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OPTICAL AND MECHANICAL PROPERTIES OF THERMALLY EVAPORATED FLUORIDE THIN-FILMS

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K. Zhang, R. Fahey, D. Jasinski, C. Scarpino, R. Dziendziel, S. Burger, D. DePoy

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KAPL ATOMIC POWER LABORATORY SCHENECTADY, NEW YORK 12301

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Optical and mechanical properties of thermally evaporated fluoride thin films

K. Zhang, R. Fahey, D. Jasinski, C. Scarpino
OFC Corporation, 2 Mercer Road, Natick, MA 01760

R. Dziendziel, S. Burger, D. DePoy
Lockheed Martin Corporation
Post Office Box 1072, Schenectady, NY 12301-1072

I. Introduction.

As a result of health and safety issues surrounding the use of radioactive materials on coated optical components, there has been renewed interest in coating materials whose optical and mechanical properties approach those offered by their radioactive counterparts. Due to the radioactive nature of ThF_4 and its widespread use in optical coatings, the coating industry is examining other low index and non-radioactive fluorides as possible alternatives. In this paper, we present the results of an experimental study on the optical and mechanical properties of thermally evaporated ThF_4, DyF_3, CeF_3, LiF, HfF_4, IRX, and IRB thin films, where the materials were deposited at different substrate temperatures. The objective is to examine this series of fluorides under comparable deposition conditions and with respect to such material properties as: n and k, film stress, and environmental stability. The optical constants of these fluorides were evaluated over the wavelength region from 1.0μm to 12.5μm.

II. Deposition Conditions.

All target fluoride materials were better than 99.9% pure. All materials were evaporated in resistance (thermal) sources and under pressures of less than 5×10^{-4} Pa. Each material was separately tested at substrate temperatures of 100°C and at 200°C. Deposition rates of 2nm/s were chosen for all evaporated materials. Each coating run included: 1mm thick Si witnesses and 0.5mm ZnSe substrates. Each coating test also included at least eight 0.1mm thick glass beams for the purpose of determining film stress.

III. Measurement.

The transmittance and reflectance of the "as deposited" films were measured from 1.0μm to 12.5μm using Perkin Elmer 330 and 983 spectrophotometers. By applying a curve fitting technique to the measured values for R% and T%, the refractive index, extinction coefficient, and thickness of the films were determined over this range. Coating stresses in the fluoride films were determined using the Cantilever method.

IV. Results and Discussion.

a) Refractive Indices.

Results indicate that the refractive indices of these fluoride films are similar; with n varying between 1.25 and 1.55, depending on the wavelength region. Of which, IRB has the lowest refractive index over the entire spectral region. When normal dispersion was assumed, the experimental data for R% and T% closely fit the theoretical calculations. One exception was LiF, which showed an abnormal dispersion in the wavelength region beyond ~7μm. Wide dispersion in this material made curve fitting impossible beyond ~7μm. Tests at 100°C and

200°C indicate that for these materials, the refractive index is not strongly temperature dependent. Tables 1 and 2 show the refractive indices of the fluoride films at various wavelengths for substrate temperatures of 100°C and 200°C.

b) Absorption.

The reflection and transmission measurements indicate that all fluoride thin films show weak absorption across most of the wavelength regions in question. With the films exhibiting only weak absorption over this spectral region, it is difficult to obtain reliable extinction coefficient data using only R% and T% measurements from conventional spectrophotometers. Table 3 lists the absorption of the fluoride films at three particular wavelengths; where 3.0μm and 6.0μm are within the water band absorption region, and where 12.5μm is the longest wavelength of interest. As absorption is directly related to film thickness, the physical thickness of the films is also included in the table.

Table 1. The refractive indices of fluoride films deposited at a substrate temperature of 100°C. Values are shown at various wavelengths.

	Wavelength (μm)						
Material	1.5	5.0	8.0	10.0	11.0	12.0	12.5
ThF_4	1.46	1.45	1.45	1.37	1.32	1.29	1.28
CeF_3	1.53	1.47	1.42	1.40	1.40	1.40	1.39
DyF_3	1.44	1.44	1.44	1.39	1.35	1.32	1.31
HfF_4	1.47	1.47	1.45	1.30	1.27	1.25	1.24
IRX	1.51	1.44	1.43	1.42	1.42	1.42	1.42
IRB	1.29	1.26	1.26	1.26	1.26	1.26	1.26
LiF	-	-	-	-	-	-	-

Table 2. The refractive indices of fluoride films deposited at a substrate temperature of 200°C. Values are shown at various wavelengths.

	Wavelength (μm)						
Material	1.5	5.0	8.0	10.0	11.0	12.0	12.5
ThF_4	1.51	150	1.48	1.37	1.33	1.31	1.30
CeF_3	1.49	1.49	1.40	1.40	1.39	1.39	1.39
DyF_3	1.51	1.51	1.50	1.41	1.38	1.35	1.35
HfF_4	1.47	1.46	1.44	1.30	1.27	1.25	1.24
IRX	1.53	1.52	1.52	1.45	1.42	1.40	1.39
IRB	1.30	1.26	1.25	1.25	1.25	1.25	1.25
LiF	1.28	1.25	-	-	-	-	-

Tables 3 and 4 show CeF_3 and DyF_3 exhibit the strongest absorption at these wavelengths, while HfF_4, IRB and LiF have absorption values comparable to ThF_4. With higher substrate temperature, the water band absorption is significantly reduced in all of the fluoride films except

DyF_3; indicating that a denser microstructure was obtained. In general, the lower the absorption in the 2.8μm - 3.2μm (O-H bond absorbing band), the lower the absorption usually observed at longer wavelengths. Table 4 shows the extinction coefficients for various fluoride films at 3.0μm, which is at, or adjacent to, the deepest point of the O-H bond absorbing band.

c) Mechanical properties.

One of the most important mechanical properties of thin films is film stress. In this study, at least eight 0.1mm thick glass beam-shaped substrates were included in each coating run to evaluate film stress. The deflection at the tip of each glass beam was carefully measured before and after deposition. The film stress was then derived from the change in deflection. By averaging the film stress over the number of beams, a more reliable value for stress can be derived, and the standard deviation is generally less than 5%.

Table 5 shows film stresses for various fluoride films when deposited on glass substrates. All of the fluoride films exhibited tensile stresses except for IRB, which exhibited a slightly compressive stress. The expected trend is that higher substrate temperature results in higher film stress, but it is unclear whether this is mainly due to the effects of thermal expansion or to changes in the microstructure of the film.

Table 3. Absorption (%) of fluoride films deposited at temperatures of 100°C and 200°C.

Material	(At 100°C) Film Thickness (μm)	(At 100°C) Wavelength (μm) 3.0	6.0	12.5	(At 200°C) Film Thickness (μm)	(At 200°C) Wavelength (μm) 3.0	6.0	12.5
ThF_4	1.46	13.5	5.1	4.2	1.47	4.2	0.1	1.9
CeF_3	1.73	30.0	8.1	9.7	1.67	21.4	6.8	8.3
DyF_3	1.35	20.5	5.8	4.6	1.26	19.9	5.5	4.9
HfF_4	1.41	12.2	5.8	4.0	1.35	2.0	1.1	2.6
IRX	1.65	23.0	5.6	6.5	1.26	9.8	3.6	3.0
IRB	2.86	7.8	1.3	2.9	2.57	5.2	3.1	2.3
LiF	-	-	-	-	1.28	2.4	2.0	7.4

Table 4. Extinction coefficients of fluoride films at 3.0μm.

Substrate Temperature	ThF_4	CeF_3	DyF_3	HfF_4	IRX	IRB	LiF
100°C	0.018	0.034	0.029	0.014	0.022	0.005	-
200°C	0.006	0.020	0.033	0.000	0.014	0.004	0.000

Table 5. Stress of fluoride films on glass substrates (Stress unit: $\times 10^8$ Pa).

Substrate Temperature	ThF_4	CeF_3	DyF_3	HfF_4	IRX	IRB	LiF
100°C	1.5	0.2	1.7	1.6	1.4	-0.1	-
200°C	1.9	0.8	1.6	2.0	1.8	-0.1	0.4