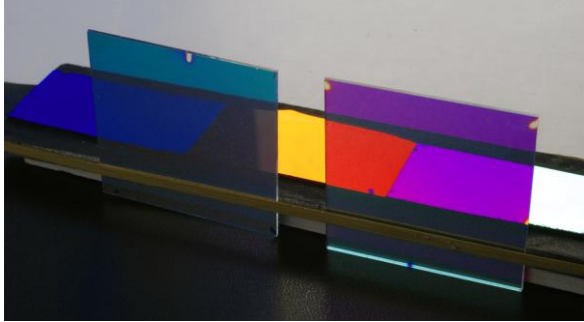


Status of Thorium Fluoride Replacement Materials



Caption: Depiction of coatings with the subtractive and additive combinations of colors produced by transmission through dichroic filters designed for the visible region. (Credit: S. Pellicori).

Non-Radioactive Coating Materials for the Infrared

Thorium fluoride (ThF_4) has been the favored low-index IR coating material since its investigation and introduction 45 years ago. However, the radioactivity of Thorium (Th) led to forbidding the use of ThF_4 by the 1980's. With that loss, subsequent studies of different fluoride compounds were conducted by scholarly groups and coating companies who sought an alternate material that would exhibit ThF_4 transparency, physical durability, and affordable cost. Those who work in the spectral range above $\sim 11 \mu\text{m}$ are already aware of suitable candidate replacements. [1, 2, 3, 4]. Although several substitute IR materials have been identified with comparable properties, none have equaled ThF_4 . This article reviews the current industry and Materion's status and progress in the pursuit.

Thorium Fluoride Properties: Desired and Not Desired

All optical coatings that are designed to provide specific functions such as reduction of surface reflection, isolation of a pass band, or definition of LW and SW separation edges, require the combination of low-index and high-index material layers. For IR wavelengths longer than $\sim 7 \mu\text{m}$, suitable materials are few in number as limited by absorption. In this region, Oxide compounds are eliminated from consideration for not meeting the highest efficiency and LDT applications. This leaves fluoride compounds for the low-index choices and zinc sulfide or zinc selenide and Ge for the high-index layers. Thus, optical coatings functioning in the thermal IR ("LWIR") are composed of a fluoride compound and a high-index material as cited above. The materials on this short list of candidates are deposited using thermal evaporation sources such as resistance- heating or E-beam evaporation. (While sputtering and ion-beam deposition is possible, those processes are not generally used for IR coatings). As is true of all fluoride compounds, the replacements have been found to require special deposition process-dependent preparation and specific deposition parameters to provide optimal properties.

The isotope component of Thorium fluoride, $\text{Th}232$, has an activity of $0.22 \mu\text{Curie}$ per gram, and emits alpha particles of 4 MeV energy, beta particles (electrons) of 0.012 MeV, and gammas at 0.0013 MeV energy. The alphas are stopped by a thickness of paper or by four inches of air. Betas can also easily be shielded against. The gammas, however, have higher penetrating power and pose a greater risk for tissue damage. Exposure by inhalation of ThF_4 dust is the preeminent hazard faced by thin-film coating personnel.

Non-Radioactive Replacements: Properties

The favorable properties provided by ThF₄ are: Low absorption; High LDT (Laser-Induced Damage Threshold) to wavelengths as long as 13 μm; Durability to humidity and moderate abrasion; Compatibility with high-index materials ZnS, ZnSe and Ge; and Ease of evaporation by resistance or E-beam heating. With the exception of lowest optical absorption above ~11μm, all of the other low-index requirements are satisfied by a variety of non-radioactive fluoride compounds. Those replacement fluoride materials include YF₃, YbF₃, LaF₃ (available from Materion), doped mixtures such as IRX™ and IRB™, and others. The best replacement materials are represented by choices from the Lanthanide series of rare earths, as indicated in **Figure 1**. In general, the heavier elements transmit to longer wavelengths.

38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53
Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
56	72	73	74	75	76	77	78	79	80	81	82	83	84	85	
Ba	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	
88	104	105	106	107	108	109	110	111	112	113	114	115	116	117	
Ra	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	
57	58	59	60	61	62	63	64	65	66	67	68	69	70		
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
89	90	91	92	93	94	95	96	97	98	99	100	101	102		
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

Figure 1. Section of the Periodic chart indicating the Rare Earth and other metals that, combined with fluorine, compose the more commonly used compounds that exhibit high IR transparency.

The following **Figure 2** shows the transmittances for LaF₃ deposited by different techniques. Absorption for these ~2 μm thick layers is noticeable at wavelength ~11 μm. Higher T is obtained by IAD-Resistance-heated evaporation. Water band spectral signatures typical of fluoride compounds are present.

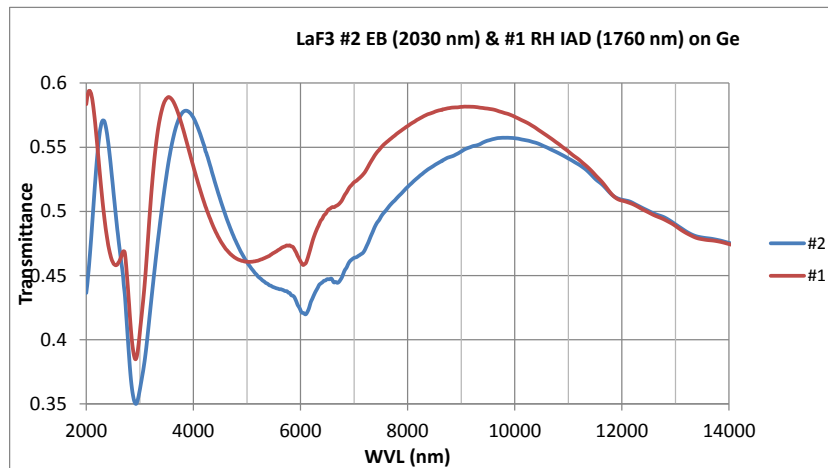


Figure 2. Transmittances of LaF₃ deposited by resistance-heated + IAD and E-Beam evaporation techniques.

Ytterbium fluoride, YbF_3 , is currently being recommended for use out to wavelengths $>12\ \mu\text{m}$. It has smooth evaporation behavior, high IR transmission, and good environmental properties. Transmittance curves for two E-beam depositions at rates 10 to $20\ \text{\AA}/\text{s}$ on ZnSe at 150°C are shown in Figure 3. At temperature 150°C , almost complete absence of water band absorptions is evident.

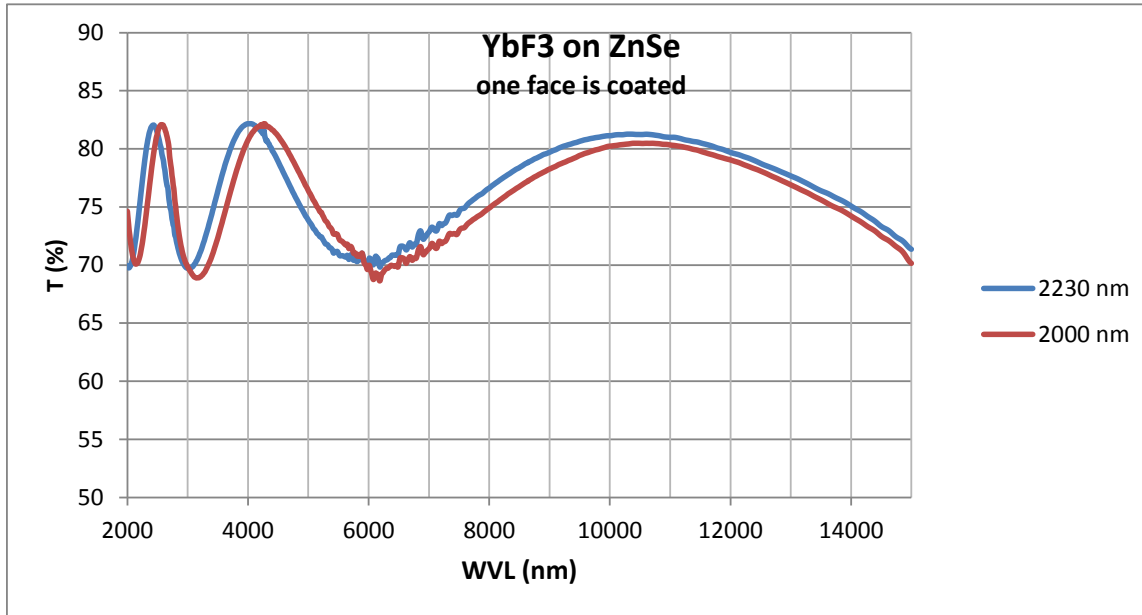


Figure 3. YbF_3 layers on ZnSe substrates. The 2000 nm layer was deposited at $20\ \text{\AA}/\text{s}$; the 2230 nm layer at $10\ \text{\AA}/\text{s}$. A very slight water absorption band at $\sim 6200\ \text{nm}$ is present.

There are a number of properties that must be considered in the choice of fluoride compound replacements. The physical thickness of a QWOT thickness for materials with index 1.35 is 1666 nm thick at wavelength $9\ \mu\text{m}$. A typical AR design for the 8 to $12\ \mu\text{m}$ region contains $\sim 2000\ \text{nm}$ of the low-index material. At that thickness, the tensile stress characteristic of fluoride compounds becomes an issue of concern relative to adhesion, cohesion, and film strength. Mixtures such as IRXTM, IRBTM, and even LaF_3 and YbF_3 , have been developed to mitigate stress accumulation in thick layers and are currently used in many IR applications. Following work cited [2], other groups are doping YbF_3 with Ba and Ca compounds.

Thin-film layers of fluoride compounds exhibit water absorption bands located at wavelengths 2.8 to $3.2\ \mu\text{m}$ and 6.0 to $7.4\ \mu\text{m}$. If the absorption band is deep, it can encroach on the 7.5 or $8.0\ \mu\text{m}$ edge of the thermal IR band [5]. A candidate replacement must, therefore, exhibit water bands at least as shallow as those exhibited by the best ThF_4 depositions. The depth of the water bands is an indication of the packing density of a film layer. Water band depth is also influenced by material composition, and the following deposition parameters: adatom energy, substrate temperature, evaporation and growth rates, and background composition and pressure [6].

The coating engineer has control of deposition parameters. Growth nano-structure and composition are important variables. High-packing density leads to high refractive index, but it also can produce high

intrinsic stress. The mixtures mentioned can be grown in thicker layers than pure materials can, and exhibit lower stress because the mixture of mutually soluble compounds (generally a selected fluoride) diffuses internal stress that otherwise would be established between structural nano-columns. Optical and mechanical properties must be stable over arid / humid exposure. A coating with high stress and high porosity will exhibit changes upon exposure to humid and arid atmospheres. A possible reaction is mechanical failure in the form of crazing, cracking, and adhesion loss. Mixed-material layers tend to form amorphous structures that are densely packed and therefore less likely to suffer the described effects [2, 3].

Corollary to the discussion of bound and therefore non-volatile water, is the component of water that is absorbed and incorporated in open pores as a result of exposure to humid atmosphere. This volatile component can affect stress and spectral properties. Refractive index increases as void volume is filled with water vapor, only to decrease upon vacuum or heating or other dehydrating atmosphere. Insuring a dense packing structure through the measures discussed will minimize this de-stabilizing phenomenon. Many fluoride compounds absorb water from the atmosphere and subsequently emit particulates during evaporation. It is important, as a further precaution against spitting, to heat the fluoride gently for a few hours in vacuum to drive off adsorbed water.

Other properties that a replacement fluoride compound material must possess are compatible chemical bonding to a variety of IR substrate materials and to the neighboring high-index layer materials (ZnS, ZnSe, Ge). Also important is the ability to provide mechanical durability, adhesive and cohesive strengths, hardness and abrasion resistance. The growth environment has a large influence on coating behavior. The combination of fluoride layers with ZnS or ZnSe layers imposes a high temperature maximum of $\sim 150^\circ\text{C}$ to prevent the sulfide and selenide materials from suffering low condensation and growth rates. Finally, some applications will require high laser-induced damage thresholds (LDT), which translate into low optical absorption (low k -value).

Comparing ThF_4 with replacement fluoride compounds, we expand on our previously published table of fluoride compounds [7]. (visit Materion webpage - http://materion.com/~media/Files/PDFs/AdvancedChemicals/CoatingMaterialsNews/Cmn14_4.pdf)

Material	ThF ₄	YF ₃	YbF ₃	IRX	IRB	LaF ₃	AlF ₃	HfF ₄
Absorp. in QW at 10 μm* (%)	~1	2-5	~1	2-3		5-10	Low-none	none
n,k at λ 10 μm	1.35, 0.001	1.35, 0.002	1.42	1.4, 0.006	1.35	1.4, 0.004	1.3, 0.04	1.35, 0.002
Water band depths*	low	low	signif.	low	Low+	signif.	low	signif
Humidity stability	Good-	good	good	good	OK	good	good	good
Abrasion durability*	good	Fine scratches	good	good	fair	good	good	good
Stress related thickness limit (μm)	~2	~2	>2	>2	>2.5	>2	>2	>2
Melt or sublimate	S	M	M	M	M	S	S	S

*Dependent on substrate temperature and IAD energy

Table 1. Properties of Thorium Fluoride and Non-radioactive Replacement Materials

Concluding Remarks

Alternates to ThF₄ exist and companies like Materion and other materials manufacturers are working on improving the preparation of the starting composition and form. One technique, mixtures (“doping”) previously mentioned, is one means for avoiding porosity. Also, low energy ion assisted deposition is useable for IR wavelengths and results in increased compaction. It is safe to conclude that work on perfecting ThF₄ replacement compounds will continue. Currently, Materion features an ever expanding selection of specialty evaporation fluorides like YF₃, YbF₃, CeF₃, BaF₂ and LaF₃.

References

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