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An infrared study of the structure of GeO_2–CeO_2 thin films

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The infrared spectra of amorphous thin films consisting of GeO_2 co-evaporated with CeO_2 are presented and interpreted in relation to the spectrum of the pure amorphous GeO_2 film. The lower frequency side of the broad absorption band within this spectrum peaking at 730 cm^{-1} is believed to be due to defect centres similar to the O_1^- and O_3^+ centres found in a-SiO_2. Absorption at higher frequencies within this band is due to the "O stretch" vibrations of the Ge–O–Ge linkage. After considering the vibrations of the O_1^- and O_3^+ centres in detail, it is shown that the band at 495 cm^{-1} cannot be due to either of these centres and must therefore by caused by some other reactive defect centres. The variation of the position of the 730 cm^{-1} peak within the series of spectra is noted and probable explanations are offered. The optical absorption edge of a-GeO_2 thin film is compared with that of a-SiO and a possible explanation of the basic differences is proposed.

1. Introduction

Several studies have been carried out in the past on the properties of thin films prepared by the vacuum co-evaporation of a Group IV oxide with CeO_2 on to a common substrate. Interest in such systems stems from a possible utilization of their dielectric properties in metal–insulator–metal (MIM) electronic devices. Electrical conductivity and optical absorption studies of films consisting of CeO_2 co-evaporated with SiO have been carried out by Hogarth and Al-Dhhan [1, 2]. Structural studies of these SiO–CeO_2 films were made by Razzaq *et al.* [3], who considered their paramagnetic properties, as well as by Singh and Hogarth [4], who measured their infrared (IR) spectra to elucidate their vibrational as well as chemical structure. In a later paper [5] these workers have also thrown some light on some possible defect centres present in the SiO–CeO_2 films.

Having considered systems containing SiO as a component, it becomes interesting to compare them with systems containing the other oxides of the group IV elements. To this end Al-Dhhan and co-workers [6–8] have considered the optical and electrical properties of the GeO_2–CeO_2 and SnO_2–CeO_2 systems.

The aim of this work is to elucidate aspects of the structure of the former of these systems through an infrared study. Further insights into their structure may be obtained by treating them as analogous to the SiO–CeO_2 studies considered earlier [4, 5].

2. Experimental work

All samples were prepared by a co-evaporation technique described by Hogarth and Wright [9]. Silicon wafers were used as substrates for the IR samples, while samples for ultraviolet visible transmission studies were prepared on Corning 7059 glass. Throughout the evaporations the substrate temperature was maintained within 100 ± 10° C, and the pressure at ≈ 1.3 mPa.

Film thicknesses were monitored using quartz crystal monitors which were, in turn, calibrated by measuring the exact thicknesses of the pure GeO_2 and CeO_2 films using multiple beam interferometry [10]. Deposition rates of the films were kept within the range 0.5 to 1.0 nm sec^{-1}.

The films were annealed for a period of 2 h at a temperature of 200° C at 1.3 mPa in the same unit as that used for their preparation.

IR spectra were run on a Perkin–Elmer SP 2000 spectrophotometer over the range 200 to 400 cm^{-1}, and on a Perkin–Elmer model 1710 FTIR over the range 400 to 2000 cm^{-1}. The ultraviolet (UV) spectra were run on a Perkin–Elmer Lambda 9UV/VIS/NIR spectrophotometer over the range 200 to 800 nm.

3. Results

Fig. 1 presents the IR spectra of the nine different compositions of GeO_2–CeO_2 thin films studied. Table I lists the important IR bands contained within the frequency range 400 to 1200 cm^{-1}, as well as those contained in the 200 to 400 cm^{-1} range obtained using a different instrument. The last row of this table shows the positions of bands belonging to the pure CeO_2 film.

All except the last entry of column 1 of this table are due to the GeO_2 component of the films. The band referred to in column 2 clearly belongs to GeO_2. Its disappearance after the 89 mol % GeO_2/21 mol % CeO_2 composition is the most striking feature of the series of spectra.

The entries of column 3 show a variation which may be quite significant to the interpretation of the spectra. The last three bands are clearly due to, or influenced by, the 710 cm^{-1} absorption of the pure CeO_2 film.

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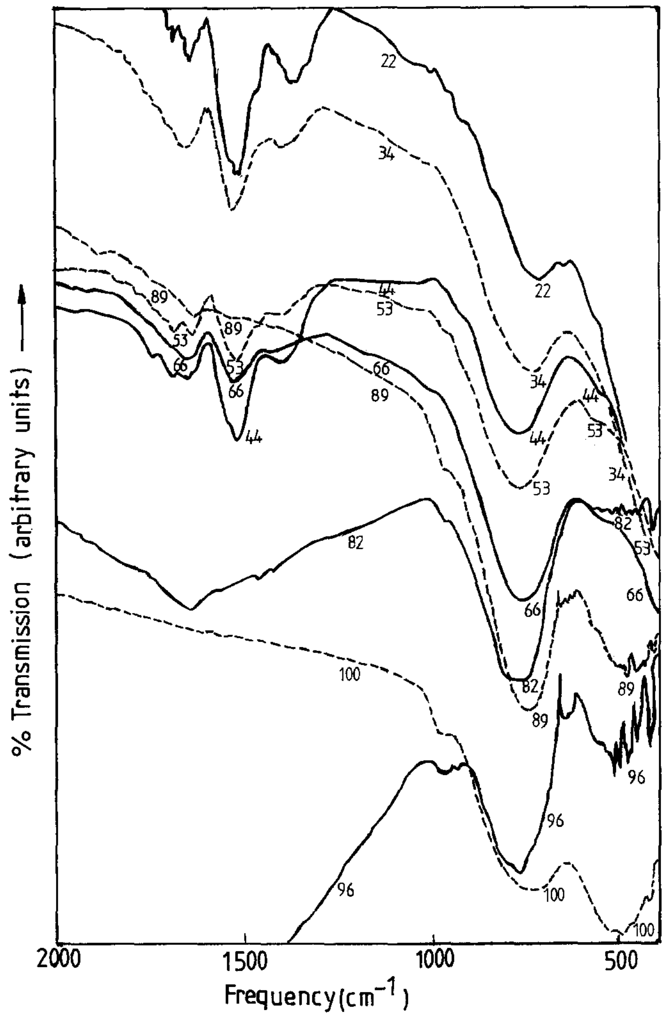

Figure 1 IR spectra of GeO_2-CeO_2 thin films of various compositions. The figures indicate film composition in mol% GeO_2.

The variations in the first five entries are discussed later. Entries of column 4 showing weak bands at 920 and 980 cm^{-1} have not been interpreted in this work. Bands occurring beyond 1200 cm^{-1} in Fig. 1 are all due to pure CeO_2 and are not discussed further.

4. Discussion

4.1. Comparisons with other spectra

To begin an interpretation of the series of spectra, one must start with a detailed consideration of the pure a-GeO_2 spectrum. As a first step it is illustrative to compare this result with others of a-GeO_2 published in the literature. Table II provides such a comparison.

In this table the $\bar{\nu}(R_2)$, $\bar{\nu}(B_2)$ and $\bar{\nu}(S_2)$ labels refer to the rocking, bending and stretching vibrations, respectively, of the oxygen atom in the Ge–O–Ge linkage, as shown in Fig. 2. This association of the observed frequencies with the modes of vibration of the oxygen atom in the Ge–O–Ge linkage are made using the calculations of Bell *et al.* [14] for vitreous GeO_2, who give 370 cm^{-1} for the $\bar{\nu}(R_2)$, 500 cm^{-1} for the $\bar{\nu}(B_2)$ and 850 cm^{-1} for the $\bar{\nu}(S_2)$ frequencies. In assigning the observed bands in this work, however, two observations need to be accounted for. Firstly a value of 730 cm^{-1} falls well below all the experimental and theoretical values assigned to the "O stretch" mode previously, and secondly the band at ≈ 500 cm^{-1} in this work is strong, unlike those of previous spectra reported for a-GeO_2 where it is very weak. It is also to be noted that the theoretical value of $\bar{\nu}(S_1)$, the frequency of the non-bridging oxygen atom formed by a

TABLE I The important IR absorption bands in the spectra of GeO_2-CeO_2 thin films. Letters refer to strength of bands: s = strong; m = medium; w = weak; sh = shoulder

	Film composition (mol% GeO_2)	Positions of IR bands (cm^{-1})			
		1	2	3	4
1.	100	350 (m)	495 (s)	730 (s)	980 (w)
2.	96	350 (m)	500 (s)	770 (s)	970 (w)
3.	89	350 (m)	485 (s)	750 (s)	970 (w)
4.	82	350 (m)	–	770 (s)	970 (sh)
5.	66	350 (m)	–	765 (s)	–
6.	53	350 (s)	–	775 (s)	920, 970 (sh)
7.	44	350 (s)	–	775 (s)	920, 970 (sh)
8.	34	350 (s)	–	730 (s)	–
9.	22	350 (s)	–	710 (s)	920, 970 (w)
10.	0 (100% CeO_2)	290 (s)	–	710 (w)	–

TABLE II Comparison of the IR bands of other a-GeO_2 spectra with that of current work

Reference	Type of a-GeO_2	Assignment band (cm^{-1})		
		$\bar{\nu}(R_2)$	$\bar{\nu}(B_2)$	$\bar{\nu}(S_2)$
1. Chakraborty and Condrate [11]	v-GeO_2	350	570	885
2. G. Lucovsky [12]	v-GeO_2	275	560	850
3. G. Lucovsky *et al.* [13]	Glow discharged a-Ge: (H, O) alloys	300	500	800
4. This study	Thin film	350(?)	495(?)	730(?)

cleavage of the Ge–O–Ge linkage, is evaluated by Bell *et al.* [14] to be $650\,cm^{-1}$. This figure is not too different from the two observed frequencies being considered above. These observations are compelling enough to suggest that the observed bands may not be due to the supposed modes of vibrations, and a careful analysis of their nature is called for.

4.2. Band assignments for the a-GeO_2 spectrum

4.2.1. Associations with Ge–O–Ge *vibrations*

An expedient technique for investigating the identities of the broad bands positioned at ≈ 730 and $495\,cm^{-1}$ is to employ a variation of the "simplified force constant model" used by Lucovsky [12] in estimating the vibrational frequencies for defect centres in v-SiO_2 i.e. vitreous silica. In his method Lucovsky estimates the frequencies of the O_1^- and O_3^+ centre vibrations by first determining effective values of the "O stretch" force constant, k_r, and the ratio, of the "O bend" and "O stretch" vibrations of the Si–O–Si linkage to the formulae given by Herzberg [15], which are respectively

$$\omega^2(B_2) = (2k_r/m_0)(\cos^2\alpha + 2\gamma\sin^2\alpha)$$

for the bending vibration of the oxygen atom in the Si–O–Si linkage, and

$$\omega^2(S_2) \approx (2k_r/m_0)\sin^2\alpha$$

for the stretching vibration of the same atom. Here ω is equal to $2\pi\nu$, ν being the vibrational frequency, m_0 is the oxygen mass, 2α is the Si–O–Si bond angle and the silicon motions are assumed negligible in the second of the formulae. Lucovsky then inserts the effective constants thus derived in the relevant formulae for the defect centre vibrational frequencies (to be given later) to estimate their corresponding values.

For the present purposes this technique may be modified to estimate the relative values of the $\bar{\nu}(S_2)$, $\bar{\nu}(B_2)$ and $\bar{\nu}(S_1)$ frequencies for a-GeO_2. This may be done by associating one observed frequency with a particular mode of vibration and using the Herzberg formulae to evaluate the frequency corresponding to the other modes. Thus, taking 2α to be 133°, the average value in v-GeO_2 [16] and a γ value of 6.2×10^{-3} [17] we first suppose that the $495\,cm^{-1}$ is the $\bar{\nu}(B_2)$ frequency. Inserting this in the first of the Herzberg formulae above yields $6.83 \times 10^2\,N\,m^{-1}$ for the value of k_r, which when used in the second formula gives for $\bar{\nu}(S_2)$ a value of $1103\,cm^{-1}$. This same value of k_r may also be used to estimate $\bar{\nu}(S_1)$ given by the simple expression

$$\omega^2(S_1) = k_r/m_0$$

On substitution into this formula, a value of $850\,cm^{-1}$ is obtained for $\bar{\nu}(S_1)$. Clearly both frequencies calculated above are far in excess of their accepted values, which indicates strongly that the $495\,cm^{-1}$ band is not due to a B_2-type vibration. We next suppose that the $730\,cm^{-1}$ frequency is due to S_2-type vibrations and substitute this value in the second of the Herzberg formulae to obtain a value of $2.99 \times 10^2\,N\,m^{-1}$ for k_r. This yields $328\,cm^{-1}$ for $\bar{\nu}(B_2)$ and $563\,cm^{-1}$ for $\bar{\nu}(S_1)$, both of which are gross underestimates of the expected values.

It thus seems unlikely either that the peak at $730\,cm^{-1}$ in the present spectrum of a-GeO_2 is due to an S_2 vibration or that the broad band at $495\,cm^{-1}$ arises from absorption by the B_2 mode of vibration. These conclusions are reinforced by the following additional facts. In the case of the $495\,cm^{-1}$ band, its strength of absorption has already been noted as contradicting other experimental observations of the $\bar{\nu}(B_2)$ frequency. This is further enhanced by the theoretical calculations of the absorption coefficients of the bands of a-GeO_2 by Bell and Hibbins-Butler [18] which reveal that the $\bar{\nu}(B_2)$ absorption should be at least an order of magnitude weaker than the $\bar{\nu}(S_2)$ absorption. Furthermore the rapid disappearance of the $495\,cm^{-1}$ band with the addition of CeO_2 supports the view that this band is due to a very reactive centre, and is thus not due to the relatively unreactive Ge–O–Ge linkage.

4.2.2. Annealing and the 730 cm^{-1} band

Further insight into the identity of the broad band peaking at $730\,cm^{-1}$ is given by the results of annealing. This shows the development of a distinct shoulder at the $800\,cm^{-1}$ side of this band (see Fig. 3). Because

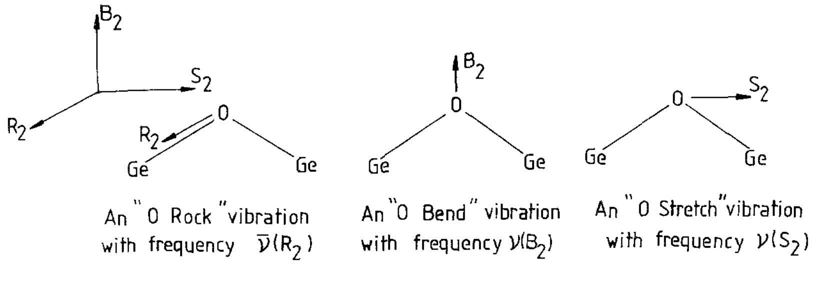

Figure 2 Motions of the oxygen atom of the Ge–O–Ge linkage in its three characteristic modes of vibrations. R_2 is perpendicular to the plane of the paper.

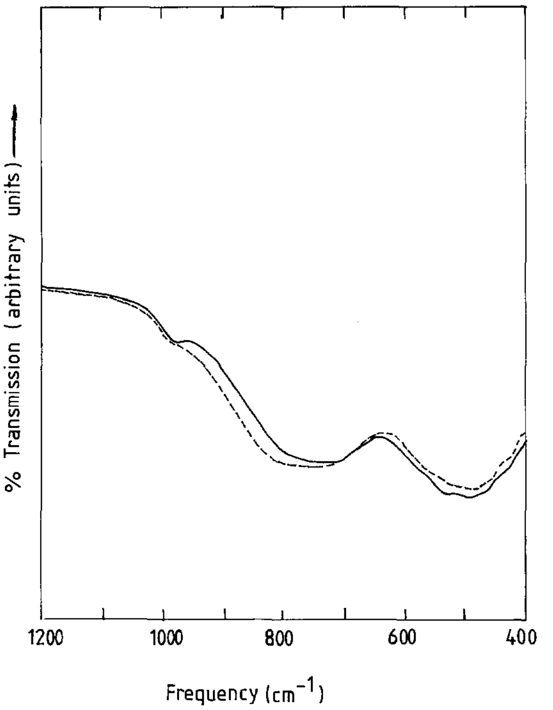

Figure 3 Annealed (— — —) and original (———) IR spectra of a pure a-GeO_2 thin film.

annealing is expected to increase the concentration of Ge–O–Ge linkages, this strongly indicates that the S_2 absorption in GeO_2 thin films also occurs closer to 800 cm^{-1}, just as it does in other forms of a-GeO_2. That is, the 730 cm^{-1} band is not due to the S_2 vibrations and must be attributed to other causes. When this new information is used to re-estimate the other frequencies, one obtains the values of 358 cm^{-1} for $\bar{\nu}(B_2)$ and 617 cm^{-1} for $\bar{\nu}(S_1)$, corresponding to a value of 3.6×10^2 for k_r.

4.2.3. Enumeration of defect centres in a-GeO_2 films

To proceed further with the analysis of the GeO_2 film of the present work it is fruitful to compare the results with those for a-SiO thin films obtained earlier [5]. It was shown that a-SiO thin films contained defect centres which were predominantly of the O_1^0 and O_3^+ types (introducing respective absorptions in the IR), the first of which was paramagnetic and thus acted as an ESR centre. This was unlike *v*-SiO_2, which contained O_1^- and O_3^+ defects instead, both of which were non-paramagmetic and thus gave a null ESR response. The absence of ESR signals in a-GeO_2 thin films [19] shows that it does not contain any paramagnetic centres (including O_1^0) in any significant quantity to produce a detectable IR response. Thus a-GeO_2 thin films behave more like bulk a-GeO_2 (which contains only very low concentrations of E′ paramagnetic centres as detected by Kordas *et al.* [20]) than a-SiO thin films do when compared to bulk v-SiO_2, this result is only to be expected.

In as far as germanium and silicon belong to the same group of the periodic table, one would expect their dioxides to have similar chemical properties. On this basis one may conjecture the presence in bulk v-GeO_2 of O_1^- and O_3^+ defects as well as vacancy bridge-type defects [21] related to the Ge–O–O–Ge linkage. Thus, similar defects are also to be expected in a-GeO_2 thin films.

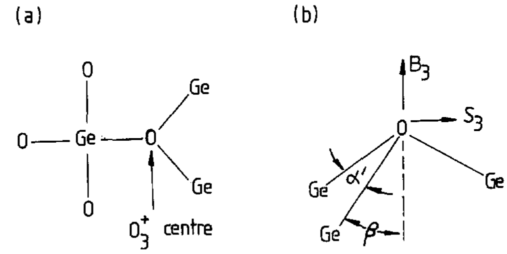

Figure 4 (a) Schematic representation of the location of the O_3^+ centre in the GeO_2 CRN. (b) Probable structure of the O_3^+ centre, with arrows showing modes of vibration B_3, S_3 of the oxygen atom.

4.2.4. IR response of the O_1^- and O_3^+ centres

To assess whether the defect centres O_1^- and O_3^+ contribute to the absorption at the two observed frequencies, one may again follow the analysis of Lucovsky for such centres in v-SiO_2. As he pointed out, the stretch vibrational frequency of the O_1^- centre will deviate from that of O_1^0 according to the scaling law

$$\Delta v/v_0 = 3\Delta d/d_0$$

where v, d refer to vibrational frequencies and bond lengths, repectively. Because the acquisition of a negative charge by the O_1^0 centre will increase its value of k_r, one expects the O_1^- vibrational frequency to be greater than the 617 cm^{-1} calculated above for the O_1^0 centre (which is the same as for a non-bridging oxygen atom). This upward scaling means that the stretch vibrations of the O_1^- centre cannot contribute to the 495 cm^{-1}, but may do so to the 730 cm^{-1} peak.

Vibrational frequencies attributable to the O_3^+ centre are more difficult to estimate. Fig. 4 shows the location of this centre in the GeO_2 continuous random network as well as its probable structure, assumed to be pyramidal with the exact shape yet to be decided. Here the Ge–O–Ge bond angle is denoted α', and the angle between the bisector of the apex angle and a Ge–O bond as β. Motions of the oxygen atoms are analysed as stretching or S_3 motions and bending or B_3 motion. Assuming that the germanium motions may be neglected (a much better assumption than for the SiO_2 case), the stretching frequency $\bar{\nu}(S_3)$ may be estimated by the relation

$$\omega^2(S_3) = (3k_r/2m_0)[\sin^{-2}\beta + 3\gamma \sin^{-4}\beta/(1 + 3\cos^2\beta)]$$

and the bending frequency $\bar{\nu}(B_3)$ by

$$\omega^2(B_3) = (3k_r/m_0)[\cos^2\beta + 12\gamma \cos^2\beta\sigma \sin^2\beta/(1 + 3\cos^2\beta)]$$

If we now assume that k_r has the value 3.6×10^2 N m^{-1}

TABLE III Vibrational frequencies of the O_3^+ centre corresponding to some possible pyramidal angles

$\beta°$	$\alpha°$	$\gamma(S_3)$(cm^{-1})	$\gamma(B_3)$(cm^{-1})
71	110	720	356
76	115	742	266
90	120	763	0

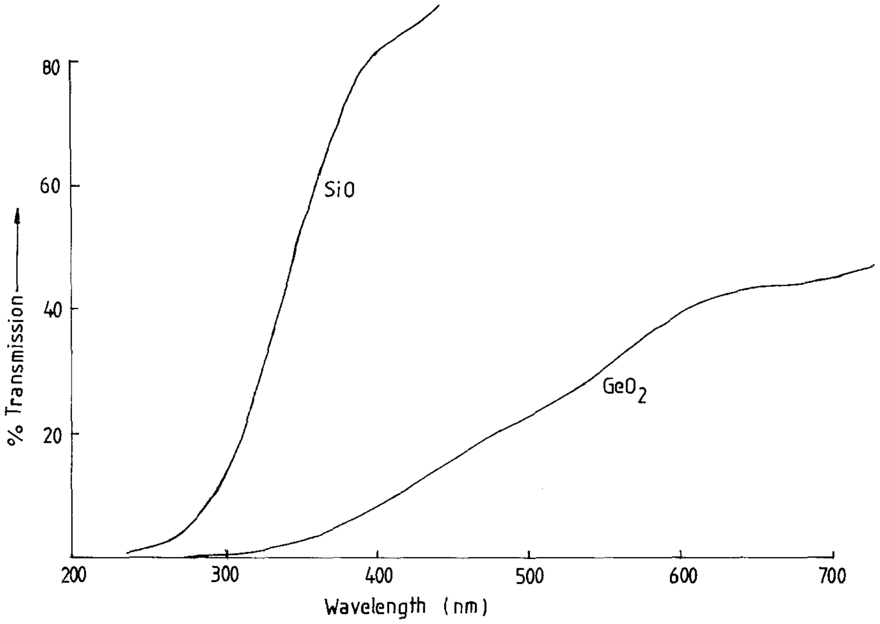

Figure 5 Optical transmission edges of SiO and GeO_2 thin films.

(i.e. that corresponding to $\bar{\nu}(S_2)$ equal to $800\,cm^{-1}$) and take γ to be 6.2×10^{-3} as before, a table of angles and frequencies such as that shown in Table III may be drawn up.

The most probable values of the angles have now to be determined. An upper limit for α' is certainly provided by the Ge–O–Ge bond angle, because the addition of a further germanium atom at the oxygen lone pair site is bound to cause repulsion among the germanium atoms. The lower limit is difficult to assess. It is best therefore to use the experimental fit of Lucovsky for v-SiO_2 as an indicator for the present case. He found the best fit for α' for the O_3^+ centre in the latter material to have the value of 106°, which is considerably lower than the upper limit of some 150° set by the Si–O–Si bond angle. We thus choose the lowest value of 110° for α' here, yielding $720\,cm^{-1}$ for $\bar{\nu}(S_3)$ and $356\,cm^{-1}$ for $\bar{\nu}(B_3)$. If we further assume that the strength of the B_3 absorption has the same relation to the S_3 absorption as B_2 did to the S_2 absorption, then the only important contribution of the O_3^+ centre to the vibrational spectrum must be one near $720\,cm^{-1}$.

To conclude, neither the O_1^- nor the O_3^+ centre appears to contribute to the $495\,cm^{-1}$ band, but both may influence the peak at $730\,cm^{-1}$. When one considers this conclusion together with the earlier assessment pertaining to the Ge–O–Ge vibrations, the final picture that emerges is that the broad band peaking at $730\,cm^{-1}$ is probably made up with contributions from O_1^- and O_3^+ centre vibrations on the $730\,cm^{-1}$ side of the band, and from S_2-type vibrations on the $800\,cm^{-1}$ side. It also becomes evident that the bulk of the energy absorption within the $495\,cm^{-1}$ band is not due to excitations of any of the vibrational modes considered so far. Thus the main cause of this absorption has still to be identified.

4.3. Addition of CeO_2

The variation in the position of the band labelled $730\,cm^{-1}$ as the CeO_2 addition begins (see the first five entries of column 3 in Table I) may be attributed to chemical reactions between this new species and defect centres contributing to the band. Two such centres have been identified as O_1^- and O_3^+. The irregular nature of this frequency shift could be due to slight differences in preparation conditions for these films, resulting in different amounts of reaction or varying amounts of centre formation, or both. Whatever the cause of the variation, it serves to show that the band in question has a more complex origin than the obvious one.

The rapid disappearance of the $495\,cm^{-1}$ absorption with CeO_2 addition strongly suggests that it originates in a reactive centre or centres. Because these cannot be the O_1^- or the O_3^+ centres, others must be enumerated as possible sources. The probable abundance of defect centres in an a-GeO_2 film *vis-à-vis* a-SiO films is probably seen in its optical absorption edge. Fig. 5 shows this edge together with that of a-SiO for comparison. The gradual change in the absorption coefficient of a-GeO_2 film with frequency clearly contrasts with that of a-SiO. One possible cause of this slow change may be the presence of a high density of defect states in the energy gap of the solid. There are other equally likely explanations, however, and one must treat the above conjecture with great caution.

To proceed by analogy with a-SiO films, the first defects other than those mentioned above that must be considerd are the vacancy bridge-type defects mentioned earlier. For conclusions regarding the nature and abundance of such defects we must await additional experimental results.

5. Conclusions

The GeO_2 band peaking at $730\,cm^{-1}$ is probably made up from contributions by O_1^-, O_3^+ centre absorptions on the lower frequency edge of the band and by "O stretch" absorptions of the O atom in the Ge–O–Ge linkage at the higher frequency edge.

The $495\,cm^{-1}$ band in the same spectrum is not due to any of the vibrations of the Ge–O–Ge group or of the two defect centres considered in this work.

The behaviour of the $495\,cm^{-1}$ band with CeO_2 addition to the films suggest it is due to some reactive site in the a-GeO_2.

The position of the 730 cm^{-1} varies irregularly with CeO_2 addition probably because of differences in preparation conditions of the films, leading to irregularities in the chemical activity between CeO_2 and the reactive sites of GeO_2. These slight changes in preparation condition may also affect the band directly by producing variations in the concentrations of the defect centres formed.

Other possible defects in a-GeO_2 thin films may include the non-paramagnetic vacancy bridge-type defects originating from a bond cleavage of the Ge–O–O–Ge linkage.

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