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B. Li, S. Y. Zhang, J. C. Jiang, B. Fan, F. S. Zhang; Improving low-temperature performance of infrared thin-film interference filters utilizing the intrinsic properties of IV-VI narrow-gap semiconductors ; Optics Express 401, Vol. 12, No. 3, (9th February 2004)

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Other: **WPI, EPODOC, TXTE, INSPEC & Internet**

(54) Title of the Invention: **Temperature invariant infrared filter**
Abstract Title: **Temperature invariant infrared filter**

(57) A temperature invariant narrow bandpass filter 5 to transmit mid-infrared radiation that may be used in a mid-infrared sensor for monitoring a species, which may be a component of a fluid or a solid material. The filter has a substrate 14, a first stack deposited on the substrate, a cavity 16 deposited on the first stack and a second stack deposited on the cavity. The first and second stacks are made from alternating high 10 and low 12 refractive index materials, and the cavity is a low refractive index material. By providing a high ratio of low refractive index material in the filter with respect to high refractive index material, the filter is configured so that wavelength transmission remains constant with varying temperature. The high refractive index material has a refractive index that decreases with temperature and the cavity is at least three full wavelengths or three half wavelengths of the transmission wavelength or the narrow band of transmission wavelengths.



21 08 15

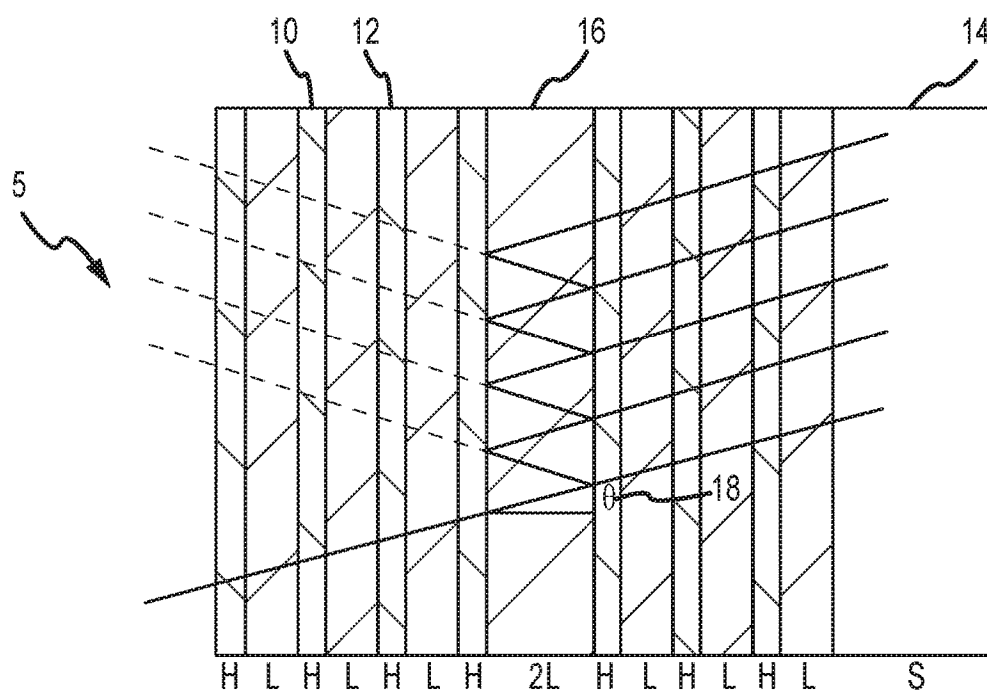


FIG.1

21 08 15

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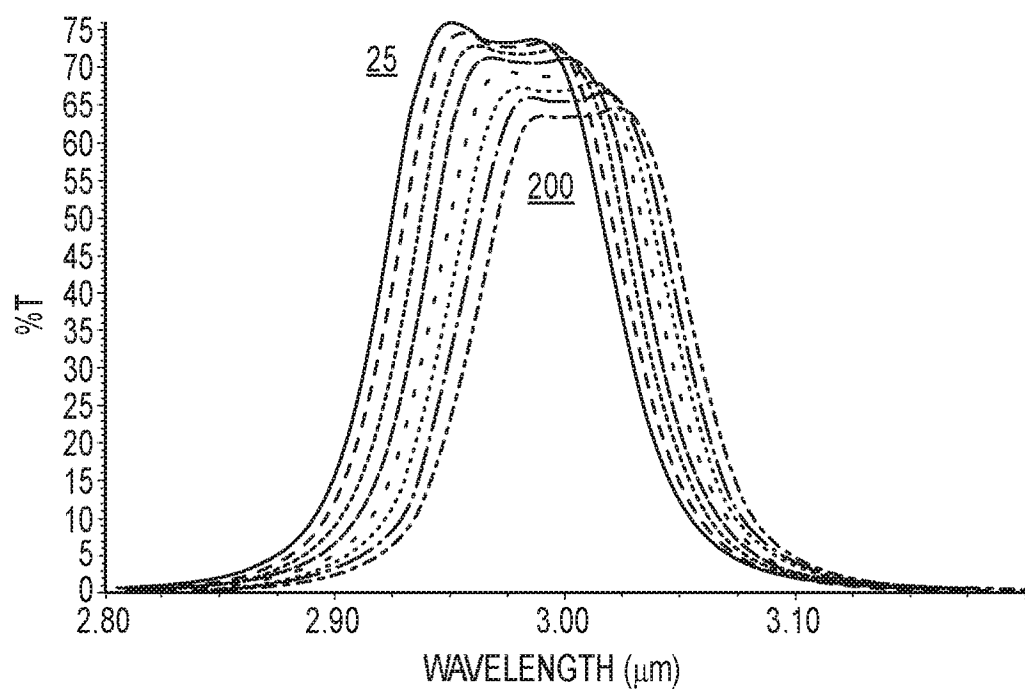


FIG.2A

21 08 15

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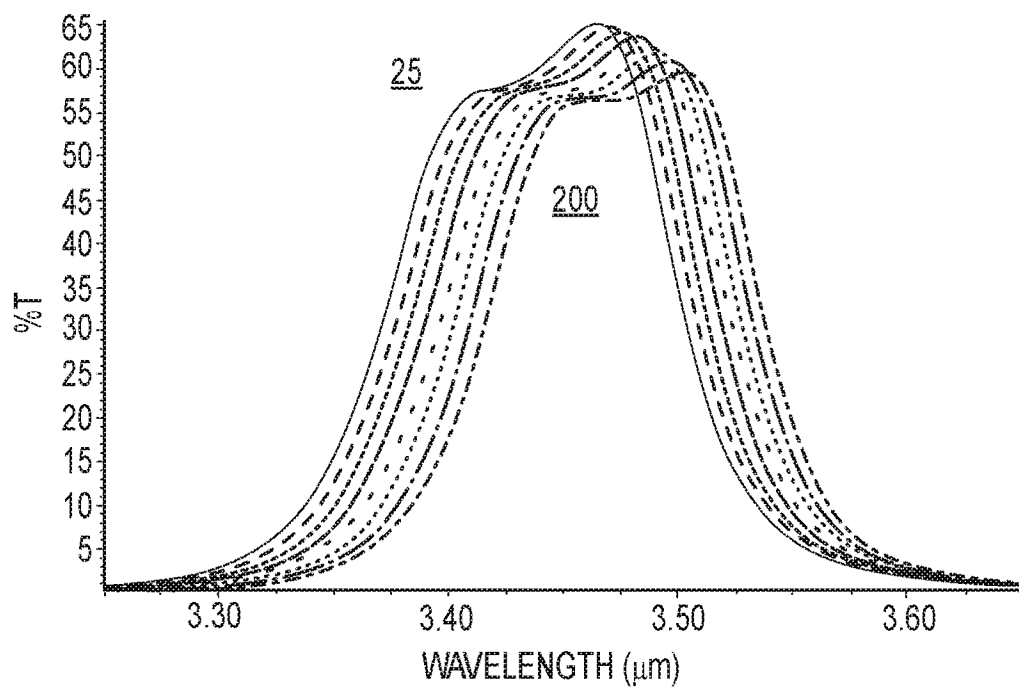


FIG.2B

21 08 15

4/20

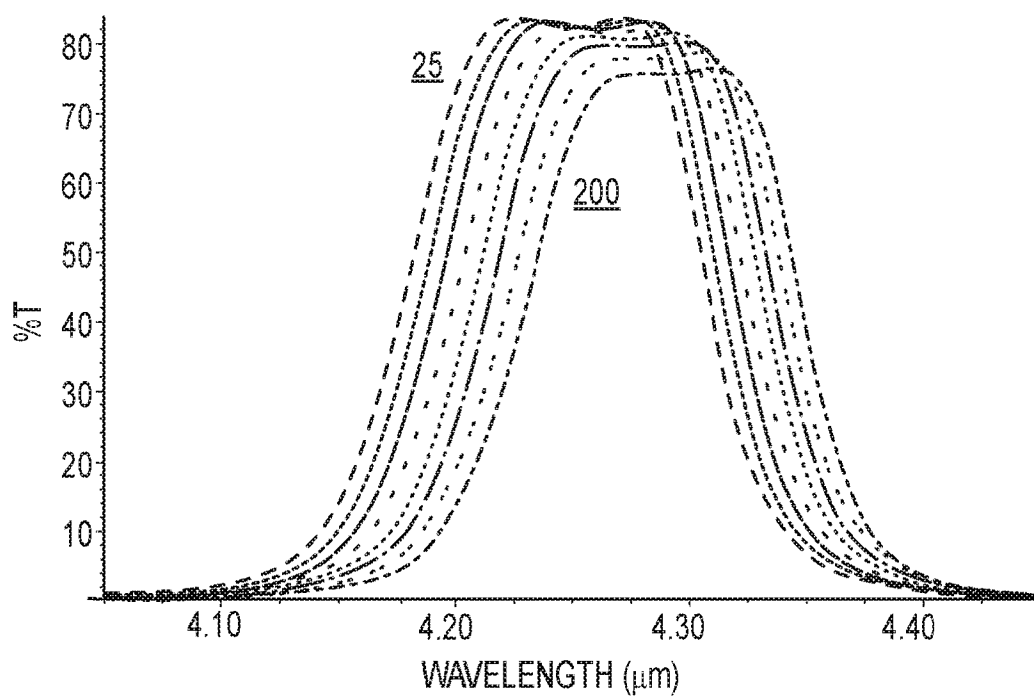


FIG.2C

21 08 15

5/20

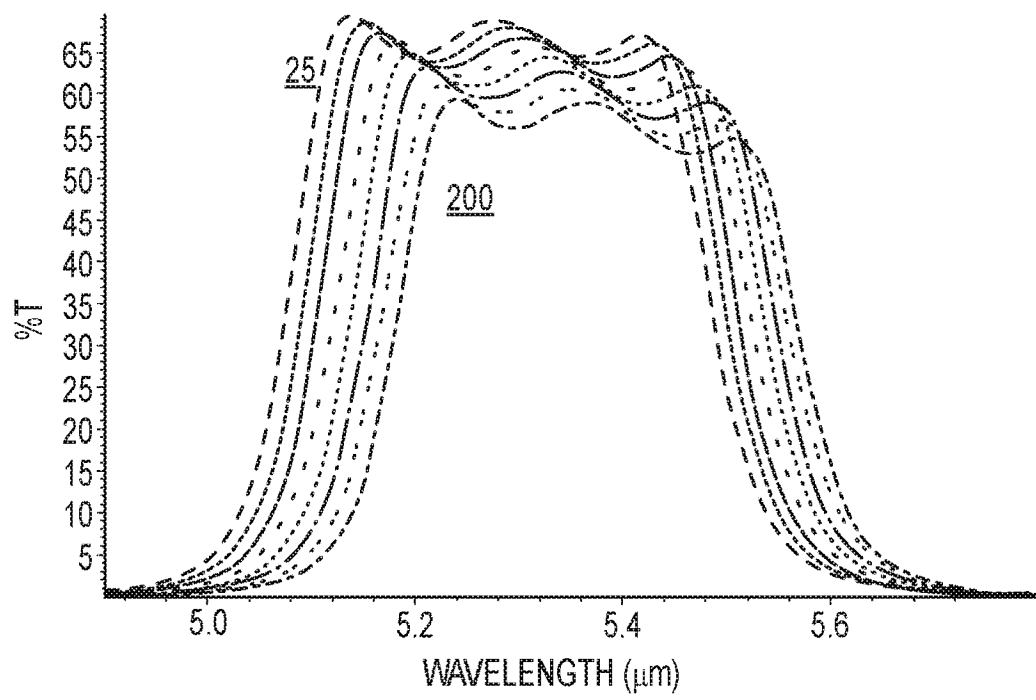


FIG.2D

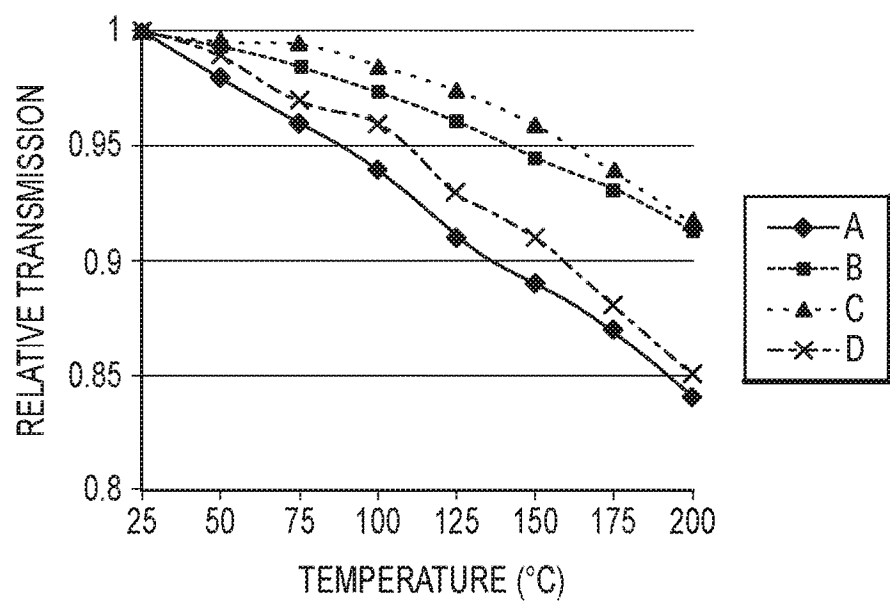


FIG.3A

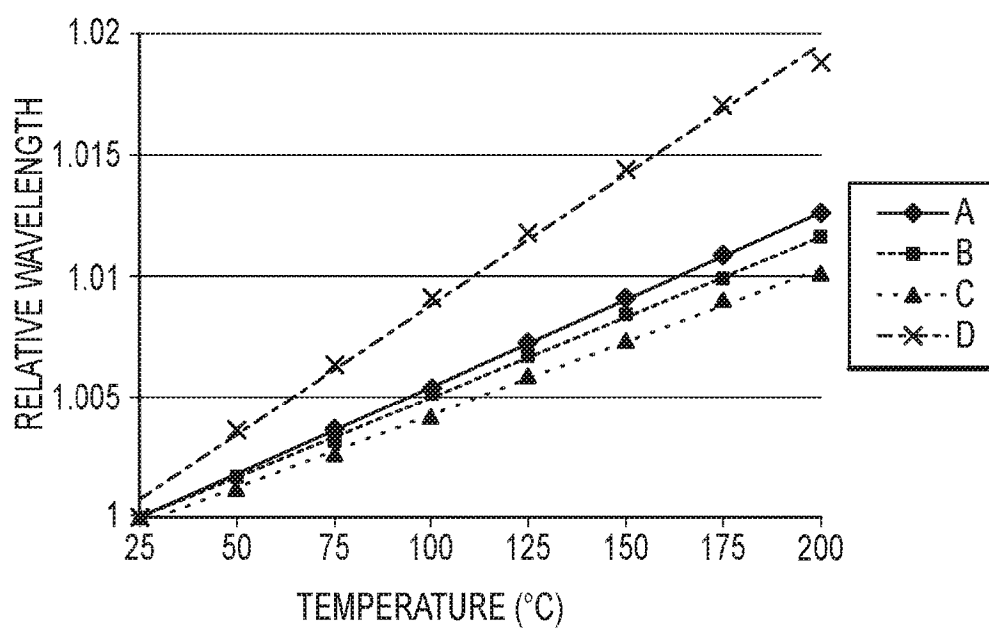


FIG.3B

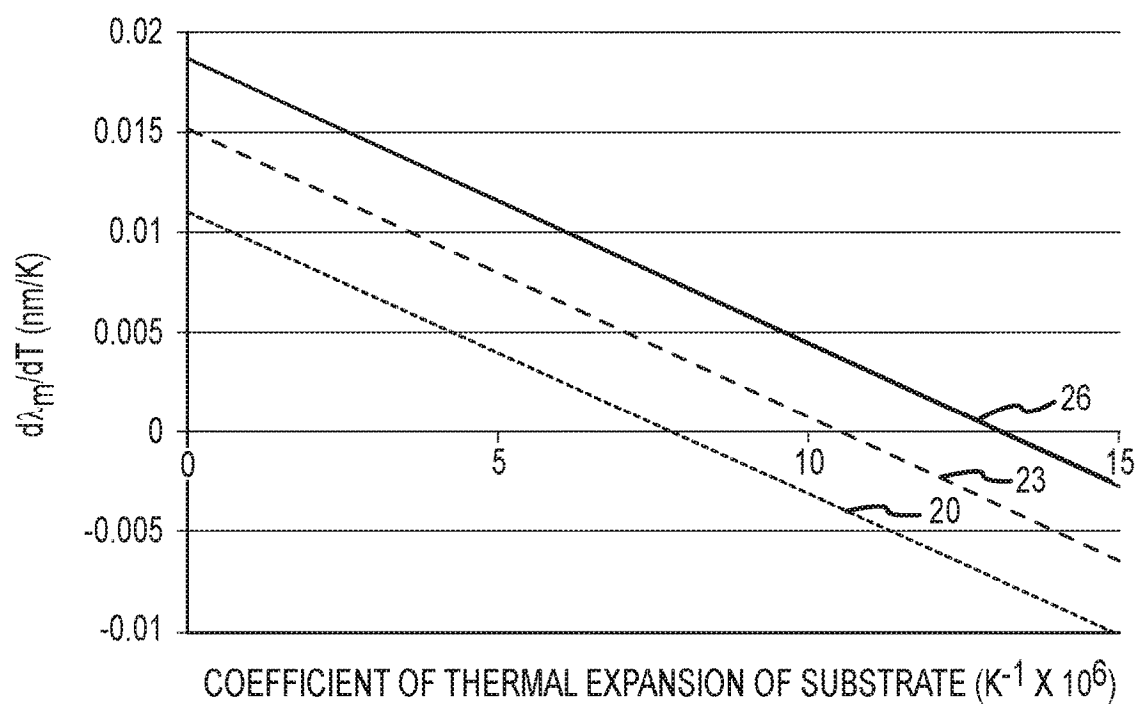


FIG.4

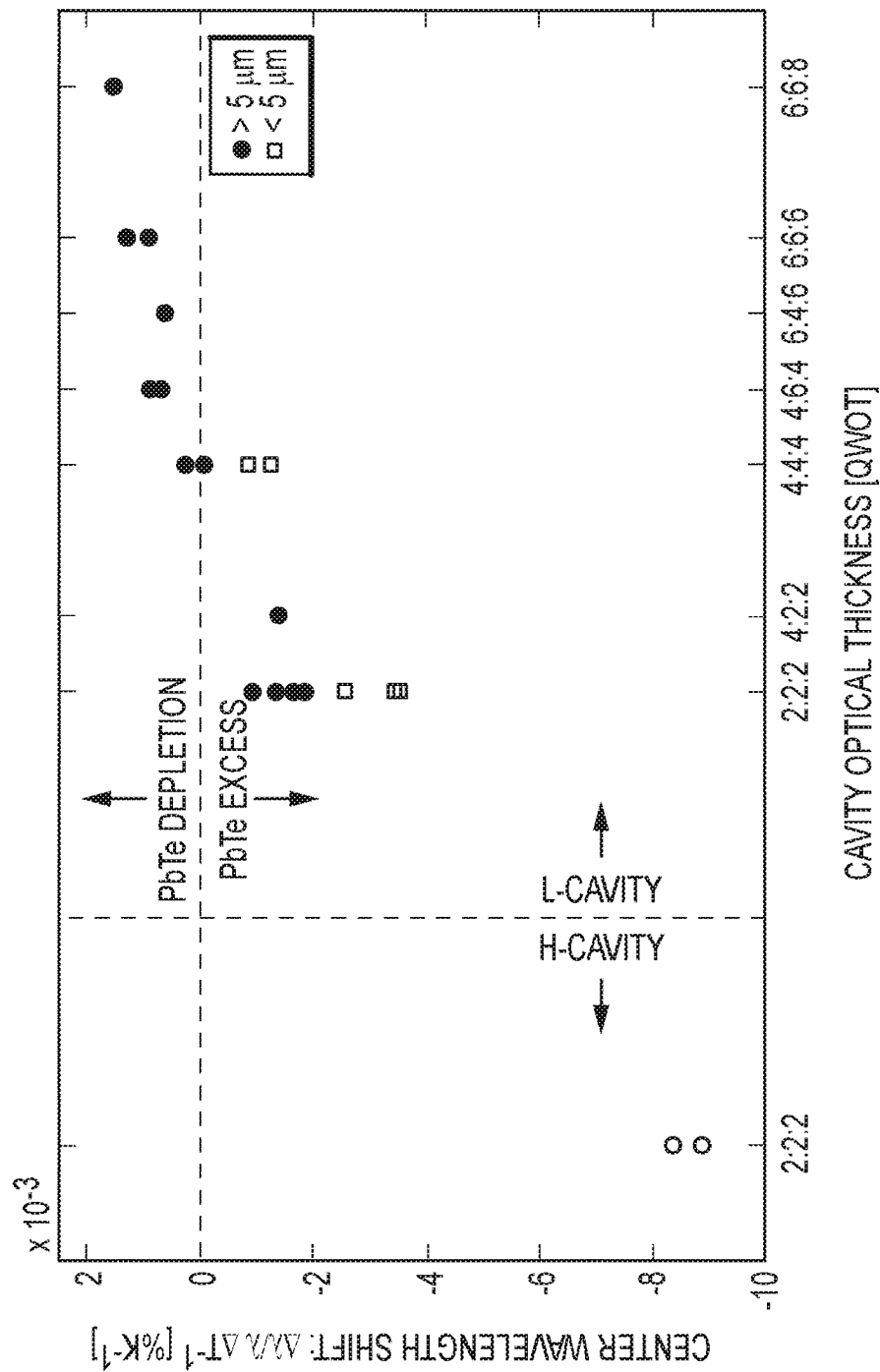


FIG.5

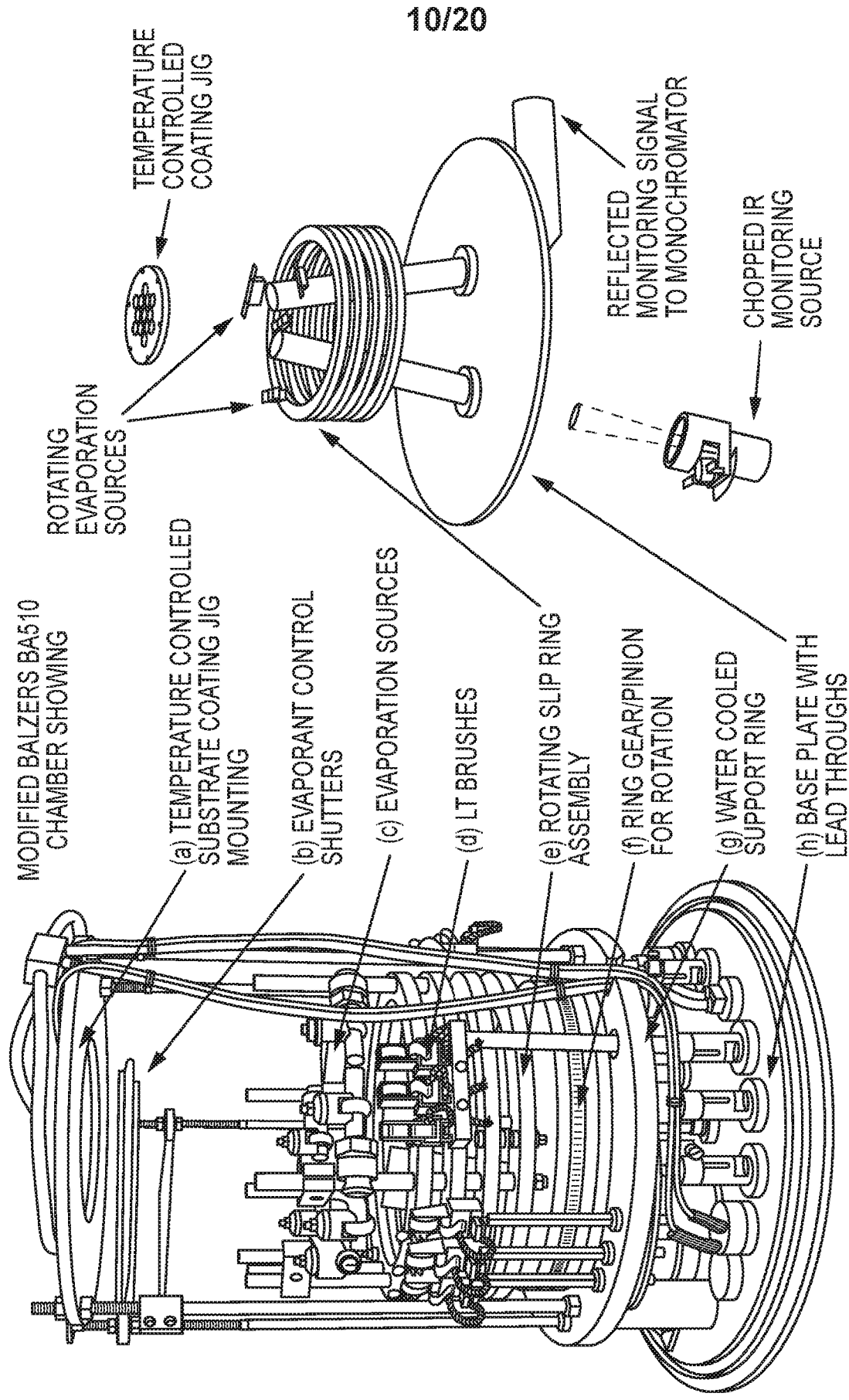


FIG.6A

FIG.6B

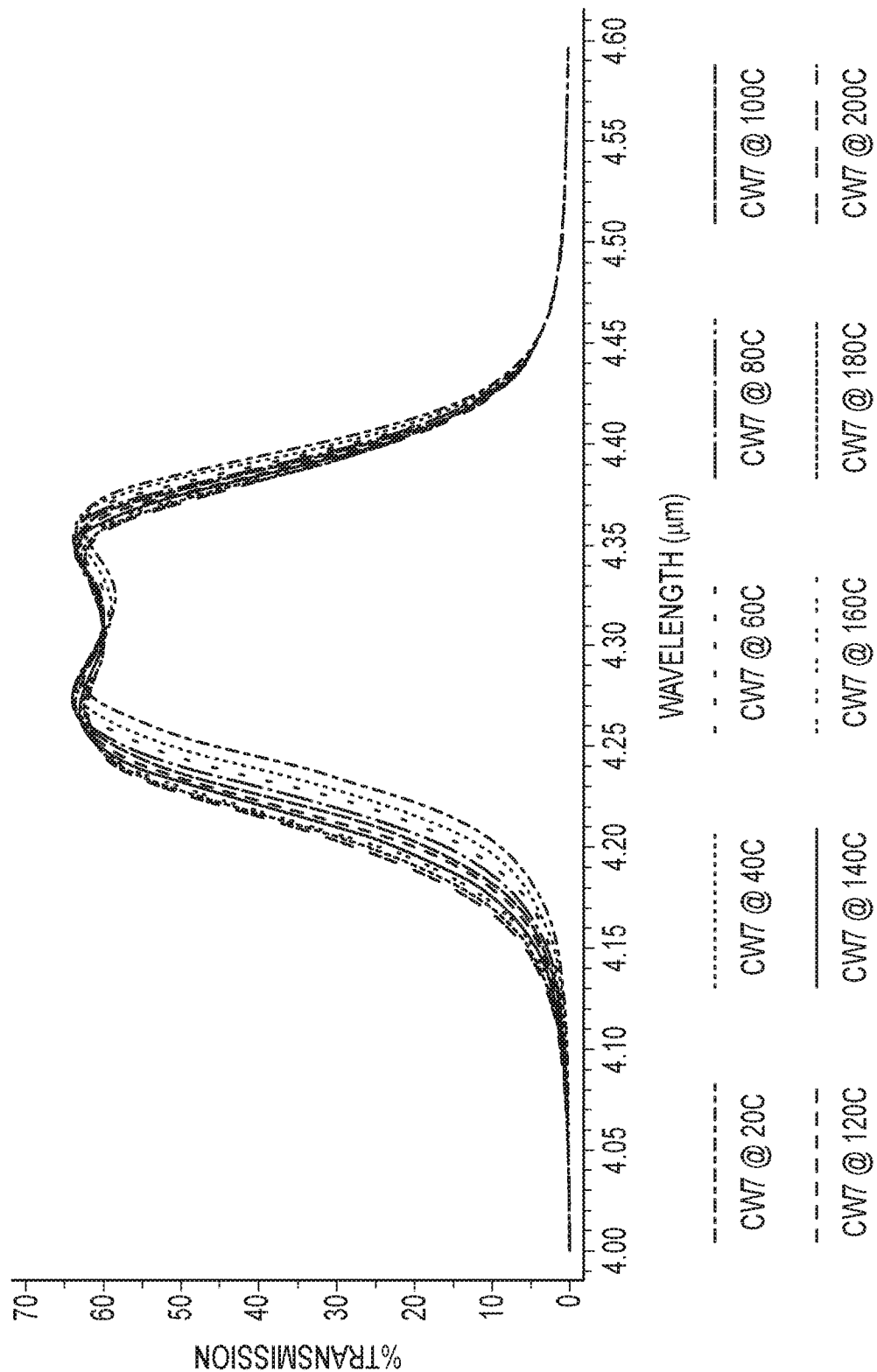


FIG.7A

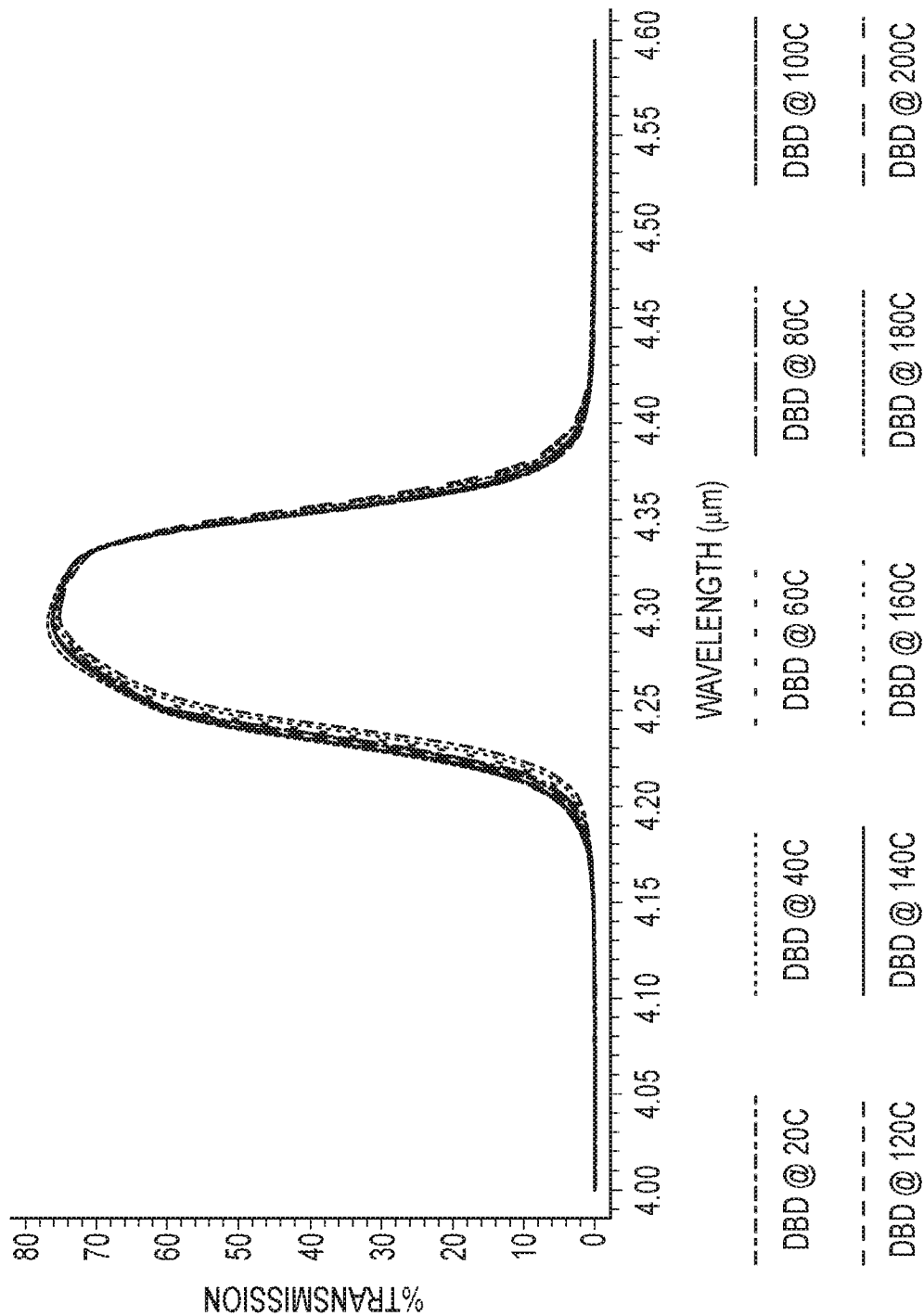


FIG.7B

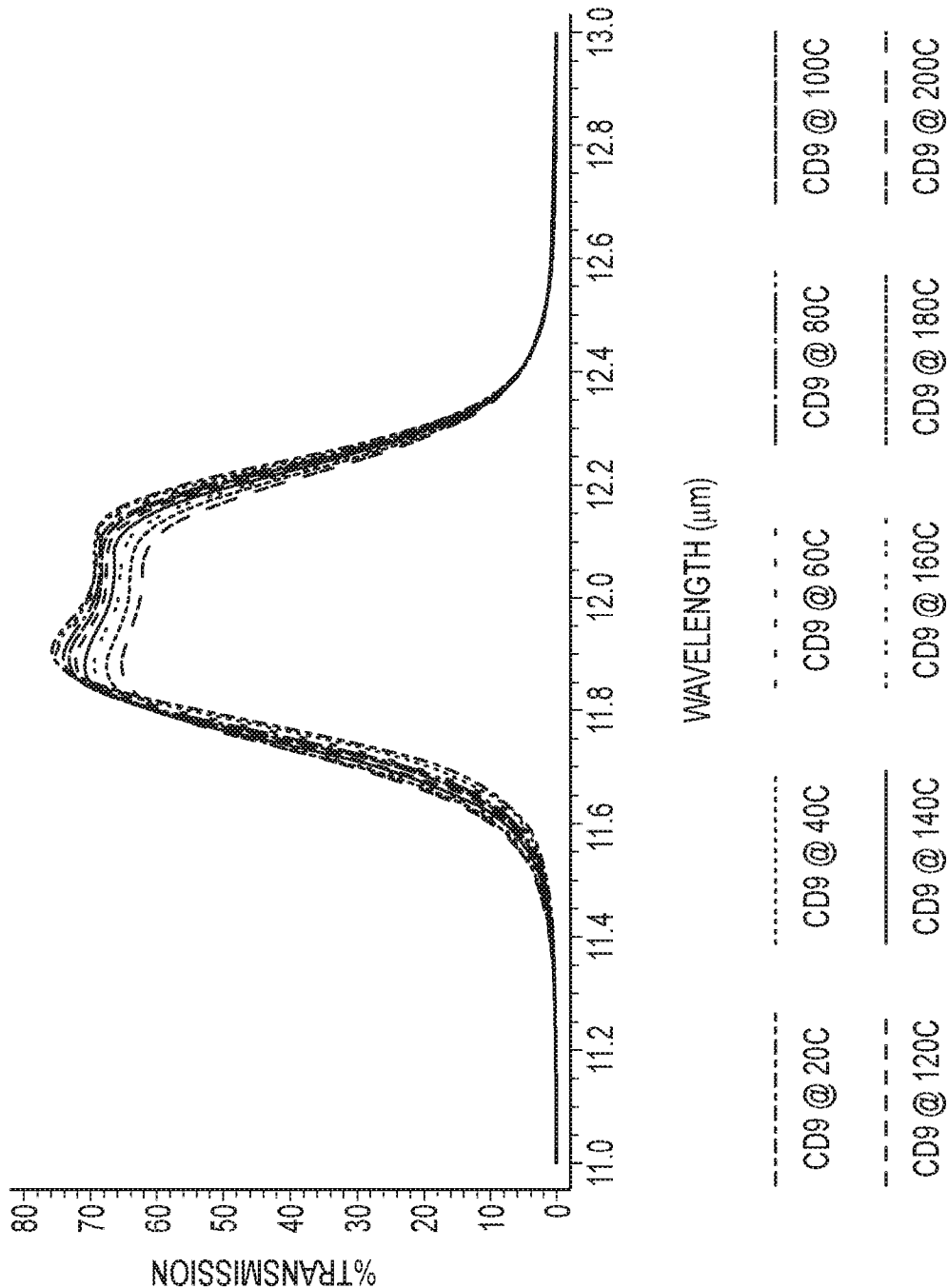


FIG.8A

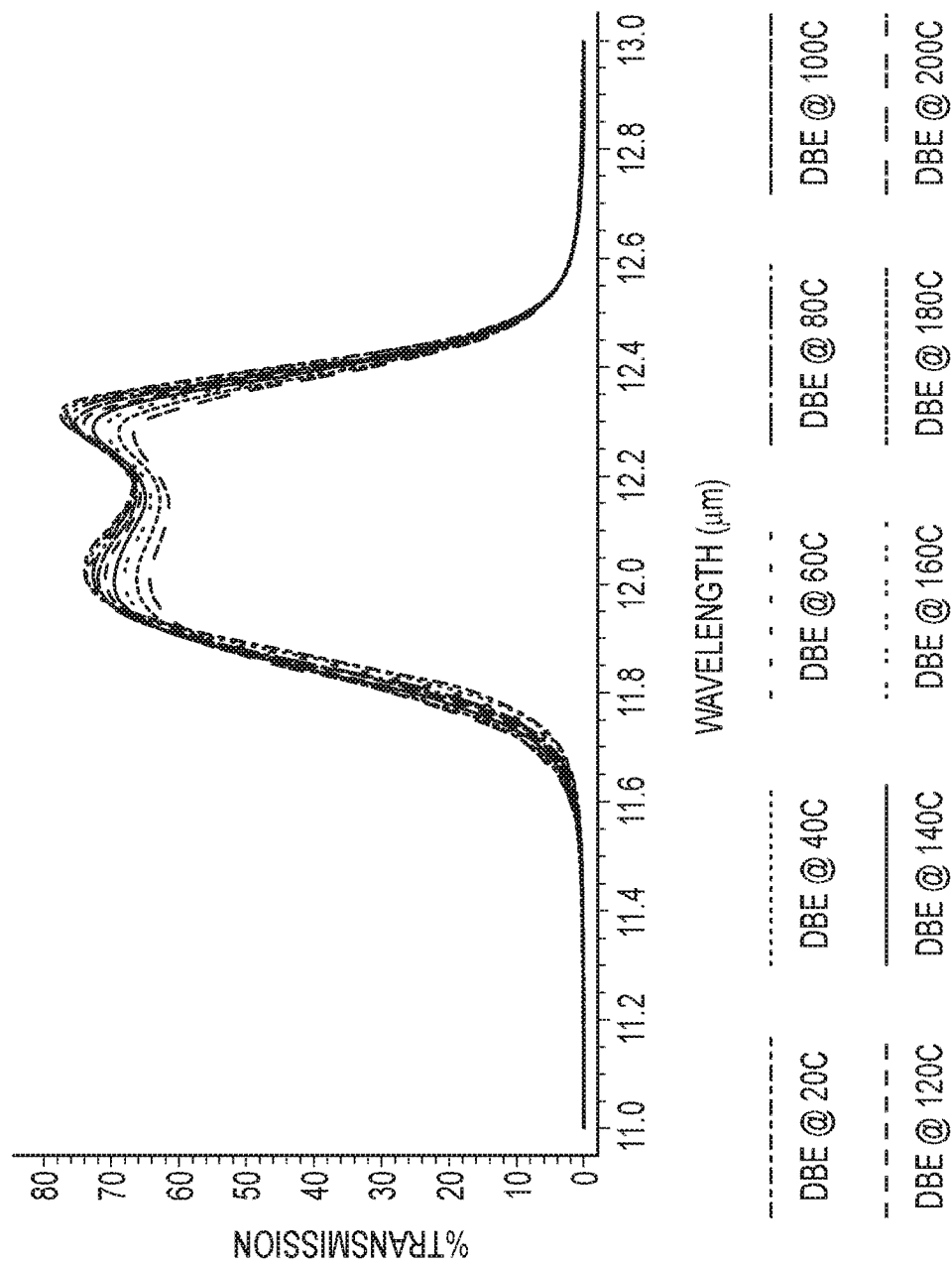


FIG.8B

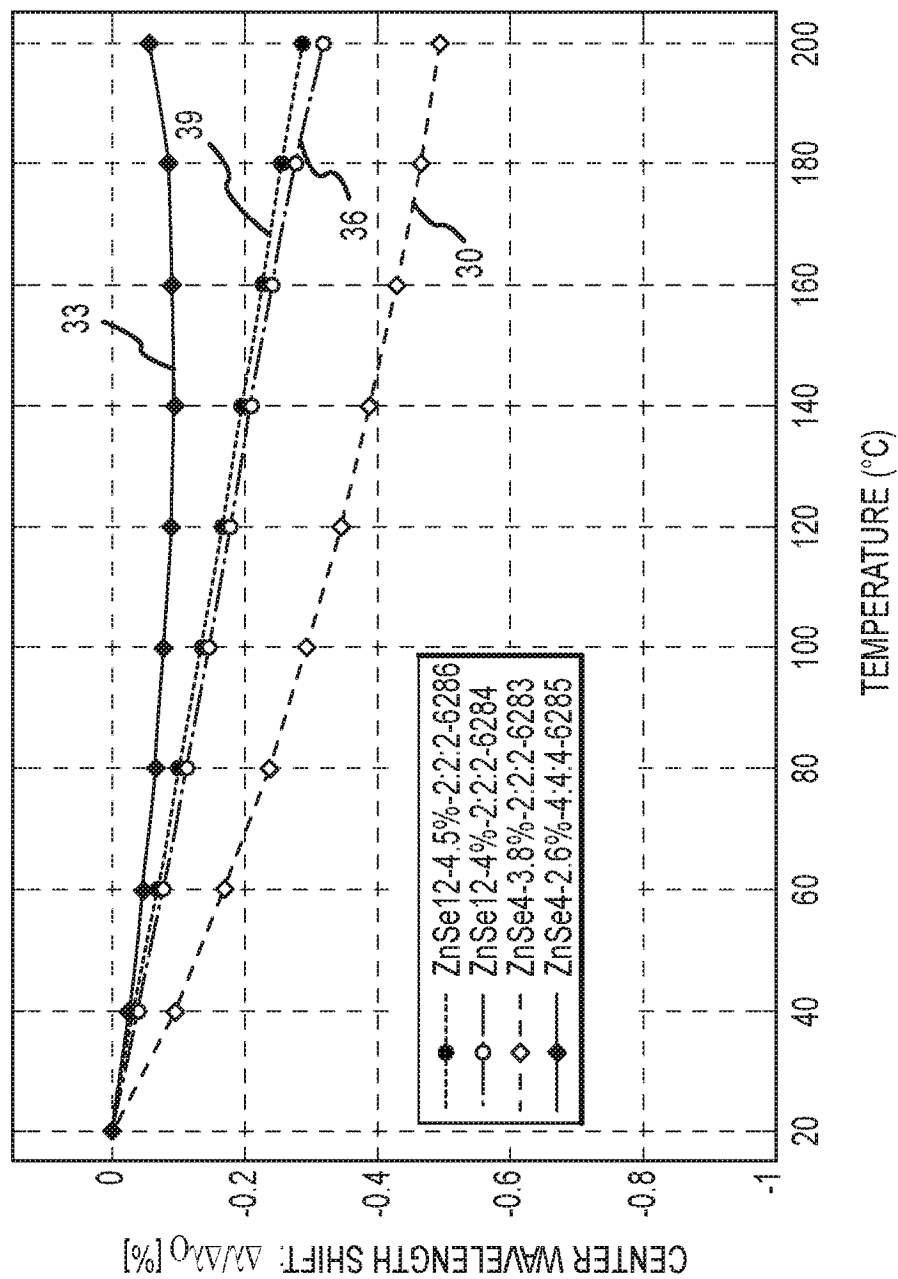


FIG.9

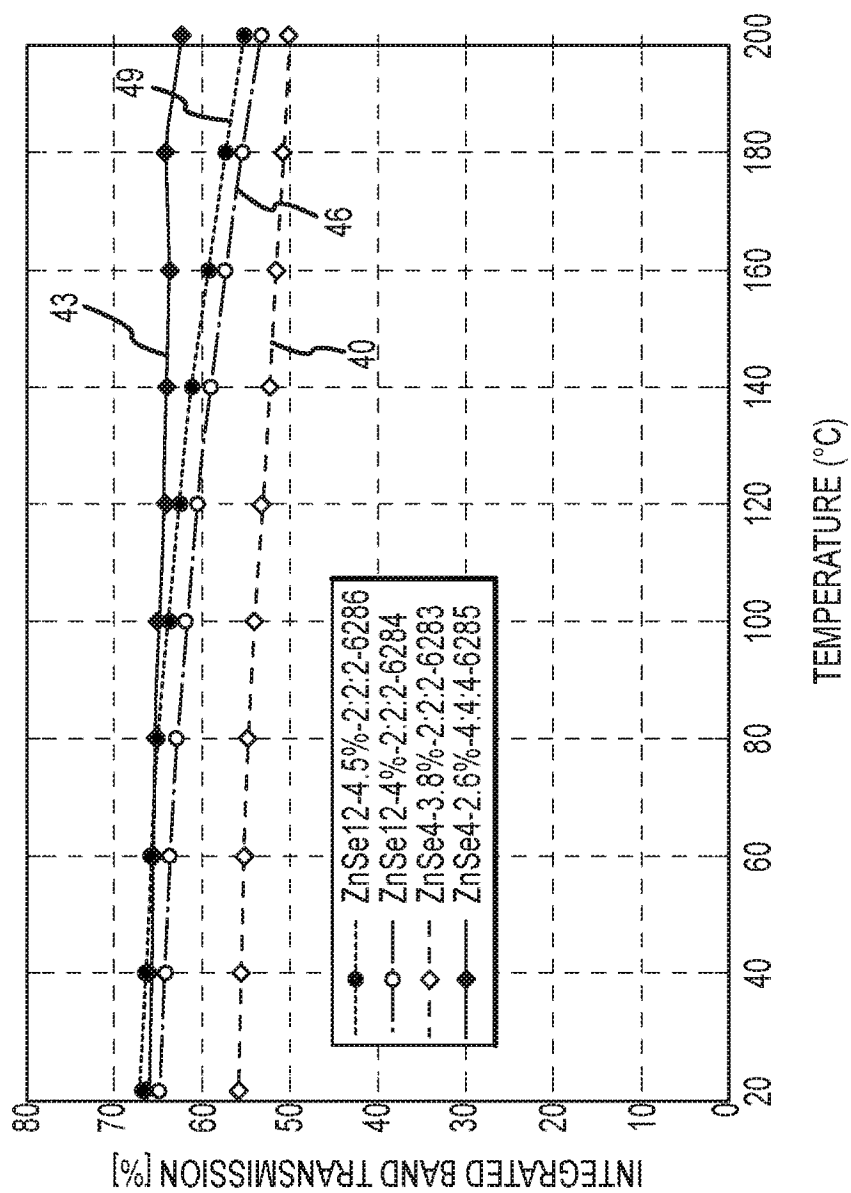


FIG.10

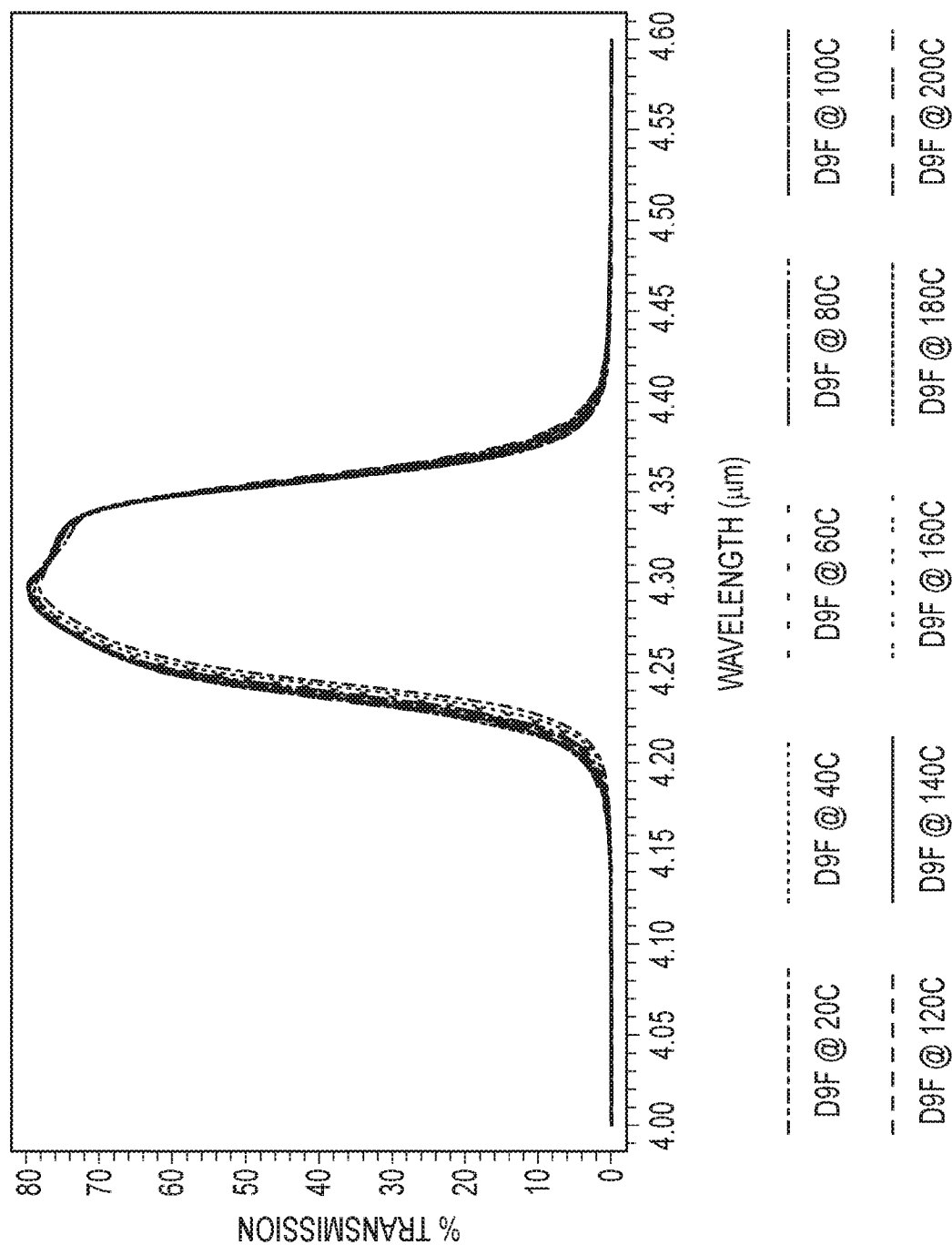


FIG.11A

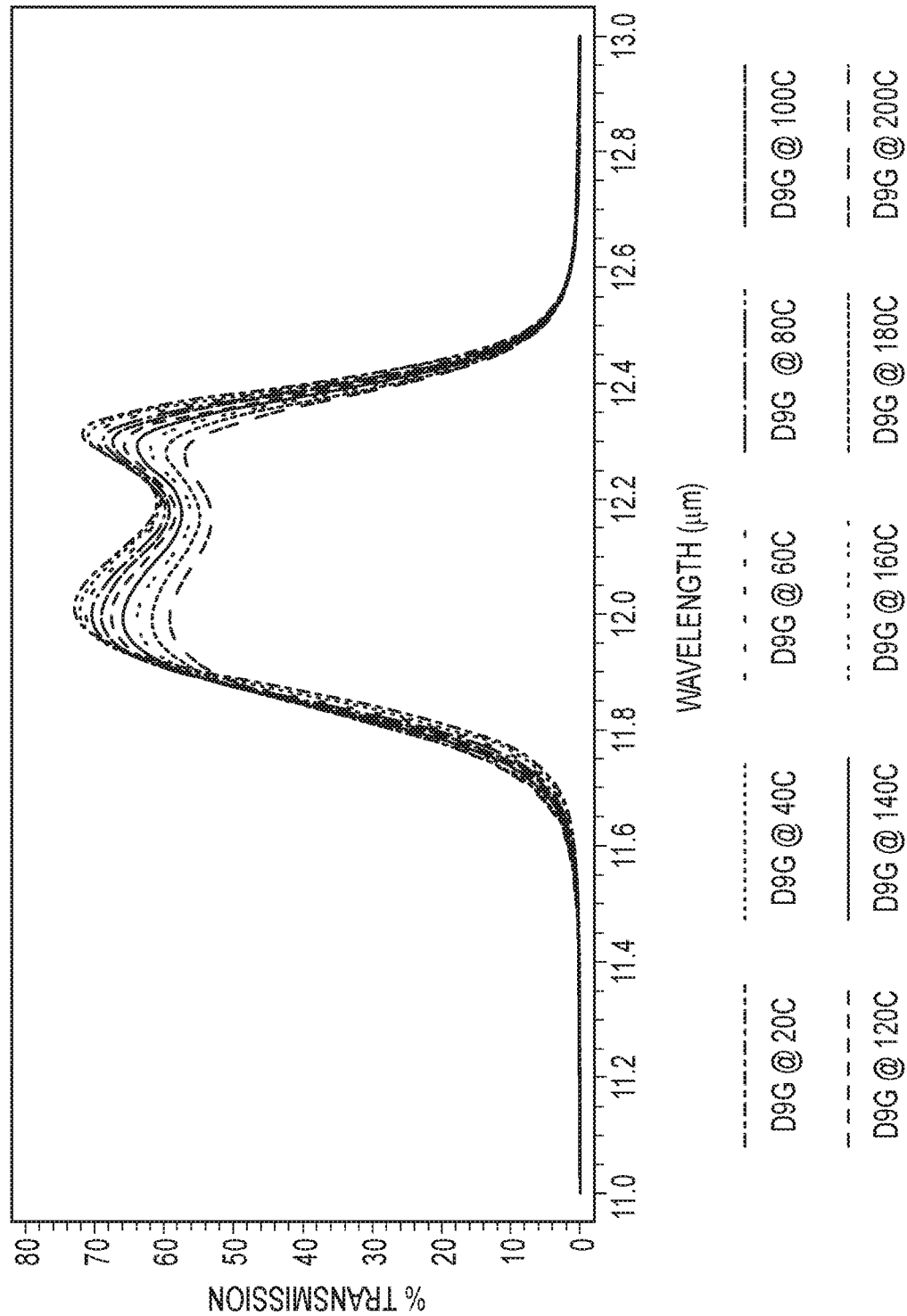


FIG.11B

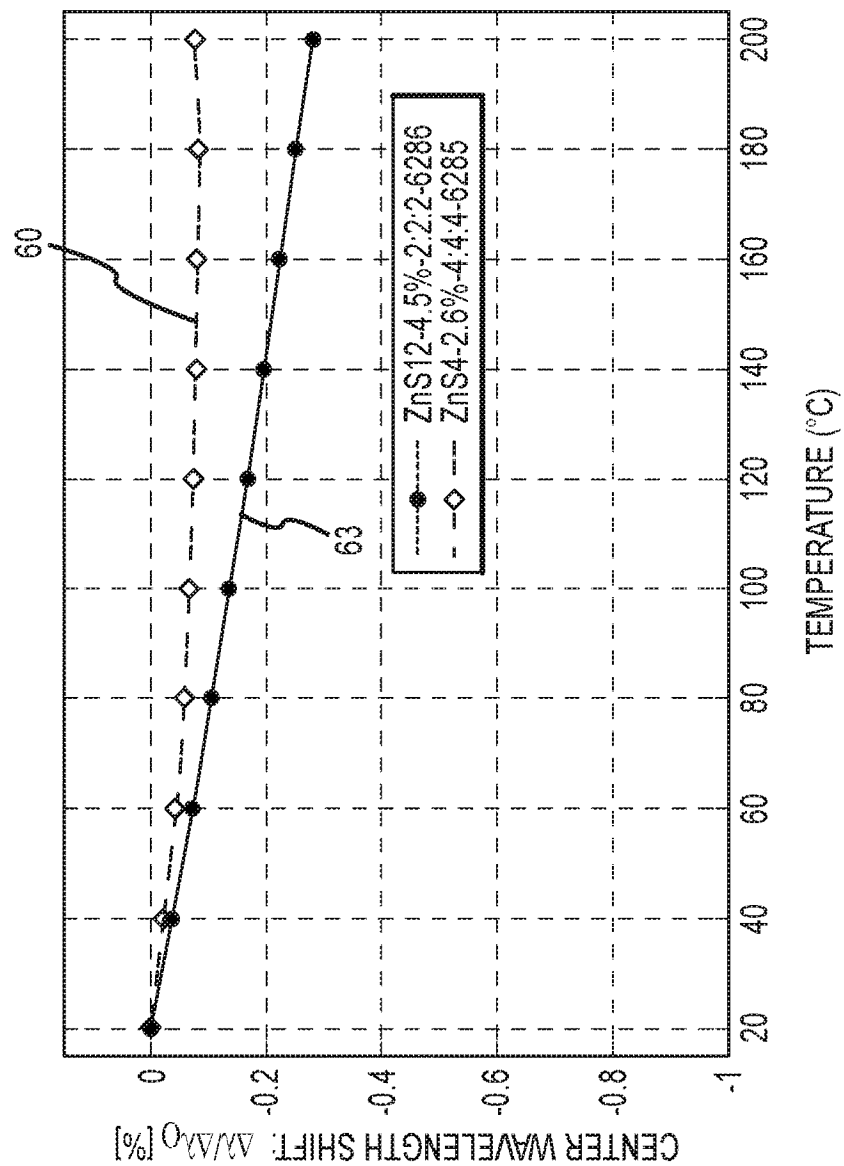


FIG.12

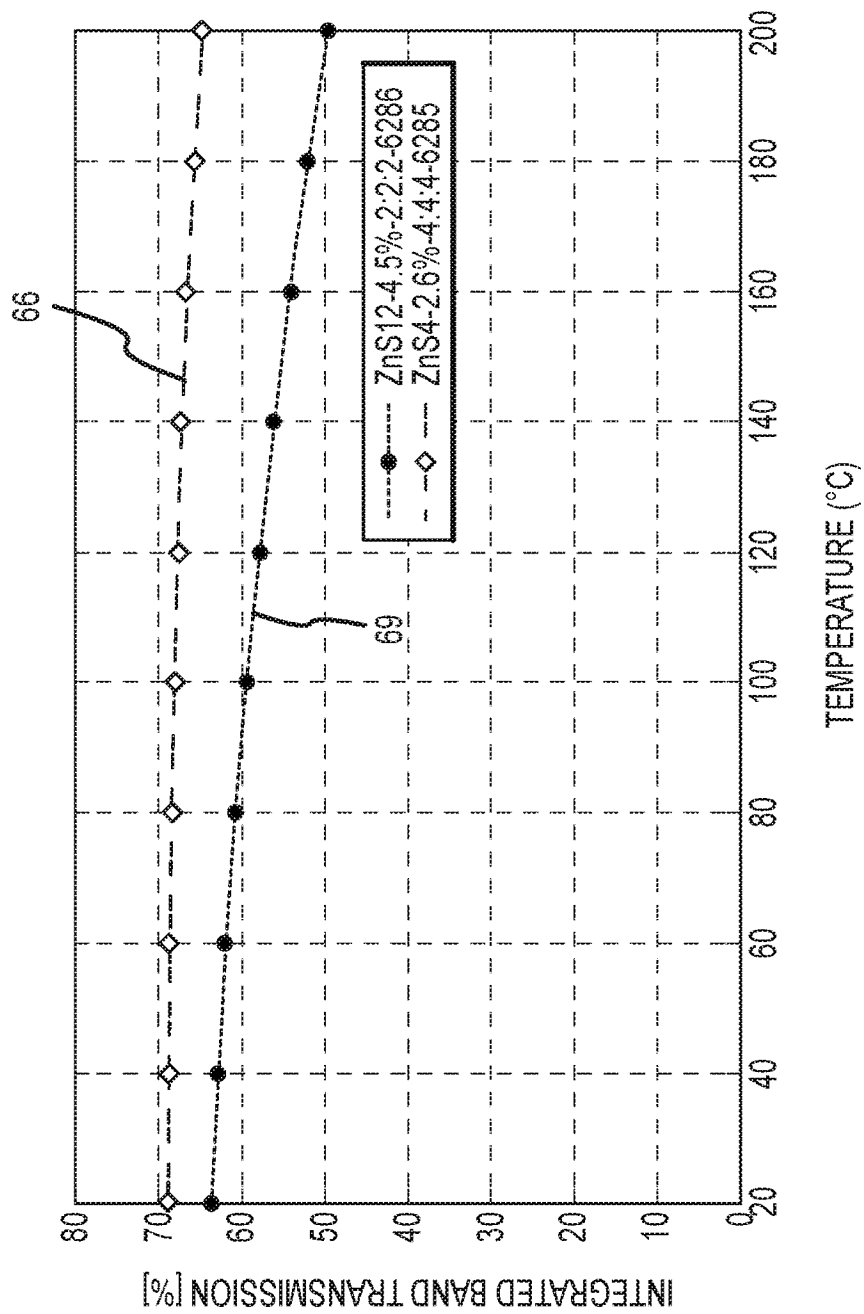


FIG.13

TEMPERATURE INVARIANT INFRARED FILTER

BACKGROUND

Embodiments of the present disclosure relate to narrow bandpass filter that may be
5 used in a mid-infrared sensor for monitoring a species, which may be a component
of a fluid or a solid material.

The analysis of chemical composition of fluid samples is important in many
industries and is often required to be performed in harsh environments. For
example, in the food and beverage and chemical processing industries, online
10 measurements are often required to be made in hot, cold, widely temperature
varying conditions and/or in the presence of reactive compounds. In the
hydrocarbon industry, online measurements are often made in hydrocarbon wells
for the determination of phase behaviour and chemical composition for the
monitoring and management of a hydrocarbon well as well as the evaluation of the
15 producibility and economic value of the hydrocarbon reserves. Similarly, the
monitoring of fluid composition during production or other operations can have an
important bearing on reservoir management decisions. Similarly, determination of
phase behaviour and chemical composition is important in pipelines and the like
used to convey/transport hydrocarbons from the wellhead, including subsea
20 pipelines.

SUMMARY

Embodiments of the present disclosure provide mid-infrared sensors for use where
temperatures may vary widely.

For purposes of the present disclosure, the term “mid-infrared radiation” means
25 that the radiation has a wavelength in the range from about 2 to 25 μm , and in
some embodiments of the disclosure from about 3 to 12 μm or from about 3 to
10 μm .

In embodiments of the present disclosure, a narrow bandpass filter may be
configured such that its wavelength transmission band is substantially temperature

invariant over all temperatures in the range from about 25 to 150°C. In some embodiments, the narrow bandpass filter may be configured for use in the petrochemical industry, where temperatures in downhole environments can vary greatly, e.g. from room temperature up to 150°C or 200°C. By using such a temperature invariant filter, the sensitivity of the sensor to shifts in temperature of its surroundings can be greatly reduced, improving accuracy and allowing for use of mid-infrared sensing techniques in locations experiencing wide temperature fluctuations.

To cover a greater range of downhole temperatures, the wavelength transmission band of the first narrow bandpass filter may be substantially temperature invariant over all temperatures in the range from about 25 to 200°C. To cover both downhole and subsea conditions (where ambient temperatures can be in the range from -25 to 25°C), the wavelength transmission band of the first narrow bandpass filter may be substantially temperature invariant over all temperatures in the range from about -25 to 125, 150 or 200°C.

In embodiments of the present disclosure, the term "substantially temperature invariant" means that the variance is at most about 0.2 nm/°C over the temperature range -25 to +200°C and over the wavelength range 2-14 μm. In some embodiments, the variance is at most about 0.05, 0.03, 0.02 or 0.01 nm/°C.

In some embodiments of the present disclosure, the filter may be an interference filter. For example, the filter may in some embodiments comprise a substrate, formed of Si, SiO₂, Al₂O₃, Ge, ZnSe and/or the like and at each opposing side of the substrate alternating high and low refractive index layers may be formed. For example, in some embodiments, the high refractive index layers may be formed of PbTe, PbSe, PbS and/or the like and the low refractive index layers may be formed of ZnS, ZnSe and/or the like.

Applicants have found that for mid-infrared filters experiencing wide temperature variations, changes in optical properties of the filter may be prevented by controlling the ratio of low to high refractive index materials in the filter so that there is a high ratio of the low refractive index material. To produce this, in some embodiments of the present disclosure, the cavities of the low bandpass filter

comprise low refractive index material. In embodiments of the present disclosure, filter comprises a cavity having an optical thickness of at least three full wavelengths of the transmission wavelength or the narrow band of transmission wavelengths or three half-wavelengths of the transmission wavelength or the narrow band of transmission wavelengths. In some embodiments, the filter comprises at least separate three cavities. For example, where the filter comprises at least three separate cavities, each of the cavities are either half wavelength ($\lambda/2$) or full wavelength (λ) of the transmitted radiation in optical thickness. And for example, where the cavity comprises a single cavity, it comprises a cavity of optical thickness $3\lambda/2$ or 3λ in optical thickness. In some embodiments, other combinations of cavities are used to obtain a narrow bandpass filter comprising a cavity with an optical thickness of three full wavelengths of the transmission wavelength or the narrow band of transmission wavelengths or three half-wavelengths of the transmission wavelength or the narrow band of transmission wavelengths, e.g., one cavity with a half wavelength ($\lambda/2$) optical thickness and one cavity with a full wavelength (λ) optical thickness.

Many conventional filters display changes in optical properties, such as high band shifts, with increasing temperature. For example, shifts in the range 0.2 to 0.6 nm/°C have typically been measured over narrow temperature ranges and/or at single wavelengths. Transmissivities of conventional filters also tend to reduce with increasing temperature. However, in embodiments of the present disclosure, by using a PbTe-based, PbSe-based, PbS-based and/or the like interference filter, it is possible to substantially reduce band shifts and transmissivity reductions. For example, a PbTe-based interference filter can, in accordance with an embodiment of the present disclosure, have a band shift of only about 0.03 nm/°C or less. As an alternative to PbTe, PbSe, PbS or mixtures of these lead chalcogenide compounds may be used in some embodiments, for the high refractive index layers of the temperature invariant filter. Moreover, applicants have found that other high refractive index materials, such as germanium, are unsuitable for such filters.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the disclosure will now be described by way of example with reference to the accompanying drawings in which:

Figure 1 shows a schematic of a typical structure of a narrow bandpass interference filter;

Figures 2A-D illustrates temperature dependence of the bandpass of commercially-available filters A, B, C and D for the temperature range 25 °C to 200 °C in increments of 25 °C;

Figure 3A shows the relative change in T_m for the four filters of Figs. 3A-D as a function of temperature;

Figure 3B shows the dependence of the relative wavelength ($\lambda_m(T)/\lambda_m(25)$) on temperature for the four commercially-available filters of Figs. A-D;

Figure 4 illustrates dependence of $d\lambda_m/dT$ on C_s for three values of $dn_e/n_e dT$; $0.75 \times 10^{-5} \text{ K}^{-1}$ (blue), $1.00 \times 10^{-5} \text{ K}^{-1}$ (red) and $1.25 \times 10^{-5} \text{ K}^{-1}$ (green);

Figure 5 illustrates variation of $d\lambda_m/\lambda_m dT$ for a suite of filters, in accordance with embodiments of the present disclosure, fabricated with ZnSe as the low refractive index material and PbTe as the high refractive index material;

Figure 6A is an illustration of a Balzers BA510 thin film deposition system and Figure 6B is a schematic of the rotating evaporation sources;

Figures 7A and B show the temperature dependence of the bandpass of two 3 cavity filters fabricated on ZnSe substrates and designed to operate at $\lambda_m = 4.26 \mu\text{m}$, in accordance with embodiments of the present disclosure;

Figures 8A and B show the corresponding performance of two narrow bandpass filters, a degenerate filter in Fig. 8A and an optimally matched filter in Fig. 8B, operating at $\lambda_m = 12.12 \mu\text{m}$;

Figure 9 compares the relative change in wavelength λ_m at peak transmission with temperature of the four filters shown in figures 7A and B and 8A and B;

Figure 10 shows the corresponding variation of the integrated band transmission T_i with temperature for the four filters of figures 7A and B and 8A and B;

- 5 Figures 11A and B show the temperature dependence of the bandpass of two 3 cavity filters fabricated on ZnS substrates that have been designed to operate at $\lambda_m=4.26 \mu\text{m}$ (4:4:4 cavity layers) and $\lambda_m=12.1 \mu\text{m}$ (2:2:2 cavity layers);

Figure 12 compares the dependence of $\Delta\lambda_m/\lambda_{m0}$ on temperature (20-200°C) for the two filters shown in figures 11A & 11B; and

- 10 Figure 13 shows the variation of T_i with temperature for the two filters of Figs 11A & B deposited on ZnS substrates.

- 15 In the appended figures, similar components and/or features may have the same reference label. Further, various components of the same type may be distinguished by following the reference label by a dash and a second label that distinguishes among the similar components. If only the first reference label is used in the specification, the description is applicable to any one of the similar components having the same first reference label irrespective of the second reference label.

DETAILED DESCRIPTION

- 20 The ensuing description provides preferred exemplary embodiment(s) only, and is not intended to limit the scope, applicability or configuration of the invention. Rather, the ensuing description of the preferred exemplary embodiment(s) will provide those skilled in the art with an enabling description for implementing a preferred exemplary embodiment of the invention, it being understood that various
25 changes may be made in the function and arrangement of elements without departing from the scope of the invention.

Specific details are given in the following description to provide a thorough understanding of the embodiments. However, it will be understood by one of

ordinary skill in the art that embodiments may be practised without these specific details. For example, well-known circuits, processes, algorithms, structures, and techniques may be shown without unnecessary detail in order to avoid obscuring the embodiments.

5 Also, it is noted that the embodiments may be described as a process which is depicted as a flowchart, a flow diagram, a data flow diagram, a structure diagram, or a block diagram. Although a flowchart may describe the operations as a sequential process, many of the operations can be performed in parallel or concurrently. In addition, the order of the operations may be re-arranged. A
10 process is terminated when its operations are completed, but could have additional steps not included in the figure. A process may correspond to a method, a function, a procedure, a subroutine, a subprogram, etc. When a process corresponds to a function, its termination corresponds to a return of the function to the calling function or the main function.

15 Moreover, as disclosed herein, the term "storage medium" may represent one or more devices for storing data, including read only memory (ROM), random access memory (RAM), magnetic RAM, core memory, magnetic disk storage mediums, optical storage mediums, flash memory devices and/or other machine readable
20 mediums for storing information. The term "computer-readable medium" includes, but is not limited to portable or fixed storage devices, optical storage devices, wireless channels and various other mediums capable of storing, containing or carrying instruction(s) and/or data.

Furthermore, embodiments may be implemented by hardware, software, firmware, middleware, microcode, hardware description languages, or any combination
25 thereof. When implemented in software, firmware, middleware or microcode, the program code or code segments to perform the necessary tasks may be stored in a machine readable medium such as storage medium. A processor(s) may perform the necessary tasks. A code segment may represent a procedure, a function, a subprogram, a program, a routine, a subroutine, a module, a software
30 package, a class, or any combination of instructions, data structures, or program statements. A code segment may be coupled to another code segment or a

hardware circuit by passing and/or receiving information, data, arguments, parameters, or memory contents. Information, arguments, parameters, data, etc. may be passed, forwarded, or transmitted via any suitable means including memory sharing, message passing, token passing, network transmission, etc.

5 It is to be understood that the following disclosure provides many different embodiments, or examples, for implementing different features of various embodiments. Specific examples of components and arrangements are described below to simplify the present disclosure. These are, of course, merely examples and are not intended to be limiting. In addition, the present disclosure may repeat
10 reference numerals and/or letters in the various examples. This repetition is for the purpose of simplicity and clarity and does not in itself dictate a relationship between the various embodiments and/or configurations discussed. Moreover, the formation of a first feature over or on a second feature in the description that follows may include embodiments in which the first and second features are
15 formed in direct contact, and may also include embodiments in which additional features may be formed interposing the first and second features, such that the first and second features may not be in direct contact.

The spectral region of narrow bandpass dielectric filters designed to operate in the near-infrared ("near-IR") and mid-infrared ("mid-IR") shift systematically to longer
20 wavelengths with increasing temperature. For example, tests have been performed to measure values of the shift in the wavelength (λ_m) at peak transmission with temperature, expressed as the temperature coefficient ($d\lambda_m/dT$), of a suite of commercially-available narrow bandpass filters operating in the near-IR spectral region ($\lambda_m=0.39\text{-}1.02\ \mu\text{m}$). Values of $d\lambda_m/dT$ have been measured in
25 the range of 0.001-0.003 nm/K with $\lambda_m=0.32\text{-}1.02\ \mu\text{m}$, and 0.0025 nm/K over the temperature range 25-60°C and 0.0036 nm/K over the temperature range 60-100°C with $\lambda_m=1.54\ \mu\text{m}$.

Significantly larger values of $d\lambda_m/dT$ have been measured for narrow bandpass filters operating in the mid-IR spectral region. For example, for a filter with $\lambda_m=2.67\ \mu\text{m}$ heated between 20°C to 150°C produced a value of $d\lambda_m/dT$ of 0.19 nm/K, while
30 for a filter with $\lambda_m=3.84\ \mu\text{m}$ cooled from 20°C cooling to -190°C produced a

corresponding value of 0.33 nm/K. Moreover, the width of the bandpass regions for mid-IR filters have been found to decrease on heating. Values of $d\lambda_m/dT$ reported in the literature for mid-IR filters are in the range 0.2-0.8 nm/K.

The origin of the change in λ_m with temperature is a change in the material properties with temperature of the dielectric materials that comprise the layers of the filters.

Figure 1 shows a schematic of a typical structure of a narrow bandpass interference filter. The narrow bandpass interference filter 5 comprises layers of high (H) refractive index material 10 and low (L) refractive index material 12 deposited on a substrate (S) 12. A Fabry-Perot cavity 2L 16 is formed in a section of the narrow bandpass interference filter 5. Ray traces are shown for an angle of incidence θ 18 for an incident radiation beam (beam refraction at the various interfaces is omitted for purposes of clarity).

The narrow bandpass interference filter 5 comprises the Fabry-Perot cavity 16 formed from low refractive index material (shown as 2L) separating two stacks of alternating high and low refractive index materials (shown as HLHLHLH). The layers are deposited onto the substrate 14, which may comprise silicon, germanium or sapphire. The cavity 16 behaves as a Fabry-Perot interferometer and the condition for the transmission of radiation of wavelength λ_o through the filter is given by:

$$\frac{m\lambda_o}{2} = n_o d_o \cos\theta \quad [1]$$

where:

n_o is the refractive index of the cavity film,

d_o is the thickness of the cavity film,

θ is the angle of incidence of the radiation and m is an integer, usually referred to as the order of the interference.

The term $n_o d_o \cos\theta$ is the optical thickness of the Fabry-Perot cavity 16, and for transmission through the narrow bandpass interference filter 5 the optical thickness must be equal to an integer number of half wavelengths, *i.e.*, the condition for

constructive interference between incident and reflected light at the boundary of the cavity. The layers bounding the Fabry-Perot cavity 16 are stacks of high reflectivity quarter wavelength layers characterised by:

$$\lambda_o/4 = n_H d_H \cos\theta \quad \text{and}$$

$$5 \quad \lambda_o/4 = n_L d_L \cos\theta$$

where the subscripts H and L refer to the high and low refractive index materials, respectively.

For narrow bandpass filters operating in the mid-infrared spectral region low refractive index materials may comprise zinc selenide and zinc sulfide, while the
10 high refractive index materials may comprise germanium and lead telluride.

At some temperature T, for the same order m and angle of incidence θ ,

$$\frac{m\lambda_T}{2} = n_T d_T \cos\theta \quad [2]$$

and combining eqns.[1] and [2] gives:

$$\lambda_T = \frac{(n_T d_T)}{(n_o d_o)} \lambda_o \quad [3]$$

or

$$\Delta\lambda = \lambda_T - \lambda_o = \lambda_o \left[\frac{(n_T d_T)}{(n_o d_o)} - 1 \right] \quad [4]$$

which identifies the source of the temperature shift in the centre wavelength of the
15 filter as the change in the optical thickness of the cavity.

The changes in n and d with temperature result from a combination of thermal expansion ($\partial d/\partial T$), thermooptic ($\partial n/\partial T$), thermomechanical ($\partial d/\partial \sigma$) and stress optic ($\partial n/\partial \sigma$) effects, where σ is the stress developed in the layers of the film and the substrate caused by differential thermal expansion effects.

20 Figures 2A-D show the temperature dependence of the bandpass of four commercially-available mid-IR filters operating in the spectral region 3.0-5.3 μm . All

four filters experience a systematic decrease in T_m and an increase in λ_m as the temperature increases from 25 to 200°C.

Figure 3A shows the relative change in T_m for the four filters as a function of temperature. Filters A and D experience a 15-16% decrease in T_m over the temperature range, while the decrease for filters B and C is only 8%. The value of dT_m/dT increases with increasing temperature for filters B, C and D but is fairly constant over the whole temperature range for filter A.

Figure 3B shows the dependence of the relative wavelength ($\lambda_m(T)/\lambda_m(25)$) on temperature for the four commercially-available filters. The corresponding values of $d\lambda_m/dT$ for filters A, B, C and D are 0.21, 0.23, 0.25 and 0.57 nm/K, which are comparable to the values (or moduli of the values) of $d\lambda_m/dT$ obtained previously (4-6, 16-19) for mid-IR filters.

Optical mechanical models of increasing complexity have been used to account for the change in optical properties, such as the shift in the centre wavelength, of narrow bandpass filters with changes in temperature. In one such model, the shift in wavelength with temperature of the narrowband pass filter, $d\lambda_m/dT$, is simply considered as being related to the coefficient of thermal expansion (C_s) of the substrate and $dn_e/n_e dT$, where n_e is the effective refractive index of the filter layers.

Figure 4 shows the dependence of the shift in wavelength at peak transmission with temperature ($d\lambda_m/dT$) as a function of the coefficient of thermal expansion (C_s) for three values of refractive index change of the materials comprising the filter with temperature ($dn_e/n_e dT$), as obtained by one such optical mechanical model. In Fig. 4, $dn_e/n_e dT$ is $0.75 \times 10^{-5} \text{ K}^{-1}$, $1.00 \times 10^{-5} \text{ K}^{-1}$ and $1.25 \times 10^{-5} \text{ K}^{-1}$.

The figure shows that $d\lambda_m/dT$ can be related to $dn_e/n_e dT$ and C_s by:

$$\frac{d\lambda_m}{dT} = k_1 \frac{dn_e}{n_e dT} + k_2 C_s + k_3 \quad [5]$$

where k_1 , k_2 and k_3 are constants. For the data shown in figure 2

$$\frac{d\lambda_m}{dT} = 1540 \frac{dn_e}{n_e dT} - 1400 C_s - 0.004 \quad [6]$$

which shows that the coefficients for the relative changes in the effective refractive index and dimensional changes of the substrate are approximately equal.

In the near-IR spectral region the modulus of the relative change in the refractive index of the dielectrics typically used to fabricate filters (SiO_2 , TiO_2 , Al_2O_3 and Ta_2O_5) is in the range $1\text{--}10 \times 10^{-6} \text{ K}^{-1}$ and therefore comparable to the values of C_s for some glass substrates. Under these circumstances it is possible to minimise the value of $d\lambda_m/dT$ by balancing the changes in n_e with the changes in the physical dimensions of the dielectric films and substrate.

The dielectric materials used to fabricate filters in the mid-IR spectral region are characterised by significantly larger values of dn/ndT than those materials used in the near-IR. Common high and low refractive index materials used to construct mid-IR filters are germanium (Ge) and zinc selenide (ZnSe), which have values of dn/ndT of $10.8 \times 10^{-5} \text{ K}^{-1}$ and $2.5 \times 10^{-5} \text{ K}^{-1}$, respectively. Application of the optical mechanical model by means of equation 6 with C_s set to zero gives $d\lambda_m/dT = 0.04 \text{ nm/K}$ for zinc selenide and $d\lambda_m/dT = 0.17 \text{ nm/K}$ for germanium. Note these are values determined from a simple model and when the values of dn/ndT for the mid-IR optical materials zinc selenide and germanium are used in equation 6, the values of $d\lambda/dT$ obtained from the model are of the order of $0.2\text{--}0.8 \text{ nm/K}$, the values of $d\lambda_m/dT$ measured experimentally for mid-IR filters. Such a large shift in wavelength at peak transmission with temperature ($d\lambda_m/dT$) for mid-IR filters limits the use of such filters in industries where the filter is to be used in temperature varying conditions.

In an embodiment of the present disclosure, a mid-infrared narrow bandpass filter is provided that has substantially temperature invariant optical properties over a wide temperature range. The temperature range is -20°C to $+200^\circ\text{C}$ and the measured modulus of the shift in the wavelength λ_m at maximum transmission with temperature, $d\lambda_m/dT$, is less than 0.2 nm/K over the wavelength range $2\text{--}14 \mu\text{m}$.

An approach to the design of filters with a predetermined thermal response can be considered by the design of the filter:

$$(\text{LH})^{x1}(\text{LL})^{y1}(\text{HL})^{x2}(\text{LL})^{y2} \dots (\text{LL})^{yN}(\text{HL})^{xN+1}$$

consisting of a total of y half wavelength spacers (cavities) LL of low refractive index material in N cycles ($y=\sum y_i$) and where LH are the stacks of x_i quarter wavelength layers of alternating high and low refractive index material in the N cycles.

- 5 The peak reflection wavelength of the quarter wavelength reflector stack, irrespective of the values of x_i and N , can be expressed as

$$\lambda_m = 2(n_L d_L + n_H d_H) \quad [7]$$

for first order reflections ($m=0$).

The temperature variation of the wavelength in the reflector stack $d\lambda_m/dT|_s$ can be expressed as

$$\left. \frac{d\lambda_m}{dT} \right|_s = 2n_L d_L \left(C_L + \frac{dn_L}{n_L dT} \right) + 2n_H d_H \left(C_H + \frac{dn_H}{n_H dT} \right) \quad [8]$$

- 10 where C_L and C_H are the coefficients of linear expansion of the low and high refractive index materials, respectively.

From eqn.[1] for first order reflection and normal incidence (*i.e.*, $m=1$ and $\theta=0^\circ$), the corresponding temperature dependence $d\lambda_m/dT|_c$ of the cavity layer of low refractive index material is given by:

$$\left. \frac{d\lambda_m}{dT} \right|_c = 2yn_L d_L \left(C_L + \frac{dn_L}{n_L dT} \right) \quad [9]$$

- 15 noting that y is the total number of half wavelength cavity layers.

The total change in wavelength with temperature $d\lambda_m/dT|_T$ is given by the sum of $d\lambda_m/dT|_c$ and $d\lambda_m/dT|_s$

$$\left. \frac{d\lambda_m}{dT} \right|_T = 2(1+y)n_L d_L \left(C_L + \frac{dn_L}{n_L dT} \right) + 2n_H d_H \left(C_H + \frac{dn_H}{n_H dT} \right) \quad [10]$$

or

$$\left. \frac{d\lambda_m}{\lambda_m dT} \right|_T = (1+y) \left(C_L + \frac{dn_L}{n_L dT} \right) + \left(C_H + \frac{dn_H}{n_H dT} \right) \quad [11]$$

noting $n_L d_L = n_H d_H$ at the temperature for which the filter is designed for use.

From the preceding, it can be seen that $d\lambda_m/dT|_T$ can only be zero if the value of dn/dT for one of the materials is negative. As such, in embodiments of the present disclosure, a high refractive index material, such as PbTe, is used in the filter to provide a negative value of dn/dT . In embodiments of the present disclosure, for close matching of the value of $d\lambda_m/dT|_T$ to zero, the wavelength dependence of n_i with temperature and wavelength dependence of dn_i/dT is taken into account.

The condition $d\lambda_m/dT|_T=0$ is given approximately by:

$$\frac{dn_H}{n_H dT} = -(1+y) \frac{dn_L}{n_L dT} \quad [12]$$

noting that C_i is considerably smaller than $dn_i/n_i dT$ for most materials used in mid-infrared filters. In embodiments of the present disclosure, the term $(1+y)$ may be chosen to satisfy eqn.[12] depending on the choice of low refractive index material. For example, in one embodiment of the present disclosure, with ZnSe for the low refractive index material and PbTe for the high refractive index material of the lens, and using the material values of bulk phases $n_L=2.43$, $n_H=6.10$, $dn_L/dT=6.3 \times 10^{-5} \text{ K}^{-1}$ and $dn_H/dT=-2.1 \times 10^{-3} \text{ K}^{-1}$ for $\lambda_m=3.4 \text{ }\mu\text{m}$, eqn.[12] is satisfied with $y=13.3$, i.e., approximately 13 half wavelength cavity layers are required to achieve the condition $d\lambda_m/dT|_T=0$.

There is considerable variation in the values of the material properties (n_H , dn_H/dT , C_H , etc.) that appear in eqn.[11] for thin films in a multilayer structure and therefore in the predicted value of $d\lambda_m/\lambda_m dT$ or the value of y required to achieve the condition $d\lambda_m/\lambda_m dT=0$. The uncertainty is particularly severe for the value of dn_H/dT for PbTe in view of its magnitude and influence on the value of y . For example, the value of dn/dT for PbTe at $\lambda_m=5 \text{ }\mu\text{m}$ has been reported to be of the order of $-1.5 \times 10^{-3} \text{ K}^{-1}$, $-2.7 \times 10^{-3} \text{ K}^{-1}$ and $-2.8 \times 10^{-3} \text{ K}^{-1}$. From eqn.[12] the corresponding values of y (to the nearest integer) are 9, 17 and 18, respectively.

In view of the uncertainties in the value of dn/dT for PbTe and, therefore, the number of low refractive index half wavelength spacers required to achieve $d\lambda_m/dT=0$, in embodiments of the present disclosure, applicants have determined an experimental value of $d\lambda_m/dT$ as a function of the optical thickness of the low refractive index cavities for a suite of filters. In determining the experimental value

the suite of filters are fabricated by the same method. From the experimental analysis it is possible, unlike with the lens models, to make a determination for a configuration of a narrow bandpass filter that has a minimal or zero value for $d\lambda_m/dT$ under specified conditions, such as a specified temperature variation.

Figures 5 shows the variation of $d\lambda_m/\lambda_m dT$ for a suite of filters, in accordance with embodiments of the present disclosure, fabricated with ZnSe as the low refractive index material and PbTe as the high refractive index material. The plot shows that, in accordance with embodiments of the present disclosure, a particular value of $d\lambda_m/\lambda_m dT$ can be achieved by controlling the ratio of low to high refractive index materials in the filter (*i.e.*, a parameter similar to y in eqns.[11] and [12]). From analysis, it was found that to obtain temperature invariance, the ration of low refractive index to high refractive index material needs to be high. As such, in embodiments of the present disclosure, the narrow bandpass filter comprises one or more cavities comprising low refractive index material. Figure 5 shows that for $\lambda_m < 5 \mu m$ the condition $d\lambda_m/\lambda_m dT = 0$ is met by a 4:4:4 (*i.e.*, 3 full wavelength or 6 half wavelength cavities ($y=6$)) filter, while for $\lambda_m > 5 \mu m$ a 6:4:6 ($y=8$) filter is required. As such, in some embodiments of the present invention, to a ratio/amount of low refractive index to provide temperature invariance the filter comprises one or more cavities that provide an optical thickness of at least three full wavelengths of the transmission wavelength.

In accordance with an embodiment of the present disclosure, a narrow bandpass filter is provided that comprises cavities having a low refractive index. In accordance with embodiments of the present disclosure, the design procedure illustrated in figure 5 may be used to fabricate substantially temperature invariant filters over the entire mid-infrared spectral range. To provide for temperature invariance, the narrow bandpass filter includes a large amount of low refractive index material, film and/or the like. Consequently, in accordance with some embodiments of the present disclosure, the temperature invariant narrow bandpass filter comprises a cavity(ies) having an optical thickness of at least three full wavelengths of the transmission wavelength or the narrow band of transmission wavelengths or three half-wavelengths of the transmission wavelength or the narrow band of transmission wavelength.

The cavity may comprise a single or a plurality of cavities that provide the optical thickness. Merely by way of example where the filter comprises three cavities of low refractive index material, each of the cavities comprises either half wavelength ($\lambda/2$) or full wavelength (λ) of the transmitted radiation in thickness. Where the filter comprises a single cavity, the cavity comprises an optical thickness of at least $3\lambda/2$ or 3λ in thickness. Other combinations, such as a two cavity, one $\lambda/2$ cavity and one λ cavity, are also possible to provide the desired optical thickness.

In some embodiments, the temperature invariant filter comprises a cavity or a plurality of cavities, where the optical thickness of the cavity or the cavities comprises at least three full wavelengths of the transmission wavelength or six half-wavelengths of the transmission wavelength, *i.e.*, an equivalent y value of 6 or greater. Such a configuration, although complicated to fabricate, provides a large ratio of low refractive index material to produce temperature invariance.

Moreover, as described herein, new materials have been used as low and/or high refractive index materials in the narrow bandpass filter to provide, amongst other things, for spectral transmission through the narrow bandpass filter, as the prior materials for fabricating narrow bandpass filters do not work or perform poorly with the configuration of the temperature invariant narrow bandpass filters of the present disclosure.

Figures 6A and B illustrate a system comprising a modified thin film deposition system with rotating thermal evaporation sources and stationary optical substrates for fabricating a temperature invariant filter in accordance with an embodiment of the present disclosure. Figure 4A is an illustration of a Balzers BA510 thin film deposition system and Figure 4B is a schematic of the rotating evaporation sources.

In an embodiment of the present disclosure, coating depositions may be fabricated using a specially modified Balzers 510 bell-jar deposition plant containing a unique geometry of rotating thermal evaporation sources and stationary substrates. In embodiments of the present disclosure, the deposition layer materials are evaporated from resistance heated molybdenum boat sources mounted on a slip ring assembly rotating at a fixed geometry beneath the substrate plane. This static-

substrate arrangement permits precise temperature control of the substrates, aided by jig mounting with intimate thermo-mechanical contact during deposition. The static substrate plant arrangement allows precise control of substrate temperature using intimate coating jig attachment to an electrically heated copper backing plate which ensures the uniformity, stoichiometry and packing density of the deposited condensed films.

In an embodiment of the present disclosure, control of the substrate temperature is achieved by intimate contact clamping using a combination of metallic lead annular washers, backing pieces and slotted disc springs. This arrangement provides a low impedance thermal path from the uncoated substrate rim to the temperature controlled coating jig maintaining a constant substrate temperature despite the variable radiated flux that originates from the evaporation sources. Temperature control is critically important as the 'sticking coefficient' of most infrared materials is strongly dependent on temperature. Reproducibility of this method also ensures that there is a minimum of variation between the filter substrate and optical monitor piece used to determine layer thickness during the deposition.

Narrow bandpass filters, in accordance with embodiments of the present disclosure, were fabricated using ZnS and ZnSe substrates with PbTe as the high refractive index material and ZnSe as the low refractive index material in the reflecting stacks and ZnSe as the low refractive index material in the cavity layers. The filters were designed with 19 layers of quarter wavelength thickness of ZnSe and PbTe with three cavity layers consisting of either half or full wavelength thickness. The multilayer bandpass design and choice of substrate material were selected for perfect optical impedance matching. However, in some embodiments, additional substrates of differing material were included in the filters to produce optical matching. These filters, in accordance with embodiments of the present disclosure, are referred to as 'degenerate' and are of considerable use for optical and environmental diagnosis purposes, particularly the identification of any dependencies on the choice of substrate.

Figures 7A and B show the temperature dependence of the bandpass of two 3 cavity filters fabricated on ZnSe substrates and designed to operate at $\lambda_m=4.26\ \mu\text{m}$, in accordance with embodiments of the present disclosure.

Figure 7A shows the performance of a degenerate filter consisting of 3 half wavelength cavities (2:2:2). Performance of the filter shows a systematic shift of λ_m to shorter wavelength with increasing temperatures (*i.e.*, $d\lambda_m/\lambda_m dT < 0$).

In contrast, the performance of the filter shown in Fig. 7B, in accordance with an embodiment of the present disclosure, a filter with optimum optical matching and 3 full wavelength thickness cavities (4:4:4) shows a significantly smaller shift with temperature.

Figures 8A and B show the corresponding performance of two narrow bandpass filters, a degenerate filter in Fig. 8A and an optimally matched filter in Fig. 8B, operating at $\lambda_m=12.12\ \mu\text{m}$. The two filters, both constructed with 3 half wavelength cavities (2:2:2), show similar behaviour, both in terms of wavelength shift and decrease in transmission with increasing temperature.

Figure 9 compares the relative change in wavelength λ_m at peak transmission with temperature of the four filters shown in figures 7A and B and 8A and B. In the figure, the degenerate $4.26\ \mu\text{m}$ (2:2:2) filter produces line 30, the optimally matched $4.26\ \mu\text{m}$ (4:4:4) filter produces line 33, the degenerate $12.1\ \mu\text{m}$ (2:2:2) filter produces line 36 and the optimally matched $12.1\ \mu\text{m}$ (2:2:2) filter produces line 39.

The change in λ_m is expressed as $\Delta\lambda_m/\lambda_{m0}$, where λ_{m0} is the value of λ_m at 20°C . The value of $d\lambda_m/dT$ for the $\lambda_m=4.26\ \mu\text{m}$ (4:4:4) filter varies from $-0.04\ \text{nm/K}$ at 20°C to $+0.03\ \text{nm/K}$ at 200°C and sensibly zero over the temperature range $80-160^\circ\text{C}$. The maximum numerical value of $d\lambda_m/dT$ for the $\lambda_m=4.26\ \mu\text{m}$ (2:2:2) filter is $-0.21\ \text{nm/K}$ at 20°C with an average value of $-0.12\ \text{nm/K}$ over the whole temperature range. The values of $d\lambda_m/dT$ for the $\lambda_m=12.1\ \mu\text{m}$ (2:2:2) optimal and degenerate filters are -0.19 and $-0.21\ \text{nm/K}$, respectively, over the temperature range $20-200^\circ\text{C}$.

Figure 10 shows the corresponding variation of the integrated band transmission T_i with temperature for the four filters of figures 7A and B and 8A and B. The value of dT_i/dT is negligible for the $\lambda_m=4.26\ \mu\text{m}$ (4:4:4) filter and $|dT_i/dT|$ is less than 0.06%/K for the other 3 filters. In the figure, the degenerate $4.26\ \mu\text{m}$ (2:2:2) filter produces line 40, the optimally matched $4.26\ \mu\text{m}$ (4:4:4) filter produces line 43, the degenerate $12.1\ \mu\text{m}$ (2:2:2) filter produces line 46 and the optimally matched $12.1\ \mu\text{m}$ (2:2:2) filter produces line 49.

Figures 11A and B show the temperature dependence of the bandpass of two 3 cavity filters fabricated on ZnS substrates that have been designed to operate at $\lambda_m=4.26\ \mu\text{m}$ (4:4:4 cavity layers) and $\lambda_m=12.1\ \mu\text{m}$ (2:2:2 cavity layers). Both filters have been optically matched to the substrate (*i.e.*, are non-degenerate).

Figure 12 compares the dependence of $\Delta\lambda_m/\lambda_{m0}$ on temperature (20-200°C) for the two filters shown in figure 11. In the figure, variation of $\Delta\lambda_m/\lambda_{m0}$ with temperature for the $4.26\ \mu\text{m}$ (4:4:4) filter 60 and the $12.1\ \mu\text{m}$ (2:2:2) 63 are shown.

The largest absolute value of $d\lambda_m/dT$ for the $\lambda_m=4.26\ \mu\text{m}$ filter is -0.05 nm/K, which is obtained at 20°C; $d\lambda_m/dT$ is sensibly zero over the temperature range 80-200°C. The $\lambda_m=12.1\ \mu\text{m}$ filter exhibits a value of $d\lambda_m/dT=-0.19\ \text{nm/K}$ over the entire temperature range.

Figure 13 shows the variation of T_i with temperature for the two filters deposited on ZnS substrates. In the figure, variation of integrated band transmission with temperature for the $4.26\ \mu\text{m}$ (4:4:4) filter 66 and the $12.1\ \mu\text{m}$ (2:2:2) 69 are shown. The decrease in T_i for the $\lambda_m=12.1\ \mu\text{m}$ filter is 15% over the temperature range 20-200°C, while the corresponding decrease for the $\lambda_m=4.26\ \mu\text{m}$ filter is less than 5%.

The foregoing outlines features of several embodiments so that those skilled in the art may better understand the aspects of the present disclosure. Those skilled in the art should appreciate that they may readily use the present disclosure as a basis for designing or modifying other processes and structures for carrying out the same purposes and/or achieving the same advantages of the embodiments introduced herein. Those skilled in the art should also realize that such equivalent constructions do not depart from the scope of the present disclosure, and that they

may make various changes, substitutions and alterations herein without departing from such scope.

All references referred to above are hereby incorporated by reference.

CLAIMS

1. A temperature invariant narrow bandpass filter configured to transmit mid-infrared radiation with a transmission wavelength or narrow band of transmission wavelengths, the filter, comprising:

5 a substrate;

a first stack comprising layers of alternating high and low refractive index materials deposited on the substrate;

a cavity comprising low refractive index material deposited on the first stack; and

10 a second stack comprising layers of alternating high and low refractive index materials deposited on the cavity, wherein:

the high refractive index materials have a refractive index that decreases with temperature over a portion of an operating temperature of the filter;

15 the cavity is disposed between the first and the second stack; and

the cavity comprises an optical thickness of at least three full wavelengths of the transmission wavelength or the narrow band of transmission wavelengths or three half-wavelengths of the transmission wavelength or the narrow band of transmission wavelengths.

2. The narrow bandpass filter of claim 1, wherein the cavity comprises three (3) separate cavities and each of the three separate cavities comprises an optical thickness of either a full wavelength (λ) of the transmission wavelength or the narrow band of transmission wavelengths or a half wavelength ($\lambda/2$) of the transmission wavelength or the narrow band of transmission wavelengths.

3. The narrow bandpass filter of claim 1, wherein the cavity comprises a plurality of separate cavities that in combination comprise an optical thickness of at least three full wavelengths of the transmission wavelength or the narrow band of transmission wavelengths or three half-wavelengths of the transmission wavelength or the narrow band of transmission wavelengths.

4. The narrow bandpass filter of claim 1, further comprising:

one or more additional stacks of alternating high and low refractive index material.

5. The narrow bandpass filter of claim 1, wherein the low refractive index material comprises at least one of zinc selenide and zinc sulphide.

6. The narrow bandpass filter of claim 1, wherein the high refractive index material comprises lead telluride.

7. The narrow bandpass filter of claim 1, wherein the high refractive index material comprises either lead sulfide or lead selenide or some combination of lead telluride, lead sulfide and lead selenide.

8. The narrow bandpass filter of claim 1, wherein a modulus of change in central wavelength of the filter with temperature is less than or equal to $0.2 \text{ nm}/^{\circ}\text{C}$ over a temperature range -25°C to $+200^{\circ}\text{C}$ for a wavelength range $2\text{-}14 \mu\text{m}$.

9. The narrow bandpass filter of claim 1, wherein a modulus of change in peak transmission of the filter is less than $0.1\%/^{\circ}\text{C}$ over a temperature range -25°C to $+200^{\circ}\text{C}$ for a wavelength range $2\text{-}14 \mu\text{m}$.

10. The narrow bandpass filter of claim 1, wherein a relationship between the number of half wavelength and full wavelength cavities and the change in central wavelength of the filter with temperature is established to obtain a particular value of said change in central wavelength with temperature, including a value that is sensibly zero, by the fabrication of a suite of filters with a varying

number of said cavities using a particular fabrication method and with particular materials for the high and low refractive index layers.

5 11. The narrow bandpass filter of claim 1, wherein the low refractive index material comprising the cavity is different to the low refractive index material of at least one of the first stack and the second stack.

 12. The narrow bandpass filter of claim 1, wherein the cavity has a value of y that is 6 or greater.

10 13. The narrow bandpass filter of claim 1, wherein the cavity comprises an optical thickness of at least three full wavelengths of the transmission wavelength.

 14. A narrow bandpass filter according to any of the embodiments described herein.

 15. A method for using a narrow bandpass filter according to any of the embodiments described herein.

15



Application No: GB1416268.9

Examiner: Mr Gareth James

Claims searched: 1-15

Date of search: 28 January 2015

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1-15	J. S. Seeley; R. Hunneman; A Whatley; Temperature-invariant and other narrow-band IR filters containing PbTe, 4-20 [micrometers]; Proceedings of the Society of Photo-Optical Instrumentation Engineers; Vol 246, pages 83-94, (1980), ISSN: 0361-0748. (SEELEY) See abstract and the Double Halfwave (DHW) filter design on page 91.
X	1-15	JP S5831307 A (TOKYO OPTICAL) See abstract and figures.
X	1-15	B. LI , S. Y. Zhang, J. C. Jiang, B. Fan, F. S. Zhang; Improving low-temperature performance of infrared thin-film interference filters utilizing the intrinsic properties of IV-VI narrow-gap semiconductors ; Optics Express 401, Vol. 12, No. 3, (9th February 2004) (LI). See whole document, especially abstract and page 403.
A	-	EP 1967872 A1 (MURATA MANUFACTURING CO) See abstract, figures, especially figure 1 and paragraphs 1-10.
A	-	WO 2012/073791 A1 (FUJIFILM CORP) see abstract and figures, especially figure 1-4 & 36.
A	-	JP 2013054368 A (PANASONIC CORP) see abstract and figure 1.

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
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Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^X :

Worldwide search of patent documents classified in the following areas of the IPC



G02B

The following online and other databases have been used in the preparation of this search report
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WPI, EPODOC, TXTE, INSPEC & Internet

International Classification:

Subclass	Subgroup	Valid From
G02B	0005/28	01/01/2006