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Review

Fluorides of some s-, p-, d-, and f-metals as prospective materials for interference optics: Present status and development

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ABSTRACT

Materials with low refractive indices based on fluorides of some s-, p-, d- and f-metals for interference optics were examined. Issues concerned with the enhancement of both optical and operational properties of the thin-film coatings based on fluorides were discussed. A doping mechanism for REF_3 (RE – Sc, La–Lu) dopants in the widely used material – magnesium fluoride – was proposed. Interaction in the metal fluoride systems was established. The influence of the initial material composition on the structure and properties of coatings was determined.

Contents

1. Introduction

Recent research in the field of solid state fluorine chemistry is aimed at the search and development of new compounds and composites based on fluorides with high optical and operational properties.

Interference optics is based on the application of multi-layer thin-film coatings obtained by thermal evaporation in vacuum, magnetron sputtering, laser ablation, etc. [1–4]. Recently some other methods, e.g. MOCVD [5], ALD [6] and sol–gel [7] were used for the thin-film coatings deposition. But thermal evaporation in vacuum is still the most widespread mode of deposition of coatings due to the high efficiency. The rate of evaporation depends on the composition of material, temperature and depth of vacuum.

Each layer is characterized by definite optical parameters, such as a refractive index, scattering factor etc. The values of refractive indices are changed from one layer to another. It is well known from the thin-film conceptions that the best design for the coating is when a pair of materials forms two layers with the contrast refractive indices [8]:

$$n_h > n_l, \qquad (1)$$

where n_h, n_l are high and low refractive indices, respectively.

A high mechanical durability is important as well as additional requirements to the non-optical properties. As a result of this general approach to design, it is necessary to optimize deposition

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conditions as well as techniques, composition of materials for targets in order to achieve the required optical and operational parameters of thin-film coatings.

Fluorides of metals are the most widely spread materials with the low refractive indices.

Layers with high and low refractive indices in the interference optics for lasers working in the UV range of spectrum are composed from fluorides of various metals, e.g. LaF_3 and MgF_2 [9,10].

A series of fluorides of s-metals (LiF, MgF_2, CaF_2, SrF_2, BaF_2), p-metals (AlF_3, PbF_2, BiF_3), d-metals (ScF_3, YF_3, LaF_3, ZrF_4, HfF_4), and f-metals (LnF_3, where Ln – Ce–Lu, and ThF_4) are mainly used now. It is well known that compounds (NaF, KF, RbF, CsF, SnF_2, AgF) with high solubility as well as d-metals fluorides with intensive absorption bands (CuF_2, NiF_2, CoF_2, etc.) are not used as materials for interference optics.

Materials (fluorides) with low refractive indices were reported [4]. To the author opinion, these optical data (especially, for PbF_2) are not enough correct. All fluorides have common negative feature, namely ability to pyrohydrolysis in the presence of the trace amounts of water even under deep vacuum [11] that negatively results to the coatings properties, in particular: increasing scattering factor and decreasing mechanical durability of the coatings deposited from them.

Thus, given work is aimed at doping of well-known binary compounds with additives (dopants) of other fluorides or even complete substitution for new ones, complex compounds and study of the resulting thin-film coatings.

2. Experimental results and discussion

2.1. Fluorides of s-, p-, d- and f-metals

The following data on the thermal characteristics are given: temperature of fusion (melting point) (T_m), temperature of boiling (sublimation, T_b), effective temperature of evaporation (T_e) of metal fluorides (Table 1). Besides, the data on optical (refractive index ($n_{\lambda = 550\ nm}$), scattering factor, σ) and operational (mechanical durability, H) characteristics of the coatings obtained from them are given here also. Some technological regularities of processes of the thermal evaporation of fluorides in vacuum are observed. The majority of fluorides of metals (with the exception of fluorides of f-metals of the end of lanthanide series) especially fluorides with composition of AlF_3 and ZrF_4, HfF_4, for which the sublimation mechanism is exclusively possible ($T_b < T_m$), evaporate in a mode of sublimation. The evaporation in vacuum of fluorides of metals is carried out from the fused state, i.e. at $T > T_m$, that is caused by more stable character of evaporation under these conditions. The most refractory fluorides of metals (LaF_3, ScF_3) are sublimated.

Some regularity in values of refractive indices was found, namely:

(a) values of refractive indices slightly increase at cationic transfer to heavier analogue (f.i. in the series MgF_2–BaF_2 or ScF_3–LaF_3);
(b) fluorides of full valence metals with small atomic weight (LiF, MgF_2, AlF_3, ScF_3) have the lowest values of n – till 1.40, while fluorides of heavy and non-full valence metals (PbF_2, BiF_3) differ significantly by great values of n (nearby 1.8);
(c) values of n for fluorides of f-metals change slightly in the lanthanide series due to the action of opposite directed factors (lanthanide compression).

Other optical and operational properties of coatings do not demonstrate such bright regularities. Values of σ in many cases are 0.1–1.0%, and mechanical durability of many coatings is lesser than for group 0 (the highest value). Abovementioned disadvantages are based on the properties of fluorides of metals, because the majority of synthesized fluorides contain residual amounts of oxygen-containing admixtures, which demonstrate sparking of the melt, interaction with the evaporator etc. at the evaporation in vacuum. Moreover, fluorides of multivalent p-, d-, f-metals are decomposed in a vaporous state with the following formation of defective

Table 1
Physical–chemical properties of some binary fluorides, optical and operational parameters of the resulting thin-film coatings.

Formula of fluoride	Temperature, K			$n_{\lambda = 550\ nm}$	σ, %[a]	H, rot.[a]
	T_m	T_b	T_e			
Fluorides of s-metals						
LiF	1121	1949	1082	1.39	0.05	1000
MgF_2	1563	2543	1439	1.38[a]	0.05	2500
CaF_2	1692	2803	1583	1.43		
SrF_2	1673	2733	1618	1.44		
BaF_2	1593	2533	1449	1.47		
Fluorides of p-metals						
AlF_3	–	1552[b]	1033	1.40		
PbF_2	1095	1566	879	1.75[a]	0.27	2500
BiF_3	1000	1173	720	1.85		
Fluorides of d-metals						
ScF_3	1825	1880[b]	1316	1.40	2.2	2000
YF_3	1428	2503	1505	1.53	0.5	2500
LaF_3	1682	2603	1513	1.59[a]	0.34	2000
ZrF_4	1183 (under pressure)	1179[b]	809	1.57		
HfF_4	1298	1247[b]	843	1.58		
Fluorides of f-metals						
CeF_3	1703	2453	1466	1.63[a]	0.27	1000
NdF_3	1650	2573	1466	1.61[a]	0.22	3000
EuF_3	1549	2553		1.57[a]	0.035	17,000
DyF_3	1430	2473	1499	1.56		
HoF_3	1416	2519	1529	1.56[a]	0.19	1000
ErF_3	1419	2503	1540	1.56		
YbF_3	1435	2473	1494	1.56[a]	1.2	8000
ThF_4	1383	1953	1205	1.53		

[a] Author's results.
[b] Sublimation point.

structures in a coating. As to the decomposition, then EuF_3 and YbF_3, i.e. fluorides of lanthanides possessing variable valence (III and II) are exception.

The influence of various bellow factors on the properties of coatings, in particular degree of crystallinity (amorphous, crystalline or mixed amorphous–crystalline, i.e. containing both an amorphous component and a crystalline phase) should be taken into account. Such mixed structure has a rather high mechanical durability. Therefore, formation of amorphous layers is favourable [12]. It is well known that most of fluorides of metals form polycrystalline coatings mainly. However, fluorides of polyvalent metals (AlF_3, ZrF_4, HfF_4) form amorphous coatings. Noteworthy, that tendency to form amorphous coatings in fluorides of f-metals in a lanthanide series is increased due to growth of their acidity. For instance, if fluorides of Y, La and light lanthanides (i.e. elements of the beginning of lanthanide series) form almost entirely crystalline coatings, then amorphous component appears in the coatings formed by fluorides of heavy lanthanides (i.e. of the end of the series).

The amorphous component is expressed in a form of halo on the diffraction curves within the interval of small angles (Fig. 1b). It is supposed, that amorphous component plays an important role in the sharp increase of mechanical durability of a coating deposited from YbF_3. Probably, the increase in the contents of amorphous component in a coating in the latter case is promoted by an increase of the actual number of components at thermal evaporation in vacuum, i.e. occurrence of fluorides of both Yb(III) and Yb(II).

2.2. Composites and complex fluorides

The further development of fluoride materials consists in substitution of binary compounds by composites or complex compounds.

Magnesium fluoride is one of the most widely used optical materials with a low refractive index, in particular as antireflective coating on glasses and optical filters [5,7,9].

Taking into account that the entire elimination of oxygen-containing admixture in MgF_2 is a rather complicated task, a series of composites based on magnesium fluoride containing additives as dopants were developed by us. These dopants had to eliminate or minimize a negative effect of the admixture. It should be considered that volatility of dopant must be smaller than volatility of magnesium fluoride. Therefore such dopants as AlF_3, ZrF_4 should be excluded.

Systems of composition MgF_2–REF_3 (RE – Sc, Y, La–Lu), with effective evaporation temperatures (T_e) of dopants close to that one for magnesium fluoride were chosen. The action of the dopant probably consists in exchange reaction, where the oxygen-containing admixture (MgO) transforms into the less active form, namely, RE oxofluoride and, then to RE oxide:

$$MgO + REF_3 \xrightarrow{t} MgF_2 + REOF, \qquad (2)$$

$$3REOF \xrightarrow{t} RE_2O_3 + REF_3. \qquad (3)$$

Results of XRDA of phases and determination of phase parameters of lattices (Table 2) demonstrate that one of the composite components is either oxofluoride (REOF) or oxide (in case of the system MgF_2–ScF_3) in particular after the thermal evaporation. Some influence of a dopant on the lattice parameters of MgF_2 in a coating is observed. This effect is more expressed in case of composites MgF_2–ScF_3 and MgF_2–NdF_3 because of the greatest affinity in volatilities of corresponding components. Moreover, amorphous components in the coatings obtained by

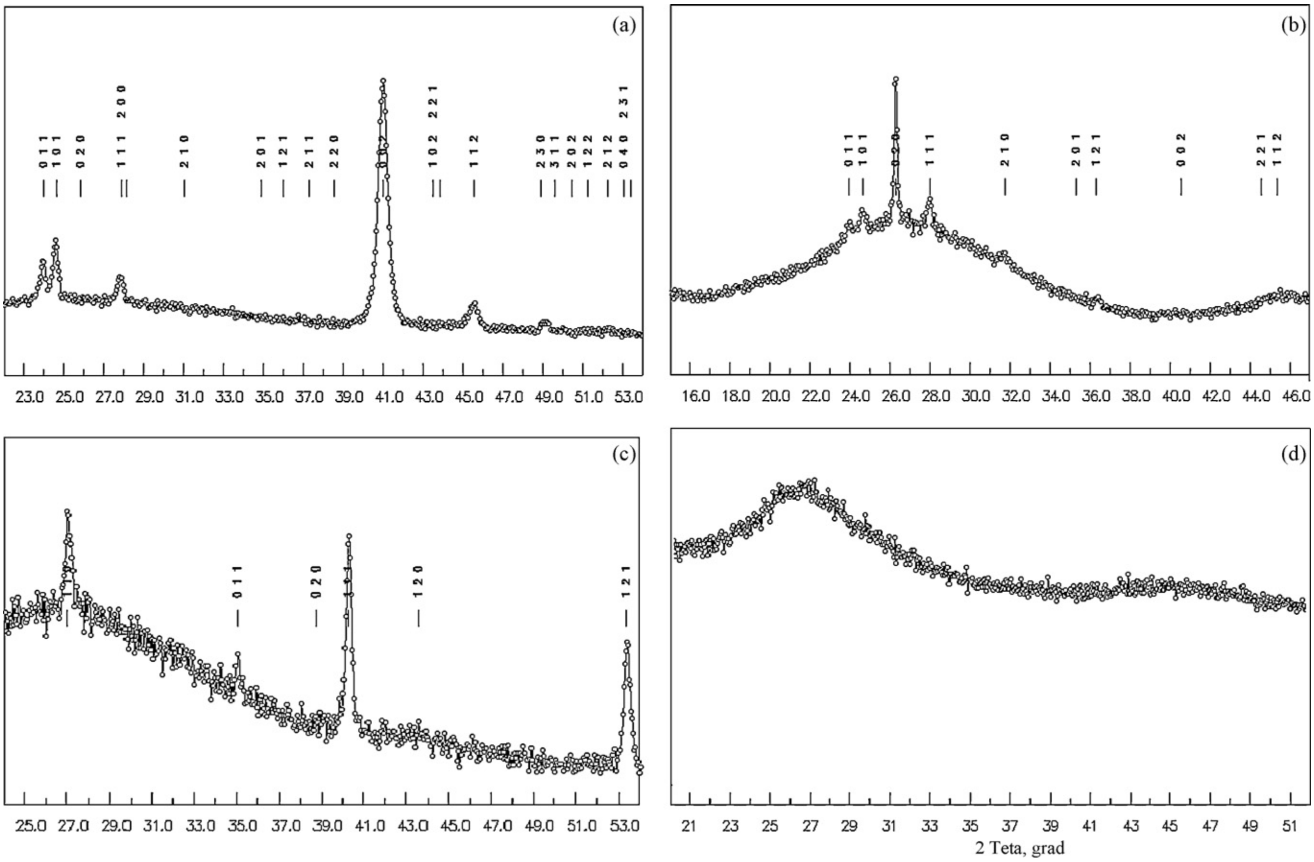

Fig. 1. Patterns of the X-ray diffraction spectra of the thin-film coatings obtained from binary and complex fluorides: YF_3 (a), YbF_3 (b), MgF_2–LuF_3 (c), BaY_2F_8 (d).

Table 2
Results of the X-ray phase analysis of the composites based on MgF_2.

Type of the sample	Phase composition	Lattice parameters of MgF_2, Å	
		$a = b$	c
Pure MgF_2			
Initial material	MgF_2	4.619(1)	3.049(2)
Residue after evaporation	MgF_2	4.619(2)	3.049(1)
Coating	MgF_2	4.611(1)	3.038(2)
Composite based on MgF_2–ScF_3 system			
Initial material	$MgF_2 + ScF_3 + ScOF$	4.622(1)	3.052(1)
Residue after evaporation	$MgF_2 + Sc_2O_3$	4.622(2)	3.051(1)
Coating	MgF_2	4.639(1)	3.060(1)
Composite based on MgF_2–LaF_3 system			
Initial material	$MgF_2 + LaOF$	4.619(1)	3.049(1)
Residue after evaporation	$MgF_2 + LaOF$	4.619(1)	3.044(1)
Coating	MgF_2	4.624(1)	3.043(2)
Composite based on MgF_2–NdF_3 system			
Initial material	$MgF_2 + NdF_3$	4.619(1)	3.049(2)
Residue after evaporation	$MgF_2 + NdF_3 + NdOF$	4.619(1)	3.049(1)
Coating	MgF_2	4.631(1)	3.054(1)
Composite based on MgF_2–LuF_3 system			
Initial material	$MgF_2 + LuF_3 + LuOF$	4.618(1)	3.049(1)
Residue after evaporation	$MgF_2 + LuOF$	4.619(1)	3.049(2)
Coating	MgF_2	4.615(2)	3.044(2)

evaporation of composites are essentially greater as compared to MgF_2 (Fig. 1c).

Therefore is important to study the influence of dopants on the optical and operational properties of obtained coatings. The obtained data are given in the Table 3. It is evident, that RE fluorides dopants appear also in coatings and affect the values of a refractive indices as compared to that ones for a coating obtained from MgF_2. Thus scattering factor of a film is decreased and mechanical durability is increased substantially in magnesium fluoride coating under the action of ScF_3 and LuF_3 dopants.

Similar or even stronger enhancement of optical and operational properties is expressed in composites based on fluorides of f-metals (CeF_3, SmF_3, EuF_3, TmF_3, YbF_3) with variable valence, but another doping mechanism is used here. The oxidation–reduction process takes place at middle temperatures simultaneously with complexation:

$$\mathrm{Ln(III)F_3 + Ce(III)F_3 \leftrightarrow Ln(II)[Ce(IV)F_6]}, \tag{4}$$

where Ln – Sm, Eu, Tm, Yb.

Thermal evaporation of the composite in vacuum results to the decomposition of complex fluoride with elimination of CeF_4 and its partial decomposition into CeF_3 and F_2, which is a powerful fluorinating agent eliminating defects in a coating. The processes described above are expressed mostly in composite EuF_3–CeF_3 due to strong ability of europium to vary its valence. Fluorinating results to significant improvement of optical and operational properties of coatings in case of composite EuF_3–CeF_3 (Table 3).

Table 3
Optical and operational properties of the coatings obtained from composites and complex fluorides of s-, d- and f-metals.

Chemical composition of initial material	Properties of the coating		
	n	σ, %	H, rot.
Composites based on MgF_2–REF_3 systems			
MgF_2–ScF_3	1.40	0.02–0.03	17,000
MgF_2–LaF_3	1.42	0.05–0.06	2000
MgF_2–NdF_3	1.43	0.06–0.07	15,000
MgF_2–LuF_3	1.43	0.05–0.06	16,000
Complex fluorides and systems			
EuF_3–CeF_3	1.59	0.017	22,000
YbF_3–CeF_3	1.55	0.11	2000
BaY_2F_8	1.49	0.5	2500–3000

Cryolyte or trisodium hexafluoraluminate $Na_3[AlF_6]$ was one of the first complex fluorides used as an optical material. Cryolyte has lower solubility in water and better adaptability to thermal evaporation as compared to NaF and AlF_3 (its initial fluorides). However, mechanical durability of the coatings obtained from cryolyte is rather low due to incongruent character of its evaporation process in vacuum.

Thus, it is important to search for complex fluorides composed of components with closer volatilities in vacuum. Such complex compounds are $BaRE_2F_8$, where RE–Y and heavy lanthanides (Tm, Yb, Lu). In fact, difference between volatilities of BaF_2 and YF_3 or, e.g. YbF_3, is not too essential (Table 1). The strong interaction between components observed in these compounds (complexation), may serve as additional factor, which favours to congruent character of evaporation in vacuum of complex fluorides of this type. Moreover, expansion of the transparency range within IR interval of spectrum must be observed due to some increase in lengths of the bonds RE–F in complex compound as compared to bonds in binary compounds, f.i. YF_3. Besides, all complex fluorides, as a rule, have essential lower T_m as compared to initial components, f.i. BaY_2F_8 has $T_m = 1233$ K ($T_m = 1593$ K for BaF_2, and $T_m = 1428$ K for YF_3), that improves the evaporation process of material in vacuum. Structure of the compound synthesized by us is in conformity with the literary data that was established by the XRDA method (Fig. 2). Crystallographic parameters of BaY_2F_8 within the limits of structural model of similar type of $BaTm_2F_8$ were determined (Table 4). The residue after evaporation contains BaY_2F_8 phase with a slightly increased lattice parameters $a = 6.977$, $b = 4.260(8)$, and $c = 10.514$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 99.68^\circ$ as compared to initial compound, as well as a very small admixture (~5%) of YF_3.

The diffraction spectrum of the coating has one expressed halo near reflection (2 0 0) of compound BaY_2F_8 that indicates its X-ray amorphous character (Fig. 1d). Thus, downturn of symmetry of fluoride in a combination with increase in number of components in a coating results to reduction of ability to crystallization, and, hence, promotes formation of amorphous component. Good adhesion to a substrate (optical glass) with enough high mechanical durability and a rather low value of scattering factor about 0.5% at 630 nm was shown by the coating. The range of

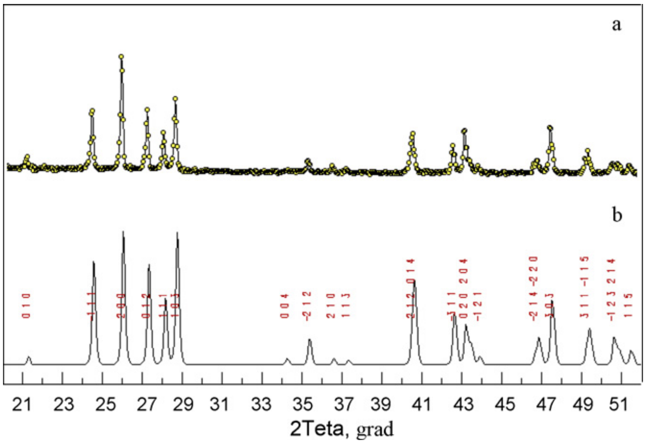

Fig. 2. The comparison of the experimental X-ray diffraction spectra of BaY_2F_8 synthesized product (a) and the graphic image of standard diffraction spectra for this compound (b).

coating transparency is 0.2–12.5 μm that allows to consider this material as alternative to rather toxic, α-emitting ThF_4 for interference optics of a middle IR range of a spectrum, e.g. for IR technological (CO_2) lasers (λ = 10.6 μm).

3. Experimental

3.1. Sample preparation

Polycrystalline samples of fluorides were synthesized by reaction of fluorination of 99.99% pure oxides (in case of MgF_2 and HfF_4, as initial compounds $MgCO_3$ and $HfOCl_2$, respectively were used) with ammonium hydrofluoride or ammonium fluoride. The processes may be described by the following equations:

$$M_2O_3 + 3NH_4HF_2 \xrightarrow{t} 2MF_3 + 3NH_3\uparrow + 3H_2O\uparrow, \tag{5}$$

where M = Al, Sc, Y, Ln,

$$MgCO_3 + NH_4HF_2 \xrightarrow{t} 2MgF_2 + NH_3\uparrow + CO_2\uparrow + H_2O\uparrow, \tag{6}$$

$$HfOCl_2 + 2NH_4HF_2 \xrightarrow{t} HfF_4 + 2NH_3\uparrow + H_2O\uparrow + 2HCl\uparrow \tag{7}$$

Synthesized fluorides were melted (excepting AlF_3, ScF_3, and HfF_4) or annealed into tablets in inert (purified Ar or He) atmosphere. Composites or complex fluorides were synthesized from initial fluorides by solid state reaction or by melting in inert atmosphere as well.

Table 4
Crystallographic data for BaY_2F_8 compound ($BaTm_2F_8$ structure type).

Atom	Site	*x*	*y*	*z*
Ba(1)	*2a*	0	0	0
Y(1)	*4h*	0.5	0.5	0.176(9)
F(1)	*8j*	0.193(2)	0.569(3)	0.140(2)
F(2)	*4i*	0.399(3)	0.213(5)	0
F(3)	*8j*	0.041(6)	0	0.739(2)
Space group		*B2/m* (no. 12)		
Lattice constants, Å		$a = 6.976(7)$, $\angle\gamma = 99.68(1)$	$b = 4.260(1)$,	$c = 10.509(1)$,
Calculated density, $g\,cm^{-3}$		$d_{cal} = 5.14$		
Independent reflections		131		
Total isotropic thermal factor, $Å^2$		$B = 0.26(7)$		
Texture parameter		$\tau = 0.90(2)$, texture axis [100]		
Reliability factor		$R_W = 0.062$		

3.2. X-ray diffraction analysis

Studies of phase composition and structural parameters of the phases in the initial material, coating and residue after evaporation were carried out by the modified Rietveld method. XRD profiles of polycrystalline samples and coatings were recorded on a DRON – 3 M device using Cu Kα filtered radiation. The data were collected in the angular (2θ) interval from 10° to 140°. Primary processing of X-ray diffraction spectra was carried out with a full-profile method. The qualitative and quantitative X-ray analysis is based on the developed software.

3.3. Coating technology and measurements

Thin-film coatings on the substrates were made from various materials (optical glass, germanium, optical ceramics, etc.) obtained through the thermal evaporation (resistive mode) of the tablets of materials in the vacuum chamber VU-1A at residual vacuum $(2–3) \times 10^{-3}$ Pa. Technological vapour pressure of the vaporizing material was ~1 Pa. The corresponding value of temperature in vacuum technology is called effective temperature of evaporation (T_e). Evaporation was carried out with various rates (100–150 nm/s) from tantalum or molybdenum crucibles. Coatings had optical thickness (nd) within the interval 0.8–2.4 μm.

Refractive indices of coatings were determined from the interference curves by measuring minimal values of the reflection *R*:

$$n_l = \sqrt{n_s \frac{1 + \sqrt{R_{min}}}{1 - \sqrt{R_{min}}}}, \tag{8}$$

where n_l, n_s are values of refractive indices of the layer and substrate, respectively, provided that $n_l < n_s$.

The scattering factor was determined on the laser device using the He–Ne laser (λ = 682 nm) by measuring relative diffuse reflection from a substrate with the coating put into the sphere coated with smoked MgO.

Mechanical durability of coatings was determined qualitatively on the device SM-55 by a number of rotations to appearance of ring-like scratches on the surface. A group 0 of mechanical durability corresponds to more than 3000 rotations, group 1 – not less than 2500 rotations, etc.

4. Conclusion

Status quo on the development of materials with low refractive indices, based on binary and complex fluorides or composite for interference optics was examined. Some regularity in the change of the optical properties (refractive index and scattering factor) and mechanical durability of the coatings, deposited from fluorides of s-, p-, d- and f-metals, was established. The effect of amorphous component in the thin-film layer on its properties, especially mechanical durability was found. It has been shown that a negative effect of the oxygen-containing admixture to MgF_2 could be minimized by addition of REF_3 (RE – Sc, Y, La–Lu) to basic material. Doping mechanism of such dopants and alternative way for improvement of properties of thin-film coatings, which consists of the application of composites of LnF_3–$Ln'F_3$, i.e. of lanthanides fluorides with variable valences were proposed. Application of complex fluorides, in particular BaY_2F_8, will allow to substitute completely toxic and radioactive ThF_4 as material for interference optics of CO_2-lasering (10.6 μm).

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