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## Effect of B<sub>2</sub>O<sub>3</sub> addition to Magnesium, Zirconium, Hafnium fluorides on the parameters of thin films formed from them

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For the first time, the influence of a B<sub>2</sub>O<sub>3</sub> additive on Magnesium, Zirconium, and Hafnium fluorides, encompassing their structural and optical properties, was subjected to investigation. The phase composition of the MgF<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> system was ascertained through the utilization of X-ray phase analysis and infrared (IR) transmission spectroscopy. Notably, a discernible presence of a newly formed phase, characterized as a complex compound of Magnesium fluoroborate (Mg<sub>3</sub>(BO<sub>3</sub>)F<sub>3</sub>), was unveiled. In the instances of the ZrF<sub>4</sub>-B<sub>2</sub>O<sub>3</sub> and HfF<sub>4</sub>-B<sub>2</sub>O<sub>3</sub> systems, the modification in the characteristics of IR spectra was attributed to the  $\alpha \rightarrow \beta$  phase transitions occurring within the respective metal tetrafluorides. Subsequently, thin-film coatings of metal fluorides treated with the B<sub>2</sub>O<sub>3</sub> additive were fabricated employing thermal evaporation under vacuum conditions. It was determined that the refractive index of MgF<sub>2</sub> experienced a slight reduction (from 1.42 to 1.41) following the incorporation of the additive, while the mechanical strength exhibited a marginal augmentation. Conversely, the refractive index of coatings derived from Zirconium and Hafnium tetrafluorides, subsequent to heat treatment with B<sub>2</sub>O<sub>3</sub>, remained nearly constant at 1.53 across all samples. Additionally, an evaluation of the volatility of the samples was carried out, revealing a slight increase in volatility following treatment with the B<sub>2</sub>O<sub>3</sub> additive, with the exception of the MgF<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> system. A plausible mechanism elucidating the influence of B<sub>2</sub>O<sub>3</sub> on oxygen-containing impurities present in metal fluorides is proposed.

**Keywords:** metal fluorides, B<sub>2</sub>O<sub>3</sub> additive, thermal evaporation in a vacuum, thin film coating, refractive index.

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## Introduction

Metal fluorides, specifically MgF<sub>2</sub>, ZrF<sub>4</sub>, HfF<sub>4</sub>, and others, serve as film-forming materials in interference optics to yield coatings characterized by a low refractive index, rendering them transparent within the ultraviolet (UV) range of the electromagnetic spectrum [1-4].

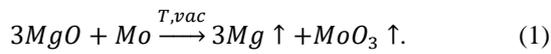
Notably, MgF<sub>2</sub> holds the distinction of being the inaugural material employed worldwide by O. Smakula, our compatriot, for the production of transmissive coatings [5].

A significant drawback inherent to fluoride materials pertains to the presence of metal oxide impurities, which exert deleterious effects on the optical and operational

attributes of the coatings derived from these materials. The methodologies proposed for the elimination or sequestration of impurities into less reactive forms [6-8] are notably time-intensive and not uniformly efficacious. In our previous work, we introduced and successfully implemented, in the case of Zinc sulfide, the utilization of Boron sesquioxide (B<sub>2</sub>O<sub>3</sub>) as an additive to bind ZnO impurities, creating a complex Zinc borate-type compound [9]. When B<sub>2</sub>O<sub>3</sub> interacts with these impurities, the oxide shell surrounding the base material grains is additionally disrupted, potentially enhancing the technological parameters governing the thermal evaporation process under vacuum conditions. Nevertheless, no prior research has investigated the

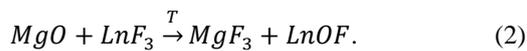
impact of the B<sub>2</sub>O<sub>3</sub> additive on the technological parameters governing the vaporization of metal fluorides in a vacuum environment or on the properties of the resultant coatings.

The primary objective of this study is to explore the interaction between B<sub>2</sub>O<sub>3</sub> and oxide impurities within Magnesium difluoride, and comparison of those for Zirconium tetrafluoride and Hafnium tetrafluoride, and its subsequent influence on the properties of these materials in both crystalline and thin-film states. It should be mentioned that Magnesium fluoride, like other metal fluorides employed in optical applications, possesses certain drawbacks, with the chief concern being the presence of oxygen-containing impurities within the material. This arises from the fact that, when focusing on the surface of MgF<sub>2</sub> crystallites (solid solutions being nonexistent within the MgF<sub>2</sub>-MgO system [10-14]), Magnesium oxide readily undergoes interactions with evaporator materials (such as Mo and Ta) during thermal evaporation in a vacuum environment, as delineated by the following chemical reaction scheme:



Thermodynamic calculations unequivocally demonstrate that Magnesium fluoride lacks the capacity for such interactions. The products arising from reaction (1), upon incorporation into the coating, lead to the degradation of its optical and operational characteristics. Oxygen-containing impurities exert analogous, if not more detrimental, effects on fiber optic materials. To mitigate their presence, a proposition is set forth involving the utilization of nonmetallic (Cl, Br) fluorides, as well as KrF<sub>2</sub> or XeF<sub>2</sub> [15]. However, it is worth noting that both the reagents themselves and the methodologies relying on them could be regarded as unconventional and, moreover, as those that pose potential hazards to the environment and human health. In the interest of completeness, it should be acknowledged that, in select instances, composites derived from the MgF<sub>2</sub>-MgO system find application as materials for the deposition of anti-reflective coatings designed for the infrared (IR) spectrum [16].

Previously, we devised a technique for immobilizing oxide impurities within Magnesium fluoride through exchange reactions involving additives of metal fluorides (LnF<sub>3</sub>, wherein Ln represents Sc, Nd, Lu) [7], as outlined by the following scheme:



The resultant lanthanide oxofluorides (their presence was confirmed through X-ray diffraction analysis) exhibit reduced susceptibility to chemical interactions with evaporator materials when compared to MgO.

In a recent study, the authors of this article demonstrated the remarkable effectiveness of Boron oxide (B<sub>2</sub>O<sub>3</sub>) as an additive for sequestering oxide impurities, notably ZnO, in Zinc sulfide and the ZnS-Ge system [9]. Furthermore, B<sub>2</sub>O<sub>3</sub> proved proficient in stabilizing Ge(II) in GeO [17, 18]. Given the ready accessibility of B<sub>2</sub>O<sub>3</sub>, primarily in the form of orthoboric acid, and the low molecular weight of the eliminated compound, it is

prudent to investigate the impact of B<sub>2</sub>O<sub>3</sub> addition on the properties of fluorides, particularly MgF<sub>2</sub>.

## I. Experimental

The initial MgF<sub>2</sub> material was procured from New Materials and Technologies (Odesa). Grade 14-3 orthoboric acid (commercially available) served as the starting material for B<sub>2</sub>O<sub>3</sub> production. The samples underwent heat treatment in a high-temperature horizontal tubular furnace, model RHTC 804-450 (manufactured by Nabertherm, Germany), within an environment of additionally purified Argon. The purification system was provided by Valco Instruments Co Inc., USA. The heat treatment occurred in multiple stages, with temperatures ranging from 250 to 400°C in increments of 50°C, with each stage having a holding time of 10 minutes. The conclusion of each stage was determined by the absence of condensation on the cold sections of the reactor. Subsequently, a series of stages at much higher temperatures, reaching up to 1000°C, were conducted with a slight excess pressure of argon. These stages featured longer holding times, with intervals of 100°C. The completion of this phase was marked by the complete absence of gas emissions. Following the heat treatment, the material was cooled to room temperature, the reactor was opened, and the material was extracted for testing. The test material underwent preliminary grinding and compression into tablets. For this study, three sample types were prepared: the original MgF<sub>2</sub>, material containing an amount of B<sub>2</sub>O<sub>3</sub> corresponding to the binding of 10% mol. MgO in MgF<sub>2</sub>, and material subjected to ethanol washing to remove residual B<sub>2</sub>O<sub>3</sub>, followed by extensive calcination to eliminate volatile Boron compounds and ethanol.

As the fundamental materials, Zirconium and Hafnium tetrafluorides of puriss grade (VO Vilnohirsik mining and metallurgical plant, Vilnohirsik, Dnipropetrovsk region) were employed, while Boron oxide, also puriss spec., was used as an additive (supplied by REAKHIM enterprise, Donetsk). Samples weighing 35g each of the ZrF<sub>4</sub>-B<sub>2</sub>O<sub>3</sub> and HfF<sub>4</sub>-B<sub>2</sub>O<sub>3</sub> systems were prepared by blending the initial components (ZrF<sub>4</sub> and HfF<sub>4</sub> with B<sub>2</sub>O<sub>3</sub>) in proportions corresponding to the content of the oxygen-containing impurity, namely the hypothetical compound ZrOF<sub>2</sub> (HfOF<sub>2</sub>), at 10% wt. Based on calculations, the B<sub>2</sub>O<sub>3</sub> content approximated 4.80% wt. and 3.07% wt. for the ZrF<sub>4</sub>-B<sub>2</sub>O<sub>3</sub> and HfF<sub>4</sub>-B<sub>2</sub>O<sub>3</sub> systems, respectively. These samples underwent heat treatment in a high-temperature vertical tubular furnace within an inert helium atmosphere. The batch was placed in a quartz glass tube, which was subsequently sealed within a reactor of identical material. The heat treatment occurred in two stages: initially, heating took place under slight vacuum conditions (10<sup>-2</sup> atm.) at 450°C for 1 hour. Following this, inert gas was introduced to achieve a pressure slightly above atmospheric (1.05-1.1 atm.), and the temperature was raised to 750°C. The samples were held at this temperature for 3 hours until a white coating appeared on the cold reactor surfaces.

X-ray phase analysis (XRD) of the products was carried out using a DRON-3M diffractometer equipped

with  $\text{CuK}\alpha$  radiation and employing the powder method. XRD patterns were acquired with focusing according to the Bragg-Brentano scheme, covering an angular range of  $10\text{--}80^\circ$  with a step size of  $0.5^\circ$  and an exposure time of 1 second. The X-ray tube anode operated at 20 mA and 30 kV, with Soler slits measuring  $002/12/025$  mm. The device exhibited an error margin of 0.01%.

Given propensity of  $\text{B}_2\text{O}_3$  for glass transition, initial identification of the samples was conducted through infrared (IR) transmission spectroscopy. Spectra were obtained from samples pressed into CsI matrices (provided by the Institute of Single Crystals of the National Academy of Sciences of Ukraine, Kharkiv) using a Fourier transform spectrometer, model Frontier, manufactured by Perkin-Elmer (USA). The wavenumber measurement spanned the range of  $200\text{--}4000\text{ cm}^{-1}$ .

Thin-film coatings were produced through thermal evaporation (resistive method) in a vacuum using the VU-1A system, with condensation onto substrates heated to  $250^\circ\text{C}$  (for  $\text{MgF}_2$  or  $\text{MgF}_2\text{--B}_2\text{O}_3$ ) and  $200^\circ\text{C}$  or  $250^\circ\text{C}$  (for  $\text{ZrF}_4$ ,  $\text{ZrF}_4\text{--B}_2\text{O}_3$ , or  $\text{HfF}_4$ ,  $\text{HfF}_4\text{--B}_2\text{O}_3$ ). The substrates employed were TF-4 glass (heavy flint), wedge-shaped plates featuring a  $12^\circ$  wedge angle. The crushed material (tablets) was placed in a molybdenum evaporator situated within a vacuum unit, which was subsequently evacuated. The molybdenum evaporator was heated by applying a current of 120-150 A, and the evaporation and coating process took place over durations of 10-30 minutes. Relative volatility of vaporized materials was estimated using a formula previously developed by our team [19]:

$$f = \frac{d_{\text{opt.}}}{\tau \cdot I^2 \cdot n}, \quad (3)$$

where  $d_{\text{opt}}$  represents the optical thickness,  $\tau$  is the coating duration in minutes,  $I$  denotes the current power passing through the evaporator in amperes, and  $n$  signifies the refractive index. The current power was carefully chosen to ensure that the coating application rates from different materials closely matched each other. The refractive index of the coating was determined by employing a wedge-shaped plate crafted from TF-4 glass. This determination was accomplished by measuring the reflection coefficient ( $R$ ) from the glass plate and identifying the extreme values of  $R$  within the interference pattern. It is noteworthy that the optical thickness ( $d_{\text{opt.}}$ ) and physical thickness ( $d$ ) are linked through the following relationship, which incorporates the refractive index ( $n$ ):

$$d_{\text{opt.}} = n \cdot d, \quad (4)$$

where  $d$  is the physical thickness of the coating.

The optical thickness was determined by the number of minima (maxima) in the interference pattern according to the formula [1]:

$$d_{\text{opt.}} = m \cdot \frac{\lambda}{4}, \quad (5)$$

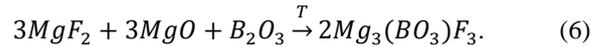
where:  $m$  is the number of minima (maxima);  $\lambda$  is the wavelength, nm.

## II. Results and discussion

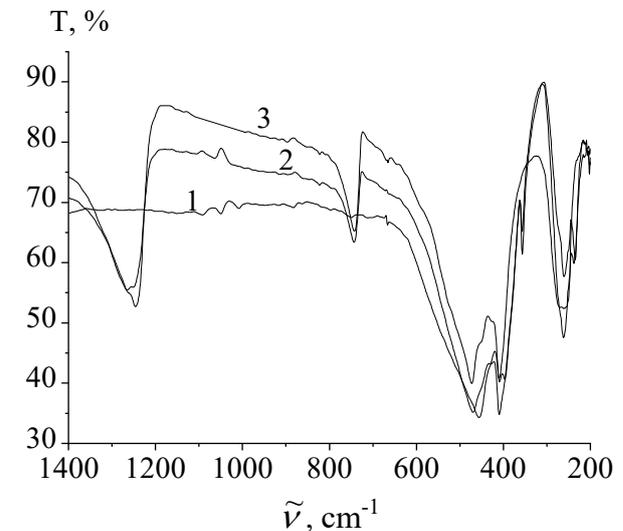
The tetragonal symmetry of  $\text{MgF}_2$  crystals in all three samples was confirmed.

The parameters of the  $\text{MgF}_2$  cell that we have refined standard value in parentheses are:

$a = 4.62485 \text{ \AA}$  ( $5.623 \text{ \AA}$ ),  $c = 3.05165 \text{ \AA}$  ( $3.0549 \text{ \AA}$ ). Space group  $P42/mnm$ . Peaks of a complex compound of Magnesium fluoroborate crystallizing in hexagonal crystal system, space group  $P63/m$ , crystallographic parameters:  $a = 8.827 \text{ \AA}$ ,  $c = 3.1021 \text{ \AA}$ ,  $\gamma = 120^\circ$ , appear due to the reaction:



The infrared transmission spectrum of the annealed  $\text{MgF}_2$  sample, in the absence of  $\text{B}_2\text{O}_3$  addition, exhibits a prominent broad band comprising two distinct bands characterized by differing widths and peak positions at  $410$  and  $456\text{ cm}^{-1}$ . Additionally, a much narrower band with a pronounced absorption peak at  $262\text{ cm}^{-1}$  is observed. Evidently, these bands correspond to the valence vibrations associated with the Mg–F bonds within the matrix and the Mg–Cl bonds present as an admixture, respectively. Furthermore, a relatively narrow yet weak peak at  $3616\text{ cm}^{-1}$  has been identified, which corresponds to the valence vibrations of the hydroxyl group (Mg–OH) (see Fig. 1).



**Fig. 1.** Infrared transmission spectra in the interval  $1400\text{--}200\text{ cm}^{-1}$  of  $\text{MgF}_2$  samples:

1 – original sample, 2 – sample after heat treatment with  $\text{B}_2\text{O}_3$ , 3 – sample after heat treatment with  $\text{B}_2\text{O}_3$ , washing off excess  $\text{B}_2\text{O}_3$  and repeated heat treatment.

The reflection spectra of coatings obtained by evaporation of  $\text{MgF}_2$  and  $\text{MgF}_2\text{--B}_2\text{O}_3$  samples on substrates are presented in Fig. 2.

The spectra exhibit a distinctive «sine wave» pattern with a variable periodicity. However, it is noteworthy that the «amplitude» of the «sine wave» for the  $\text{MgF}_2$  film appears somewhat larger in comparison to the reflection spectrum of the  $\text{MgF}_2\text{--B}_2\text{O}_3$  film. This observation provides evidence in support of the higher refractive index

of the former coating. Indeed, the calculated refractive index values at  $\lambda = 500$  nm stand at 1.42 and 1.41 for the MgF<sub>2</sub> and MgF<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> films, respectively, both significantly exceeding the value for pure MgF<sub>2</sub> films ( $n = 1.38$ ). Moreover, it is worth mentioning that the number of extremities on the curves remains practically identical, which is unsurprising considering the very close values of the optical thickness of the coatings, approximately 1300 nm (as presented in Table 1).

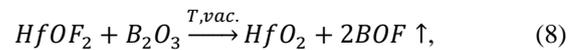
The calculated values of effective volatility, as determined by the formula provided earlier, yield results of 4.52 and 2.74 (averaged)  $10^{-3}$ . Consequently, an intriguing phenomenon emerges wherein the material subjected to heat treatment with B<sub>2</sub>O<sub>3</sub> exhibits a decrease in volatility. One plausible explanation for this phenomenon is as follows: MgF<sub>2</sub>, akin to other fluorides of active metals, encompasses MgO and MgCl<sub>2</sub> within its composition, a finding that has been previously discovered and substantiated by our research [20, 21]. These components combine to form a highly robust compound, Magnesium oxychloride (Mg<sub>2</sub>OCl<sub>2</sub>). This compound likely possesses a polymeric, and possibly amorphous structure, rendering it undetectable by X-ray phase analysis methods. When B<sub>2</sub>O<sub>3</sub> interacts with MgF<sub>2</sub> containing this particular compound, an acid-base reaction takes place at elevated temperatures, as delineated by the following potential scheme:



During the heat treatment process, a portion of MgCl<sub>2</sub> is lost, but the majority of evaporation occurs within a vacuum chamber. Given that the refractive index of MgCl<sub>2</sub> significantly exceeds that of MgF<sub>2</sub> (1.68 and 1.38, respectively), the sample heat-treated with B<sub>2</sub>O<sub>3</sub> exhibits

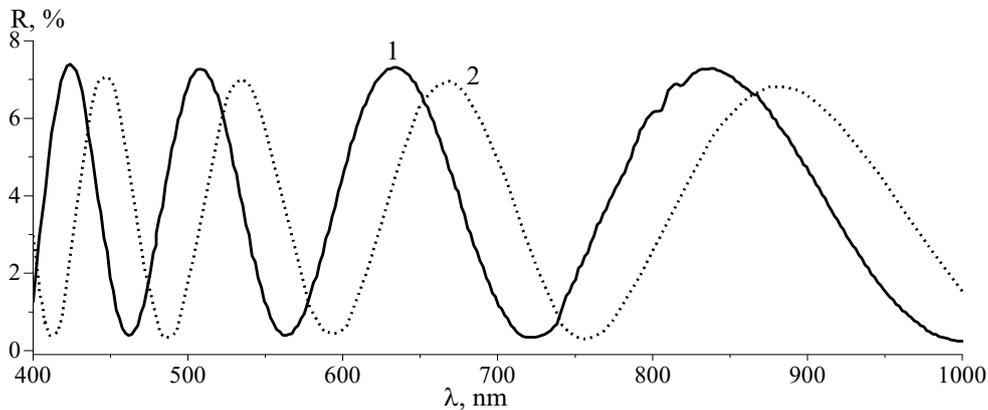
comparatively less growth in refractive index. This discrepancy is evidently attributable to the loss of a portion of MgCl<sub>2</sub>, which results in a substantial reduction in volatility (by over 1.5 times) for the treated sample. This phenomenon also has repercussions on the mechanical strength of the coatings, as outlined in Table 1. Specifically, the mechanical strength of these coatings is notably lower than that of coatings comprised of pure MgF<sub>2</sub> (2500 rotations), but it experiences an approximately 20% increase following heat treatment with B<sub>2</sub>O<sub>3</sub>.

The infrared transmission spectra of the ZrF<sub>4</sub>, ZrF<sub>4</sub>-B<sub>2</sub>O<sub>3</sub>, HfF<sub>4</sub>, and HfF<sub>4</sub>-B<sub>2</sub>O<sub>3</sub> samples exhibit overall similarity. Each spectrum features characteristic peaks within bands corresponding to the lattice (valence) vibrations of Zr(Hf)-F bonds, typically near 500 cm<sup>-1</sup> [4]. Additionally, certain IR spectra manifest bands indicative of various B-O bond vibrations. It is evident that a reaction takes place between the B<sub>2</sub>O<sub>3</sub> additive and Hafnium fluoride during thermal evaporation in a vacuum, potentially following a scheme akin to the one proposed below:



as a result of which the additive is removed by evaporation of the volatile Boron-containing product.

In these systems, the interference pattern is positioned below the contoured spectral reflectance curve of the substrate (Fig. 3) [4]. The spectral characteristics of all thin-film systems display remarkable similarity, reflecting the close alignment of their thicknesses and refractive indices, along with their nearly identical optical heterogeneity. However, subtle distinctions do exist. In the case of coatings lacking the B<sub>2</sub>O<sub>3</sub> additive, the



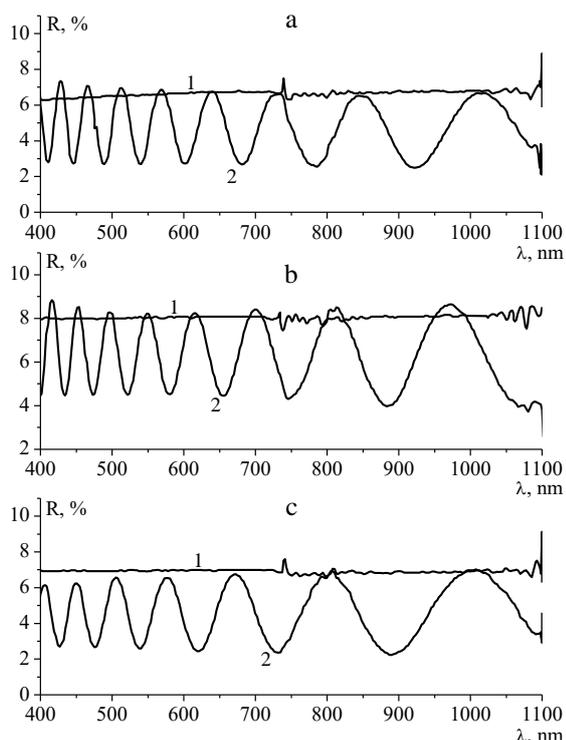
**Fig. 2.** Interference spectra of coatings fabricated from MgF<sub>2</sub> (1) and MgF<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> (2).

**Table 1.**

Parameters of thermal evaporation in vacuum and characteristics of coatings

Parameters	$I$ , A	$\tau$ , min.	$n$ ( $\lambda = 500$ nm)	$d_{\text{opt}}$ , nm	$f \cdot 10^3$ , nm/min $\cdot$ A <sup>2</sup>
MgF <sub>2</sub>	140	10	1.42	1258	4.52
MgF <sub>2</sub> -B <sub>2</sub> O <sub>3</sub>	140-150	16	1.41	1300	2.94-2.56
ZrF <sub>4</sub>	140	25	1.53	2000	2.66
ZrF <sub>4</sub> -B <sub>2</sub> O <sub>3</sub>	120	30	1.53	2000	3.03
HfF <sub>4</sub>	140	20	1.57	2000	3.25
HfF <sub>4</sub> -B <sub>2</sub> O <sub>3</sub>	120	20	1.53	2000	4.54

interference curves marginally intersect with the substrate's reflection characteristic, and the count of peaks varies slightly. Notably, the interference curve of the  $\text{HfF}_4\text{-B}_2\text{O}_3$  coating gently curves beneath the substrate's base reflectance curve, indicative of superior optical uniformity within the system. The reflection spectra featured in were employed to compute the optical parameters of the coatings, as outlined in Table 1. Additionally, the technological parameters of thermal evaporation in a vacuum are provided in the same table, from which the evaporation coefficient (volatility) is derived.



**Fig. 3.** Spectral characteristics of reflection from wedge-shaped samples of TF-4 glass without coating (1) and with coating (2): a)  $\text{ZrF}_4\text{-B}_2\text{O}_3$ ; b)  $\text{HfF}_4$ ; c)  $\text{HfF}_4\text{-B}_2\text{O}_3$  [4].

It is noteworthy that the refractive index of the coatings remains essentially constant at approximately 1.53, except for the  $\text{HfF}_4$  sample. This deviation might suggest the partial formation of certain side compounds during the evaporation process of  $\text{HfF}_4$ . In general, the  $f$  values exhibit a noticeable increase from  $\text{ZrF}_4$  to  $\text{HfF}_4$ , and this increase is further amplified when  $\text{B}_2\text{O}_3$  is added, compared to the original  $\text{ZrF}_4$  and  $\text{HfF}_4$  samples. This phenomenon suggests the higher volatility of  $\text{HfF}_4$  relative to  $\text{ZrF}_4$  under conditions of high vacuum and sufficiently low temperatures, which is an unexpected result warranting further investigation.

Concerning the impact of adding  $\text{B}_2\text{O}_3$  to  $\text{ZrF}_4$  and  $\text{HfF}_4$  on the increase in their volatility, the explanation is straightforward. It is known that fluorides and chalcogenides of metals typically contain impurities of oxides, which are primarily located on the surface of the

grains and possess higher melting and boiling temperatures, thereby impeding their evaporation. The addition of  $\text{B}_2\text{O}_3$  serves to disrupt these «shells», thereby facilitating the process of evaporation. A similar phenomenon of increased volatility was observed in the case of purified  $\text{ZnS}$ , compared to the original material containing Zinc oxide impurities. It is worth noting that the effectiveness of the  $\text{B}_2\text{O}_3$  additive is significantly lower in the case of  $\text{ZrF}_4$  compared to  $\text{HfF}_4$ , as evidenced by the ratio of  $f$  values (1.14 and 1.40, respectively). This discrepancy suggests weaker durability of oxide «shells» in  $\text{ZrF}_4$ , as well as the heightened reactivity of  $\text{B}_2\text{O}_3$  with respect to  $\text{HfO}_2$  «shells» within  $\text{HfF}_4$ .

## Conclusions

The study focused on the influence of  $\text{B}_2\text{O}_3$  addition during heat treatment on various thin-film coatings. It was observed that  $\text{B}_2\text{O}_3$  addition led to an improvement in the refractive indices of  $\text{MgF}_2$ -based coatings, enhancing their optical properties for potential optical applications.

Conversely, in the case of  $\text{ZrF}_4$  and  $\text{HfF}_4$  coatings,  $\text{B}_2\text{O}_3$  addition significantly increased their volatility. This effect was attributed to the disruption of oxide impurities on grain surfaces, with a more pronounced impact observed in  $\text{HfF}_4$  coatings compared to  $\text{ZrF}_4$ .

These findings underscore the multifaceted effects of  $\text{B}_2\text{O}_3$  in thin-film coating processes, emphasizing its potential for tailoring optical properties and volatility in different material systems. Further research is warranted to delve into the underlying mechanisms and refine the optimization of these coatings for specific applications.

**Conflicts of interest:** *The authors declare no conflict of interest.*

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## Вплив додавання $V_2O_3$ до фторидів Магнію, Цирконію, Гафнію на параметри утворених з них тонких плівок

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Вперше досліджено вплив добавки  $V_2O_3$  на фториди Магнію, Цирконію та Гафнію, що охоплює їх структурні та оптичні властивості. Фазовий склад системи  $MgF_2-V_2O_3$  встановлено за допомогою рентгенівського фазового аналізу та інфрачервоної (ІЧ) спектроскопії пропускання. Примітно, що було виявлено помітну присутність новоутвореної фази, яка характеризується як комплексна сполука – фторборат Магнію ( $Mg_3(VO_3)F_3$ ). У випадках систем  $ZrF_4-V_2O_3$  і  $HfF_4-V_2O_3$  зміна характеристик ІЧ-спектрів пояснюється фазовими переходами  $\alpha \rightarrow \beta$ , що відбуваються у відповідних тетрафторидах металів. Згодом методом термічного випаровування в умовах вакууму були виготовлені тонкоплівкові покриття з фторидів металів, оброблених добавкою  $V_2O_3$ . Було визначено, що показник заломлення  $MgF_2$  зазнав незначного зниження (з 1.42 до 1.41) після введення добавки, тоді як механічна міцність продемонструвала незначне збільшення. І навпаки, показник заломлення покриттів, отриманих з тетрафторидів Цирконію та Гафнію, після термічної обробки  $V_2O_3$ , залишався майже постійним і становив 1.53 для всіх зразків. Крім того, була проведена оцінка леткості зразків, яка виявила незначне збільшення леткості після обробки добавкою  $V_2O_3$ , за винятком системи  $MgF_2-V_2O_3$ . Запропоновано вірогідний механізм, що пояснює вплив  $V_2O_3$  на оксигенвмісні домішки, присутні у фторидах металів.

**Ключові слова:** фториди металів, добавка  $V_2O_3$ , термічне випаровування у вакуумі, тонкоплівкове покриття, показник заломлення.