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A comparison of the optical properties of glass and of evaporated amorphous thin films of BaO–TeO$_2$

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Two series of glass and thin film specimens of BaO–TeO$_2$ were prepared. The optical absorption edges and infrared absorption spectra were investigated. It was found that the fundamental absorption edge is a function of BaO content in both kinds of films and that the absorption is due to indirect electronic transitions. The values of optical gap for blown films were greater than those of thin evaporated films, but the widths of the band tails were greater for the evaporated thin films, which were expected to be more disordered than the thin blown glass films.

1. Introduction

In amorphous, as in crystalline materials, useful information can be deduced both from the optical absorption edge and from infrared absorption spectral measurements, even though in such materials the edge is less sharp and the absorption peaks are broader than is normally the case for non-metallic crystals. Al-Ani and Hogarth [1] reported the optical properties of TeO$_2$ thin films of different thicknesses and related them to those characteristic of TeO$_2$ glass and they analysed their results in terms of a density-of-states diagram as shown in Fig. 1. A comparison of the optical properties of bulk and thin film samples was described by Fagen and Fritzsche [2] for mixed chalcogenide glasses. They found that the optical energy gap, E_{opt}, for thin films which were prepared by vacuum evaporation has a smaller value than that of bulk glassy films of similar composition. Infrared spectra of TeO$_2$ films which exhibit a minor absorption band at 715 cm^{-1} and one pronounced absorption band at 600 cm^{-1} have been investigated by Al-Ani and Hogarth [1] who found their results to be in a good agreement with the published results for the pertinent oxides by Hilton and Jones [3].

In the present work, optical absorption edge and infrared absorption spectra measurements were taken for BaO–TeO$_2$ as a glass and also as thin vacuum-evaporated films of different compositions. In a search of the literature we have found no examples of such measurements pointing to differences in structure between melt-cooled glasses and thin amorphous films, other than the examples cited above.

Following the earlier work on the simple TeO$_2$ system [1] and also having regard to the results of Fagen and Fritzsche [2], it was expected that the values of the optical energy gap for films of both kinds having nominally the same composition, should be of broadly the same value but that as a consequence of the increased disorder in the thin evaporated films, the band tailing and hence the derived values of Urbach energy should be lower in the case of the glass. Certainly the simpler structural defects such as dangling bonds should be present in lower concentrations in the glass samples.

2. Experimental work

Thin evaporated films of BaO–TeO$_2$ 300 nm thick and of different compositions were prepared in a vacuum 4×10^{-6} torr in a Balzers BA 510 coating unit using the technique of Hogarth and Wright [4]. Tantalum and molybdenum boats were used for TeO$_2$ and BaO respectively and the Corning 7059 glass substrates were kept at a temperature of 100° C. In the case of the BaO–TeO$_2$ glass system, very thin films were obtained

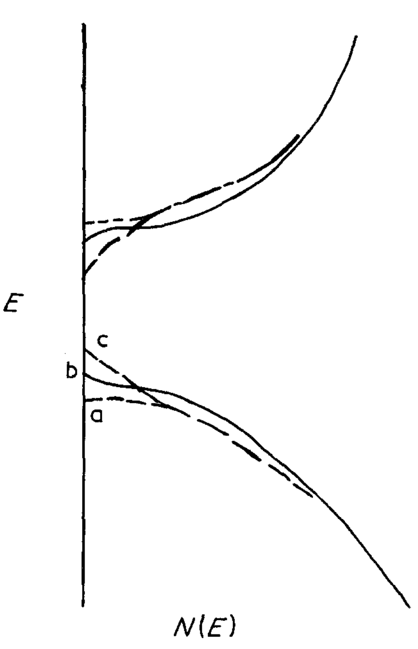

Figure 1 Proposed density-of-states diagram for three systems. (a) ---- crystalline, (b) —— blown glass film, (c) – – – evaporated film.

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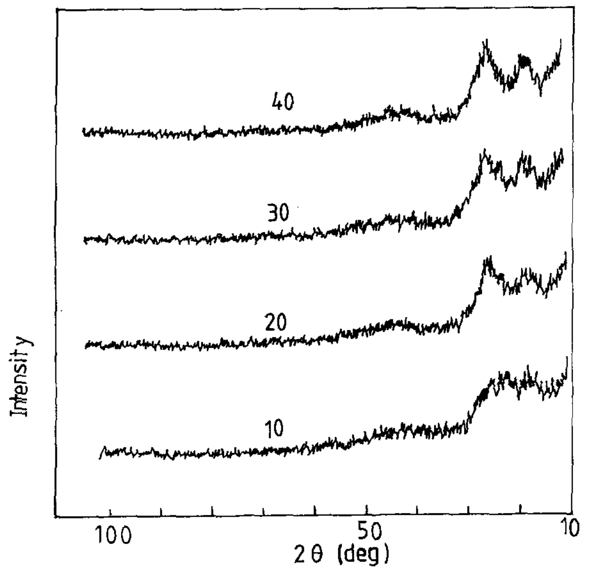

Figure 2 X-ray diffraction patterns of different compositions of BaO–TeO_2 glasses.

by blowing techniques and the details have been given earlier by Hassan and Hogarth [5].

Infrared absorption spectra for both kinds of films were investigated using a Perkin–Elmer spectrometer, Model 1710, in the range 400 to 4000 cm^{-1}. The absorption measurements in the ultraviolet and visible regions were carried out in the range 200 to 900 nm using a Perkin–Elmer Lambda 9 spectrophotometer. The absorption coefficient $\alpha(\omega)$ can be calculated from the relation

$$\alpha(\omega) = (1/d) \ln I_0/I_t \qquad (1)$$

where I_0 and I_t are the intensities of the incident and transmitted beams respectively, corrected for any reflection at the first surface, and d is the thickness of the sample.

3. Results and discussion

3.1. X-ray diffraction and thermal analysis

All glass samples were tested by X-ray diffraction and the results showed the absence of crystalline characteristics. Fig. 2 shows X-ray diffraction patterns typical of the whole range of compositions, recorded with a Phillips type PW 1050 diffractometer, using a copper tube and nickel filter.

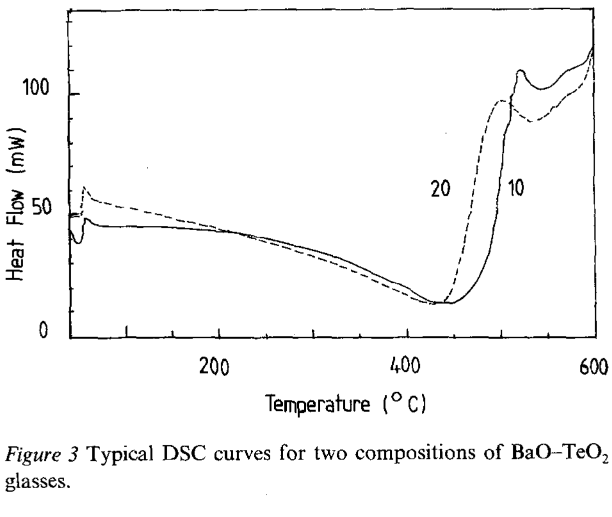

Figure 3 Typical DSC curves for two compositions of BaO–TeO_2 glasses.

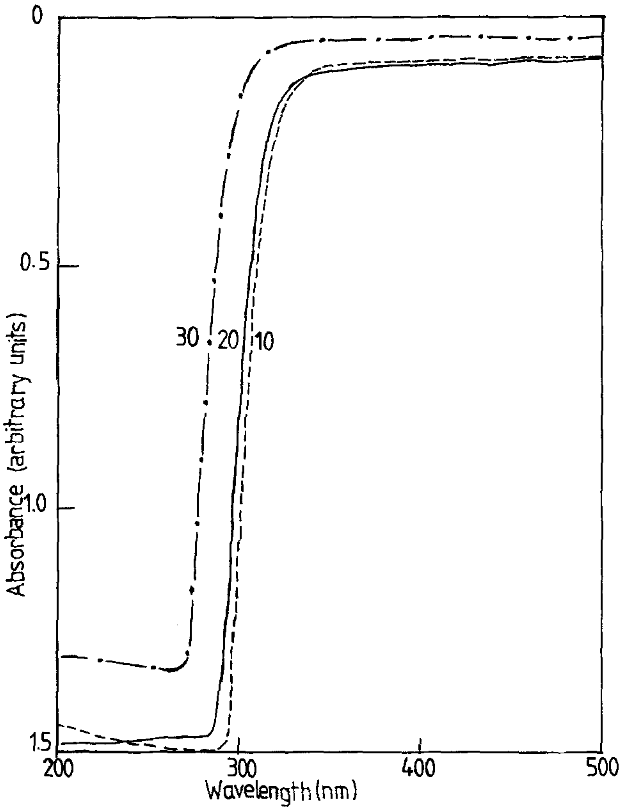

Figure 4 Optical absorption spectra of BaO–TeO_2 glasses. (Content of BaO shown in mol %).

In the investigation of thermal analysis the differential scanning calorimetry (DSC) technique was used. An important use of DSC in glasses is to measure the glass transition temperature, T_g. The thermal stability of the glasses was studied in a Perkin–Elmer DSC 7

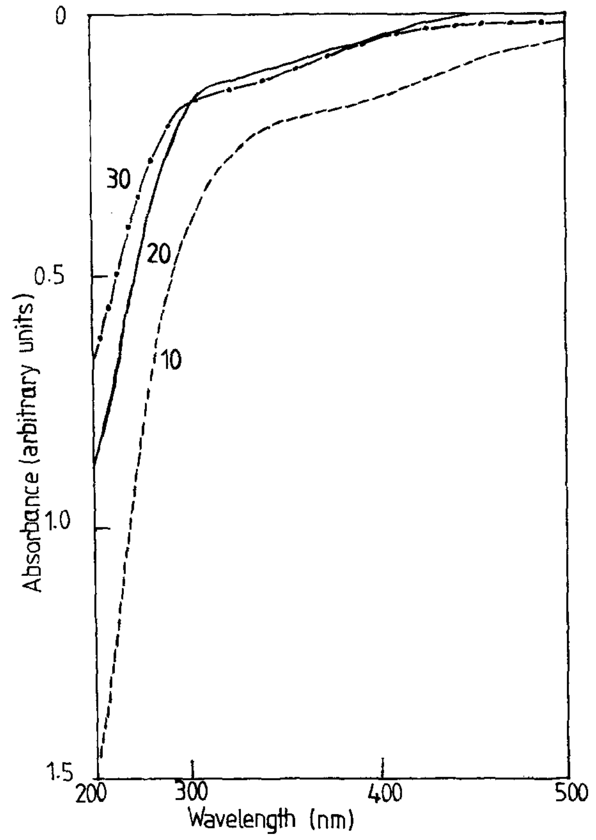

Figure 5 Optical absorption of BaO–TeO_2 thin films. (Content of BaO shown in mol %).

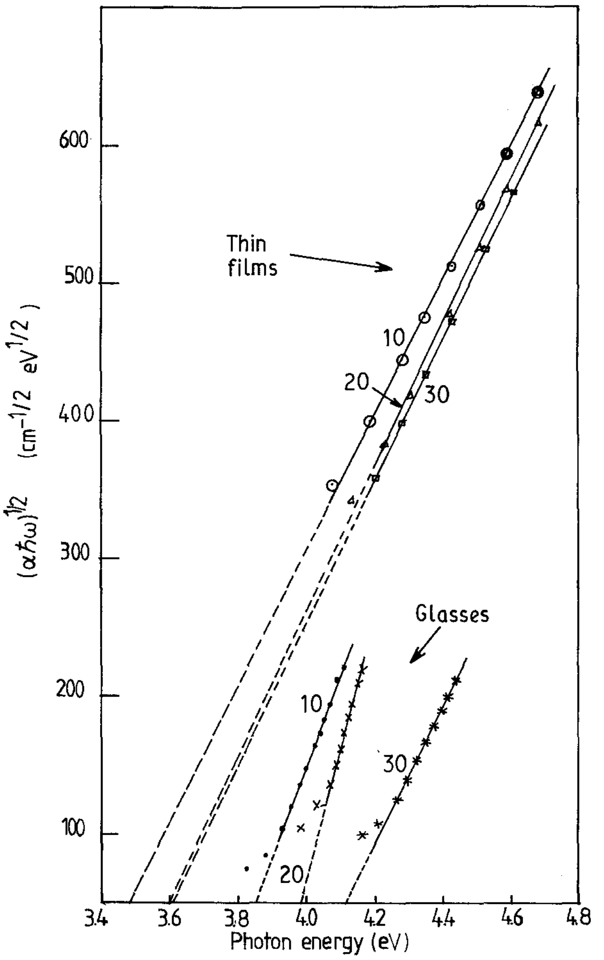

Figure 6 $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy for a series of BaO-TeO_2 glasses and thin films.

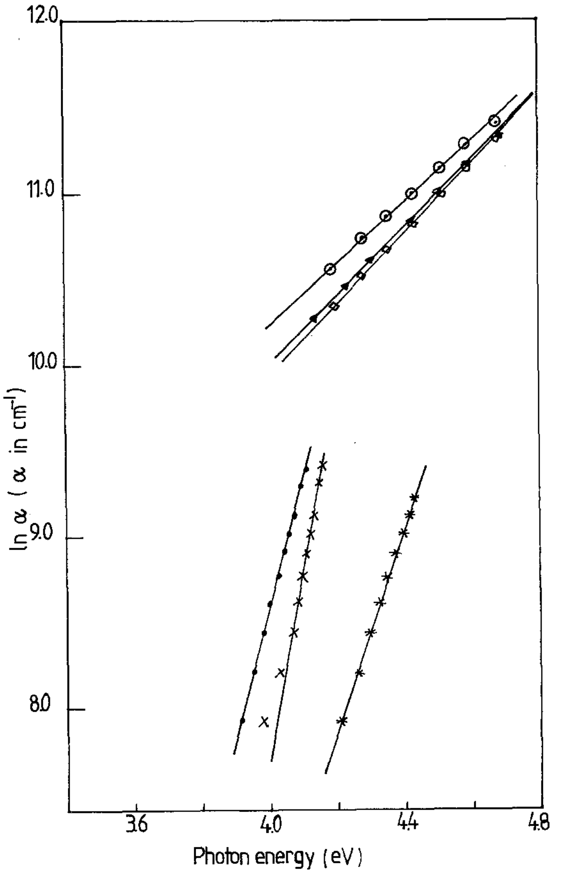

Figure 7 Optical absorption edges of BaO-TeO_2 glasses and thin films plotted in accordance with the Urbach rule. (Content of BaO shown in mol %).

equipment for two compositions, in the temperature range 50 to 600° C. The heat flow to the sample was measured under thermally controlled conditions. DSC gave very sensitive results showing that the transitions started at a lower temperature than expected. Fig. 3 shows typical curves of the transitions and Table I gives a summary for the glass endothermal peak values, exothermal peak values and the amount of heat ΔH absorbed by the glass in the endothermal transitions.

3.2. Optical measurements and analysis

The optical absorption spectra at different compositions for both kinds of films as a function of wavelength are shown in Figs 4 and 5. It is clear that by increasing the content of BaO, the absorption edge shifts towards lower wavelengths. The absorption coefficients $\alpha(\omega)$ were determined near the edge for the whole range of glass and thin film compositions and the results may be displayed in a number of ways as a function of photon energy $\hbar\omega$. The most satisfactory results were obtained by plotting the quantity $(\alpha\hbar\omega)^{1/2}$ as a function of $\hbar\omega$ as suggested by Tauc *et al.* [6] and by Davis and Mott [7]. For absorption by indirect transitions their equation takes the form

$$\alpha(\omega) = \frac{B(\hbar\omega - E_{\mathrm{opt}})^2}{\hbar\omega} \qquad (2)$$

and applies particularly in the region of absorption for which the absorption coefficient $\alpha(\omega) \geqslant 10^4\,\mathrm{cm}^{-1}$. In this equation B is a constant and $\hbar\omega$ is the energy of the incident photons. Fig. 6 shows the plot of $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ for both kinds of films. The values of E_{opt} for the materials are obtained by extrapolating the linear plots of the curves to $(\alpha\hbar\omega)^{1/2} = 0$ and are given in Table II. The graphs show straight lines with some deviations at the lower photon energies which were suggested by Redfield and Afromowitz [8] to be due to imperfections in the materials. The fundamental absorption edge in most amorphous semiconductors in the lower absorption region usually obeys an

TABLE I Exothermal and endothermal temperature transition peaks for some glass samples using DSC in the range from 50 to 600° C

BaO content (mol %)	Endothermal peak temperature (° C)	Exothermal peak temperature (° C)	$-\Delta H$ ($\mathrm{J\,g^{-1}}$)
10	446	519	729
20	435	502	756

TABLE II Optical parameters of BaO-TeO_2 samples in the form of blown glass and evaporated thin films

BaO content (mol %)	E_{opt} (eV)		E_0 (eV)	
	Glass	Thin film	Glass	Thin film
10	3.85	3.48	0.134	0.557
20	3.98	3.60	0.090	0.500
30	4.12	3.61	0.178	0.474

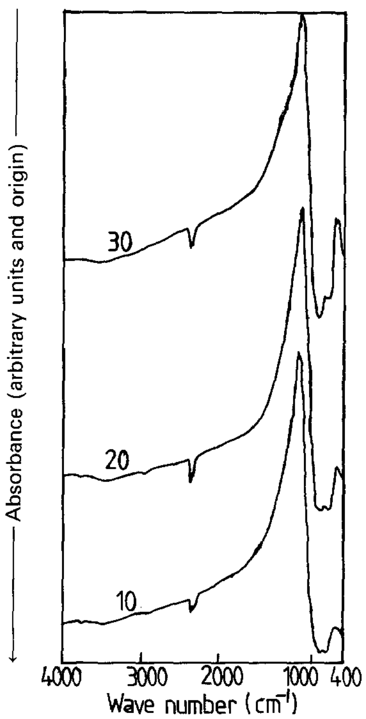

Figure 8 Infrared absorption spectra of BaO–TeO$_2$ glasses.

empirical relation due to Urbach [9]

$$\alpha(\omega) = C \exp(\hbar\omega/E_0) \tag{3}$$

where E_0 is usually identified with the width of the band tails of the localized states in the band gap and C is a constant. The values of absorption coefficient $\alpha(\omega)$ estimated by using Equation 1 are shown on an Urbach plot in Fig. 5 for various BaO–TeO$_2$ glasses and thin films. The values of E_0 are calculated from the slopes of the straight lines of these curves and included in Table I. The curves of Fig. 7 show that the exponential behaviour of the absorption edge (Urbach law) can be demonstrated for both types of sample.

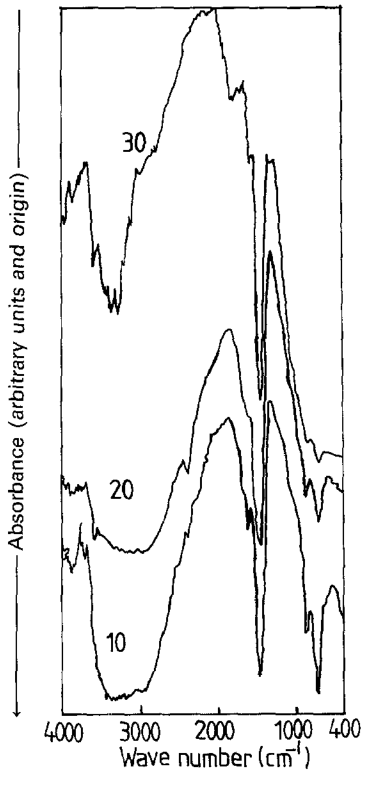

Figure 9 Infrared absorption of BaO–TeO$_2$ thin films.

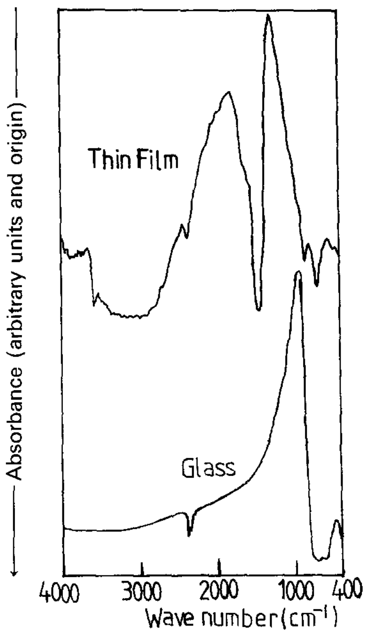

Figure 10 Infrared absorption spectra of (20 mol % BaO–80 mol % TeO$_2$) glass and thin film samples.

As shown in Table II the values of E_0 for evaporated films are greater than those of the blown films whereas the E_{opt} values show the opposite trend. These differences in the band structure can be explained by visualizing that in the case of blown films the localization of electronic states is more concentrated nearer to the band edges. Since the amount of band tailing was shown by Anderson [10] to be associated with disorder

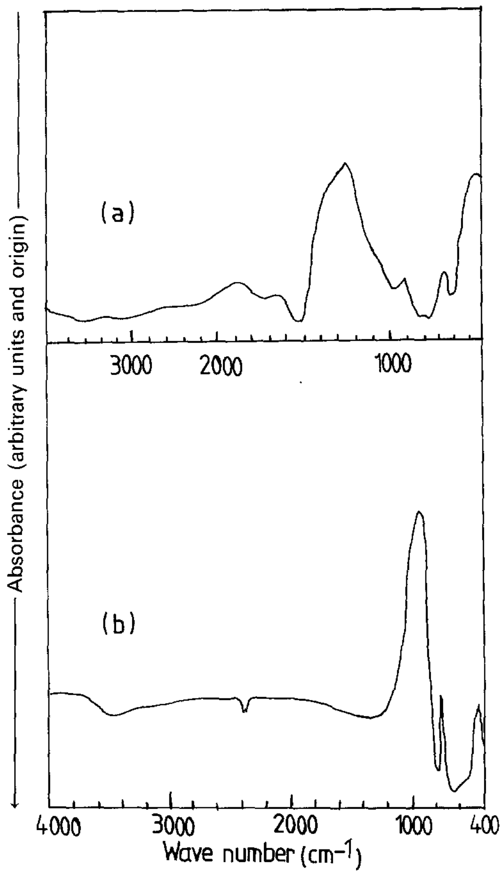

Figure 11 The infrared absorption spectra of (a) BaO crystalline, (b) TeO$_2$ crystalline.

TABLE III The positions of absorption peaks in both kinds of films of BaO–TeO_2

Content of BaO in glass (mol %)	Position of bands (cm^{-1})				
10	600	691	–	–	–
20	609	705	–	–	–
30	593	711	–	–	–
Content of BaO in thin film (mol %)					
10	–	698	837	1425	–
20	–	686	846	1437	–
30	–	687	837	1413	–
TeO_2 crystalline	580	660	771	3427	–
BaO crystalline	580	700–800	920	1450–1500	1600–1720

in the system, this is consistent with the idea that the bulk glassy films are more ordered than the evaporated layers, and our results on simple oxides are entirely consistent with the results for the chalcogenides, namely that our blown glass samples are more highly ordered and possess lower values of Urbach energy. Our results are in a good agreement with the published results of Fagen and Fritzsche [2] for mixed chalcogenide glasses and of Al-Ani and Hogarth [1] for tellurite.

The infrared spectra of BaO–TeO_2 glasses and thin films are shown in Figs 8, 9, 10 and 11. Table III summarizes the characteristic infrared absorption band positions. The intensity and the absorption band positions in these spectra show evidence of some chemical interaction between the two oxides rather than simply retaining absorption bands characteristic of a simple oxide mixture. The position of the main absorption band of the TeO_2 glass is at 640 cm^{-1} as observed by Al-Ani *et al.* [11].

The structure of the tellurite glasses investigated indicates that the inclusion of BaO destroys the three-dimensional network typical of TeO_2 but that, where the Ba^{2+} ion is located, strongly polarized non-bridging Te–O bonds are formed [12]. With the incorporation of BaO the absorption peaks for the TeO_4 group shift from 593 to 609 cm^{-1} and from 691 to 711 cm^{-1}. As has been shown earlier [13, 14] this is due to the deformation of TeO_4 to TeO_{3+1} polyhedra due to the polarization of the Te–O bonds. The spectra of BaO–TeO_2 evaporated thin films exhibit absorption bands which shift from 686 to 698 cm^{-1} and from 837 to 846 cm^{-1} and which are also due to the vibrations of the Te–O bonds. Finally the shift in absorption band from 1425 to 1437 cm^{-1} in the thin film which disappears in the glassy state may be due to the stretching vibrations of the Ba–O bonds.

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