



Determination of doping elements of synthetic crystals by direct current glow discharge mass spectrometry



Jiangli Dong^{a,b}, Rong Qian^{b,*}, Wei Xiong^b, Haiyun Qu^b, Bilige Siqin^b, Shangjun Zhuo^b, Jun Jin^b, Zhaoyin Wen^b, Pingang He^a, Peter Kenneth Robinson^c

^a Department of Chemistry, East China Normal University, Shanghai 200062, China

^b Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

^c MassCare, Ltd., 11 Waterside Way, Middlewich, Cheshire CW10 9HP, UK

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ABSTRACT

Direct current glow discharge mass spectrometry (dc-GD-MS) was applied for the determination of doping elements in synthetic crystals. To get stable discharge, the surface coating method and tantalum carrier method were used to support the sputtering and ionization of samples respectively. For the analysis of BaF₂, Y₃Al₅O₁₂ (YAG), Bi₄Si₃O₁₂ (BSO), La₃Ga₅SiO₁₄ (LGS), CsI and Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PMN-PT), the stable discharge current and the matrix signals were investigated by using these two methods. While for the analysis of CaF₂ and γ-Al₂O₃, the tantalum carrier method could sustain much stable discharge to achieve fine intensity of matrix elements compared to the surface coating method. Furthermore, two Y₃Al₅O₁₂ (YAG) samples were also studied by inductively coupled plasma optical emission spectrometer (ICP-AES) to validate the precision, accuracy and reproducibility of these two methods. The results suggested that the dc-GD-MS would be a good choice to determine the doping elements in synthetic crystals by these two methods.

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1. Introduction

Lattice vacancies exist in crystal materials during the growth process, they could be created thermally by the substitution of ions with incorrect valences, which have been reported to strongly affect the optical and scintillation properties of the material [1–3]. Such as the CsI crystals doped with thallium atoms present high stopping power and good energy resolution, they are since decades employed in nuclear physics as charged particle detectors [4]; the LiYF₄ crystal doped with rare-earth ions has been proved to be an efficient all-solid-state lasing media that covers varied wavelength regions due to its good chemical durability and thermal stability, high optical transparency, and lower phonon energy [5]. More and more researchers are trying to get crystal materials with different properties by doping some elements such as transition metals, rare earth, actinides elements [5,6] and so on. In the synthesis of the synthetic crystals, the concentrations of doping elements and impurities may affect the quality and performance of the crystals, such as radiation hardness, thermoluminescence characteristics [7,8], light yield [9]. For example, the fluorescence yield and fluorescence spectra of CsI crystals are affected by the concentration and distribution of doping element thallium [4]; the properties

of lead tungstate (PbWO₄) can be modified by doping some trivalent ions, including La³⁺, Y³⁺, Lu³⁺, Gd³⁺, an optimum doping concentration would result in considerable improvement of its emission and scintillation characteristics [10]. Therefore, a better understanding of the doping elements in synthetic crystal materials appears desirable.

X-ray fluorescence spectrometry (XRF) [11–13], atomic spectrometry (AES/AAS) [14–16] and inductively coupled plasma mass spectrometry (ICP-MS) [17–19] methods have been used to monitor the doping elements and impurities in crystals. For instance, Zhuo et al. had used XRF to determine both major components and dopants in PbWO₄ and bismuth germanate (Bi₄Ge₃O₁₂, or BGO) scintillation crystals [13]; Sheina et al. had used inductively coupled plasma atomic emission spectrometry (ICP-AES) and flame spectrometry (FAES/FAAS) to establish the stoichiometric composition of cerium-doped crystals [16]; Takahashi et al. had used the ICP-MS fitted with an octopole reaction system collision/reaction cell to analyze boron (B) and phosphorus (P) elements doped in photovoltaic-grade silicon [19]. Although XRF could be used to analyze samples in various forms (such as solid, powder, melting tablets, liquids, etc.), the analytical sensitivity is not enough for the analysis of trace elements. Similarly, ICP-MS has high sensitivity for a wide range of analytes and wide linear dynamic range [20,21], it needed the solid samples to be dissolved into solution and diluted, it is time-consuming and contamination would be caused in this process [22].

* Corresponding author. Tel.: +86 21 52413101; fax: +86 21 52415609.

E-mail address: qianrong@mail.sic.ac.cn (R. Qian).

Glow discharge mass spectrometry (GD-MS) has been widely used for the direct analysis of trace elements in metals and semiconductors [23]. Its main advantages include the ability to obtain isotopic information across the periodic table down to ng g^{-1} detection limits [24], high mass resolution and high sensitivity [25–27]. Moreover, solid materials could be directly analyzed by dc-GD-MS without the need for dissolution and dilution, thus avoids the possible contamination. With the development of sample preparation methods and ion sources, GD-MS has been successfully used to analyze some non-conductive samples such as glass, ZrO_2 , Macor and others. For instance, Marcus et al. had used the rf-GD-MS for the analysis of glass and Macor [28–30], and Schelles et al. had used the secondary cathode method for the analysis of glass, ZrO_2 , Macor [31–33]. For analysis of powder samples, the powders could be mixed with conducting materials and then the mixture pressed into a pin or a disk; or the powders could also be embed evenly onto the surface of a pure and conductive host. However, grinding of the solid materials might be troublesome or cause some contamination. For block or plate samples, radio frequency glow discharge mass spectrometry (rf-GD-MS) [34,35] or secondary cathode method [36] could be applied for direct analysis without any sample preparation. The disadvantage of secondary cathode method is the restricted measurement conditions [25].

In our recent research work, a surface coating method was developed and successfully used to analyze some non-conductive materials using the pin cell of a dc-GD-MS [37]. In the present work, dc-GD-MS was used to analyze the doping elements and impurities in synthetic crystals with the surface coating method and tantalum (Ta) carrier method. Eight types of crystals including BaF_2 , $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG), $\text{Bi}_4\text{Si}_3\text{O}_{12}$ (BSO), $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ (LGS), CsI, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PMN-PT), CaF_2 and $\gamma\text{-Al}_2\text{O}_3$ were studied by dc-GD-MS. Typical elements of different crystals were analyzed to investigate the precision, accuracy and reproducibility of these two methods. Two YAG samples were analyzed quantitatively by ICP-AES to validate the precision, accuracy and reproducibility of these two methods. Some flat crystal samples were also analyzed by the secondary cathode method in our work, no stable signals of matrix could be acquired except for the CsI. Compared to the secondary cathode method, the surface coating method and Ta carrier method could sustain stable discharge and enhance the stability of signals. Moreover, Ta carrier method could avoid some interferences of indium (In) for the analysis of the rare earth elements, and was available to analyze the samples with large bond energy such as $\gamma\text{-Al}_2\text{O}_3$ and CaF_2 . The results indicated that the dc-GD-MS would be a good choice to analyze the doping elements in synthetic crystals by combining the surface coating method and Ta carrier method.

2. Experimental

2.1. dc-GD-MS experiments

The dc-GD-MS experiments in this work were performed with a VG 9000 glow discharge mass spectrometer (Thermo Elemental, UK). It is a double-focusing magnetic sector instrument with reverse Nier–Johnson configuration. The discharge cell used was a pin cell designed for pin-shaped samples. The cell was pre-cooled to about -180°C by liquid nitrogen to reduce the background caused by residual gases. The discharge process was supported by high-purity argon (>99.9999%). The accelerating voltage was set to 8 kV. The intensity of the ion beams was detected by a Daly detector for small current (10^{-19} – 10^{-13} A) and a Faraday cup for large current (10^{-13} – 10^{-9} A). For most of the measurements, the working resolution used was better than 4000.

2.2. Materials and sample preparation

The high-purity indium (>99.9999%) was purchased from Emei Semiconductor Material Factory & Institute (Sichun, PR China). The high-purity tantalum was purchased from Goodfellow Cambridge Limited (>99.999%). The samples, including BaF_2 , PMN-PT, YAG, BSO, LGS, CsI, CaF_2 and $\gamma\text{-Al}_2\text{O}_3$, were provided by the Shanghai Institute of Ceramics, Chinese Academy of Sciences. The pictures of some raw materials containing doping elements were presented here (Table 1). For the surface coating method, the raw materials were manufactured into pin samples with square ($2\text{ mm} \times 2\text{ mm}$) cross-section, and length of 20 mm (Fig. 1a). For the Ta carrier method, the raw materials were manufactured into pin samples with square ($2\text{ mm} \times 2\text{ mm}$) cross-section, and length of about 5–10 mm (Fig. 1c). All the samples were then cleaned with dilute nitric acid solution, and then pure water, and finally cleaned with anhydrous ethanol.

According to our previous report for surface coating method [37], the pure indium was melted in a clean ceramic crucible at a temperature of around 200°C . The pin sample was held by titanium tweezers and dipped into the indium, submerging around 75% of the length, and the surface coating layer thickness of indium was about $400\ \mu\text{m}$. It was important that the indium should cover the entire surface that would be exposed to the plasma, and to a length sufficient to ensure that the cathode voltage was applied from the sample holder [37]. Meanwhile, Ta carrier with square ($2\text{ mm} \times 2\text{ mm}$) cross-section, and length of 20 mm was made from high-purity tantalum. The pin sample was put in the Ta carrier for analysis (Fig. 1). Although there is no relevant literature was reported about the Ta carrier method, the similar method was used by some companies such as Evans Analytical Group (EAG), Mass Spectrometry Instrument Ltd. (MSI) and so on. All the prepared samples and Ta carriers were kept in anhydrous ethanol before the analysis was started.

2.3. Spectral interference

Because argon was used as the discharge gas, argon and the related clusters would have some interference with the matrix [37]. For example, ^{40}Ar was always a strong interference to ^{40}Ca , so the isotopes ^{42}Ca or ^{44}Ca were chosen to determine the concentration of Ca. The VG 9000 dc-GD-MS is a double focusing magnetic sector mass spectrometer and can separate much isobaric interference, such as ^{52}Cr from the interference ion $^{40}\text{Ar}^{12}\text{C}$, ^{56}Fe from the interference ions $^{28}\text{Si}_2$ and $^{40}\text{Ar}^{16}\text{O}$, and so on.

In our research work, the similar possible interferences were also investigated. In surface coating method, the indium and argon might produce some interference to some rare earth elements, such as $^{115}\text{In}^{36}\text{Ar}$ to ^{151}Eu , $^{115}\text{In}^{40}\text{Ar}$ to ^{155}Gd , $^{115}\text{In}^{27}\text{Al}$ to ^{142}Nd , and so on. In the case of Ta carrier method, the ^{180}Ta and ^{181}Ta would not cause interference to most of the rare earth elements (Fig. 2).

3. Results and discussion

3.1. Analysis of impurities of indium pin and Ta carrier

At the beginning of our experiments, the impurities of the used indium pin and tantalum carrier were measured by dc-GD-MS, the condition used was a 1.5 kV/0.6 mA discharge. Both of the indium pin and the tantalum carrier were pre-sputtered for about 20 min before analysis. The results of panoramic analysis indicated that the concentrations of almost all elements were investigated below a level of 0.01 (ppm wt, relative to In), except for sodium (Na) which was below a level of 0.1 (ppm wt, relative to In) in indium pin. In the Ta carrier, only the concentration of niobium (Nb) was 3.32

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