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Accepted Version

Hawkins, G. and Stolberg-Rohr, T. (2015) Determination of the embedded thermo-optical expansion coefficients of PbTe and ZnSe thin film infrared multilayers. Optics Express, 23 (12). pp. 16348-16355. ISSN 1094-4087 doi: https://doi.org/10.1364/OE.23.016348 Available at http://centaur.reading.ac.uk/40470/

Published version at: https://www.osapublishing.org/oe/abstract.cfm?uri=oe-23-12-16348
To link to this article DOI: http://dx.doi.org/10.1364/OE.23.016348

Publisher: The Optical Society

Determination of the embedded thermo-optical expansion coefficients of PbTe and ZnSe thin film infrared multilayers

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Abstract

This paper reports the first derived thermo-optical properties for vacuum deposited infrared thin films embedded in multilayers. These properties were extracted from the temperature-dependence of manufactured narrow bandpass filters across the 4-17 µm mid-infrared wavelength region. Using a repository of spaceflight multi-cavity bandpass filters, the thermo-optical expansion coefficients of PbTe and ZnSe were determined across an elevated temperature range 20-160 ºC. Embedded ZnSe films showed thermo-optical properties similar to reported bulk values, whilst the embedded PbTe films of lower optical density, deviate from reference literature sources. Detailed knowledge of derived coefficients is essential to the multilayer design of temperature-invariant narrow bandpass filters for use in non-cooled infrared detection systems. We further present manufacture of the first reported temperature-invariant multi-cavity narrow bandpass filter utilizing PbS chalcogenide layer material.

1. Introduction

The optical and semiconductor properties of group IV-VI Lead chalcogenide compounds has been a subject of thin film research for several decades [1]. Lead Telluride (PbTe) has been deployed in multilayers extensively over this period as a mid-infrared interference material, being particularly valuable in the coating design due to its high refractive index ($n \approx 5.5$) and long-wave spectral location of its electronic absorption edge. It is also distinctive amongst other transparent infrared materials because of its negative refractive index temperature coefficient which enables the unique construction of temperature-invariant narrow bandpass filters [2-4] across both cooled and elevated operating temperatures.

We previously conducted a systematic investigation into the design of temperature-invariant narrow bandpass filters, from which we demonstrated the thermo-optical properties of PbTe films accessible from literature sources were insufficient to accurately predict the temperature-induced wavelength shift of PbTe/ZnSe multi-cavity narrow bandpass filters across an elevated temperature range 20-200 ºC [5]. Thus, an improved and refined understanding of thin film thermo-optical properties is essential to simulate, and gain control of the behavior of bandpass temperature-invariance demanded by non-cooled infrared optical systems [6]. We further introduced a thermo-optical expansion coefficient term (γ), which denotes the expansion in optical thickness (δ) with increasing temperature. The optical thickness, being the product of the physical thickness (l) and the refractive index (n) $\delta = nl\ 2\pi/\lambda$, whilst the temperature derivative of δ is the sum of the temperature derivatives of l and n;

$$\gamma = \frac{1}{\delta}\frac{d\delta}{dT} = \frac{1}{l}\frac{dl}{dT} + \frac{1}{\delta}\frac{dn}{dT}$$

The thermo-optical expansion coefficient (γ) is a crucial term, as it is primarily this material property that is responsible for the wavelength shift with temperature exhibited by any optical thin film multilayer. In a binary material narrow bandpass filter, we showed in [5] that the center wavelength shift with temperature obeys the linear relation in Eq. (1).

$$\frac{1}{\lambda_C}\frac{d\lambda_C}{dT} = s_L\,\gamma^L + s_H\,\gamma^H \qquad (1)$$

Where γ^L and γ^H are the thermo-optical expansion coefficients of the low and high index layers respectively, and S_L and S_H are sensitivity factors describing the proportional weighting of the two materials (S_L+S_H=1) which are determined as a function of the multilayer design. However, wavelength-dependence is not a direct function of material quantity; cavity layers dominate sensitivity, whilst the influence of reflector layer count reduces sensitivity in proportion with distance between cavities, as described by [2]. Equation (1) shows that temperature-invariance naturally requires one of the materials to exhibit negative optical expansion ($\gamma < 0$). This property is however known only to exist in thin film materials with a lead (Pb) based composition, i.e., PbTe and other lead chalcogenides, which strongly motivates improved understanding for these thermo-optical properties.

In this paper we utilize the elevated temperature measurements from a comprehensive repository of historic spaceflight bandpass filters, previously described in [5] to derive a new, realistic and practical data set of thermal-optical properties (γ) for embedded polycrystalline thin films of PbTe and ZnSe within a multilayer. We further consider the application of other alternative Pb-salts (PbSe, PbS) to broaden the range of temperature-invariance towards shorter wavelengths, and present the first reported thin film SWIR bandpass filter at 3.0 μm exhibiting temperature-invariance and utilizing the negative thermo-optical expansion of lead sulphide (PbS).

2. Thermo-optical source data

In [5] we conducted a literature survey to determine the existing sources of thermo-optical properties for PbTe and ZnSe in both bulk and thin film form with a particular focus on elevated temperatures across the 20-200 ºC range. Our investigation concluded that the optical data available for these materials is exceptionally scarce. Where temperature measurements currently exist, this data is very coarse, or unsuitable for the desired wavelength regions. Valuable reference databases exist [7], which aim to create easy access to reported refractive index properties of various optical materials, however its temperature-dependence (dn/dT) property is rarely specified. A further challenge of incorporating thermo-optical properties in thin film simulations remains the non-specific physical condition from reported measurements which will differ to layers embedded within a multilayer assembly. Many reported thin film measurements are performed on single films exposed to ambient environments [8, 9] which are likely to deviate in their stress condition from embedded films in the multilayer structure. Other thin films are epitaxial single-crystalline films, which in [10] were found to resemble bulk properties, whilst the thin films deposited by physical vapor deposition are typically of a polycrystalline columnar structure, as is the case for our selection of manufactured bandpass filters. In addition to this, variations in deposition conditions affect stoichiometry, crystal morphology, and packing density all of which influence the opto-mechanical properties of the deposited films.

For evaporated PbTe layer material, refractive index temperature measurements were reported for exposed polycrystalline [9] and single-crystalline films, [10] and, as anticipated, omission of any data for embedded polycrystalline films. Data on thermal expansion was expectedly only found in bulk form [11]. For ZnSe we found no reported thin film measurements of the refractive index temperature coefficient, however bulk refractive index coefficient data is available from Feldman [12]. The thermal expansion coefficient was measured for exposed thin films in [13] however the experimental coefficients were of such high magnitude that they were dismissed as unrealistic in proportion to embedded thin film properties and behavior.

3. Experimental data and simulation method

To acquire the embedded thermo-optical data properties for thin film simulations, we characterized and correlated the thermal behavior from a historic repository [14-16] of PbTe/ZnSe narrow bandpass filters, manufactured over a course of two decades, and covering a wide range of wavelengths, bandwidths, and multilayer design types. These filters were manufactured by thermal evaporation using a modified Balzers BA510 deposition chamber. This deposition system is especially fitted with a tooling arrangement of rotating evaporation sources and stationary substrates. This static substrate arrangement is particularly important for the deposition of precision thin-film multilayers, as the need for accurate elevated temperature control is essential to maintain good opto-mechanical properties of the materials, particularly as the stoichiometry and sticking coefficient of chalcogenides are highly temperature dependent. The selection of bandpass filters used in this study were deposited with substrate temperatures between 185-210 °C. Further deposition details are discussed in the papers where the filters were first published [14-16]. The filters were all newly characterized by extraction from high temperature FTIR spectral measurements across the range of 20-200 ºC, where the observed wavelength displacements were correlated with multilayer design properties in [5]. The wavelength shift with temperature was accurately modelled using Eq. (1).

In order to determine the thermo-optical expansion coefficient for the embedded thin films of both PbTe and ZnSe layer materials, only a minimum of two filters is required with common center wavelength, but of significantly different multilayer design. This establishes two or more simultaneous equations to solve with respect to the two unknown optical properties. This requirement was achieved at three different wavelengths; 4.3 µm, 10.4 µm, and 12.1 µm. The sensitivity factors were determined from the multilayer properties, and presented in [5] for the relevant designs. In Fig. 1, the measured center wavelength shift with temperature is shown for three center wavelengths as a function of the low-index sensitivity weighting factor S_L. Equation (1) contains only one independent variable, since the high- and low-index sensitivity weighting factors adds up to unity ($S_L + S_H = 1$). Thus, the equation can be written and solved as a linear function of either variable, e.g., $\frac{1}{\lambda_c}\frac{d\lambda_c}{dT} = (\gamma^L - \gamma^H)S_L + \gamma^H$. Hence in Fig. 1, the intersection with the y-axis ($S_L = 0$) shows γ^H, whilst the slope gives $\gamma^L - \gamma^H$. As we have more than two filters at each of the three wavelengths, comprising; 11 filters at 4.3 µm, 4 filters at 10.4 µm, and 10 filters at 12.0 µm, we performed a multivariate least squares fit to obtain the desired material properties of γ^{PbTe} and γ^{ZnSe} at the selected wavelengths. The shift in center wavelength on the y-axis is the mean shift across the 20-160 ºC temperature range. The upper limit was chosen to avoid non-linear behavior which was exhibited by some filters at temperatures greater than 160 ºC. Filters in the 4 µm region showed a temperature displacement with a tendency to reduce when approaching the higher temperatures, even within this range. This was primarily due to the reduced influence of electronic absorption in the PbTe material, shifting to shorter wavelengths on heating. The value fitted at the 4.3 µm wavelength is thus an average value over the temperature range, and will be slightly higher at room temperature.

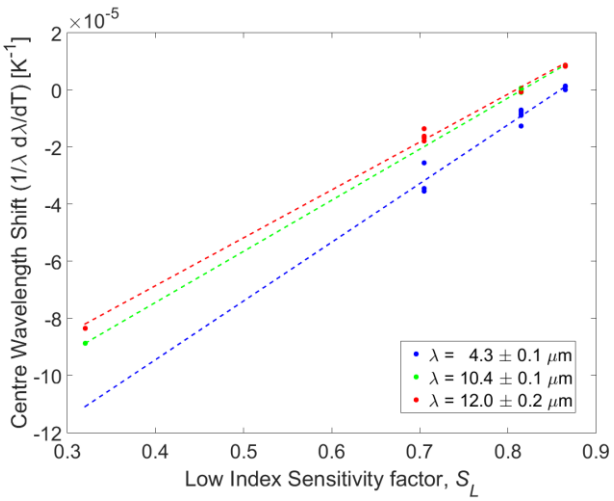

Fig. 1. Measured center wavelength shift with temperature as a function of multilayer design specified by the low index sensitivity factor (dots) shown together with the results of multivariate least square fits (lines).

4. Results

Applying the measured wavelength shift properties with temperature, a thermo-optical expansion coefficient for the embedded thin films was derived for both PbTe and ZnSe at three different mid-infrared wavelengths. The resulting coefficients are given in Table 1, and shown in Fig. 2 together with corresponding literature data.

Table 1. Thermo-optical expansion coefficients derived for embedded PbTe and ZnSe films.

λ [µm]	γ^{PbTe} [10^{-5} K^{-1}]	γ^{ZnSe} [10^{-5} K^{-1}]
4.3	-17.7 ± 2.3	2.9 ± 0.8
10.4	-14.6 ± 0.7	3.3 ± 0.2
12.0	-13.6 ± 1.1	3.2 ± 0.6

To each extracted coefficient we have given a variance which was generated by fixing one coefficient in Eq. (1) at a time and calculating the resulting sample standard deviation for the temperature coefficient of the alternate material. The stated variances in table 1 represent twice the sample standard deviation (±2σ) and is further

included in Fig. 2 as vertical error bars. Whilst these variations may appear large in value, they are small compared to the discrepancies within the currently existing knowledge of thin film PbTe properties.

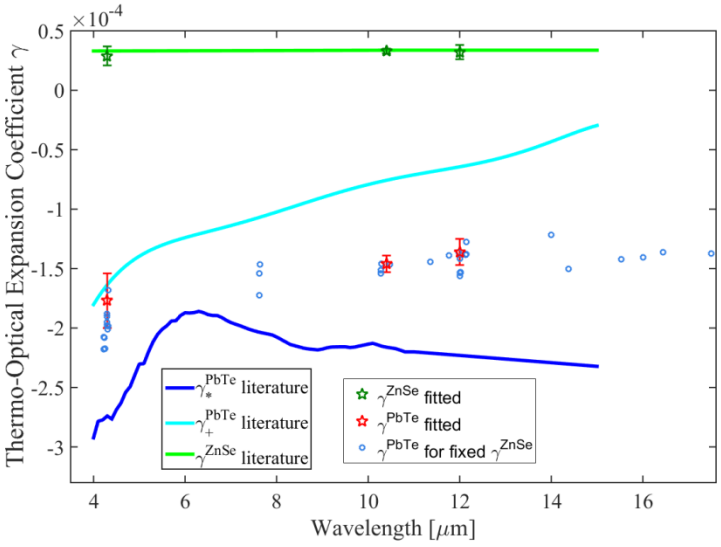

Fig. 2. Thermo-optical expansion coefficients of embedded PbTe and ZnSe determined by multivariate least square fit to Eq. (1) shown together with literature data, the origin of which are listed in Table 2. Additionally, a value for $\boldsymbol{\gamma^{PbTe}}$ was extracted from each bandpass filters based on a fixed $\boldsymbol{\gamma^{ZnSe}}$ value.

Reference literature values for ZnSe offers a near wavelength-independent value of γ based on bulk samples; $\gamma^{\mathrm{ZnSe}} = 3.4 \cdot 10^{-5}\ \mathrm{K}^{-1}$. This value is in very good agreement with our findings of $3.25 \cdot 10^{-5}\ \mathrm{K}^{-1}$ in the long wavelength region. At 4.3 µm, we extract a slightly lower value of $2.9 \cdot 10^{-5}\ \mathrm{K}^{-1}$. Although still within the experimental variation, we consider that the low value is a consequence of the electronic absorption edge influence of PbTe receding from the bandpass filter as the temperature increases and skewing the measurement of $d\lambda/dT$. In total, it appears that embedded polycrystalline thin films of ZnSe exhibit optical properties similar to those of bulk ZnSe, whilst in contrast for PbTe, we obtain values that are significantly different from the literature data. This can be understood in terms of a lower optical density of deposited PbTe film [17], compared to single-crystal material which is the origin of the γ_*^{PbTe} data [10]. In contrast, the polycrystalline γ_+^{PbTe} data was obtained from exposed PbTe film [9], which is not subject to the similar mechanical stresses experienced by the embedded films. It is therefore reasonable to conclude the embedded thin film values lies between these two extrema.

Table 2. Origin of reference α and β literature data

$\gamma = \alpha + \beta$	$\alpha = \frac{1}{l}\frac{dl}{dT}$	$\beta = \frac{1}{n}\frac{dn}{dT}$
γ_*^{PbTe} $-21 \cdot 10^{-5}\ \mathrm{K}^{-1}$	*bulk* [11] $2.0 \cdot 10^{-5}\ \mathrm{K}^{-1}$	*Single-crystal, exposed film* [10] $-23 \cdot 10^{-5}\ \mathrm{K}^{-1}$ (at 10 µm)
γ_+^{PbTe} $-7.9 \cdot 10^{-5}\ \mathrm{K}^{-1}$		*Polycrystalline, exposed film* [9] $-9.9 \cdot 10^{-5}\ \mathrm{K}^{-1}$ (at 10 µm)
γ^{ZnSe} $3.4 \cdot 10^{-5}\ \mathrm{K}^{-1}$	*bulk* [18] $0.77 \cdot 10^{-5}\ \mathrm{K}^{-1}$	*Bulk* [12] $2.6 \cdot 10^{-5}\ \mathrm{K}^{-1}$

At wavelengths where bandpass filters with two distinct multilayer designs were not available to permit a multivariate fit, we applied the method of fixing γ^{ZnSe} to literature values. This is justified by the good agreement obtained with literature γ^{ZnSe} established using the multivariate fits. In this manner we obtained a value for γ^{PbTe} for each bandpass filter by the solution of Eq. (1);

$$\gamma^H = \left(\frac{1}{\lambda_c}\frac{d\lambda_c}{dT} - s_L \gamma^L \right) \Big/ s_H \qquad (2)$$

The resulting extracted coefficients are shown in Fig. 2 along with the multivariate fit results, which offer an indication of the experimental variations together with additional information about wavelength-dependence.

5. PbS temperature-invariant narrow bandpass filter

Whilst the concept of temperature-invariance has been governed by the opposing negative temperature coefficients of PbTe and complementary dielectric layer pair, extending the application of invariant narrow bandpass filters towards the shorter infrared wavelength region (SWIR) requires the use of a lighter molecular mass lead chalcogenide salt. The deployment of Galena, lead (II) sulphide (PbS) multilayer was first suggested as a material by Braithwaite [19] in 1954, from which attempts to manufacture interference layers were unsuccessful at that time due to unexpectedly high absorption, induced by poor stoichiometry decomposition during deposition. PbS has subsequently remained an unutilized layer material that has been extensively reported for its semiconductor properties in opto-electronic quantum dot infrared photodetectors and photovoltaic devices, but as a transparent infrared layer material has been scarcely reported in literature sources for over 60 years. Here we present the manufacture of the first fully-transparent temperature-invariant narrow bandpass filter comprising a PbS/ZnSe 3-cavity multilayer of 8% FWHM bandwidth at 3.0 µm. The PbS/ZnSe bandpass is deposited on a Sapphire substrate and similarly exhibits invariant wavelength behavior throughout the 20-200 °C temperature range (Fig 3).

Manufacture of the filter was performed by conventional thermal deposition using the same experimental conditions as PbTe, however avoiding the differential stoichiometric loss and free carrier absorption were compensated by the introduction of a partial pressure of oxygen into the chamber during PbS layer deposition. This was best performed at a pressure of $4x10^{-5}$ Torr, from which transparency becomes fully restored. The lower absorption properties of PbS in comparison with PbTe subsequently offers transparency across the SWIR wavelength region down as far as 2.3 µm ($\alpha<1x10^{4}$ cm^{-1}) [20]. Simulations of refractive index matching, based on the bandpass FWHM and bandwidth broadening with temperature (0.1 nm K^{-1}), suggests a deposited PbS thin film refractive index of 4.0 at 20 °C decreasing to 3.82 at 200 °C. The center wavelength stability is better than 0.02 nm K^{-1}. The thermo-optical expansion coefficient for bulk PbS is close to PbTe at long wavelengths ~2.3 K^{-1} (8-10 µm) with a rapid decrease towards the absorption edge at 2.3 µm [10,11]. The experimental data available for PbS is still too scarce to extract a reliable experimental value, but preliminary results indicate that thin film temperature coefficient (as for PbTe) is significantly less negative than the bulk value. Further determination of γ^{PbS} is of ongoing research.

Environmental durability of this deposited PbS/ZnSe multilayer was assessed by subjecting 1-inch diameter witness samples to the general provisions of military specification MIL-F-48616. This testing included a visual surface quality assessment, adhesion testing, moderate abrasion, humidity testing at 50 °C for 24 hours in >95% relative humidity, together with additional cryogenic to high temperature thermal cycling (20–473 K) and liquid nitrogen thermal shock testing. Further extreme testing included dicing by diamond saw in deionized water lubricant, all of which passed with satisfactory compliance.

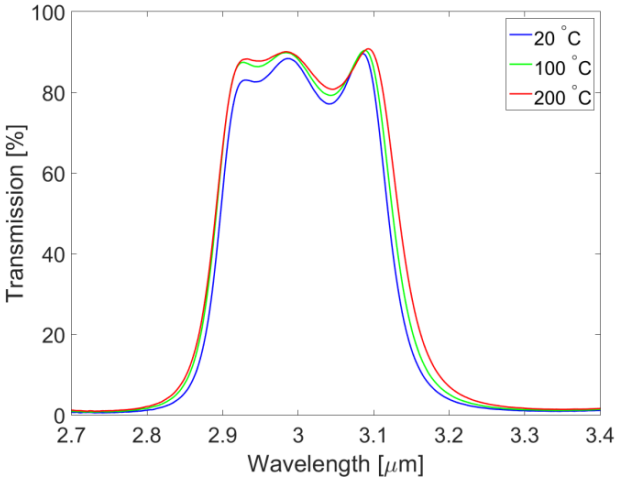

Fig 3. Temperature-invariant PbS/ZnSe 8% FWHM narrow bandpass filter at 3.0 µm on Sapphire
(Single-side coating inclusive of rear surface reflection losses)

6. Discussion

The narrow bandpass filter set from which the presented data was extracted, are all double-side coated complete manufactured optical filters, that contain continuous out-of-band wavelength blocking and antireflection matching layers. The passband ripples of these subsidiary blocking stacks may exert some influence to modulate the final shape and center wavelength positioning of the bandpass profile. However, in [5] we showed that random layer thickness errors have negligible influence on the temperature-invariance transmission profile, as this is dominated by the design and materials interdependence. The substrate has previously been reported to influence temperature dependence of narrow bandpass filters [21] but in [5] the choice of substrate, or substrate thickness did not appear to affect the temperature behavior of the bandpass filter profile. Further, although all of the filters studied were of triple half-wave (3-cavity) multilayers, we can consider the extracted thermo-optical values to be representative also for embedded thin films in other multilayer structures, particularly as variations in cavity order and number of inter-cavity layers did not appear to affect the thermo-optical behavior. However, the precise deposition conditions may conceal further opto-mechanical stress dependence of the extracted thermo-optical properties.

7. Conclusions

In this investigation we have derived the thermo-optical expansion coefficients for embedded thin films of polycrystalline PbTe and ZnSe. Embedded thin film ZnSe was found to exhibit bulk thermo-optical properties, whilst embedded thin film PbTe deviated significantly from reported literature values. This was attributed to the lower density of deposited PbTe film compared to single-crystal material. A thin film bandpass filter based on thermally deposited PbS material was demonstrated, extending the range of temperature-invariant behavior to shorter wavelengths and a wider range of bandwidths.

Acknowledgements
The authors thank colleagues at Schlumberger Cambridge Research for discussions and grateful support under contract reference QU-RDU-01274-C, Thomine is an industrial PhD student at Danfoss IXA A/S and her work is supported by the Danish Agency of Science, Technology and Innovation (DASTI). Thanks also to Richard Sherwood and Karim Djotni at the University of Reading for their assistance with spectral measurements and thin film depositions, which is gratefully acknowledged.

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