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(54) Title: NON-LINEAR OPTICAL DEVICES

(57) Abstract: Adjacent non-linear optical layers in a stack of at least two such layers are joined by a glass layer to form a device such as a parametric oscillator, frequency doubler or birefringent phase matched device. The indices of the layers and glass are preferably matched within 30%, and for non-linear infra-red or thermally sensitive materials such as gallium arsenide, zinc selenide, lithium niobate and ZnGeP₂ the glass is preferably a low melting chalcogenide glass comprising Ge, As, Se and Te. The non-linear layers may comprise a grating, e.g. striated or periodically poled.



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Non-Linear Optical Devices

The present invention relates non-linear optical devices comprising a stack of two or more non-linear layers.

5 The present invention provides a non-linear optical device comprising a stack of at least two layers of non-linear optical material, adjacent said non-linear layers being joined by a glass layer.

The present invention also provides a method of making a non-linear optical device comprising a stack of at least two layers of non-linear optical material, in which method the surfaces of adjacent said non-linear layers are joined by a glass layer
10 under the action of heat and pressure.

Our copending UK Patent Application No. GB 0123731.2 relates generally to the joining of optical components, and claims a method of joining opposed surfaces of two optical components, the method comprising the steps of providing at least one said surface with a thin layer of bonding glass having a glass transition temperature
15 T_g substantially lower than the glass devitrification temperature T_{c1} , placing the said surfaces together with only the coating or coatings therebetween to form an assembly, and heating the assembly under pressure to a temperature T_b which lies between T_g and T_{c1} and is sufficiently high to soften the glass and bond the components together.

In the present invention, optical components to be joined using an intermediate glass
20 layer are specifically layers of non-linear optical material. While the invention encompasses the joining of a relatively small number of non-linear layers, e.g. 2, 3, 4 or 5, as will be explained in due course there exists a group of non-linear devices which comprise a stack of a significantly larger number of non-linear optical layers through which optical energy is intended to propagate in series. As the number of
25 optical interfaces increases, so does the problem of providing interfaces of high optical quality, without which the efficiency of the stack decreases unacceptably.

As explained in our copending application, which inter alia deals generally with this type of problem, the presence of gaps or spaces between faces which should be in optical contact can arise from such sources as imperfections in the surfaces to be

joined, or the presence of contamination at the surfaces, particularly particulate contamination, and leads inter alia to optical losses due to reflection (because of index mismatch) and scattering. Consequently, a number of tried and tested techniques have been developed to avoid light losses at optical interfaces in composite optical devices, including the provision of a direct interface, i.e. where the surfaces are in direct optical and mechanical contact, the interposition of an adhesive layer between the components, and, where possible, diffusion bonding.

Direct interfacing requires very accurate physical preparation of the surfaces of the components, and extremely high standards of cleanliness. For this reason, while this technique is used in practice, it is difficult and best avoided if possible.

The diffusion-bonding approach mentioned above is difficult to realise due to a number of practical considerations. The individual layers must be highly polished and optically flat and the surfaces of the layers must be free of particulate contamination. It has been observed that a particle as small as $1\mu\text{m}$ can result in a void between layers with a diameter of 1 mm (D Bollmann et al, Jpn J Appl Phys, vol 35, pp3807-3809). Such voids are a source of optical loss, which can build up significantly over a stack of many layers. The temperature and pressure needed to diffusion bond the layers may also degrade the optical properties of the material (D Zheng et al, J Electrochem Soc, vol 144, no 4, pp 1439-1441).

Bonding of components with an intermediate layer of a material such as an adhesive can serve to reduce or remove light loss and so increase device efficiency. For example, Canada Balsam, which has a refractive index very similar to that of conventional silica based optical glasses, was used for many years as an adhesive for mounting microscope slides and for joining lens components. Many modern optical components are of materials with indices much greater than conventional glass, for example semiconductor electro-optic devices and glasses, and this commonly occurs with components for use in the infrared region, for example. The refractive indices of conventional adhesive compositions fail to match these greatly increased indices, so that reflection at the interfaces is again increased, and it has often been necessary to resort to direct interfacing.

It is as a result of such considerations that our copending application proposes the use of an intermediate glass layer to bond adjacent optical components together. By appropriate choice of a thin layer of a glass with optical and thermal characteristics, and of the layer thickness and bonding conditions, it can be arranged that the glass provides an effective bond between the components without adversely affecting them in any way, and that the optical interfaces thus produced are not significantly detrimental to optical transmission from one component to the other, e.g. by selection of the refractive index, transmissivity and thickness of the glass layer.

As mentioned above, certain non-linear devices comprise a stack of non-linear optical layers where it is desirable to have the best optical interfaces possible.

Non-linear optical materials are useful for the production of new wavelengths via conversion of existing laser wavelengths (e.g. M Fejer, Physics Today, May 1994)). Common applications of non-linear optical materials include frequency-doubling and optical parametric oscillators. In such devices, fundamental (input) and generated (output) optical waves propagate together through the material and energy is transferred from the fundamental to the generated waves (forward-conversion). The reverse process, in which energy is transferred from the generated waves to the fundamental wave(s), can also occur. This is known as back-conversion.

The direction and efficiency of the non-linear process is determined by the phase relationship between the various interacting waves. In general, the phase relationship changes as the waves propagate through the non-linear optical material, resulting in alternating sections of forward- and back- conversion. The maximum useful length of material is the length of one such section and is known as the coherence length for the material. This is the distance over which the interacting waves retain a suitable phase relationship for forward conversion. If the waves propagate beyond this distance, energy is transferred back from the generated waves to the fundamental wave. In general, the coherence length is too short to be useful unless a technique known as phase matching can be employed.

By way of example, when frequency doubling, the coherence length L_{coh} is given by the following formula:

$$L_{coh} = \frac{\pi}{\Delta k} = \frac{\lambda_{\omega}}{4(n_{2\omega} - n_{\omega})}$$

The term in brackets in the denominator of the above equation represents the dispersion of the material between the original or pump frequency ω and the up-converted frequency 2ω . With birefringent materials, the quantities $n_{2\omega}$ and n_{ω} are polarisation dependent, and where the birefringence is sufficient the optical design can be adapted so that the dispersion term is made to approach or to reach zero, desirably from the point of view of the above equation alone by choosing a propagation direction such that $n_{2\omega} = n_{\omega}$, making L_{coh} infinite. In practice, values of L_{coh} can be provided such that it is much larger than the necessary operative length of the non-linear material.

With non-linear materials which have only a relatively small degree of birefringence or zero birefringence, or where the use of a desired non-linear coefficient (normally a more advantageous coefficient) is not possible along, or sufficiently close to, a direction for which phase matching by birefringence is possible, the dispersion term cannot be made to approach zero, and L_{coh} then becomes finite and commonly relatively small.

For example, for gallium arsenide (which is not birefringent) L_{coh} is around 100 microns for a pump wavelength of 10 microns. Lithium niobate is an example of a material which does have a sufficiently large birefringence to allow phase matching - however the propagation direction necessary to ensure phase matching does not coincide with that required to exploit the largest non-linear coefficient in this material.

In such cases positive steps must be taken to extend the interaction length that gives rise to constructive forward conversion in the non-linear material. To achieve this there is an alternative approach to phase matching known as quasi-phase matching. In this technique the non-linear optical material is divided into sections exactly one coherence length (or an odd multiple of coherence lengths) long, either by producing

striated crystals during growth, or by appropriate poling of a crystal, or by assembly of a stack of multiple layers with different crystal orientations. Within each section a useful non-linear optical interaction can occur as the waves get progressively out of phase. If the material axis is reversed in the following section then the interaction can
5 continue. By reversing the axis in successive sections in this manner, an arbitrary interaction length can be achieved (J McMullen, J Appl Phys, vol 46 no 7, p3076-3081). Quasi-phase matching allows the use of non-linear optical materials that cannot be phase-matched using birefringence, such as gallium arsenide, or the use of propagation directions that maximise effective non-linear coefficients in birefringent
10 materials such as lithium niobate. It is of particular importance in optical wavebands for which there are few good birefringent non-linear optical materials available.

Striated crystals and poled crystals tend to be useful only for low aperture devices, because of their manner of production. However, the assembly method has potential for providing larger aperture devices useful in high power applications where it is
15 necessary to minimise the possibility of optical damage to the device. It will be understood that because the coherence length in quasi-phase matched assemblies or stacks tends to be relatively short, a relatively large number of layers is required to provide a practically useful effect, and commonly there are over 50, and often over 100 layers non-linear layers with individual thicknesses of the order of a hundred
20 microns in a quasi-phase matched stack.

However, when different sections of non-linear material are assembled into a quasi-phase matched stack there is a primary difficulty in producing a structure of sufficient quality to be useful. There are major problems both in providing high quality optical joins between adjacent sections, and in producing or maintaining accurate control of
25 section lengths and distances between sections, and the penalties associated with poor quality joins or inaccuracy in section lengths generally increase as the number of layers in the stack increases.

In practice it is normally vital to bond the layers of a quasi-phase-matched stack together to obtain a device with a useful degree of efficiency, but the type of bonding
30 used may give rise to further problems. By joining non-linear layers with a glass layer

according to the invention, it is possible to provide good quality optical interfaces, good bonding, and control of the section lengths, as will be amplified later.

It has already been made clear that the invention is not limited to stacks with large numbers of non-linear layers, and as few as two non-linear layers may be present.

- 5 Indeed, the most common form of phase matching as described above requires non-linear optical materials that are birefringent crystals, and the birefringent non-linear stacks next to be discussed commonly use very much lower numbers of layers.

10 In a birefringent non-linear crystal, the direction of propagation and polarisation of the various waves is chosen so that a suitable phase relationship for forward conversion is maintained throughout the crystal and the coherence length is longer than the crystal. Various drawbacks can be encountered using this approach:

1. The phase-matching constraint defines the direction of propagation, which may not be the direction for which the non-linear interaction is strongest, as in lithium niobate mentioned above.
- 15 2. Even where the phase matching constraint allows a suitable propagation direction in relation to non-linear coefficients, the various beams may 'walk-off' and become spatially separated within the crystal. The strength of walk-off depends on the material and the type of birefringent phase matching employed. Since conversion occurs throughout the optical path of the input beam, the spatial
20 characteristics of the converted beam can also be affected. Beam walk-off reduces the length of non-linear material that gives rise to constructive conversion, and hence introduces a maximum sample length, preventing exploitation of longer crystals if available.
3. The presence of optical loss within a birefringent material may limit the useful
25 length of a single sample.
4. It is not always possible to satisfy the phase-matching condition at all wavelengths for which the crystal is transparent.
5. The number of non-linear materials suitable for use in parts of the infrared spectrum which are also birefringent is rather limited.

Particularly in situations where walk-off is a problem or useful crystal lengths are short (see points 2 and 3 above), it should be possible to create a crystal with long effective length whilst arranging the orientation of the different layers so that the stack assembly method may also be of considerable use. By replacing a monolithic
5 block of the material by plurality of birefringent non-linear layers thereof, the orientations of the different layers may be adjusted so that the converted optical energy may be caused substantially to track the originating optical energy.

With stack assemblies of birefringent non-linear layers, since it is possible to obtain phase matching within individual layers the thicknesses thereof can be, and in practice
10 will tend to be, much greater (of the order of millimetres) than the layer thicknesses employed for quasi-phase matched stacks.

Any relatively thin non-birefringent material introduced between the birefringent non-linear layers, such as the glass layer(s) of the present invention, tends to have a relatively small effect on phase matching in subsequent layers. This effect is
15 minimised by choosing a non-birefringent material whose dispersion is closely matched to that of the birefringent non-linear layer. Any detrimental effect can be minimised by ensuring that the intermediate layer is as thin as possible and that the overall number of layers is kept to a minimum. The bonding of birefringent non-linear layers of a stack together is significantly advantageous, for example in that it provides
20 a monolithic device with improved efficiency.

When making a quasi-phase matched stack, if an intermediate bonding layer is to be employed, it is necessary to be able to provide such a layer with a thickness which can be accurately controlled, to preserve the coherence length. In both quasi-phase matched and birefringent non-linear stacks, it is preferred to have an intermediate
25 layer thickness which is as low as possible. Neither are particularly easy using the adhesive or other intermediate materials conventionally used in the art. As will be explained in greater detail below, the use of intermediate bonding optical glass layers enables thin intermediate layers of accurately controlled thickness to be provided in the bonded product. Particularly for quasi-phase matched stacks, the thickness of the
30 intermediate layer(s) can be tailored prior to bonding to adjust the layer spacing and to preserve phase coherence.

Ideally, the dispersion of the bonding glass should equal that of the non-linear material. This is not always possible, but the detrimental effect of not matching the dispersion is expected to be small if the glass layers are thin. In quasi-phase matched stacks, compensation is possible by adjusting the thickness of the non-linear optical layers. In birefringence phase matched stacks, there is expected to be a slight reduction in efficiency, but the use of thicker non-linear layers is again advantageous in reducing the amount of dispersion induced inefficiency.

The choice of preferred glass for use in the invention, including its thermal properties and refractive index, will be further explained with reference to the accompanying drawings, in which:

Figures 1 to 3 are differential thermal analysis plots for three different chalcogenide glasses; and

Figure 4 illustrates the effect of refractive index mismatch in a stack of alternating layers.

To reduce optical loss by index-mismatch reflection at the interfaces, the refractive index of the glass layer is preferably close to, and ideally equal to, that of the non-linear optical material. This reduces undesired reflections at the surface which is coated. For devices having at least 10 layers of non-linear optical material, more probably 40 layers, and even more probably at least 80 layers, the index of the glass should be chosen so that the total theoretical reflection from all the interfaces is no greater than 20%, preferably no greater than 10%, and more preferably no greater than 5%, and most preferably substantially zero. Alternatively, the glass has a refractive index which is preferably within 15% of the refractive index of the non-linear optical material (i.e. $R \pm 15\%$), more preferably within 10% and even more preferably within 5%, and most preferably within 2%. These numbers of layers are more likely to be encountered with quasi-phase matched stacks.

As noted above, birefringent stacks may involve relatively few layers, so that the requirement for index matching may be relaxed somewhat. Thus, more generally, the glass has a refractive index which is preferably within 30% of the refractive index of

the non-linear optical material (i.e. $R \pm 30\%$), more preferably within 20% and even more preferably within 10%, and most preferably within 5%.

Figure 4 illustrates the effect of refractive index mismatch in a stack of alternating layers of gallium arsenide and a glass. It will be seen that the transmission of the stack reduces progressively with departure from unity of the ratio of the refractive indices, and also with increasing numbers of layers in the stack. For example, a stack of 51 layers of gallium arsenide, each layer bounded on either side by a glass layer with a refractive index matched within 5% (100 GaAs to glass interfaces) provides an overall transmission of around 94%.

10 The method of the present invention may be performed by the steps of providing two layers of non-linear optical material, providing a surface of at least one said layer with a thin layer of bonding glass having a glass transition temperature T_g substantially lower than the glass devitrification temperature T_{c1} , placing the said layers together with only the coating or coatings therebetween to form an assembly, and heating the
15 assembly under pressure to a temperature T_b which lies between T_g and T_{c1} and is sufficiently high to soften the glass and bond the layers together.

This enables the non-linear optical layers to be joined with a strong, low optical-loss bond and with very precise and controllable spacing. By appropriate choice of materials and conditions it can be arranged that during bonding the glass engulfs any
20 particulate contamination on either surface minimising the impact of scattering loss, and it can also soften sufficiently to flow into any surface indentations thus making this technique particularly useful for bonding to crystalline materials that are inherently difficult to polish, such as $ZnGeP_2$.

In addition to a glass devitrification temperature T_c , corresponding to a change from a
25 glassy phase to a melt phase or a crystalline phase, many glasses have at least one glass transition temperature T_g where a glassy phase is retained but with somewhat different properties. In particular, heating the glass through a temperature T_g to obtain a higher temperature glassy phase (the reader will appreciate that the phase change may require other conditions, and in particular the phase change may take a
30 significant time) can provide a phase which is appreciably softer or more mobile.

Glass phase transitions may be detected by differential thermal analysis, wherein heat is supplied at a controlled rate to a sample and the temperature of the sample is plotted over time. During differential thermal analysis the temperature initially follows a generally linear plot, and phase transitions are indicated by deviations from linearity. In particular a glass transition temperature T_g may be identified by a discontinuity in the plot, generally in the form of a knee. Further transition points may be identified at higher temperatures, and at least one of these may correspond to the devitrification temperature. The latter may be identified since upon performing the reverse measurement by cooling the sample the corresponding knee is absent or at least does not occur at the same temperature.

Figure 1 shows a differential thermal analysis plot for the material $\text{Ge}_{15}\text{As}_{15}\text{Se}_{29}\text{Te}_{41}$, using the following cycle:

1. Hold at 20.00°C for 1.0 minutes
2. Heat from 20.00°C to 450.00°C at 10.00°C/minute
3. Hold for 10.0 minutes at 450.00°C
4. Cool from 450.00°C to 20.00°C at 10.00°C/minute

Two inflection points on the rising part of the curve at 120°C and 240°C are respective first and second glass (glass/glass) transition temperatures T_{g1} and T_{g2} . Steeper transitions T_{c1} and T_{c2} at 290°C and 380°C are transitions associated with crystal phases, and the lower of these temperatures, T_{c1} , will be the devitrification temperature since at that point the material ceases to be in a glassy phase. In Figure 1 it will be observed that the curve is not retraced upon cooling, shows no (reverse) glass/glass transition points corresponding to T_{g1} and T_{g2} , and does not return to the starting point. Thus any thermal processing of this material is likely to be associated with marked changes in the properties of the material, and these changes may be dependent on a number of factors (e.g. times, temperatures, heating rates, atmospheres) so that any change may well be difficult to reproduce reliably.

As used herein, “first glass transition temperature” refers to the lowest glass transition temperature above ambient.

Figure 2 shows a differential thermal analysis plot for the material $\text{Ge}_{15}\text{As}_{15}\text{Se}_{17}\text{Te}_{53}$ using the following cycle:

1. Hold for 1.0 minute at 20.00°C
2. Heat from 20.00°C to 440.00°C at 10.00°C/minute
- 5 3. Cool from 440.00°C to 80.00°C at 10.00°C/minute
4. Hold for 20.0 minutes at 80.00°C
5. Heat from 80.00°C to 440.00°C at 10.00°C/minute
6. Cool from 440.00°C to 80.00°C at 10.00°C/minute
7. Hold for 20.0 minutes at 80.00°C
- 10 8. Heat from 80.00°C to 440.00°C at 10.00°C/minute
9. Cool from 440.00°C to 20.00°C at 10.00°C/minute
10. Hold for 60.0 minutes at 20.00°C

Compared with Figure 1 this plot is a relatively simple trace involving first and second glass (glass/glass) transition temperatures T_{g1} and T_{g2} at 145°C and 260°C, and a single devitrification temperature T_{c1} 330°C. On cooling, while the curve is not retraced, reverse glass transition points T_{g1} and T_{g2} at 275°C and 160°C are exhibited. The trace is repeatable, as evidenced by measurements over three cycles with heating to 330°C.

Figure 3 shows a differential thermal analysis plot for the material $\text{Ge}_{19}\text{As}_{11}\text{Se}_{17}\text{Te}_{53}$, using the following cycle:

1. Hold at 20.00°C for 1.0 minutes
2. Heat from 20.00°C to 500.00°C at 10.00°C/minute
3. Hold for 10.0 minutes at 500.00°C
4. Cool from 500.00°C to 20.00°C at 10.00°C/minute
- 25 5. Hold for 60.0 minutes at 20.00°C

This plot is even simpler than that of Figure 2, showing just a single glass/glass transition temperature T_g at 170°C, and no devitrification point up to a temperature in excess of 470°C. There is a large temperature interval between T_g and the highest temperature investigated.

In practising this bonding method with respect to the present invention, the conditions, including the choice of Tb and the glass material, are preferably selected so that there is no undesired change in either of the non-linear optical layers, for example by destroying or distorting them or their surfaces, or producing an irreversible phase change therein. In most cases the ideal is that the non-linear optical layers remain substantially wholly unaffected by the bonding process, or at least that subsequent to the bonding process they correspond substantially to the starting non-linear optical layers even if some form of change has occurred in the meantime. However, it is envisaged that there may be occasions when Tb is selected to cause a desired change such as an irreversible phase in the material of the non-linear optical layers so as to produce modified but desired properties.

The conditions under which bonding is effected are preferably selected such that there is no substantial extrusion of the glass out from between the bonded surfaces and/or so that the thickness of the glass layer or layers remains substantially constant.

Where the glass exhibits a plurality of glass transition temperatures above ambient, Tb is preferably selected to lie between the first and second glass transition temperatures.

The glass needs to be suited to the non-linear material being used, i.e. subject to the constraints such as refractive index matching and thermal characteristics as described herein. It is preferably an inorganic glass for example a chalcogenide glass. In particular embodiments the optical glass may comprise Ge, As, Se and Te, and one range of preferred glasses has the general formula $\text{Ge}_{(x-a)}\text{As}_a\text{Se}_{(100-x-b)}\text{Te}_b$ where $25 < x \leq 55$ (preferably $25 < x \leq 40$); $10 \leq a \leq 25$; $40 < b \leq 70$, and $(100-x-b) > 0$ (see our copending UK Patent Application No. GB 0123743.7).. The glasses of Figures 1 to 3 conform to this formula. More preferably, particularly for example where the substrate is of GaAs, $30 \leq x \leq 40$; and $50 < b \leq 70$. In these ranges there exist glasses having good to very good thermal characteristics with indices closely matching those of GaAs and ZnGeP_2 .

Alternatively the glass may be amorphous arsenic sulphide.

Preferably the glass is selected such that it undergoes the bonding cycle reversibly, so that its properties at the end of the cycle are substantially identical to those at the commencement of the cycle. The glass of Figure 1 does not conform to this criterion and so is not a preferred material. The glasses of Figures 2 and 3 are preferred materials according to this criterion.

Preferably the glass has only one glass transition temperature before the devitrification temperature is reached, making the glass of Figure 3 more preferable than that of Figure 2.

Preferably there is an interval of at least 50°C, more preferably at least 100°C, and even more preferably at least 150°C, between the (first) glass transition temperature and any other transition temperature, whether a further glass transition temperature or the devitrification temperature. On this criterion the glass of Figure 3 is again more preferable to that of Figure 2, although both conform to the wider criteria.

Infrared transmitting chalcogenide glasses based on the Ge-As-Se-Te system have been prepared with refractive indices in the range $n=3.00$ to 3.45 . These glasses have also been successfully coated onto silicon ($n=3.43$) and GaAs ($n=3.28$) substrates, with layer thicknesses of from 0.1 microns to greater than 3 microns, using a RF sputtering technique.

The thickness of the coating applied to the or both surfaces to be joined will be dictated at least in part by the characteristics of the surfaces and their manner of preparation. It is extremely difficult to prepare some surfaces with a high degree of optical precision (surface quality and form – the surfaces are commonly required to be optically flat, although other shaped surfaces fall within the invention), or the conditions are such that optical cleanliness cannot be guaranteed. Under such conditions a somewhat thicker layer may be required to ensure that surface defects however caused are effectively surrounded by the bonding glass and do not contribute excessively to light scattering or separation of closely adjacent regions of the substrate surfaces.

The layer or layers of glass may be deposited by any standard method, such as RF sputtering, flash evaporation, solvent evaporation or spin coating, and preferably, but not necessarily, it is deposited on both said surfaces to be joined.

Commonly the thickness of the coating on one or both surfaces lies in the range 0.1 to 20 microns, more preferably 1 to 10 microns, and is most preferably no more than 5 microns. The maximum thickness of the glass in the bonded device is preferably 20 microns, more preferably 10 microns, even more preferably 6 microns and most preferably no more than 4 microns. However, layers of greater thickness can be provided for reasons mentioned above.

10 In particular, it is possible to use the glass layer to compensate or correct for any deviation in the optical thickness of the non-linear optical layers, e.g. from a coherence length or integral multiple thereof in the case of non-linear optical stacks for wavelength conversion and the like. After deposition of the glass coating on a non-linear optical layer, the optical thickness of the coated item may be measured
15 (taking into account the intended propagation direction and polarisation if necessary), and the thickness of the glass layer may then be suitably reduced, e.g. by mechanical milling using any known technique, until the requisite optical thickness is obtained. Alternatively, if the coated item is too thin, further glass could be deposited, optionally followed by part removal thereof. In an on-line glass coating process,
20 continuous measurement of optical thickness of the item could be effected until the necessary thickness is achieved (or exceeded, if subsequent polishing to the correct thickness is deemed appropriate).

The facility of being able accurately to control the optical thickness and spacing of the different layers becomes extremely important when the stack is more than a few
25 layers thick, and can substantially reduce or avoid optical loss by back-conversion and the concomitant inefficiency of the stack.

Preferably the bonding step is carried out under a controlled atmosphere. This may involve an increased or reduced pressure, or a near vacuum, and the atmosphere may be inert or active.

Individual layers of a stack may be added and bonded sequentially, or all the layers may be joined in a single step, or any intermediate process may be employed. It is likely that a very large stack will be assembled in parts each comprising a lesser plurality of layers, and the parts will then be joined together in a similar manner.

- 5 The non-linear optical material may be gallium arsenide, zinc selenide, lithium niobate, or ZnGeP_2 , for example. ZnGeP_2 is used in near-IR pumped optical parametric oscillators operating in the mid-infrared.

10 Either or both ends of the stack may be supplemented by a protective layer. Techniques for improving the optical damage threshold characteristics of optical crystals have been described. See, for example, DeMaria et al, "Apparatus for improving the optical intensity induced damage limit of optical quality crystals", US Patent No. 5,680,412 October 1997. These involve the attachment of thick pieces (several mm) of optically transparent material to the end-faces of an optical crystal. Materials are usually selected that offer improved optical damage and thermal
15 characteristics over those of the bulk optical crystal and in some cases offer improved surface finishes for subsequent dielectric coating.

The principal requirement for the material is to have a refractive index similar to that of the bulk optical crystal in order to minimise reflection loss at the material/crystal interfaces. An example of such a selection might be the attachment of GaAs ($n=3.3$)
20 to ZnGeP_2 crystals ($n=3.1$) to produce improved non-linear optical crystals in the mid-infrared. Attachment techniques demonstrated to date are based on direct optical contacting. This requires careful surface preparation of both the bulk crystal, which may in itself be difficult, and the end-face material.

Preferably the stack includes a protective window which is joined to an end face of
25 the stack via a glass layer. The glass layer may be chosen and provided according to the criteria laid down above when discussing joining the non-linear layers. If necessary, once contacted in place the attached material can then be anti-reflection coated using standard dielectric coating methods.

The attached material can take the form of a plane layer, e.g. a disc, or a Brewster cut prism which further avoids the need for an AR coating.

Alternatively, or additionally, an external face of the stack may be provided with a dielectric or anti-reflection coating. This may be a conventional dielectric coating, or
5 it may be formed of a glass coating (preferably but not necessarily of the same material as is used to bond the layers together) in which is formed a “moth-eye” structure for example by embossing or etching, as more particularly described in our copending UK Patent Application No. GB 0123744.5. As explained therein, the glass coating overcomes difficulties associated with the adherence of conventional
10 dielectric anti-reflection coatings on certain substrates, and also with the difficulty of preparation of the optical surfaces of some materials, since it can surround surface defects and contamination, and, if necessary, can itself be polished relatively easily. Again, the glass layer may be chosen and provided according to the criteria laid down above when discussing joining the non-linear layers.

15 Thus far the discussion has centred on quasi phase matched stacks in which the light propagates through each layer in turn, i.e. stacks where the non-linear layers lie normal or at an angle to the optical propagation direction. However, the provision of layers of non-linear material either side of a central non-linear layer may itself be advantageous, even where the light propagates in the plane of the central layer. For
20 example, it was mentioned above that quasi phase matching could also be achieved by the use of periodically poled or striated crystal layers providing gratings. By their very manner of production, these layers, or at least the regions where the gratings are located, tend to be thin. Our copending UK Patent Application No. GB 0123742.9 relates to non-linear optical arrangements in which layers of non-linear optical
25 material providing gratings are stacked in spaced relation to form a multi-grating assembly, and discloses constructions in which the layers of the stack are joined and spaced by glass layers.

When pumping a single such layer, for example a periodically poled (PP) layer of lithium niobate in an optical parametric amplifier, it is currently necessary to ensure
30 that the pump beam diameter is sufficiently small in the layer thickness direction to

avoid clipping the edge(s) of the layer, since otherwise multiple reflections (total internal reflection) can give sufficient gain to support off-axis modes, leading to poor beam quality and spectral broadening. If a layer of (the same) unpoled non-linear material is bonded either side of the PP layer using an index matched glass, the optical aperture of the PP layer is effectively increased although the dimension of the gain region is unaltered. Slightly larger pump beams can then be used without fear of the detrimental effects just mentioned.

Thus the invention encompasses stacks of non-linear optical layers joined by glass layers, both where the intended optical propagation direction is normal or at an angle to the planes of the layers, and where it is parallel thereto. Considerations set out above in relation to stacks of quasi-phase matched layers apply also to stacks where the intended optical propagation direction lies parallel to the layers. However, the refractive index matching condition may be relaxed somewhat.

A stack provided by the present invention may be transmissive in part of the infrared spectrum. However, the invention extends to the production of devices for use in the visible and/or UV parts of the spectrum.

A stack provided by the present invention may provide, or form part of, an optical device such as a harmonic generator, e.g. a frequency doubler or tripler, a frequency mixer, and a parametric device such as an optical parametric oscillator, amplifier or generator.

Further features and advantages of the invention will become clear upon a reading of the appended claims, to which the reader is referred, and also upon consideration of the following more detailed description of embodiments of the invention.

1. Quasi-Phase Matched Devices

Quasi-phase matched techniques offer a route to the production of efficient non-linear optical materials for laser wavelength conversion. The basis of the technique is to create a structure consisting of a stack of crystalline layers with alternating crystal orientations. This construction makes possible the use of materials which have outstanding optical properties (high non-linear coefficient, low-loss, high damage

threshold etc.) but which cannot be phase-matched by conventional techniques. The technique is especially valuable for the mid-infrared spectral region where there are few useful non-linear crystals.

5 Because of the high number of interfaces involved in a quasi-phase matched device comprising a stack of spaced non-linear crystalline layers, the quality of each interface must be very high (very low reflection and scattering losses) if an efficient quasi-phase matched device is to result. The optical losses of a stack of crystalline plates separated by air gaps are high due to the large number of surface reflections, and effective techniques for producing quasi-phase-matched devices rely on reducing
10 these losses.

In the case of gallium arsenide the current technique relies on the high temperature diffusion bonding of thin (ca 100 μ m) polished wafers and it is necessary to have precise control of wafer thickness, which is extremely onerous. The process is inherently unreliable because of the requirement for ultra-clean surfaces, free from
15 any particulate material. The present invention enables the use of a technique for forming the phase-matched material, which is inherently simpler, more cost effective, and which can involve a significant relaxation of the control of wafer thickness. The technique is likely to lead to more efficient non-linear conversion devices and higher performance laser sources.

20 Wafers of suitably oriented non-linear optical material are polished to an appropriate thickness and then cleaned. The thickness of the wafers at this stage can be measured by any convenient technique. Any trimming can be carried out by a suitable controlled thinning technique such as ion beam milling, using optical interferometry for the basis of the control technique. The wafers are then coated with low glass transition point
25 Tg glass using any standard method to a total thickness calculated according to the required application. The coating method should provide precise thickness control. Examples of suitable methods include sputtering and flash evaporation. To improve wetting of the non-linear optical material it is convenient to deposit approximately half the required thickness of low glass transition point Tg glass onto both sides of
30 each wafer, rather than depositing it all on one surface. The stack of wafers is then

assembled by placing the wafers, one on top of another, in the correct orientation. Care should be taken to prevent the incorporation of undue particulate material between the layers. However, small particles of diameter less than the thickness of the glass layer, although undesirable, will not prevent the layers from bonding since the glass will ultimately flow around and engulf them on heating. Provided that their optical loss characteristics are not too high, they will not unduly compromise the performance of the stack at high laser fluences. Imperfections such as roughening or scratches introduced by the processing can similarly be accommodated.

The stack of wafers is then placed in an oven and heated to the softening point of the glass. The atmosphere within the oven may be controlled, e.g. to remove air which would otherwise become trapped within the finished structure. In a preferred method, the assembled stack of coated wafers is baked in an oven for about 1 to 2 hours at a baking temperature above 100° C but substantially lower than the glass transition (or softening) temperature with the intention of boiling off any volatile contamination including moisture, and the temperature is then raised to the region of the softening point. While the structure is hot, pressure is applied to force out any remaining air and to encourage the glass to flow and adjacent layers to bond. A preferred pressure range is 50 to 250 kg/cm² (500 to 2500 Newtons/cm²). The temperature and pressure are maintained for a suitable period, e.g. around 4 hours, before the oven is finally cooled. The finished structure can then be removed from the oven.

In the simplest form, the thickness of each layer of non-linear optical material is chosen to be close to the coherence length (or an odd multiple thereof) of the material at the intended wavelengths of use. The thickness of the adjacent glass layer is chosen such that either the combined optical thickness of the non-linear optical layer and the glass layer provides an odd number of coherence lengths (odd length case), or the combined optical thickness of the non-linear optical layer and the glass layer provides an even number of coherence lengths (even length case).

Note that the coherence lengths may be different in the two materials and the combined thicknesses should be calculated with this in mind. For example, if the non-linear optical material has a coherence length of 100µm and the glass has a coherence

length of 50 μ m, then a 90 μ m layer of non-linear optical material (0.9 coherence lengths) together with a 5 μ m layer of glass (0.1 coherence length) would form a total of one coherence length.

5 In the odd length case, the crystal axis of the subsequent non-linear optical layer must be rotated by 180 degrees with respect to that of the current layer. In the even length case, the two axes should be parallel. The odd length case is preferred since this maximises the proportion of non-linear optical material in the device.

10 In a first example of a quasi-phase matched device, GaAs has a number of useful optical properties as a non-linear optical material for use in the infrared but is not birefringent. GaAs has a refractive index of 3.27 at 10 μ m and the coherence length of GaAs for frequency doubling of CO₂ laser radiation is approximately 106 μ m. A suitable glass is Ge₁₅As₁₅Se₁₇Te₅₃ which has a refractive index of 3.23 at 10 μ m, i.e. matching within 2%. The composition of the glass can be varied slightly in order to improve the index match at one or more of the operating wavelengths.

15 In a second example, zinc selenide is potentially a better non-linear material than GaAs in that it has a higher non-linear coefficient and transmits in the visible range. It has a refractive index of 2.43 at 5 microns, and it is believed that the low glass transition point Tg glass arsenic trisulphide As₂S₃ may prove a good bonding material device for a quasi-phase matched device using zinc selenide. Arsenic trisulphide has a
20 refractive index $n=2.4$ and a softening temperature of about 210°C.

By way of a third example, the wafers are of unpoled lithium niobate, which is used for non-linear conversion in the visible, near infrared and mid infrared bands and has a refractive index of $n=2.2$. The wafers are oriented to exploit the higher or highest non-linear coefficient, while the QPM stack facilitates the maintaining of a large
25 aperture. Reflection losses at each surface are expected to be no more than 0.2%. The maximum operating temperature of arsenic trisulphide glass is about 150°C, which is sufficiently high to allow heating of the bonded stack to prevent problems associated with photo-refractive damage.

The invention is also applicable to the assembly of more complex structures, which may require extensive calculations to determine the thickness and orientation of each layer according to the intended application. An example of a more complex structure might be a device designed to frequency-triple the input. In its simplest form this
5 would consist of a simple frequency-doubling structure directly bonded to a frequency-mixing structure. Such a monolithic device would have the advantage over a pair of discrete structures of eliminating the need for multiple anti-reflection coatings as well as reducing device size and complexity.

1.1. Frequency doubler

10 In order to make a frequency-doubling device for use with CO₂ laser radiation, 30 GaAs wafers are polished to a thickness of 305μm (just under three coherence lengths). Layers of Ge₁₅As₁₅Se₁₇Te₅₃ are sputtered onto both sides of each wafer to bring the total thickness of each wafer to three coherence lengths. (Polishing techniques for GaAs can typically achieve wafer thickness tolerances of around plus
15 or minus 2μm.) The layers are then assembled in a clean environment to form a stack, which is placed in an oven. The oven is evacuated and then heated to temperatures in the range 140 to 240 degrees centigrade. A pressure of 10-100 kg/cm² is applied for 2-4 hours before cooling the oven to room temperature. The resulting structure can be used as-is or anti-reflection coatings may be applied to the ends to improve the
20 efficiency of the device.

Calculations suggest that between 100 and 150 wafers are necessary for an efficient frequency-doubling device for use with CO₂ laser radiation. This could be formed as a single stack, but it is more likely that (for example) 3 stacks of 50 layers each would be made with suitable antireflection coatings on each stack. A potential advantage of
25 this multi-stack structure is that small phase mismatches which build up between pump and harmonic in one stack might be compensated by adjusting the relative orientations of the stacks, or by introducing a transparent dispersive element between each stack, the orientation of which can be adjusted for precise compensation.

1.2. Parametric Oscillator

In the production of a quasi-phase matched optical parametric oscillator device fabricated from GaAs wafers and designed to produce output wavelengths in the 3-5 μm band from a pump wavelength around 2 μm , low glass transition point T_g index-matching glass is employed as an intermediate layer between the wafers. The prospective facing surfaces of the wafers are each coated with an index-matching glass film by sputtering and then pressed together at moderate temperatures (ca 140-240°C). This technique results in a low-temperature bonding process incorporating an amorphous layer which can deform to accommodate imperfections (including particulate contamination) in the wafer surfaces. An important feature of the above technique in both frequency doubling and optical parametric oscillators cases is the precise control of layer thicknesses provided by the sputtering process.

All the wafers may be coated as appropriate and formed into a stack prior to bonding of the entire stack. This is the simplest and most preferred process. However, each pair of prospective facing surfaces may be coated and bonded in turn, or any intermediate process may be employed.

The glass is chosen to have a refractive index close to that of the wafer material to minimise the reflection losses. The glass must also have good optical transmission at the wavelengths at which the quasi-phase-matched device is designed to operate. For use in the mid-infrared waveband, chalcogenide glasses have the required properties. Glasses in the Ge-As-Se-Te system which satisfy the index-matching condition for GaAs have been identified, and samples of the glass have been prepared.

2. Birefringent Phase Matched Devices

In a variant of the above process, the wafers are of a series of birefringent ZnGeP_2 components cut for use in a mid-infrared optical parametric oscillator, and the bonding process is performed at a temperature of less than 200°C, and the glass of the Ge-As-Se-Te system has the formula $\text{Ge}_{15}\text{As}_{15}\text{Se}_{17}\text{Te}_{53}$. The extreme difficulty of obtaining long, low optical loss, crystals of ZnGeP_2 is thereby overcome. A further

advantage is that the resulting construction enables walk-off compensation to be introduced, by rotating each short crystal layer relative to its neighbours.

It is important to note that quasi-phase-matching and birefringent phase matching also have important applications in the visible waveband, where lower refractive index
5 non-linear materials would permit the use of commercially available glasses for bonding, providing they meet the index matching and glass transition temperature requirements.

Other optical components, for example a lens or suitably cut window material, may be similarly bonded to the end of a phase-matched stack, producing a compact
10 monolithic device. For example a major face of a protective lamina of GaAs ($n=3.3$) and a major face of a ZnGeP_2 crystal ($n=3.1$) at the end of a stack thereof are each coated with a thin layer of a low melting glass based on the Ge-As-Se-Te system, the lamina and crystal are assembled with the coated surfaces in contact, and heat and pressure are applied to bond them together without affecting the mechanical or optical
15 properties of either the lamina or the crystal.

CLAIMS

1. A non-linear optical device comprising a stack of at least two layers of non-linear optical material, adjacent said non-linear layers being joined by a glass layer.
2. A device according to claim 1 wherein the glass has a refractive index which
5 is within 30% of the refractive index of the non-linear optical material.
3. A device according to claim 1 or claim 2 wherein the stack comprises three said non-linear layers, and the central said non-linear layer comprises a grating.
4. A device according to claim 3 wherein said central layer is a striated or periodically poled layer.
- 10 5. A device according to claim 1 or claim 2 wherein the layers of the stack are arranged for quasi phase matching for propagation through the layers in turn.
6. A device according to claim 5 wherein the optical thickness of each non-linear layer plus glass is substantially equal to a coherence length or an integral multiple thereof.
- 15 7. A device according to claim 6 wherein the optical thickness of each non-linear layer plus glass is substantially equal to a coherence length or an odd integral multiple thereof, and the crystal axes of adjacent non-linear optical layers are relatively rotated by substantially 180 degrees.
8. A device according to claim 6 wherein the optical thickness of each non-linear
20 layer plus glass is substantially equal to an even integral multiple of the coherence length, and the crystal axes of adjacent non-linear optical layers are substantially parallel.
9. A device according to any one of claims 1, 2, and 5 to 8 wherein the stack comprises at least 10 layers of non-linear optical material.
- 25 10. A device according to any one of claims 5 to 10 wherein the glass has a refractive index such that the total theoretical reflection from all the interfaces when traversed in sequence is no greater than 50%.

11. A device according to any preceding claim wherein the glass is a chalcogenide glass.
12. A device according to claim 11 wherein the glass comprises Ge, As, Se and Te.
- 5 13. A device according to claim 12 wherein the glass has the general formula $\text{Ge}_{(x-a)}\text{As}_a\text{Se}_{(100-x-b)}\text{Te}_b$, where $25 < x \leq 40$; $10 \leq a \leq 25$; $40 < b \leq 70$, and $(100-x-b) > 0$.
14. A device according to claim 11 wherein the glass is amorphous arsenic sulphide.
15. A device according to any preceding claim wherein the non-linear optical
10 material is selected from gallium arsenide, zinc selenide, lithium niobate and ZnGeP_2 .
16. A non-linear optical device according to any preceding claim wherein the non-linear material is birefringent.
17. A non-linear optical device according to any one of claims 1 to 15, wherein the non-linear material is non-birefringent.
- 15 18. A method of making a non-linear optical device comprising a stack of at least two layers of non-linear optical material, in which method the surfaces of adjacent said non-linear layers are joined by a glass layer under the action of heat and pressure.
19. A method according to claim 15 wherein the glass is selected to have a
20 refractive index which is within 30% of the refractive index of the non-linear optical material.
20. A method according to claim 18 wherein the glass is selected to have a refractive index which is within 30% of the refractive index of the non-linear optical material.
21. A method according to any one of claims 18 to 20 wherein the glass has a
25 refractive index such that the total theoretical reflection from all the interfaces is no greater than 50%.

22. A method according to any one of claims 18 to 21 wherein opposed surfaces of two said layers of non-linear optical material are joined by the steps of providing at least one said surface with a thin layer of bonding glass having a glass transition temperature T_g substantially lower than the glass devitrification temperature T_{c1} ,
5 placing the said surfaces together with only the coating or coatings therebetween to form an assembly, and heating the assembly under pressure to a temperature T_b which lies between T_g and T_{c1} and is sufficiently high to soften the glass and bond the surfaces together.

23. A method according to claim 22 wherein the thickness of said coating or
10 coatings is controlled so that the optical thickness of each non-linear layer plus glass is substantially equal to a coherence length or an an integral multiple thereof.

24. A method according to claim 23 wherein the optical thickness of each non-linear layer plus glass is substantially equal to a coherence length or an odd integral multiple thereof, and the crystal axes of adjacent non-linear optical layers are
15 relatively rotated by substantially 180 degrees.

25. A method according to claim 23 wherein the optical thickness of each non-linear layer plus glass is substantially equal to an even integral multiple of the coherence length, and the crystal axes of adjacent non-linear optical layers are substantially parallel.

20 26. A method according to any one of claims 22 to 25 wherein the thickness of the glass is controlled by removal of part thereof after deposition thereof.

27. A method according to any one of claims 22 to 25 wherein the thickness of the glass is controlled during deposition.

28. A method according to any one of claims 22 to 27 wherein bonding is effected
25 under conditions such that there is no substantial extrusion of the glass out from between the bonded surfaces.

29. A method according to any one of claims 22 to 27 wherein bonding is effected under conditions such that the thickness of the glass layer or layers remains substantially constant.
30. A method according to any one of claims 22 to 297 wherein the glass is
5 selected such that it undergoes the bonding cycle reversibly.
31. A method according to any one of claims 22 to 30 wherein the glass is deposited by a method selected from RF sputtering, flash evaporation, solvent evaporation or spin coating.
32. A method according to any one of claims 22 to 31 wherein the glass is
10 deposited on both said surfaces to be joined.
33. A method according to any one of claims 18 to 32 wherein the glass exhibits a plurality of glass transition temperatures above ambient and T_b is selected to lie between the first and second glass transition temperatures.
34. A method according to any one of claims 18 to 32 wherein the glass has only
15 one glass transition temperature before the devitrification temperature is reached.
35. A method according to any one of claims 18 to 34 wherein the bonding glass is selected such that there is an interval of at least 50°C, between the first glass transition temperature and the next higher transition temperature, whether a further glass transition temperature or the devitrification temperature.
- 20 36. A method according to any one of claims 18 to 35 wherein the glass is an inorganic glass.
37. A method according to claim 36 wherein the glass is a chalcogenide glass.
38. A method according to claim 36 wherein the glass comprises Ge, As, Te and Se.
- 25 39. A method according to claim 38 wherein the glass has the general formula $\text{Ge}_{(x-a)}\text{As}_a\text{Se}_{(100-x-b)}\text{Te}_b$, where $25 < x \leq 40$; $10 \leq a \leq 25$; $40 < b \leq 70$, and $(100-x-b) > 0$.

where x is in the range 20 to 50, a is in the range 5 to 30, and b is in the range 30 to 80.

40. A method according to claim 36 wherein the glass is amorphous arsenic sulphide.

5 41. A method according to any one of claims 18 to 40 wherein said non-linear material is selected from gallium arsenide, zinc selenide, lithium niobate and ZnGeP_2 .

42. A method according to any one of claims 18 to 41 wherein at least some non-linear layers of the stack are separately added and joined thereto.

43. A method according to any one of claims 18 to 42 wherein at least some non-
10 linear layers of the stack are joined together in a single step.

44. A non-linear optical device made by the method of any one of claims 18 to 43.

45. A harmonic generator, e.g. a frequency doubler or tripler, a frequency mixer, and optical parametric amplifier or an optical parametric generator comprising a device as claimed in any one of claims 1 to 17, and 44.

15 46. A non-linear optical device substantially as hereinbefore described with reference to the accompanying drawings.

47. A method of making a non-linear optical device substantially as hereinbefore described with reference to the accompanying drawings.

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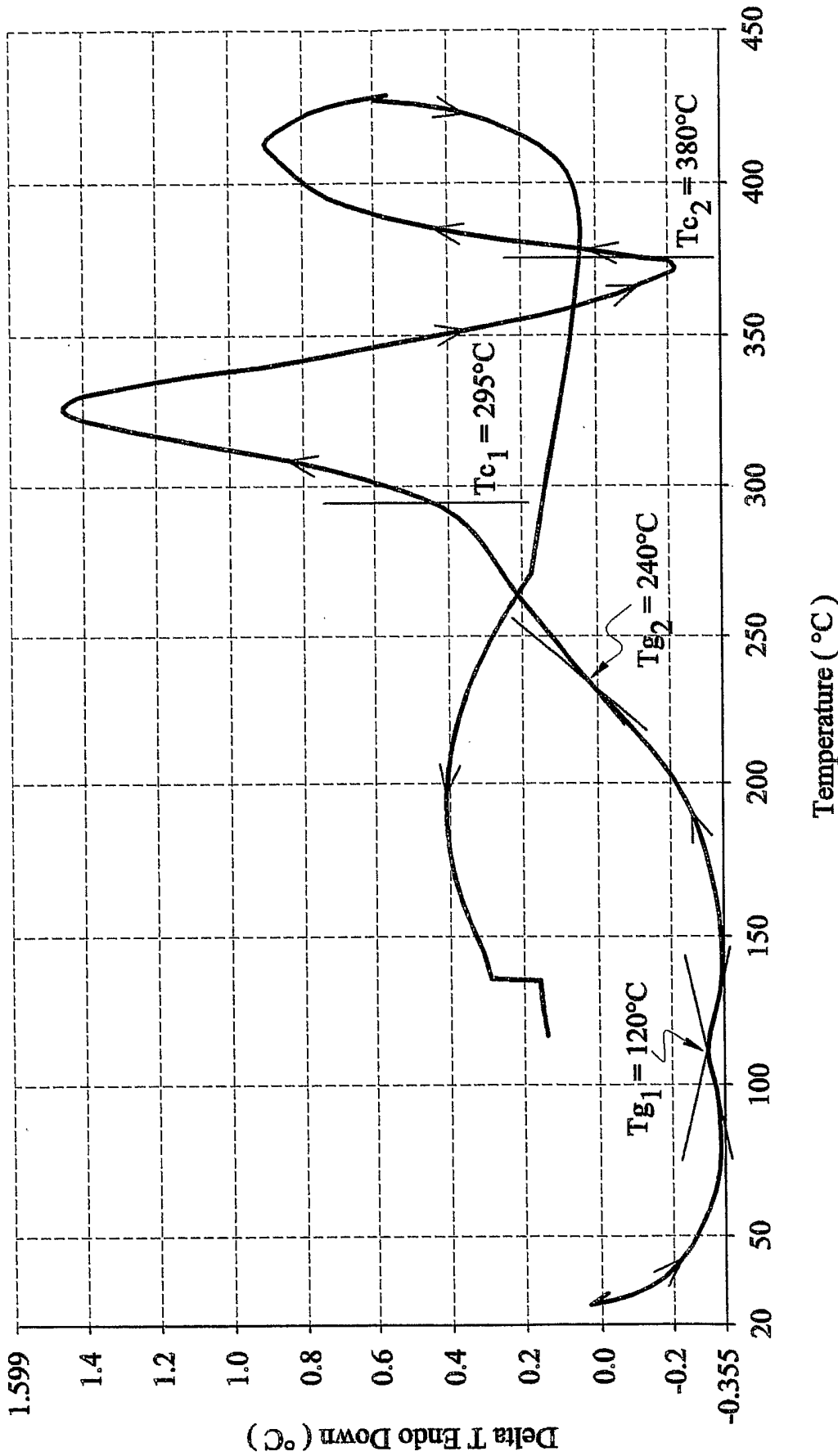


FIG. 1

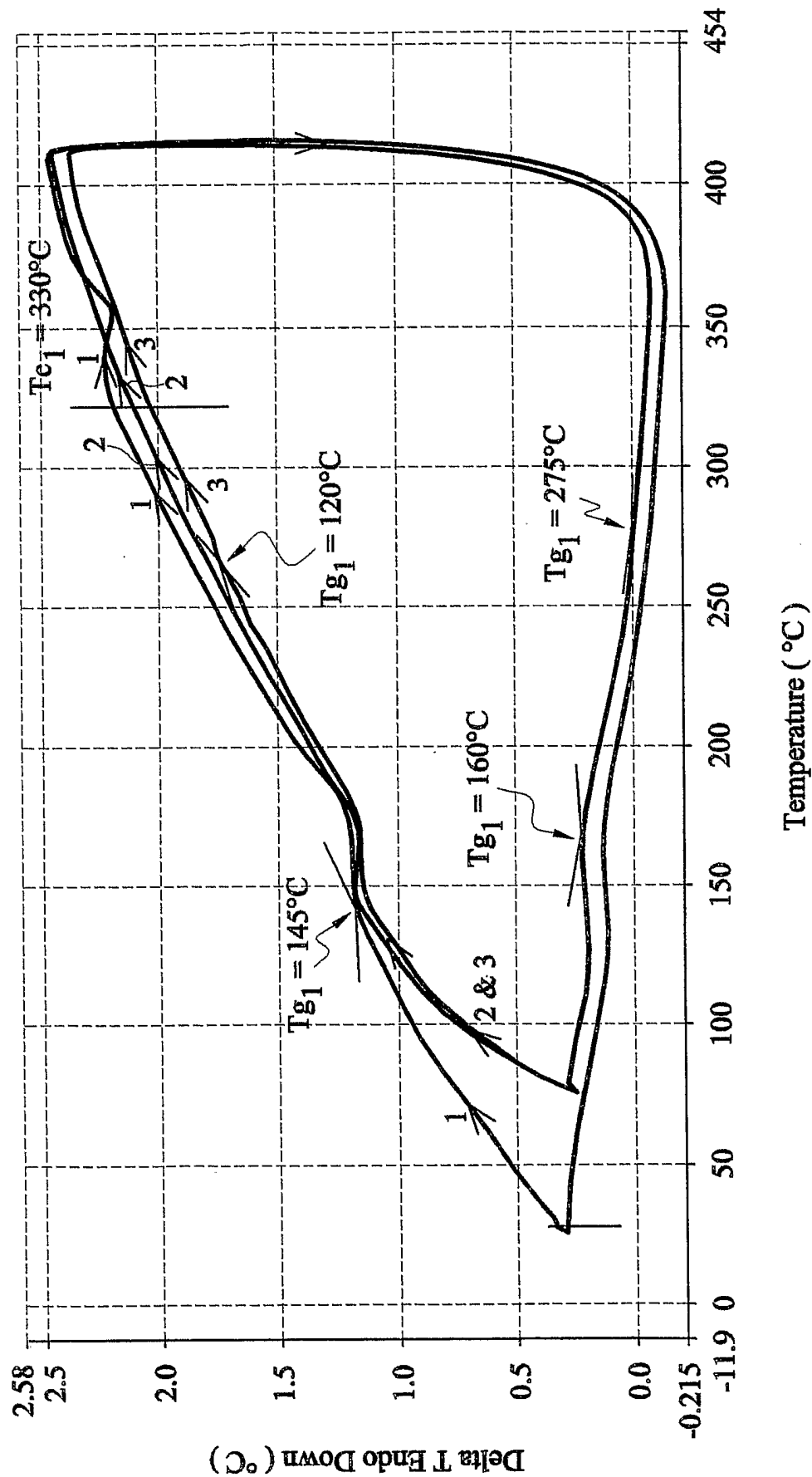


FIG. 2

-3/4-

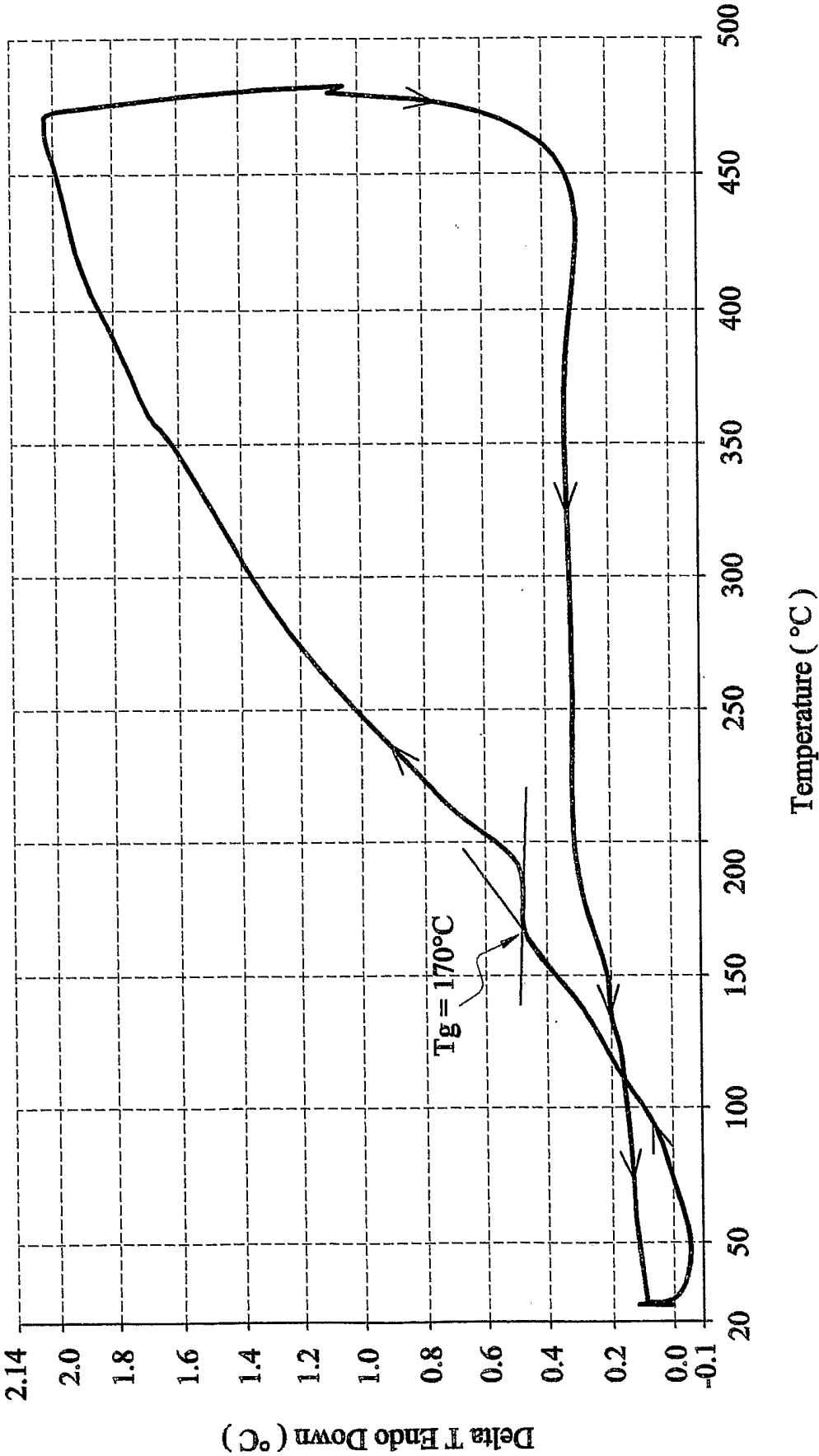


FIG. 3

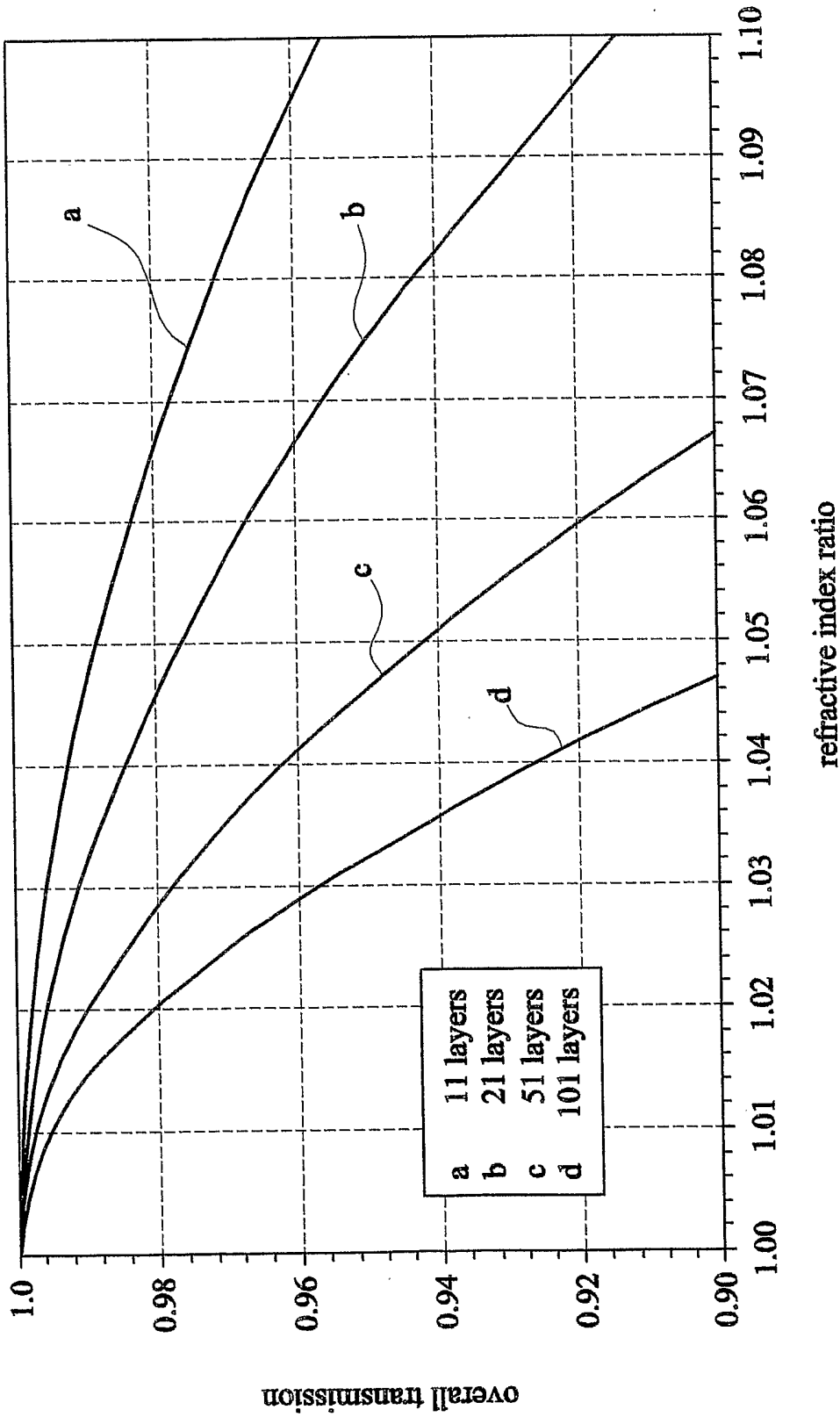


FIG. 4