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Infrared absorption spectra of evaporated V_2O_5 and co-evaporated V_2O_5/B_2O_3 thin films

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The Fourier transform infrared spectra of different compositions of evaporated V_2O_5/B_2O_3 thin films have been investigated. Most of the absorption bands corresponding to V_2O_5 and B_2O_3 films coincide with those reported by other authors. The short-range order in amorphous V_2O_5 films is found to be conserved. The absorption spectra indicate a boroxol ring structure for B_2O_3 films. In co-evaporated V_2O_5/B_2O_3 films the boron is observed to substitute in the V_2O_5 network such that the coordination number of vanadium ion remains unchanged. The presence of a number of bands corresponding to –OH groups indicates the hygroscopic character of the films.

1. Introduction

The molecule in a solid can undergo two different types of movements, rotational and vibrational. The total energy of a molecule in a solid in comprised of three different parts, the energy related to the rotational motion, that related to the vibrational motion, and the energy responsible for the motion of the electrons in the molecule itself. The energies corresponding to rotational spectra lie in the low frequency (1 to 100 cm^{-1}) range because in this case the translations occur between the closely spaced rotational levels. On the other hand, the vibrational levels in solids are separated by comparatively greater energy differences, normally in the range (10^4 to 10^2 cm^{-1}), so that the vibrational spectra of a solid can be recorded in the infrared range of energy.

Valuable information about the various energies taking part in the bonding can be achieved with the help of infrared absorption which is a useful measuring technique because it is one of the few methods that allow direct examination of the absorbed molecules on the solid surface. The infrared absorption spectra have been used to ascertain whether any kind of local disorder characteristic of the constituent oxides is maintained in the glass.

West [1] suggested that the B_2O_3 glass contains BO_3 triangular units and borate glasses contain a mixture of BO_3 triangles and BO_4 tetrahedra, depending upon composition. According to him an important constituent of vitreous B_2O_3 is the boroxol group which is a planar, six-membered ring of alternate boron and oxygen atoms. These groups are linked into a three-dimensional network by a bridging oxygen.

While studying the vibrational spectra of vitreous B_2O_3, Windisch and Risen [2] suggested that the boroxol rings involving three linked BO_3 triangular units are the major constituents of vitreous B_2O_3. Walrafen *et al.* [3] have shown that at higher temperatures, the networks of vitreous B_2O_3 and of B_2O_3 melts consist of BO_3 triangles as a basic structural unit instead of boroxol rings. From the study of nuclear magnetic resonance (NMR) spectra, Jellison *et al.* [4] proposed a boroxol ring model for the structure of vitreous B_2O_3. Elliott [5] suggested a continuous random network (CRN) of planar BO_3 units in his model for vitreous B_2O_3. He disagreed with the proposed existence of the boroxol group in this material. Recently, Kanehisa and Elliott [6] proposed that B_2O_3 glass is an infinite network of planar boroxol rings, B_3O_3, interconnected via oxygen bridges as proposed by West [1].

In V_2O_5, the V^{5+} ion exists in six-fold coordination. It is generally recognized that as long as the coordination of the cations remains the same, the infrared absorption bands of a given compound are the same [7, 8]. For a similar composition of V_2O_5, the absorption band corresponding to the V–O vibration will not change for both the crystalline and the vitreous state. If the absorption bands corresponding to crystalline and amorphous V_2O_5 are similar, then it can be concluded that the V^{5+} ions in the glassy state of V_2O_5 will also exist in six-fold coordination.

Rivoalen *et al.* [9] have suggested that the *g*-values in the electron spin resonance (ESR) spectra for both amorphous and orthorhombic V_2O_5 are the same, indicating that the short-range order remains the same in both cases. They also proposed that the unpaired 3d electron is not always localized on a single vanadium nucleus. It moves from one nucleus to another according to the hopping process which is responsible for the semiconducting properties of the oxide. Kahn *et al.* [10] reported a difference in the short-range order of crystalline and amorphous V_2O_5 based on ESR investigations. On the other hand, and also by means of ESR studies, Henri *et al.* [11] reported that the short-range order characteristic of crystalline V_2O_5 is conserved in amorphous V_2O_5. From the infrared spectra of GeO_2–P_4O_{10}–V_2O_5 glasses, it is observed that V^{5+} ions do not change their coordination when the samples change from the crystalline state to the glassy state [7]. Culea *et al.* [12] and Sharma *et al.* [13] investigated the infrared spectra of V_2O_5–B_2O_3 glasses. We have studied the infrared spectra of both evaporated V_2O_5 and co-evaporated V_2O_5/B_2O_3 thin films.

2. Experimental procedure

For infrared absorption studies, the evaporated films of V_2O_5 and V_2O_5/B_2O_3 were deposited on the substrates of silicon wafers using a co-evaporation technique as developed by Hogarth and Wright [14]. The Fourier transform infrared absorption spectra from 400 to 4000 cm^{-1} for evaporated films were recorded on a Perkin–Elmer 1710 Fourier transform infrared spectrometer. While recording the absorption spectra, an uncoated silicon wafer (substrate) was placed in the reference beam in order to compensate the effect of substrate. The spectrometer was set to record an absorption spectrum for each sample from an average of ten scans.

3. Results and discussion

The Fourier transform infrared (FTIR) transmission spectra for evaporated V_2O_5, B_2O_3 and co-evaporated V_2O_5/B_2O_3 films, each of thickness about 300 nm, are shown in Fig. 1. The spectrum of B_2O_3 films was recorded immediately after the evaporation in order to minimize the hygroscopic effect. The absorption bands corresponding to different compositions of V_2O_5/B_2O_3 films are listed in Table I. Firstly we shall try to assign the different bands to the vibrations of various structural units of simple V_2O_5 and B_2O_3 films and then we shall consider the co-evaporated films. All compositions are quoted in mol%.

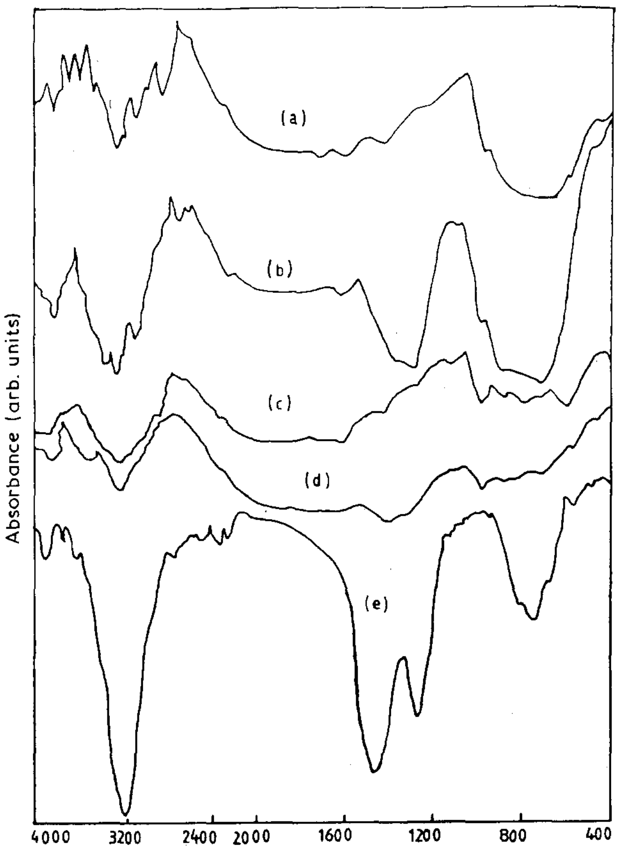


Figure 1 FTIR spectra of vacuum-evaporated V_2O_5/B_2O_3 (300 nm) thin films of different compositions: (a) simple V_2O_5, (b) $80\%V_2O_5/20\%B_2O_3$, (c) $70\%V_2O_5/30\%B_2O_3$, (d) 65% $V_2O_5/35\%B_2O_3$, (e) simple B_2O_3.

TABLE I Various absorption bands recorded in the Fourier transform infrared spectra of evaporated V_2O_5 and co-evaporated V_2O_5/B_2O_3 thin films; (sr) represents a shoulder and (sp) represents a sharp band

100% V_2O_5 (cm^{-1})	80% V_2O_5 (cm^{-1})	70% V_2O_5 (cm^{-1})	60% V_2O_5 (cm^{-1})	100% B_2O_3 (cm^{-1})
460 (sr)	480 (sr)	—	—	470 (sr)
—	—	—	—	560 (sp)
600 (sr)	—	600 (sr)	600 (sr)	—
660 (sp)	660 (sp)	660 (sp)	660 (sp)	690 (sr)
—	720 (sp)	720 (sp)	720 (sr)	730 (sp)
—	900 (sr)	890 (sr)	900 (sr)	—
990 (sr)	990 (sr)	990 (sp)	990 (sp)	—
—	1100 (sr)	1120 (sp)	—	1150 (sr)
—	1290 (sp)	1290 (sr)	1290 (sr)	1270(sp)
1440 (sp)	—	1440 (sr)	1420 (sp)	1470 (sp)
1620 (sp)	1630 (sp)	1630 (sp)	1630 (sr)	—

3.1. B_2O_3 films

The various absorption peaks observed in the FTIR spectra of evaporated amorphous thin films of B_2O_3 can be seen in Table I. While investigating the infrared spectra of V_2O_5–B_2O_3 glasses, Sharma *et al.* [13] recorded the different bands for the crystalline B_2O_3 at 545, 650, 740 to 800, 890, 960, 1020, 1195, 1430 to 1500, 2260, 2360, 2560 and 3200 cm^{-1}. On the other hand, during the study of infrared spectra of V_2O_5–B_2O_3 glasses, Culea *et al.* [12] recorded the bands at 565, 800, 1200, 1420, 1640, 3215 and 3405 cm^{-1} for vitreous B_2O_3.

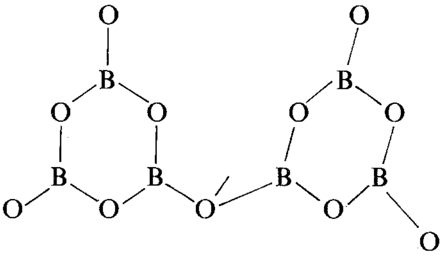
We observe that in our samples of evaporated thin films of B_2O_3 films, most of the bands recorded by other authors [12, 13] are present, although there are some generally small shifts in the frequencies corresponding to some of the bands. The different bands observed by us for amorphous films of B_2O_3 may be related to different modes of vibrations of structural units as below [15, 16].

The absorption band around 470 cm^{-1} may be related to the ring-angle bending [17, 18]. The band at 560 cm^{-1} is related to the vibration of the B–O–B bending motion [17]. The shoulder corresponding to about 690 cm^{-1} can be assigned to B–O′ wagging [18] where O′ does not belong to a ring.

The sharp band appearing at 730 cm^{-1} arises from the bond bending motion of B–O–B centres in the network [17, 19, 20]. The absorption band appearing at 1260 cm^{-1} can be attributed to the symmetric B–O′ stretching vibrations [18]. Tenney and Wong also found this strong band in B_2O_3 [19]. The bands at 1150 and 1470 cm^{-1} may be related to B–O–H bending and B–O stretching vibrations, respectively, as proposed by Parsons and Milberg [17].

The bands observed by us at the higher wavenumbers for evaporated simple B_2O_3 and V_2O_5 and co-evaporated V_2O_5/B_2O_3 films (not shown in the Table I) are evidently summation or overtone bands involving B–O and V–O bending and stretching vibrations. Such bands have also been observed by Parsons and Milberg [17] and Krogh-Moe [18] for B_2O_3 glasses. A very sharp and strong band near 3200 cm^{-1} indicates the presence of –OH groups which may be present due to the hygroscopic character of B_2O_3 films. Tomozawa and Tomozawa [21] suggested that the peak at 3600 cm^{-1} may be related to free hydroxol while that at 2750 cm^{-1} is due to hydrogen-bonded hydroxol in borosilicate glasses.

With the support of these observations, we propose the structure of our evaporated B_2O_3 film to consist of boroxol rings linked by bridging oxygen as shown below.



(I)

Our proposed structure agrees with that suggested by West [1] and Kanehisa and Elliott [6].

3.2. V_2O_5 films

The first column of Table I shows the absorption bands in the FTIR spectra of evaporated amorphous thin films of V_2O_5. Sharma *et al.* [13] recorded the infrared absorption bands at 300, 370, 470, 590, 825 and 1025 cm^{-1} for crystalline V_2O_5. They also noted that water bands or –OH stretching modes were not present in the infrared spectrum of crystalline V_2O_5. Culea *et al.* [12] recorded two main infrared absorption bands at 825 and 1020 cm^{-1} for crystalline V_2O_5. Hogarth and Hosseini [22] observed absorption peaks in the infrared spectra of crystalline V_2O_5 at 280, 370, 480, 660, 800, 1040, 1260, and 1275 cm^{-1}. They related the relatively sharp peak at 1040 cm^{-1} to the V–O stretching frequency and further suggested that the V–O stretching frequency for the compounds in which the vanadium atoms are totally ionized to V^{5+} lies in the range 1025 to 1005 cm^{-1}, and for V^{4+} lies in the range 900 to 1025 cm^{-1}. Two narrow bands at the frequencies 1040 and 985 cm^{-1} were recorded by Hevesi *et al.* [23] in the infrared spectra of V_2O_5 single crystals. They attributed these bands to the transition of vanadium ions from ground level to an excited level.

It has been observed that the band corresponding to the stretching vibration of a V–O bond appears at 1015 cm^{-1}. The presence of V^{4+} ions appears to reduce the V–O stretching frequency and it lies between 1015 and 900 cm^{-1} [24]. We propose that in our case of evaporated thin films of V_2O_5, one shoulder which appears at 990 cm^{-1} is due to the V–O stretching vibration mode [7, 25–27]. The presence of the peak at about 990 cm^{-1} in all our samples indicates that the site symmetry of the vanadium cation in glasses may be similar to that in crystalline V_2O_5.

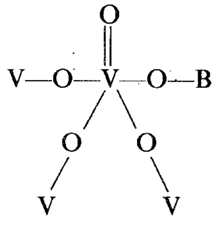
It is reported by Dimitriev *et al.* [26] that vitreous V_2O_5 can contain more than one short V=O bond, having two close absorption frequencies. The bands at 660 and 600 cm^{-1} may be attributed to V=O double bonds as suggested by Hogarth and Ahmad [28]. This is also in agreement with the suggestion made by Dimitriev *et al.* [26]. The bands appearing at frequencies around and higher than 1440 cm^{-1} may be attributed to the summation and overtone bands corresponding to stretching vibrations of V–O and V=O bonds. These types of band have also been recorded by Sharma *et al.* [13] for V_2O_5–B_2O_3 glasses.

3.3. V_2O_5/B_2O_3 films

Columns 2, 3 and 4 of Table I show the various absorption bands for different compositions of co-evaporated V_2O_5/B_2O_3 thin films. Almost all the main absorption peaks observed for the spectrum of evaporated B_2O_3 films are also observed to be present in the spectra of co-evaporated V_2O_5/B_2O_3 thin films.

While studying the infrared spectra of lithium borosilicate glasses with V_2O_5, Sanad *et al.* [29] recorded bands at 1375, 1080, 940, 890, 790, and 760 cm^{-1}. They related the band at 980 cm^{-1} to the presence of non-bridging oxygen vibrations and the bands at 790 and 1220 cm^{-1} to the stretching vibration of the boroxal ring. The strong and wide bands around 1420 and 3200 cm^{-1} which appear in composite V_2O_5/B_2O_3 films such as V_2O_5–B_2O_3 glasses, may be attributed to the bending and stretching vibration of the –OH group [12] which may be present in our samples because of their hygroscopic nature.

The shoulder observed at 990 cm^{-1} for simple V_2O_5 films is converted into a sharp band on increasing the content of B_2O_3 in co-evaporated V_2O_5/B_2O_3 films as can be seen in Fig. 1. This band can be attributed to V–O stretching as observed by Anderson and Compton [25]. Dimitriev *et al.* [26] suggested that in V_2O_5–B_2O_3 glasses, boron participates only in the substitutional positions without interacting with an isolated V=O bond and because of this reason no changes occur in the high wave number of infrared spectra. In the present case, the position of this band remains almost unchanged for all compositions of co-evaporated V_2O_5/B_2O_3 films and that for simple V_2O_5 which indicates that the co-ordination of vanadium remains unchanged. We propose that the boron ions substitute in the network in the manner as shown below.



(II)

A similar structure has also been suggested by Dimitriev *et al.* [26].

The new peak at 890 cm^{-1} which appears on adding B_2O_3 to V_2O_5 in co-evaporated V_2O_5/B_2O_3 and is present in all the co-evaporated samples is attributed to the boroxol ring structures. It also indicates that the boroxol ring is conserved in all co-evaporated V_2O_5/B_2O_3 films.

The band appearing at 1620 cm^{-1} is present in all compositions of co-evaporated V_2O_5/B_2O_3 films. This band shifted slightly towards the higher frequencies on increasing the B_2O_3 content and may also be attributed to –OH bending vibrations due to their hygroscopic nature. A similar type of band has also been recorded by Sharma *et al.* [13] for V_2O_5–B_2O_3 glasses. This band was absent in the spectra of V_2O_5–B_2O_3 glasses as recorded by Culea *et al.* [12].

For simple V_2O_5 there is a weak shoulder around 800 cm^{-1}. This band is absent for V_2O_5 contents up to 80% in co-evaporated V_2O_5/B_2O_3 films. On lowering the V_2O_5 content further, this band reappears and becomes sharper on increasing the V_2O_5 content.

Sharma *et al.* [13] reported a broad absorption peak between 740 and 800 cm^{-1} in crystalline B_2O_3 and at 825 cm^{-1} for crystalline V_2O_5. It has been reported [9] that there is no apparent change in the frequencies corresponding to the bands for crystalline and amorphous V_2O_5. In the present studies, for co-evaporated V_2O_5/B_2O_3 films the main absorption bands corresponding to simple B_2O_3 and V_2O_5 simple films are conserved, although their intensity goes on decreasing on increasing the B_2O_3 content in the co-evaporated films. From the appearance of a band around 900 cm^{-1}, we conclude that the structural unit of V_2O_5 becomes more infrared active on increasing the content of B_2O_3 in co-evaporated V_2O_5/B_2O_3 films.

A number of small bands appearing at 490, 560 cm^{-1} for simple B_2O_3 films are absent in the co-evaporated V_2O_5/B_2O_3 films suggesting some sort of structural re-arrangements of B_2O_3 during the co-evaporation process. We propose that the band at 690 cm^{-1} recorded for simple B_2O_3 films may be conserved in co-evaporated V_2O_5/B_2O_3 films, but it is indistinguishable from that at 660 cm^{-1} corresponding to V=O stretching frequency.

The sharp band appearing at 730 cm^{-1} for simple B_2O_3 films becomes a wider band and moves towards the lower frequency for co-evaporated V_2O_5/B_2O_3 films, indicating some sort of bonding changes in boron and oxygen-deformed sublattices.

The band at 1270 cm^{-1} for B_2O_3 films also becomes wider and moves towards the higher frequencies on increasing the B_2O_3 content in co-evaporated V_2O_5/B_2O_3 films. The new band appearing at 1100 to 1120 cm^{-1} for co-evaporated V_2O_5/B_2O_3 films may be attributed to the loss of oxygen by V_2O_5 to convert itself into V_2O_4. This spare oxygen may be used to yield BO_4 tetrahedra in V_2O_5/B_2O_3 films. A similar type of band has also been observed by Quan and Adams [30] and Borrelli *et al.* [31] for rubidium borate and Na_2O–B_2O_3 glasses, respectively.

4. Conclusion

The evaporated thin films of simple B_2O_3 and simple V_2O_5 show infrared absorption bands which have been commonly observed during previous studies for these materials. For co-evaporated V_2O_5/B_2O_3 films the main absorption bands corresponding to B_2O_3 and V_2O_5 are present with a small frequency shift and decreased intensity. Boron is substituted in the network such that the co-ordination number of vanadium is not changed. The B_2O_3 films show a boroxol ring type structure.

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