and on titanium backings. However, as long as

the bismuth atoms remain in an oxygen binding that raises the melting temperature sufficiently, the durability and performance during irradiation experiments seems not to be affected much by the actual structure or oxygen content. In the case of titanium backing, the titanium might act as a getter material for the oxygen thus reducing the oxide especially at elevated temperatures. This might be avoided with magnetron sputtering.

7 Outlook

For better statistics, more beam time experiments are planned with comparable beam conditions to identify possible differences in the durability of foils produced with the different methods. Preferably, each target set should be irradiated until a defined degradation state is reached. This has to be negotiated well with the scientists performing the experiments since beam time is precious and rare. Furthermore, the degradation on air with time for foils with alternative methods in order to understand the mechanism behind the effect will be observed. The targets produced on titanium backing have to be tested in a beam time to see if their durability differs significantly from those deposited on carbon backings. Also very important will be to investigate the layer composition of targets produced with different methods with analytic methods more sensitive to the chemical bonding and quantitative composition of the constituents, as e.g. infrared or Raman spectroscopy.

References

1. B. Lommel, D. Gembalies-Datz, W. Hartmann, S. Hofmann, B. Kindler, J. Klemm, J. Kojouharova, J. Steiner, Nucl. Instr. and Meth. A **480**, 16-21 (2002).
2. B. Lommel, W. Hartmann, B. Kindler, J. Klemm, J. Steiner, Nucl. Instr. and Meth. A **480**, 199-203 (2002).
3. B. Kindler, D. Ackermann, W. Hartmann, F. P. Hessberger, S. Hofmann, B. Lommel, R. Mann, J. Steiner; Nucl. Instr. and Meth. A **561**, 107-111 (2006)
4. H. A. Harwig, A. G. Gerards, Termochimica Acta **28** (190) 121-131.
5. A. M. Azad, S. Larose, S. A. Akbar, J. of Mat. Sci. **29** (1994) 4135-5151
6. F. Schröder, N. Bagdassarov, F. Ritter, L. Bayarjargal, Phase Trans. **83**:5, 311-325 (2010)
7. L. A. Klinkova, V. I. Nikolaichik, N. V. Barkovskii, V. K. Fedotov, Russ. J. of Inorgan. Chem., **52**, No. 12, 1822-1829 (2007)
8. B. Kindler, W. Hartmann, J. Klemm, B. Lommel, J. Steiner, Nucl. Instr. and Meth. A **521**, 222-226 (2004)
9. B. Kindler, W. Hartmann, A. Hübner, B. Lommel, J. Steiner, V. Yakusheva; J. of Radioanalyt. and Nucl. Chem. **305**, 703-706 (2015)