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Infrared study of EPOXS–TEOS–TPOT gels

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The thermal changes in the structure of EPOXS–TEOS–TPOT (where EPOXS = epoxysilane, 3-glycidyloxypropyltrimethoxysilane, TEOS = tetraethylorthosilicate, and TPOT = tetraisopropylorthotitanate) derived sol–gel coating materials were followed by infrared spectroscopy. The study showed that for the low-temperature treated gels, the Si–O–Si network was very "open", with many organic side groups connecting to it. One of the prominent characteristics of the structure was the presence of four-fold siloxane rings. TiO_2 plays a part in the formation of the network by Ti–O–Si bonding. With increasing the TiO_2 content in the system, the tendency towards the formation of the four-fold siloxane ring decreased. With increasing heat-treatment temperature, the organic side groups gradually disappeared and, at the same time, the siloxane ring structure decomposed and a more rigid and condensed Si–O–Si network was gradually established.

1. Introduction

It is well known that the sol–gel method for making inorganic materials has many advantages over conventional methods, such as high purity and homogeneity, low processing temperatures, ease with which a thin film may be formed, and so on [1, 2]. By introducing organic-substituted alkoxisilane, $R_nSi(OR')_{4-n}$ ($n = 1, 2$ and 3; R and R′ = organic groups), into a sol–gel system, a new kind of inorganic–organic composite, ORMOSILs, can be obtained [3, 4]. This kind of new material has many very interesting characteristics relating to their special properties and molecular structure.

Recently, in our laboratory, an inorganic–organic sol–gel coating material was obtained from the epoxysilane, 3-glycidyloxypropyltrimethoxysilane–tetraethylorthosilicate–tetraisopropylorthotitanate (EPOXS–TEOS–TPOT) system. The results of ^{29}Si nuclear magnetic resonance (NMR) study on the hydrolysis and condensation of the system, as well as the preparation and properties of the material will be reported in the future. In this paper, the thermal evolution in the structure of the materials with different composition and curing conditions was followed by infrared spectroscopy.

2. Experimental procedure

2.1. Raw materials and composition

Commercially available EPOXS, TEOS and TPOT were used as the starting materials, and butanol, ethanol and acetic acid were used as solvents and catalyst. The sol–gel samples studied in this work have the following composition

$$5EPOXS \cdot (6 - x)TEOS \cdot xTPOT$$

where $x = 0$–6. For every sample, the theoretical amount of water required to replace all the –OR groups was added. Clear sol–gel solutions were obtained by mixing all the components in the solvents.

2.2. Infrared spectra measurement

Air-dried gels were cured at different temperatures for 2 h, and then infrared spectra of the gels were taken using a Nicolet 5PC FT–IR spectrometer over the wave number range 400–4000 cm^{-1}. The KBr pellet method was employed, and each KBr sample pellet was formed by mixing 100 mg KBr with 1.0 mg sol–gel sample.

3. Results and discussion

Infrared spectra were measured for all the sol–gel samples with different compositions and different curing conditions. Figs 1–4 show infrared spectra of the sol–gel samples with $x = 0, 2, 4$ and 6.

3.1. The peak in the region from 570–600 cm^{-1}

For all the as-prepared sol–gel samples, there is a weak, slightly broad but clearly identifiable small peak in the region from 570–600 cm^{-1}. The thermal behaviour of this peak for samples with low x is quite different from that with a high x value (see Fig. 5).

3.1.1. Low x value

In this case, the small peak tends to disappear when heating the gels at higher temperature (see Fig. 5, $x = 0$–3).

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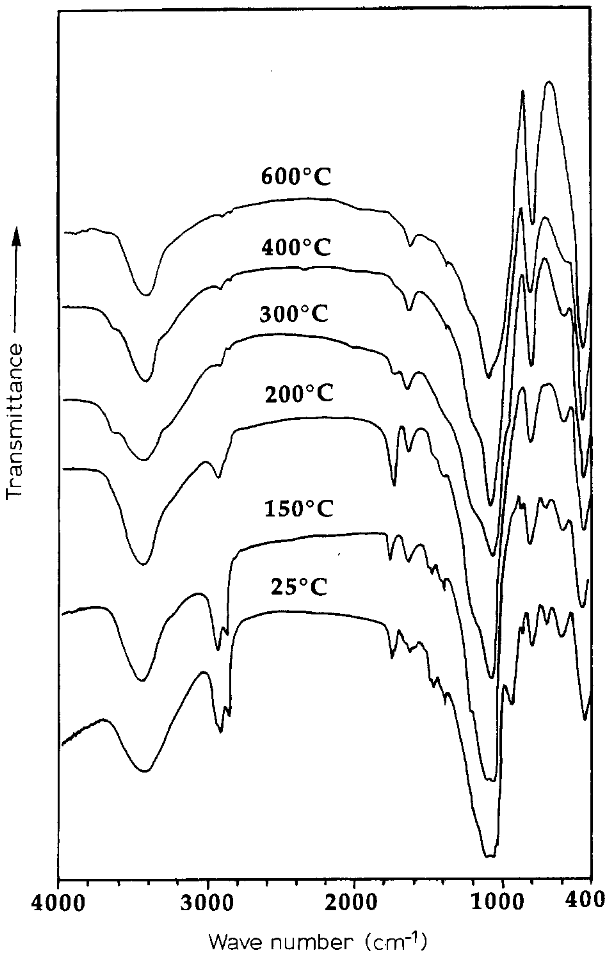


Figure 1 Infrared spectra of the gel with $x = 0$ heated at different temperatures.

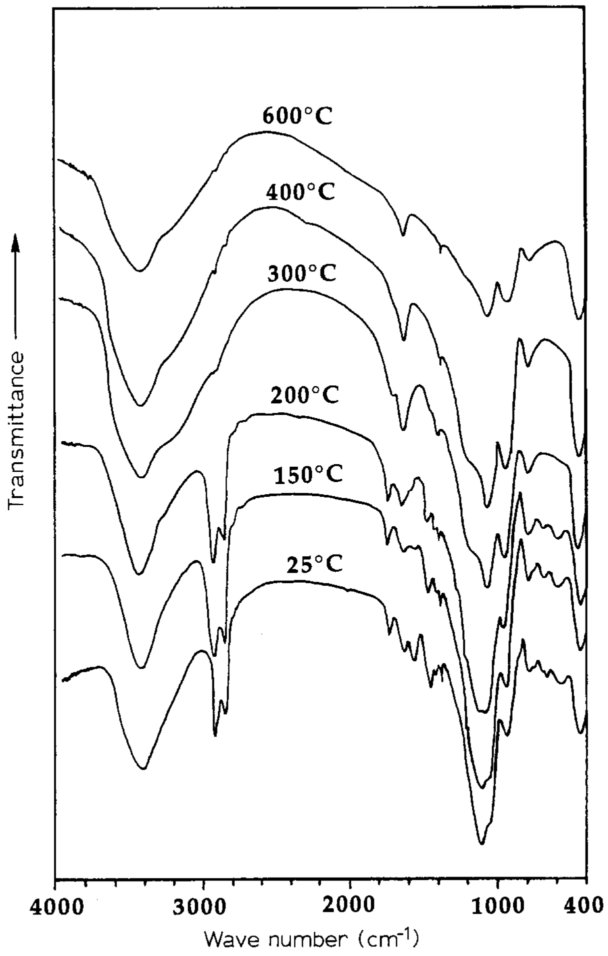
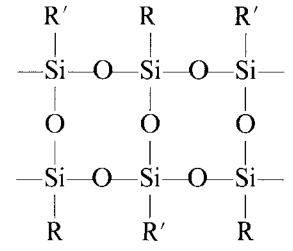
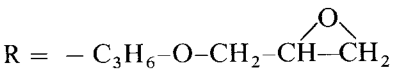


Figure 2 Infrared spectra of the gel with $x = 2$ heated at different temperatures.

A weak infrared peak around 550–600 cm^{-1} has been observed in some silicate glasses and some silicate crystals with high alkali content, which have a high concentration of Si–O$^-$ bonds [5, 6]. In these cases, the small peak has been considered to come from the terminal Si–O$^-$ vibration, which gives a prominent infrared peak around 950 cm^{-1} at the same time. This interpretation of the peak is quite doubtable for our sol–gel samples. It can be seen from Fig. 1 that no changes in intensity of the peak were observed when the peak at 945 cm^{-1} completely disappeared after heating the sample with $x = 0$. It seems that the small peak is in no way connected with the strong peak at 945 cm^{-1}. On the other hand, infrared spectra of many siloxanes with the general formula $R_{0.5}SiO_{1.5}$, which are composed of four-fold siloxane rings, have the same peak around this region [7, 8]. Recently, Hiroyuki Yoshino *et al.* [9] studied the nature of this small peak very carefully, by comparing it with that of many cyclic siloxanes and silicate minerals. This study demonstrated that the small peak in the region from 550–600 cm^{-1}, which appears in the infrared spectra of some sol–gel systems, results from the skeletal deformation of the four-fold siloxane rings.

It is believed that the small peak existing in the infrared spectra of our samples with low x values originates from the same structural group, the four-fold siloxane ring which may be as shown in Structure I,





where R = $-C_3H_6\text{-}O\text{-}CH_2\text{-}CH\text{—}CH_2$ (with O bridging CH and CH_2) and R' = OEt, OMe, OH.

It is noticed that the four-fold siloxane ring structure tends to decompose at high temperature, as indicated by the gradual disappearance of the small peak with increasing curing temperature (see Fig. 5, $x = 0$–3). Increasing x, that is, increasing the amount of substitution of SiO_2 by TiO_2, the decomposition temperature of the ring structure tends to decrease. For $x = 0$, the temperature is higher than 400 °C, while for $x = 2$ and 3 it is below 300 °C (see Fig. 5, $x = 0$–3).

3.1.2. High x value

Unlike samples with low x value, for samples with high x values the small peak in this region does not tend to disappear with increasing heat-treatment temperature: it still exists when the temperature is as high

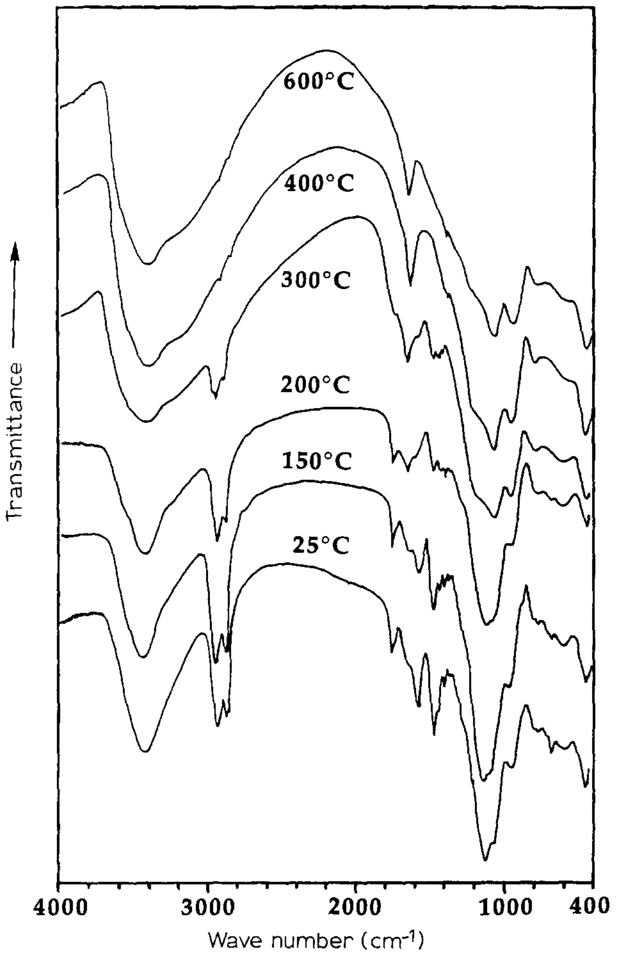


Figure 3 Infrared spectra of the gel with $x = 4$ heated at different temperatures.

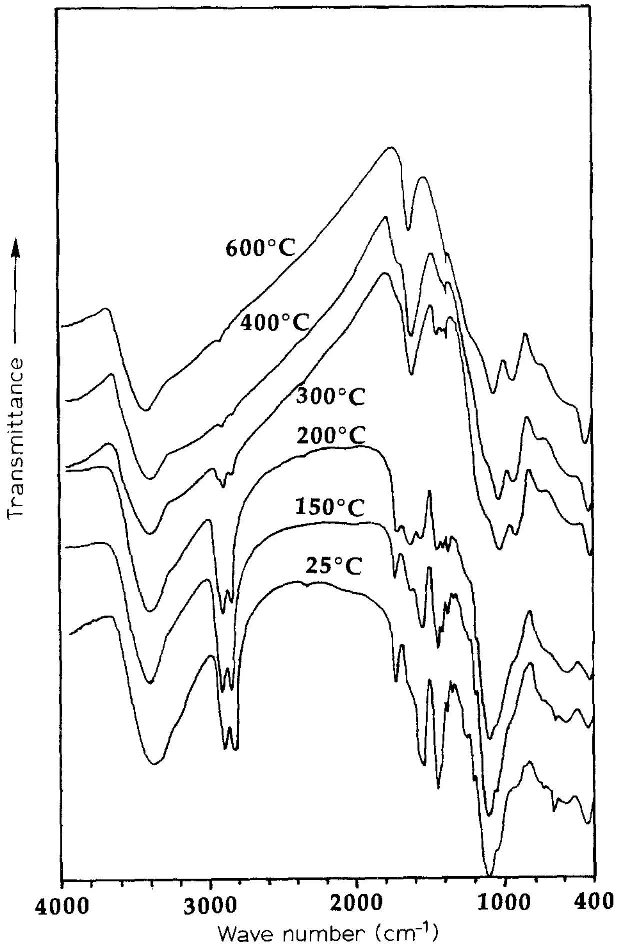


Figure 4 Infrared spectra of the gel with $x = 6$ heated at different temperatures.

as 600 °C. This indicates that it must be caused by a different structural group compared with that when x is low.

In infrared spectra of pure TiO_2 or high TiO_2-containing materials, there is a very strong and broad absorption band ranging from 400–800 cm^{-1} centred around 600 cm^{-1} [10, 11]. This band comes from the vibration of Ti–O–Ti bonds. With increasing TiO_2 content in our samples, a significant increase in infrared absorption in the same region can be attributed to this reason. It can be seen in our spectrum that the small peak is just in the centre of the large region. So, it is reasonable to think that with high TiO_2 concentration this small peak is mainly due to the vibration of Ti–O–Ti bonds. Perhaps there is still a small contribution in the peak from the four-fold siloxane rings when the heating temperature is low.

3.2. The peaks at 800, 940 cm^{-1} and 1050–1100 cm^{-1}

The infrared peak at 940 cm^{-1} of the air-dried sample with $x = 0$ disappears when it is cured at 150 °C for 2 h. After TiO_2 was added to the system, this peak did not decrease in intensity with increasing temperature, but became a little more prominent (see Figs 1–4). Many researchers assigned the peak around 950 cm^{-1} to the vibration of $Si–O^-$ or Si–OH bonds [12, 13]. This is quite possible for our sample with $x = 0$, and the disappearance of the peak on heating can be explained by the condensation reaction of siloxane groups

$$\equiv Si–OH + OH–Si\equiv \xrightarrow{\text{heating}} \equiv Si–O–Si\equiv + H_2O \quad (1)$$

Nevertheless, this explanation is unacceptable for samples containing TiO_2. In some TiO_2-containing silicate glasses and sol–gel systems, this peak is also observed [13]. It should be attributed to the Si–O–Ti stretching vibration in the case of TiO_2-containing systems. In this case, Ti^{4+} is four-coordinated and acts as a network former, forming the network structure of the sol–gel materials, together with Si^{4+}.

It is clear that the peak at 800 cm^{-1} and the strong peak in the region from 1050–1100 cm^{-1}, which is overlaid with another strong peak at 1105 cm^{-1} when the curing temperature is low, are caused by the symmetric and asymmetric vibrations of Si–O–Si, respectively. With increasing x value, the two peaks gradually shift to lower wave numbers (see Fig. 6 and Table I), which indicates that the Si–O bond is weakened by the addition of TiO_2. The two peaks for all samples gradually move to higher wave numbers with increasing heat-treatment temperature. This suggests that the Si–O bonding in the sol–gel network becomes

TABLE I Changes of Si–O–Si asymmetric and symmetric stretching bands with x and curing temperature

x	200 °C		300 °C		400 °C		600 °C	
	Asym.	Sym.	Asym.	Sym.	Asym.	Sym.	Asym.	Sym.
0	1063	799	1083	800	1088	801	1103	799
1	?	790	1067	795	1075	797	1085	798
2	1058	787	1059	790	1070	793	1077	792
3	1054	785	1057	788	1064	791	1071	790
4	1049	768	1052	783	1060	?	1066	789
5	?	?	1041	783	1052	784	1063	787
6	?	?	1034	756	1047	780	1056	?

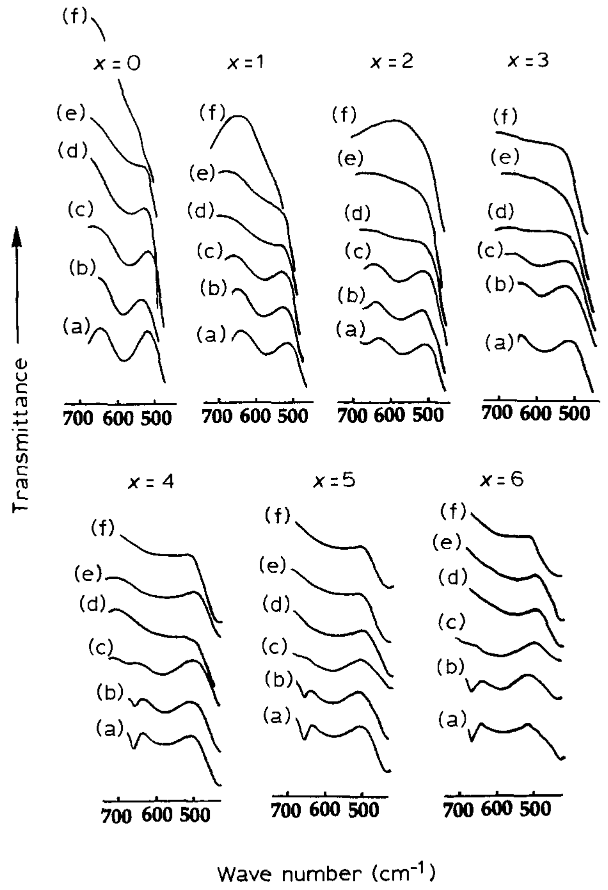


Figure 5 Changes of the infrared peak in the region from 570–600 cm^{-1} with different x values and different heating temperatures: (a) = 25 °C, (b) = 150 °C, (c) = 200 °C, (d) = 300 °C, (e) = 400 °C, (f) = 600 °C.

stronger and more rigid as the sol–gel condensation reaction goes to completion.

3.3. The peaks related to organic groups

As can be seen from the infrared spectra of air-dried gels, the middle peaks from 2850–2950 cm^{-1} and the weak peaks from 1300–1500 cm^{-1} are related to the vibration of the C–H bond in organic groups. The strong peak centred at 1100 cm^{-1}, which is overlaid with the Si–O–Si asymmetric vibration peak, is believed to come from the vibrations of the residual side groups such as Si–OEt and Si–OMe. In addition to these, there is the group R(–C$_3$H$_6$–O–CH$_2$–CH–CH$_2$O), which bonds directly to the silicon atom and cannot take part in the hydrolysis and condensation reactions.

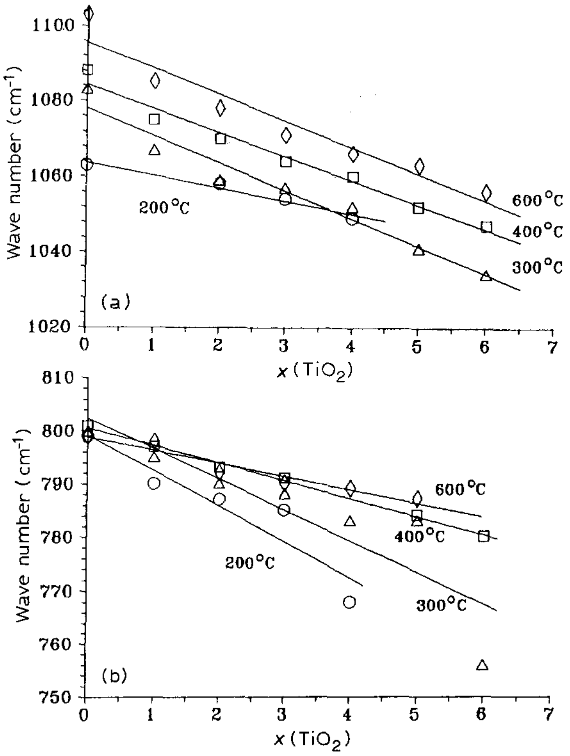


Figure 6 Changes of Si–O–Si (a) asymmetric and (b) symmetric stretching bands with x at different temperatures. Errors are smaller than the point size.

The existence of these organic residues and side groups makes the Si–O–Si network very "open", and there are many breaking points in it because of this. The vibration peaks caused by C–H around 2900 and 1400 cm^{-1} begin to decrease in intensity at 200 °C, and they almost disappear at 300 °C. The infrared peak at 1100 cm^{-1} also disappears for all samples after treatment at 300 °C for 2 h. The decrease in intensity and the disappearance of the peaks related to these organic groups are caused by the completion of the condensation reaction, and by the evaporation of residual alcohol, as well as by the oxidation of organic side groups and residues. As a result of this, many of the breaking points in the Si–O–Si network disappear, and the network structure becomes more condensed and more rigid, as indicated by the gradual shift of Si–O–Si stretching infrared peaks towards higher wave numbers (see Fig. 6).

It is also noticed that the small peak in the region from 550–600 cm^{-1}, which is caused by the four-fold siloxane ring, disappears in the same temperature range where these organic groups disappear. This phenomenon may suggest that these organic side groups play an important role in the formation and the deformation of the four-fold siloxane ring structure.

From Figs 1–4 we can see that two new peaks appear at 1560 and 1455 cm^{-1} when $\mathrm{Ti(OR)_4}$ is added into the system, and their intensities are clearly increased with increasing $\mathrm{Ti(OR)_4}$ content. These two peaks are believed to result from the carboxylate anion [14], the formation of which is promoted by the $\mathrm{Ti(OR)_4}$ component. It disappeared quickly when heating the samples at relatively low temperatures (see Figs 1–4).

4. Conclusions

The $\equiv$Si–O–S$\equiv$ network structure of the air-dried and low-temperature treated ($< 150\,^{\circ}\mathrm{C}$) gels is very "open", with many breaking points caused by the organic side groups which connect to it. One of the prominent characteristics of the network is the presence of the four-fold siloxane ring. The organic side groups play an important role for the formation of the four-fold siloxane ring structure.

The organic side groups gradually disappear from the structure in the curing temperature range from 200–400 °C. This results in the gradual disappearance of the breaking points in the structure and leads to the deformation of the four-fold siloxane ring. At the same time, a more condensed and more rigid sol–gel network structure with higher degree of the linkage between the $[\mathrm{SiO_4}]$ tetrahedra is built up.

The $\mathrm{Ti^{4+}}$ ion in the system takes part in the formation of the $\equiv$Si–O–Si$\equiv$ network by Ti–O–Si bonding. On increasing the $\mathrm{TiO_2}$ content, the strength of the Si–O bonds in the network and the tendency towards the formation of the four-fold siloxane ring in this system are decreased.

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References

1. C. J. BRINKER, D. E. CLARK and D. R. ULRICH (eds.), in "Better Ceramics Through Chemistry II", (Materials Research Society, Pittsburgh, PA, 1986).
2. J. D. MACKENZIE, *J. Non-Cryst. Solids* **100** (1988) 162.
3. H. SCHMIDT, *Mater. Res. Soc. Symp. Proc.* **32** (1984) 237.
4. *Idem, J. Non-Cryst. Solids* **112** (1989) 419.
5. H. TOYUKI, *Yogyo-KyoKai-Shi* **85** (1977) 554.
6. A. N. LAZAREV, in "Vibrational Spectra and Structure of Silicates" (Consultants Bureau, New York, 1972).
7. O. K. JOHANSON and C. L. LEE, in "Cyclic Monomers", edited by K. C. Frisch (Wiley, New York, 1971) p. 459.
8. M. G. VORONKOV and V. I. LAVREN'YEV, *Topics Curr. Chem.* **102** (1982) 199.
9. HIROYUKI YOSHINO, KANICHI KAMIYA and HIROYUKI NASU, *J. Non-Cryst. Solids* **126** (1990) 68.
10. K. A. MAURITZ and C. K. JONES, *J. Appl. Polym. Sci.* **40** (1990) 1401.
11. B. E. YOLDAS, in "Ultrastructure Processing of Ceramics, Glasses and Composites", edited by L. L. Hench and D. R. Ulrich (Wiley, New York, 1984) p. 65.
12. GAN FUXI, HUANG GUOSONG and CHEN SHIZHENG, *J. Non-Cryst. Solids* **52** (1982) 203.
13. D. L. WOOD and E. M. RABINOVICH, *Appl. Spectrosc.* **43** (1989) 263.
14. R. M. SILVERSTEIN, G. C. BASSLER and T. C. MORRIL (eds.), in "Spectrometric Identification of Organic Compounds", 4th Edn (Wiley, New York, 1981) p. 121.

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