

V.F. Zinchenko¹, G.V. Volchak¹, O.V. Mozkova², O.H. Yeriomin¹, P.H. Doha¹

Effect of B₂O₃ Addition on Optical Properties of Zirconium and Hafnium Tetrafluorides in Polycrystalline and Thin Film States

¹O.V. Bogatsky Physico-Chemical Institute of National Academy of Sciences of Ukraine, Odesa, Ukraine, vfzinchenko@ukr.net
²State Enterprise for Special Instrument Making «Arsenal», Kyiv, Ukraine, olgamozk@ukr.net

For the first time, the effect of B₂O₃ additive on the IR transmission spectra of ZrF₄ and HfF₄ samples and the optical properties of the coatings obtained from them was investigated. A significant difference in the shape of the absorption bands and the position of the vibration peaks of the Zirconium tetrafluoride and Hafnium tetrafluoride bonds was revealed. An assumption is made about the influence of ZrF₄ polymorphism on the ratio of the vapor pressures of the specified compounds in the region of the conditional temperature of evaporation in a deep vacuum. The positive effect of the B₂O₃ additive on the rate of evaporation of system samples and condensation on substrates is shown. The values of the refractive indices of the coatings are about 1.53. An exception is the refractive index of the HfF₄ coating (1.57), which can be attributed to the alternative (monoclinic) syngony of its crystal structure.

Keywords: Zirconium tetrafluoride, Hafnium tetrafluoride, B₂O₃ additive, IR transmission spectra, thermal evaporation in vacuum, coating, refractive index.

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Introduction

Metal fluorides, in particular MgF₂, ZrF₄, HfF₄ and some others, are used as film-forming materials (FFM) in interference optics to obtain coatings with a low refractive index, transparent in the UV range of the spectrum [1-3]. A significant disadvantage of fluoride materials is the presence of impurities of oxides of the metals themselves, which negatively affect the optical and operational properties of the coatings obtained from them. The proposed methods of removing or binding impurities into less active forms [4-6] are quite time-consuming and not always effective. We proposed and successfully implemented in the case of zinc sulfide the use of Boron sesquioxide (B₂O₃) additive as a binder of ZnO admixture [7] in a complex zinc borate-type compound. When B₂O₃ interacts with the admixture, the oxide shell of the grains of the base material is additionally destroyed, which should improve the technological parameters of the process of thermal evaporation of FFM in a vacuum. Research on the influence of B₂O₃ additive on technological parameters of vaporization of metal

fluorides in vacuum and properties of coatings obtained from them was not carried out. The aim of the work is to study the interaction of B₂O₃ with oxide impurities in Zirconium (ZrF₄) and Hafnium (HfF₄) tetrafluorides and its effect on the properties of materials in crystalline and thin-film states.

It is generally accepted that ZrF₄ has higher volatility (vapor pressure) compared to HfF₄. At the same time, it is important to evaluate it both in the high-temperature region (boiling or sublimation temperature at P = 1 atm.) and in the region of relatively low temperatures during thermal evaporation in a deep vacuum (P = 10⁻⁵ atm.). The last value is an important technological parameter and it is called the conditional or working temperature of the process of thermal evaporation in a vacuum. At the same time, it should be taken into account that ZrF₄ exists in at least two polymorphic modifications – cubic and monoclinic [8] with a transition temperature of 690°C (according to other data – 450°C [9]).

I. Methods of synthesis and experimental research

As basic materials – Zirconium and Hafnium tetrafluorides – reagents of the qualification of *puriss.* are used: (VO Vilnohirs'k mining and metallurgical plant, Vilnohirs'k, Dnipropetrovsk region), and as an additive material – Boron oxide – a reagent of qualification of *puriss. spec.* (REAKHIM enterprise, Donetsk).

Samples of the ZrF₄–B₂O₃ and HfF₄–B₂O₃ systems weighing of 35 g each were obtained by mixing the initial components (ZrF₄ and HfF₄ with B₂O₃) in the ratio provided by the content of the oxygen-containing impurity – the hypothetical compound ZrOF₂ (HfOF₂) in 10% wt. At the same time, it was considered that the interaction between the impurity and the B₂O₃ additive occurs according to the following schemes:



According to the calculations, the B₂O₃ content is about 4.80 %wt. and 3.07%wt. for the ZrF₄–B₂O₃ and HfF₄–B₂O₃ systems, respectively.

Samples of the above systems were subjected to heat treatment in a high-temperature tubular (vertical) furnace in an inert gas (helium) medium. The batch was placed in a tube made of quartz glass, and it, in turn, was placed in a sealed reactor made of the same material. Heat treatment was carried out in two stages. The first of them was heated with holding under a shallow vacuum (10⁻² atm.) at a temperature of 450°C for 1 hour. Next, inert gas was introduced to a pressure slightly higher than atmospheric (1.05–1.1 atm.), and the temperature was raised to 750°C, at which the samples were kept for 3 hours until the appearance of a white coating on the cold parts of the reactor. After cooling, the samples of the systems were weighed on analytical balances; mass loss was 0.2286 g, or 0.65 %wt. and 0.2565 g or 0.73 %wt. for the ZrF₄–B₂O₃ and HfF₄–B₂O₃ systems, respectively. In terms of the amount of substance that flew out, it is 1.367·10⁻³ and 1.008·10⁻³ mol, respectively, for the ZrF₄–B₂O₃ and HfF₄–B₂O₃ samples. Judging by the latest data, the volatility of ZrF₄ at a temperature of 750°C is significantly higher than that of HfF₄. The film-forming material ZrF₄–B₂O₃ (HfF₄–B₂O₃) is a white sintered sample with a slight greyish tint.

The starting reagents, the heat obtained and the residues after thermal evaporation in a vacuum were studied by the method of IR transmission spectroscopy. IR transmission spectra were recorded for the samples pressed into the CsI matrix of the qualification *puriss. spec.* (Institute of Single Crystals of the National Academy of Sciences of Ukraine, Kharkiv), pre-dehydrated by heating at 180°C, in the mass ratio sample: matrix as 1:20. Spectra were recorded on a Frontier Fourier transform spectrophotometer (Perkin-Elmer, USA) in the range of wave numbers ($\tilde{\nu}$) 4000–200 cm⁻¹. All the studied materials were ground in an agate mortar immediately before recording the spectra.

Thin-film coatings were obtained by thermal evaporation (resistive version) in a vacuum on the VU-1A installation and condensation on substrates heated to 200°C, of two types: TF-4 glass (heavy flint, wedge-shaped plate with a wedge angle of 12°) and calcium fluoride (plane-parallel plate 1 mm thick).

The crushed material was placed in a molybdenum evaporator, which was placed in a vacuum unit, evacuated, and the heater was turned on. Evaporation and coating mode: current through molybdenum evaporator – 120–140 A; duration of evaporation and coating – 20–30 min.

The relative volatility of vaporized materials was estimated according to the formula proposed by us earlier [10]:

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

where $d_{\text{opt.}}$ – optical thickness, which is a constant value of 2000 nm; τ – coating duration, min.; I is the current through the evaporator, A; n is the refractive index.

The power of the current was chosen in such a way that the speed of applying coatings from different materials was close to each other.

The refractive index of the coating was determined on a wedge-shaped plate made of TF-4 glass by measuring the reflection coefficient (R) from it, determining the extreme values of R in the interference pattern. It should be noted that the optical ($d_{\text{opt.}}$) and physical (d) thicknesses are related by the ratio through 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]:

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

where m is the number of minima (maxima); λ is the wavelength, nm.

Measurements were performed on an Epsilon device (Izovak, Belarus) and calculated using the OptiLayer program. The spectral transmittance curves of the calcium fluoride substrate and the coatings applied to it were recorded using a Shimadzu UV 2501-PS device (Shimadzu, Japan).

II. Experimental results and their discussion

IR transmission spectra of samples of ZrF₄–B₂O₃ (a) and HfF₄–B₂O₃ (b) systems are presented in Fig. 1, and the position of the bands is in Tab. 1.

In general, they are quite similar to each other. All of them contain characteristic peaks in the bands corresponding to lattice stretching vibrations of Zr(Hf)–O bonds near 500 cm⁻¹ and bending vibrations near 250 cm⁻¹.

Table 1

Positions of absorption peaks on the IR spectra of crystalline Zirconium and Hafnium tetrafluorides

Sample	Wave number, cm ⁻¹
Initial ZrF ₄	3420 1637 1410 1060 668 515 375* 293 270
ZrF ₄ , residue after evaporation	3426 2319 1636 1066* 678* 612* 515 451* 406 376 285
ZrF ₄ -B ₂ O ₃ , sintered	3568 3487 1622 1411* 873 744 670 609 502 439* 376 355 282* 270 255 238
Initial HfF ₄	3451 1644 694* 670 624* 531 467* 416 301* 254 248 244 225
HfF ₄ , residue after evaporation	3489 1630 901 763 619 516 470 420 365 338 266
HfF ₄ -B ₂ O ₃ , residue after evaporation	2328* 707* 531* 514* 457 410 259

Note: * – Bend, shoulder. High intensity peaks are highlighted in bold.

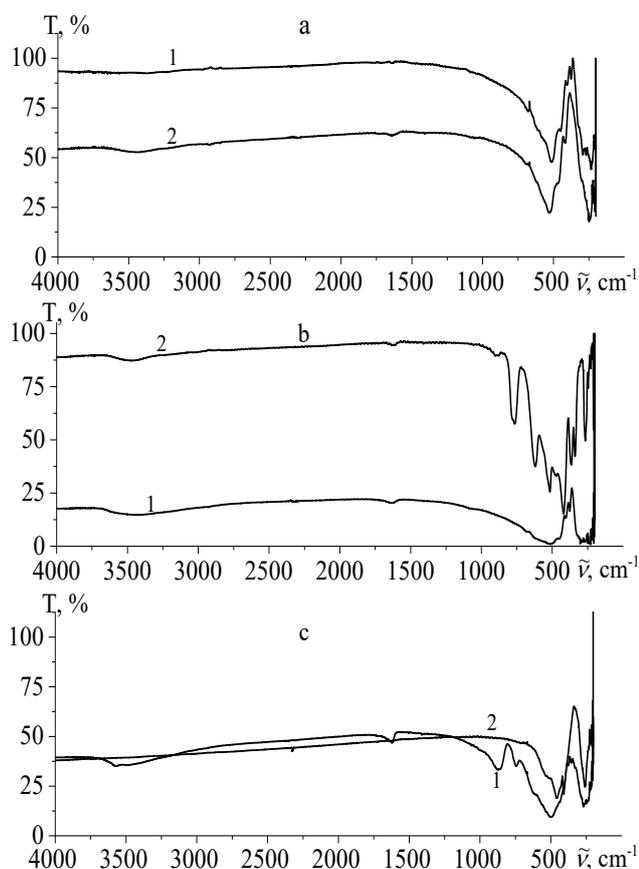
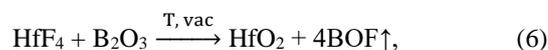


Fig. 1. IR transmission spectra of samples of the ZrF₄-B₂O₃ (1) and HfF₄-B₂O₃ (2) systems: a – initial samples (ZrF₄, HfF₄); b – residues after evaporation of ZrF₄, HfF₄ in a vacuum; c – sintered ZrF₄-B₂O₃ sample, residue after evaporation of HfF₄-B₂O₃ in vacuum.

There are also bands of valence and O-H bending vibrations of sorption (crystallization) water, especially for samples based on ZrF₄. IR spectra of ZrF₄-B₂O₃ samples reveal bands characteristic of B-O bond oscillations of various types. The transmission spectrum of the residue after evaporation of HfF₄ with a significant number of well-separated peaks of high intensity is interesting. Obviously, in this case, the monoclinic modification of HfF₄ was found in a more or less individual form. The high level of transmission of the

material of this modification in the IR range of the spectrum is also characteristic (twice as high as other samples). At the same time, the level of transmittance of the residue after evaporation of ZrF₄ is extremely low (about 10%), which perhaps indicates the favor of the cubic modification of this FFM sample. In all other cases, there is obviously a mixture of tetragonal (cubic) and monoclinic modifications. The complete absence of vibration peaks of B-O bonds in the transmission spectrum of the residue after evaporation of the HfF₄-B₂O₃ sample is incomprehensible. Obviously, a reaction occurs between the B₂O₃ additive and Hafnium fluoride during thermal evaporation in a vacuum according to a possible scheme:



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

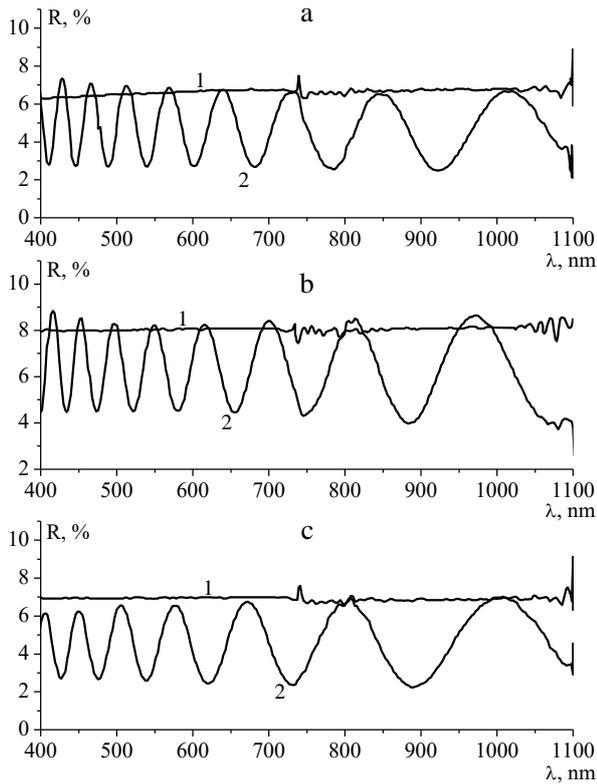
Wedge-shaped substrates made of TF-4 glass (heavy flint) with a high refractive index coated with ZrF₄-B₂O₃, HfF₄, and HfF₄-B₂O₃ are obscured optical systems, since the interference pattern is located below the contoured spectral reflectance curve of the substrate.

The spectral characteristics of all systems are very similar to each other, which reflects the proximity of the thicknesses and refractive indices of the coatings and their approximately the same optical heterogeneity. However, certain differences still exist. Thus, in the case of FFM coatings not doped with B₂O₃ additive, the interference curves slightly cross the reflection characteristic of the substrate, and the number of peaks is somewhat different. The interference curve of the HfF₄-B₂O₃ coating slightly bends below the base reflectance curve of the substrate, which indicates greater optical homogeneity of the system.

From the reflection spectra presented in Fig. 2, the optical parameters of the coatings were calculated (Tab. 2). The technological parameters of thermal evaporation of FFM in a vacuum are also given there, from which the evaporation coefficient (volatility) is calculated.

Table 2Parameters of thermal evaporation in vacuum and characteristics of coatings of MF₄ (M – Zr, Hf)–B₂O₃ systems

Parameters Sample	I, A	τ , min.	$n(\lambda = 500 \text{ nm})$	$d_{\text{opt.}}$, nm	$f \cdot 10^3$, nm/min·A ²
ZrF ₄	140	25	1.53	2000	2.66
ZrF ₄ –B ₂ O ₃	120	30	1.53	2000	3.03
HfF ₄	140	20	1.57	2000	3.25
HfF ₄ –B ₂ O ₃	120	20	1.53	2000	4.54

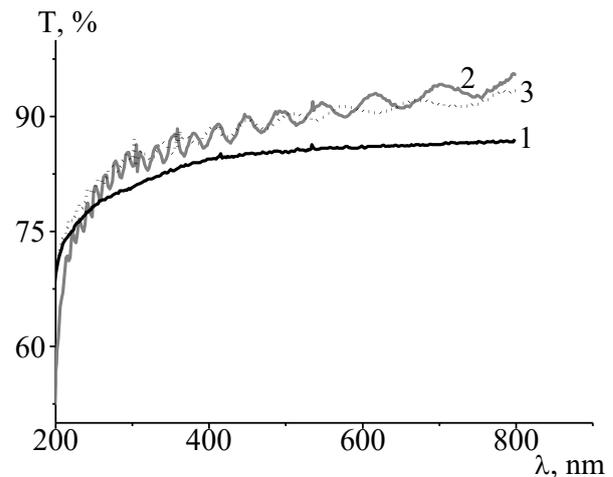
**Fig. 2.** Spectral characteristics of reflection from wedge-shaped samples of TF-4 glass without coating (1) and with coating (2): a) ZrF₄–B₂O₃; b) HfF₄; c) HfF₄–B₂O₃.

It should be noted that the value of the refractive index of the coatings is practically constant (1.53), except for the HfF₄ sample. Perhaps this indicates the partial formation of some side compounds in the process of evaporation of HfF₄. In general, f values increase noticeably from ZrF₄ to HfF₄ and when adding B₂O₃ compared to the initial ZrF₄ and HfF₄ samples. The former purportedly indicates the higher volatility of HfF₄ initial to ZrF₄ under conditions of high vacuum and sufficiently low temperatures, which is a somewhat unexpected result that needs further verification.

As for the effect of adding B₂O₃ to ZrF₄ and HfF₄ on the growth of their volatility, its explanation is clear. It is known that fluorides and chalcogenides of metals, as a rule, contain impurities of oxides that are localized on the surface of the grains of the main FFM and, having higher melting and boiling temperatures, prevent its evaporation. The addition of B₂O₃ contributes to the destruction of these «shells» and thereby unlocks the process of

evaporation of FFM. A similar phenomenon of increased volatility was observed in the case of ZnS purified from zinc oxide impurities compared to the original material. It should be noted that the effectiveness of the addition of B₂O₃ in the case of ZrF₄ is significantly lower compared to HfF₄ (the ratio of f values is 1.14 and 1.40, respectively); on the one hand, this should indicate the weak durability of oxide «shells» in and, on the other hand, the higher activity of B₂O₃ with respect to HfO₂ «shells» in HfF₄.

Spectral characteristics of substrates made of different materials with different refractive indices and coatings of various FFMs are presented in Fig. 2, 3.

**Fig. 3.** Spectral characteristics of coating samples on a Calcium fluoride substrate: 1 – substrate without coating; 2 – HfF₄-coated substrate; 3 – substrate with HfF₄–B₂O₃ coating.

In the case of coatings on a substrate of Calcium fluoride, which has a lower refractive index than that of HfF₄, the coating is translucent, and the transmission spectra lie above the corresponding curve for the substrate in a significant interval; only in the region below 400 nm do they converge. At a wavelength of about 250 nm, the spectral transmittance curve of the HfF₄ coating crosses the corresponding curve for the substrate, indicating the position of the short-wavelength limit of the transparency region. Taking into account the value of the refractive index of HfF₄ and HfF₄–B₂O₃ coatings, which are 1.57 and 1.53, respectively, it is possible to explain the ratio of their optical transparency limits. As follows from Moss's law, their ratio is:

$$\lambda_1/\lambda_2 = (n_1/n_2)^4. \quad (7)$$

In the region where the fundamental absorption begins (transmission less than 70 %), the values of λ_1 and λ_2 are respectively equal to 220 and 200 nm, which qualitatively corresponds to the equation written above: indeed, the ratio on the left side of the equation is ≈ 1.10 , while with of the right side – 1.11. The interference coatings are located above the substrate transmission curve in almost the entire spectral range for both HfF₄ and HfF₄-B₂O₃.

Conclusions

1. The nature of the IR transmission spectra of the starting substances ZrF₄ and HfF₄ and composites with the addition of B₂O₃ indicates the influence of the latter on the crystal structure of the material with stabilization of low-temperature modification, probably cubic (tetragonal) for ZrF₄ and monoclinic for HfF₄.

2. The value of the refractive index of the studied

samples was established, which is 1.53 (1.57 for HfF₄). The introduction of the B₂O₃ additive significantly increases the rate of application of coatings, and therefore the volatility of materials. The volatility of HfF₄ when evaporated in a deep vacuum and at room temperature exceeds that of ZrF₄.

Zinchenko V.F. – Professor, Doctor of Chemistry, Head of the in Chemistry of Functional Inorganic Materials Department;

Volchak G.V. – PhD (in chem.), Senior Research Fellow in Chemistry of Functional Inorganic Materials Department;

Mozkova O.V. – Head of the laboratory of optical coatings;

Yeriomin O.H. – PhD (in chem.) in Chemistry of Functional Inorganic Materials Department;

Doha P.H. – Junior Researcher in Chemistry of Functional Inorganic Materials Department.

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В.Ф. Зінченко¹, Г.В.Вольчак¹, О.В. Мозкова², О.Г. Єр'омін¹, П.Г. Дога¹

Вплив добавки B_2O_3 на оптичні властивості тетрафторидів Цирконію та Гафнію у полікристалічному й тонкоплівковому станах

¹Фізико-хімічний інститут ім. О.В. Богатського НАН України, Одеса, Україна, vzinchenko@ukr.net

²Казенне підприємство спеціального приладобудування «Арсенал», Київ, Україна, olgamozk@ukr.net

Уперше досліджено вплив добавки B_2O_3 на ІЧ спектри пропускання зразків ZrF_4 та HfF_4 та оптичні властивості одержаних з них покриттів. Виявлено суттєву відмінність форми смуг поглинання та положення піків коливань зв'язків тетрафториду Цирконію та тетрафториду Гафнію. Висунуто припущення про вплив поліморфізму ZrF_4 на співвідношення пружностей пари зазначених сполук в області умовної температури випаровування у глибокому вакуумі. Показано позитивний вплив добавки B_2O_3 на швидкість випаровування зразків систем та конденсації на підкладках. Значення показників заломлення покриттів становлять біля 1,53. Виняток становить показник заломлення покриття з HfF_4 (1,57), який можна віднести на рахунок моноклінної сингонії його кристалічної структури.

Ключові слова: тетрафторид Цирконію, тетрафторид Гафнію, добавка B_2O_3 , ІЧ спектри пропускання, термічне випаровування у вакуумі, покриття, показник заломлення.