The study of the optical constants of BaYF₅ and SrY₂F₈ films

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Abstract. Double fluoride films are used as low-refractive films in the mid-IR range of the spectrum. They have better moisture resistance and hardness than fluorides. Their using in the interference coatings requires knowledge of the optical constants of the films. The paper describes a spectrophotometric method for determining the optical constants of films with absorption based on the correction of the reflection and transmission spectra. The results of a study of optical constants also are presented in this paper: the refractive indices \( n \) and the extinction coefficients \( k \) of BaYF₅ and SrY₂F₈ films in the spectral range of 1.5–16 \( \mu \)m.

Fluoride films are highly transparent and have a low refractive index in the mid-IR spectral range of 1-15 \( \mu \)m [1-3]. Therefore, they are widely used as the film-forming materials with a low refractive index. The films BaF₂ have the lowest absorption among fluoride films. Their disadvantage is a low mechanical strength and a poor moisture resistance. In this regard, a permanent search of materials for low-refractive films free from these disadvantages is being carried out.

Among the fundamental optical characteristics of substances one of the main places belongs to optical constants (OC) - refractive index \( n \) and absorption coefficient \( k \) [4]. OC of the films of the substances are needed for the design of multilayer interference coatings. There are a number of methods for the investigation of OC. The spectrophotometric methods are the most widespread. They are based on the measurement of spectral values of the reflection \( R \) and transmission \( T \). They are traditional for studying the optical constants of thin films and are well covered in the literature [1-5]. They are usually called the \((R, T)\) - methods.

Spectrophotometric methods give us a possibility to obtain the dispersion characteristics of refractive and absorption indices of the film over the entire required spectrum range. The accuracy of the method is determined by two factors. First, the error in measuring the transmission (or reflection), i.e. measurement technique. Secondly, the method of processing spectral characteristics, i.e. finding OC from the spectra.

Currently, there is no single universal method for determining the optical constants of the real films from spectrophotometric data. The solution to such inverse problem is difficult. This is due to the incorrectness and ambiguity of the problem of obtaining optical constants from spectra [3, 6, 7]. Analytical and numerical methods are used to find OC films from \( T, R \) spectra. The first group involves the search of convenient analytical expressions for direct calculation of optical constants in various special cases [3, 8]. It is used when finding OC of non-absorbent films. The second group is based on various optimization methods [3, 6, 9]. The search is based on solving of a system of nonlinear equations.
for the energy reflection and transmission coefficients of the film-substrate system at a wavelength $\lambda$ by minimizing the quality function $F$:

$$F = \sum_{i=1}^{N} \left| L_{\text{calc}}(d, n_i, \lambda_i) - L_{\exp}(\lambda_i) \right| W(\lambda_i),$$  

where $L_{\text{calc}}(d, n_i, \lambda_i)$ and $L_{\exp}(\lambda_i)$ are the calculated and specified or experimentally obtained value of the transmission spectrum $T$ or reflection $R$ for the current value of the wavelength $\lambda_i$, $d$ is the film thickness. $W(\lambda_i)$ is the weight multiplier at the point $i$ specified by the user. This method, which was proposed for studying the thin films in [9], was also previously used to find OC of nonabsorbent films.

In this work, the third direction of the search for OC films and materials of transmission optics is implemented. It is based on the correction of the spectra for their absorption [10, 11] with the subsequent use of minimization methods for the spectra of films free of the absorption [3, 5, 6, 9]. After correction, the absorption in the spectra is zero ($A=0$). Thus, one variable is excluded from the processing of spectra. It makes easier the task of searching for OC using the known methods. For this one can find the average refractive index $\langle n \rangle$ and the film thickness $h$ using a region of the spectrum of the film free from absorption [9].

The examples of binary optical films of fluorides, including PbF$_2$ - YF$_3$, BaF$_2$ - YF$_3$ and Ba$_{1-x}$Mg$_x$F$_2$ are given in works [3, 11]. It is noted that optical scattering losses are reduced in the binary films, mechanical strength and moisture resistance increase. Other variants of binary and, in some cases, ternary systems of fluorides, chalcogenides and tellurides are also possible. The study of properties of their thin films has the great practical importance. Therefore, in this work we study films of binary fluorides BaYF$_3$ and SrY$_2$F$_8$ in the spectral range of 1.3-16 $\mu$m. To determine the optical constants, we used the original technique of the authors [11], based on correction of the reflection and transmission spectra of the films for absorption in them.

Let us consider the method for correcting the spectra of films for absorption [11]. ZnSe was used as a non-absorbing substrate. The spectrophotometric method is used to find the experimental spectra $T$ and $R$ from where the absorption spectra $A=1-T-R$ are found. Transmission $T$, reflection $R$ and absorption $A$ are connected by the energy conservation law $T+R+A=1$. Absorption $A$ can be divided into two parts. One is that part of the energy that is lost in transmission - $A_T$, the second is that part of the energy that is lost in reflection $A_R$:

$$A = A_T + A_R,$$  

$A_T$ and $A_R$ are calculated using the formulas:

$$A_R = R_0 - R, \quad A_T = T_0 - T,$$  

where $R_0$, $T_0$ are the reflection and transmission coefficients of the nonabsorbent film. The correction functions [10, 11] $f_r$ and $f_i$ are used to find $A_R$ and $A_T$, which determine the contribution of the total absorption $A$ to $A_R$ and $A_T$:

$$A_R = f_r A, \quad A_T = f_i A,$$  

$f_r$ and $f_i$ are normalized as follows from formula (1):

$$f_r + f_i = 1$$  

The correction functions $f_r$ and $f_i$ can be defined as

$$f_r = \frac{R_0 - R}{A}, \quad f_i = \frac{T_0 - T}{A}.$$  

Formulas (6) are valid for nonzero absorption. If the absorption is $A \rightarrow 0$, then the uncertainty is $0/0$. Therefore, a small absorption is introduced in the entire region of finding the correction function.
By calculating $A_R$ and $A_T$ according to formulas (4, 6) and adding them to the reflection and transmission coefficients for each wavelength it is possible to correct the spectra for absorption and obtain the values of $R_0$ and $T_0$:

$$R_{cor0} = R_0 = R + f_r A, \quad T_{cor0} = T_0 = T + f_t A$$

(7)

A calculation of $f_r$ and $f_t$ is possible only if we know $R_0$ or $T_0$ that we want to find. In other words, it is also a reverse incorrected problem. Therefore, the film model was used to find $f_r$ and $f_t$. The model contains absorption spectra similar to the absorption spectra of real films, as well as the refractive index and thickness, close to the investigated film. We used the refractive index $<n>$ and the film thickness $h$ found from the absorption-free spectral regions. The models were used to calculate the correction functions.

We used the FilmManager spectra analysis and synthesis program [13] to find the optical constants of the correction functions and calculates the spectra. The program provides the possibility of introducing an experimental or synthesized spectrum with the subsequent finding of optical constants in the selected part of the spectrum.

The optical films BaYF$_5$ and SrY$_2$F$_8$ were prepared by thermal evaporation of the sintered starting materials in vacuum at a substrate temperature of 150°C. To increase the adhesion and mechanical strength of the films during deposition, an ion-assistance was used [14]. The spectra of the films were recorded on a Bruken Vertex 70 Fourier spectrophotometer. Mechanically, BaYF$_5$ and SrY$_2$F$_8$ films are much harder and more moisture resistant than similar films of barium fluoride. Yttrium fluoride films are mechanically the most durable. However, YF$_3$ films are destroyed at a thickness of several micrometers.

Figure 1 and figure 2 show the experimental spectra of BaYF$_5$ and SrY$_2$F$_8$ films: transmission (curve 1), reflection (curve 2) and absorption (curve 3) of the film, before correction and transmission (curve 4) and reflection (curve 5) spectra after correction.

The numerical values of the correction functions $f_r$ and $f_t$ were found according to (6) to correct the spectra. They were found using the model described above. As shown in [12], an exact coincidence with the experimental spectra is not required. Approximate values are sufficient. The calculation of the correction functions showed that in the region of real absorption bands (3 and 6 μm) the correction functions differ little from the averaged values of the correction functions $<f_r>$=0.36 and $<f_t>$=0.65. The difference of these spectra from the spectra with precise correction does not exceed (in the range up to 12 μm) 0.005.

All calculations: spectra, correction functions, optical constants and processing of spectra were carried out using the FilmAnalysis program [13]. The program provides the calculation of spectra and the search of the optical constants of films and interference coatings using the minimization of the quality function $F$ by the random search method and the Powell method [6]. For a single film, $F$ has the form given by (1).

The method of calculation the refractive index using the FilmAnalysis program is as follows. The corrected spectra were used to find the geometric thickness of the film. We selected the spectral region corresponding to the first three extrema (1.45–2.1 μm) on the corrected transmission spectrum $T_0(\lambda)$. Then, the geometric film thickness $h_2$ and the average value of the refractive index $<n_2>$ were calculated using the FilmAnalysis program.

The average value $<n_2>$ is taken as an initial approximation. Then the original spectrum is divided into small sections of 0.25 μm. After that, for the first section, search $n_3$, giving the minimum discrepancy between the initial and calculated spectra. For the next section, its own $n_2$ is searched, which differs from the previous value by ±0.01. Then these actions are repeated until the end of the spectrum.
Analysis of the use of the program showed that the calculation of optical constants by numerical methods has a drawback. There is the possibility of "jumping" from one refractive index to another at some point of the spectrum due to the ambiguity of solution of the equation. To avoid this, variations in refractive index were minimized. For each subsequent part of the spectrum, the possibilities of varying the refractive indices were limited and $n_2$ was taken, which differed from the previous value by ±0.01. This made it possible to eliminate "jumping" to the adjacent solution of the equation for the spectrum of films. We have not found a discussion of such "jumping" in the literature.

To find the extinction coefficient $k$ we used the absorption spectra of the substrate of a zinc selenide $A_S$ and the absorption spectra of a substrate with a film $A_{FS}$. The absorption in the film $A_F$ was determined based on the following considerations. The total absorption $A_{FS}$ can be expanded in a power series in $A_S$ and $A_F$. Since $A_S^2 \ll 1$, $A_F^2 \ll 1$, $A_S \cdot A_F \ll 1$, neglecting the terms of the second order of smallness, we have $A_{FS} = A_F + A_S$, $A_F = A_{FS} - A_S$, whence we find the absorption in the film $A_F$.

The calculation of $k$ was carried out numerically. For this, we used the FilmAnalisyS program [13], which has possibility of the calculation of $A_{FS}$, $A_S$, and $A_F$ from the given values of the extinction coefficient of the film and substrate and their thicknesses, as well as the inverse problem. The absorption in the film $A_F$ and the extinction coefficient $k$ are related by the relationship [4]:

$$A_F = 4\pi nk d / \lambda.$$  \hspace{1cm} (8)
Here $d=1.841 \, \mu m$ is the geometric thickness of the film, which is determined from the spectra. The results of calculations of the absorption spectra $A_F$ and extinction coefficients $k$ for CaY$_2$F$_8$ and MgBaF$_4$ are shown in figure 3 and 4.

Figure 3 show the results of calculations of the refractive index $n$ and the extinction coefficient $k$ of BaYF$_5$, and figure 4 - SrY$_2$F$_8$ in the range of 1.5–16 $\mu m$ obtained by the above method.

![Figure 3. Spectra of BaYF$_5$ films: the refractive index $n$ and the extinction coefficient $k$.](image1)

![Figure 4. Spectra of SrY$_2$F$_8$ films: the refractive index $n$ and the extinction coefficient $k$.](image2)

In this paper, we consider a method of finding the optical constants of absorbing films (refractive indices $n$ and extinction coefficients $k$) from the reflection and transmission spectra. The spectra of the films were preliminarily corrected for absorption in them. For films by now free from absorption, the dispersion dependences of the refractive index and extinction of SrY$_2$F$_8$ and BaYF$_5$ in the range 1.5–16 $\mu m$ on a zinc selenide substrate have been calculated by numerical methods. There are no literature data on the optical constants of the described bifluorides. The films of BaYF$_5$ have the minimum absorption almost like that of BaF$_2$ film. Optical films of double fluorides are mechanically strong, moisture resistant and did not change their parameters after long-term storage.
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