Investigation of structural and optical properties of solid solution films in PbF$_2$-YF$_3$ system

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Abstract. This work deals with the physical chemistry of metal fluorides and their thin films applicable in thin-film optics and is related to the investigation of the structural and optical properties of solid solution films in the system PbF$_2$-YF$_3$ for the creation of interference coatings for the near- and mid-infrared spectra.

1. Introduction

Nowadays, the thin-film optical coating technology requires films based on low-refractive film-forming materials transparent in the spectral range with wavelengths exceeding 10–12 µm [1].

Traditionally, films with a low refractive index are obtained from fluorides of the following metals: calcium (CaF$_2$), barium (BaF$_2$), lead (PbF$_2$), yttrium (YF$_3$) and some others [2, 3]. However, there are a number of constraints to the successful application of the films prepared from these materials [1].

The problem of practical application of films with a low refractive index arises from the fact that the production of coatings operating in the mid-infrared region requires sufficiently thick layers with the physical thickness up to 1 µm or more. As a result, severe mechanical stresses build up both in the layers themselves and in the multilayer structures based on these layers, which often causes the coating to peel.

For example, the coatings containing YF$_3$ layers with the overall thickness of several micrometers become extremely unstable with changes in the temperature and are prone to peeling from the surface of optical parts due to mechanical stresses arising in YF$_3$ films.

In this case, using mixtures and solid solutions of metal fluorides can probably provide an effective solution. In particular, the prospects of using solid solution films in the PbF$_2$-YF$_3$ system seem good. However, data on studying these films in terms of their application in the optics of thin-film coatings have not been reported in the scientific literature.

In this regard, the purpose of the work was to study the properties of the film-forming materials and their thin films in the PbF$_2$-YF$_3$ system for creation on their basis multilayer interference coatings applicable in the near- and mid-infrared spectral ranges.

The object of the study: film-forming materials of the fluoride system PbF$_2$-YF$_3$ and their thin films prepared by electron-beam vacuum evaporation onto substrates of single-crystal silicon, germanium and silicate glass.

Subject of the research: physicochemical properties of the film-forming materials in the PbF$_2$-YF$_3$ system, optical and structural properties of the thin films formed from the investigated materials.
Research methods and instruments:
– X-ray diffraction analysis (a diffractometer "Dron-2.0», Cu-Kα);
– Scanning Electron Microscopy (a complex SUPRA 55VP-25);
– Fourier Transform Infrared Spectroscopy (an IR Fourier spectrometer FSM 1201).

2. Experimental setup
PbF$_2$ and YF$_3$ as well as specially synthesized solid solutions in the system PbF$_2$-YF$_3$ having different compositions were used as the starting film-forming materials. Data on the composition of the samples and the results of X-ray diffraction analysis of initial film-forming substances are listed in table 1.

Table 1. Results of X-ray diffraction analysis of film-forming materials.

| Sample number | Composition: mole fraction | Structure |
|---------------|----------------------------|-----------|
| 1             | ≈100% PbF$_2$              | Corresponds to the structure β-PbF$_2$, cubic lattice |
| 2             | 75% PbF$_2$ + 25% YF$_3$   | β- PbF$_2$ based solid solution |
| 3             | 50% PbF$_2$ + 50% YF$_3$   | Corresponds to the structure Pb$_{0.52}$Y$_{0.48}$F$_{2.48}$, tetragonal lattice. The main diffraction lines of this structure coincide with the lines of PbF$_2$ but with a reduced parameter |
| 4             | 25% PbF$_2$ + 75% YF$_3$   | Corresponds to the structure Pb$_{0.52}$Y$_{0.48}$F$_{2.48}$ + YF$_3$ |
| 5             | ≈100% YF$_3$               | Corresponds to the structure YF$_3$, orthorhombic lattice |

The films of the materials under the investigation had thickness of ~1 µm and were produced by E-beam evaporation in the vacuum unit VU-2M. The pressure in the vacuum chamber was not lower than 5·10$^{-5}$ Torr and the temperature of substrates during deposition was 100 °C. Single crystal silicon (111), germanium and silicate glass served as substrate materials. The rate of film deposition was about 2 nm/s. The thickness of the layer in the process of deposition was monitored by a broad-band optical monitoring system IRIS 1017 operating in the reflection mode.

3. Results and discussion
Dispersion of film optical constants was studied on samples obtained on the germanium substrates. X-ray diffraction analysis was performed on the film samples formed on single-crystal silicon and silicate glass substrates. Analysis of structural features showed that the properties of films formed on single crystal silicon substrates are identical to those of the films formed on silicate glass substrates. Table 2 lists the results of X-ray diffraction analysis of the films. The number of each film sample corresponds to the number of the film-forming material sample from table 1.

Table 2. Results of X-ray diffraction analysis.

| Film number | Structure |
|-------------|-----------|
| 1           | Corresponds to the structure β-PbF$_2$, texture along the plane (111). The orthorhombic phase of PbF$_2$ can be present in small quantities. The diffraction patterns from the films having such compositions practically coincide with each other and correspond to β-PbF$_2$ with the texture along the plane (111), but with a modified parameter. This change in the lattice parameter can be due to both the stressed state of the film and the formation of the structure Pb$_{0.52}$Y$_{0.48}$F$_{2.48}$ |
| 2–4         | The film is X-ray amorphous |

The analysis of the film microstructures indicates that film № 1 is polycrystalline and has the grain size of 40 to 100 nm, 60 nm on the average. Film № 2 is more homogenous in the grain size with the
average value there of 50 nm. The films on samples № 3–5 are fine-grained and an average grain size is of 20 nm.

The elemental composition of films № 1–3 corresponds to PbF$_2$ and the composition of film № 5 corresponds to YF$_3$. Film № 5 exhibits drop-shaped defects with sizes of about 5 µm (figure 1). The elemental composition of the defects corresponds to the elemental composition of the film.

Figure 1. Microphotograph of a YF$_3$ film defect.

The elemental composition of film № 4 (atomic %): F $-$ 74.36 %, Y $-$ 13.94 %, Pb $-$ 11.69 % is similar to that of Pb$_{0.52}$Y$_{0.48}$F$_{2.48}$.

Dispersions of the film refractive index $n(\lambda)$ and the absorption coefficient $k(\lambda)$ were calculated from the transmittance and reflection spectra of films formed on the germanium substrate with known optical constants. Calculation results are presented in figure 2.

Figure 2. Refractive index (a) and extinction coefficient (b) curves of investigated films: 1 $-$ YF$_3$; 2 $-$ Pb$_{0.52}$Y$_{0.48}$F$_{2.48}$; 3 $-$ PbF$_2$.

The values of refractive indices for the examined PbF$_2$ and YF$_3$ films are close to the known values [2, 3]. The refractive index for Pb$_{0.52}$Y$_{0.48}$F$_{2.48}$ film has some intermediate values.

4. Conclusions
We have studied the structural and optical properties of films obtained from new film-forming materials, namely from solid solutions with different compositions in the PbF$_2$-YF$_3$ system. Our results
have shown that the structure and composition of the films deposited by E-beam evaporation in the vacuum from the starting materials containing 75 % PbF$_2$ + 25 % YF$_3$ and 50 % PbF$_2$ + 50 % YF$_3$ correspond to those of films obtained from PbF$_2$. The structure of the films prepared from the material containing 25 % PbF$_2$ + 75 % YF$_3$ corresponds to Pb$_{0.52}$Y$_{0.48}$F$_{2.48}$.

Dispersions of optical constants in the spectral range from 2 to 12 µm have been calculated for PbF$_2$, YF$_3$ and Pb$_{0.52}$Y$_{0.48}$F$_{2.48}$ films.

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