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Experimental studies on the transition from xerogels to glasses for the system SiO_2–PbO–B_2O_3 with added DMSO using the thermal-mass spectroscopy coupling technique

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Abstract

The thermal-mass spectroscopy coupling technique (TG–DTA–MS) was used to study the thermal decomposition behaviour of the transition from xerogels to glasses for the gradient refractive index materials SiO_2–PbO–B_2O_3 with added dimethyl sulphoxide (DMSO). Compared with the TG–DTA–MS results for C_2H_5OH-system xerogels, the MS curves for DMSO-system xerogels show (in addition to CH_3^+ (*m*/*z*, 15)) the CH_3O^+ (*m*/*z*, 31), $C_2H_5O^+$ (*m*/*z*, 45), $[(CH_3)_2SO]^+$ (*m*/*z*, 78), etc., positive-ion mass spectrum peaks. This indicates that adding DMSO enables many residual OR groups to remain in the forming xerogels. This was beneficial for the condensation of the incompletely hydrolysed product and for preventing cracking of the xerogels. A preliminary study on the mechanism of thermal decomposition for DMSO-system xerogels is also given in this paper.

Keywords: Dimethyl sulphoxide (DMSO); SiO_2–PbO–B_2O_3; TG–DTA–MS; Transition from xerogels to glasses

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1. Introduction

An advanced research project in the field of glass materials is to use the sol-gel method to prepare gradient refractive index materials from, e.g., the SiO_2–PbO–B_2O_3system [1–2]. Because of the cracking of xerogels during heat treatment, various organic solution systems have been used by many researchers for preparing monolithic xerogels without cracks [3]. C_2H_5OH was used as the solvent in traditional sol-gel proceedings. However, this kind of solution is easily volatilized, so that the xerogels formed were cracked as a result of capillary attraction. Wei and Chen [3] used the polar solvent DMSO, which has a low surface tension, to prepare SiO_2 xerogels. They studied the thermal decomposition behaviour by DTA/GC, FTIR and TGA techniques. Brinker et al. [4] used DTA and other techniques to study the thermal decomposition of the transition from xerogels to glasses for the SiO_2 system. They found that the exothermic DTA peaks at 200–400°C are related to the combustion of the residual organic matter and carbon. All the authors mentioned above failed to report the experimental characterization of the organic and inorganic components evaporated in the thermal decomposition of the xerogels. The work presented here uses the thermal-mass spectroscopy coupling technique (TG–DTA–MS) to study the thermal decomposition behaviour of the transition processes from xerogels to glasses for the SiO_2–PbO–B_2O_3 system with added DMSO.

2. Experimental

2.1. Sample preparation

$Si(OCH_3)_4$ (16 ml) and $Si(OC_2H_5)_4$ (4 ml), with 30 ml of H_3BO_3(0.8 mol l^{-1}) and 10 ml of DMSO or alcohol were mixed and stirred for 10 min. HCl (8 ml) of pH 2 was added and the reaction carried out for 1 h. Then 3 ml of HOAC and 36 ml of $Pb(OAC)_2$(1.25 ml l^{-1}) were added and stirred for 5 min. The sol formed was sealed in a mould for gelling. The gels were aged at 30°C for seven days. After release from the mould, the gels were dried at a heating rate of 20°C h^{-1}, then kept at 40, 65, 100 and 120°C for 15 h, respectively, yielding the xerogels.

2.2. TA–MS measurements

A Netzsch Simultaneous Thermal Analyser coupled with a Swiss Balzers QMG-511 Quadrupole Mass Spectrometer were used in the experiments. DMSO-system xerogels (110 mg) and alcohol-system xerogels (110 mg) were weighed in Al_2O_3 crucibles respectively. TG full-scale was 25 mg; DTA full-scale was 0.2 mV. The region of temperature increase was 20–600°C. The heating rate was 10°C min^{-1}. The experiments were carried out in an oxygen atmosphere. The MS system was under vacuum, 2.0×10^{-5} mPa. The mass scanning speed was 1 amu s^{-1}. The time for mass filtering was 0.03 s. The receiving device was a Faraday cup. The other parameters for mass spectroscopy analysis are shown as Table 1.

Table 1
Parameters for quadrupole mass spectroscopy analysis

Proposed positive ion	CH_3^+	H_2O^+	CH_3O^+	CO_2^+	$C_2H_5O^+$	SO^+	SO_2^+	$[(CH_3)_2SO]^+$
m/z	15	18	31	44	45	48	64	78
Intensity (A)	10^{-9}	10^{-9}	10^{-11}	10^{-11}	10^{-11}	10^{-11}	10^{-11}	10^{-9}
Amplifying rate	× 10	× 10	× 1	× 1	× 1	× 1	× 1	× 10

3. Results and discussion

3.1. TG–DTA–MS results for the DMSO-system xerogels

The TG–DTA–MS results for the DMSO-system xerogels are shown in Figs. 1 and 2. The TG curve in Fig. 1 shows a big step at 67–500°C and some overlapping steps at 67–500°C. The total mass loss equals 27.3% of the total sample weight. The first mass-loss rate maximum at 210°C is probably associated with the elimination of DMSO. The corresponding DTA curves show two endothermic peaks at 220 and 260°C respectively. The endothermic peak at 220°C is stronger. The corresponding MS curves in Fig. 2 show eight positive-ion mass spectra peaks: CH_3^+ (*m/z*, 15), H_2O^+ (*m/z*, 18), CH_3O^+ (*m/z*, 31), CO_2^+ (*m/z*, 44), $C_2H_5^+$ (*m/z*, 45), SO^+ (*m/z*, 48), SO_2^+ (*m/z*, 64) and $[(CH_3)_2SO]^+$ (*m/z*, 78). The SO^+, SO_2^+ and CH_3^+ peaks are probably formed from DMSO in the mass spectrometer. The DTA curve shows a strong exothermic peak at 348°C. The corresponding MS channels detected five positive mass spectra peaks: CH_3^+ (*m/z*, 15), H_2O^+ (*m/z*, 18); CH_3O^+ (*m/z*, 31), $C_2H_5O^+$ (*m/z*, 45) and CO_2^+ (*m/z*, 44). Compared with decomposition in the first step, there were no SO^+ (*m/z*, 48), SO_2^+ (*m/z*, 64) or $[(CH_3)_2SO]^+$ (*m/z*, 78) peaks. However, the CO_2^+ (*m/z*, 44) peak was higher.

3.2. TG–DTA–MS results for the C_2H_5OH-system xerogels

In order to study the influence on the transition processes from xerogels to glasses as a result of adding DMSO, we also carried out a TG–DTA–MS determination for the C_2H_5OH-system xerogels and compared the two results. The TG–DTA–MS results from room temperature to 600°C for the C_2H_5OH-system xerogels are shown in Figs. 3 and 4. The TG curve in Fig. 3 also shows a big step at 67–500°C. The mass loss equals 15.7% of the total sample weight. The corresponding DTA curve shows a strong endothermic peak at 253°C and a strong exothermic peak at 347°C. In the corresponding MS curves, H_2O^+ (*m/z*, 18) peaks appear at 100 and 390°C, respectively. The first H_2O^+ peak indicates the release and evaporation of the physically adsorbed water on the surface of the xerogels. The second H_2O^+ peak indicates the condensation water of $\equiv$ Si–OH released and evaporated at 390°C. The CH_3^+ (*m/z*, 15) peaks appear at 180 and 300°C respectively. But the CH_3O^+ (*m/z*, 31) and $C_2H_5O^+$ (*m/z*, 45) peaks did not appear. In addition, the CO_2^+ (*m/z*, 44) peaks appear at 210 and 330°C, respectively.

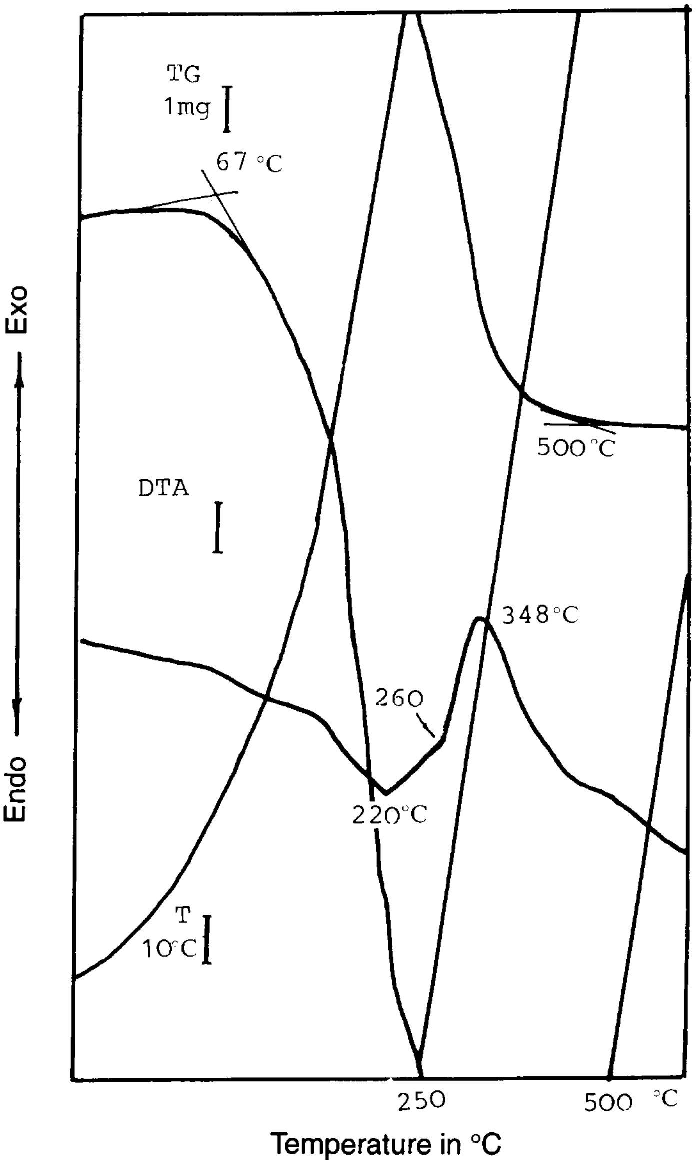


Fig. 1. TG and DTA curves for the DMSO-system xerogels.

3.3. Possible thermal decomposition mechanism for the DMSO-system xerogels

The TG–DTA–MS results mentioned above show that there are some obvious differences in the thermal decomposition of gels in the DMSO and C_2H_5OH systems. The MS curves of the DMSO system show three positive-ion mass spectra peaks

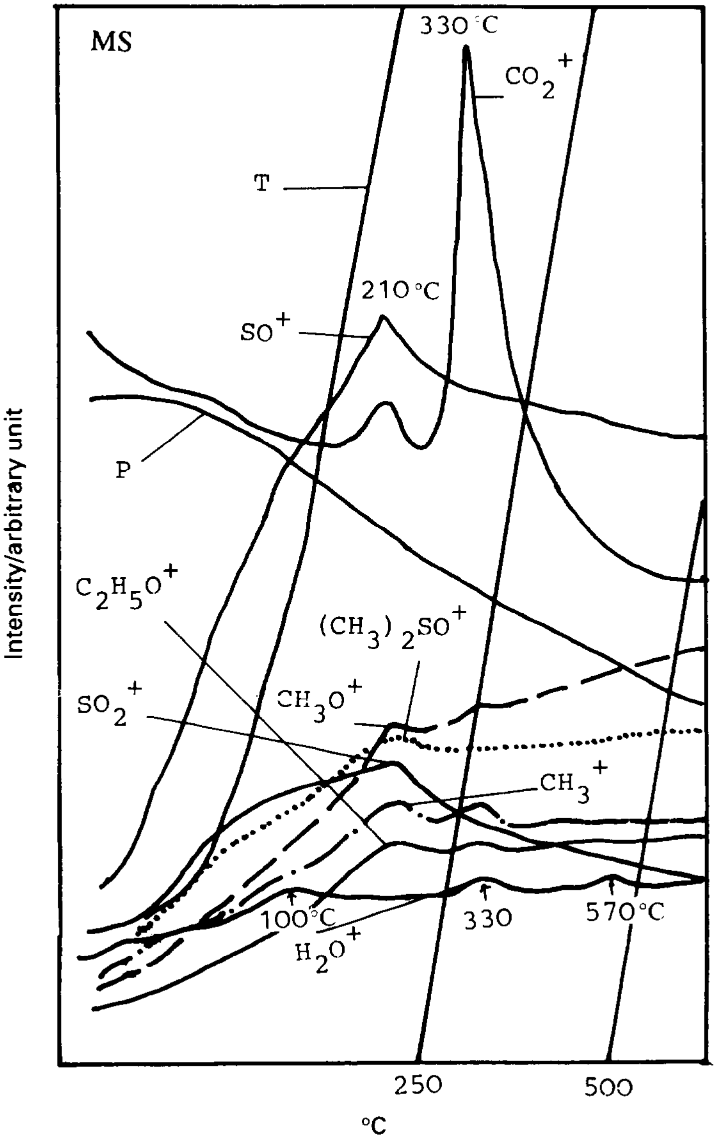


Fig. 2. Mass spectra for the DMSO-system xerogels.

containing S and the five peaks, $C_2H_5O^+$ (m/z, 45), CH_3O^+ (m/z, 31), CH_3^+ (m/z, 15), H_2O^+ (m/z, 18) and CO_2 (m/z, 44). The C_2H_5OH system shows no $C_2H_5O^+$ (m/z, 45) or CH_3O^+ (m/z, 31) (compare Figs. 2 and 4). The MS results indicate that there are more residual OR organic groups in the DMSO system. This is related to the complexing action of DMSO with Si atoms in $Si(OC_2H_5)_4$ or $Si(OCH_3)_4$. However, the excess

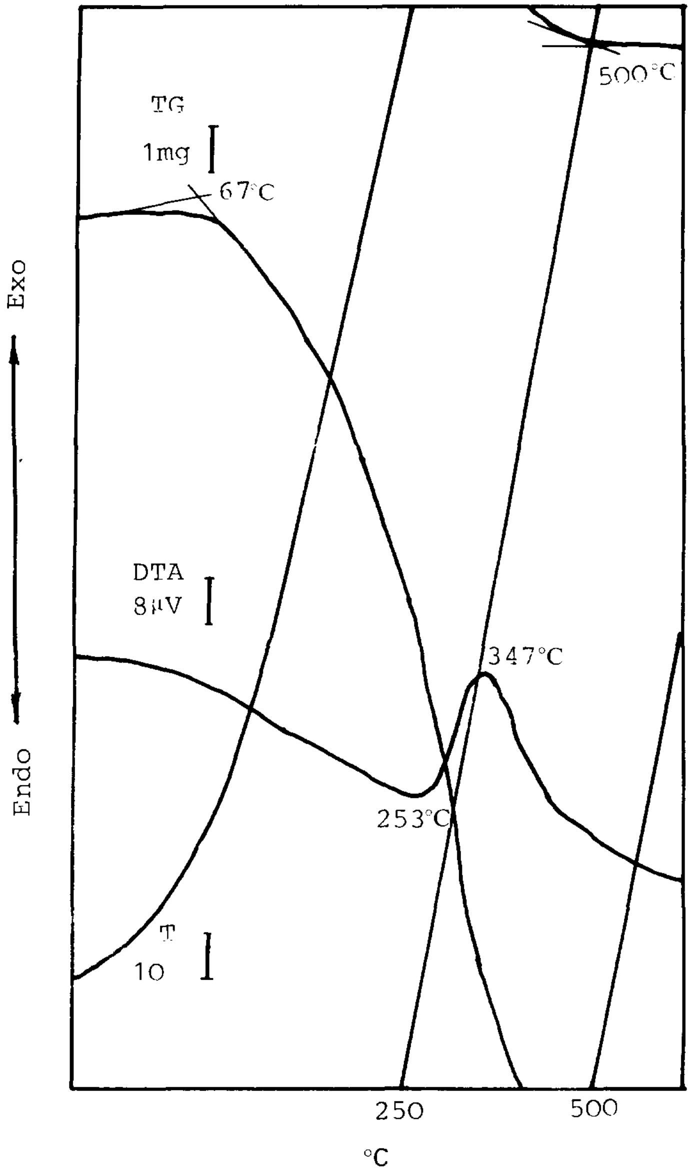
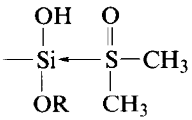


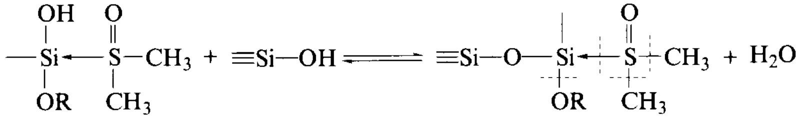
Fig. 3. TG and DTA curves for the C_2H_5OH-system xerogels.

ethanol as a reaction product will decrease the hydrolysis of $Si(OC_2H_5)_4$ or $Si(OCH_3)_4$, thus leaving more groups in the ethanol-containing system [5] at higher temperatures. Due to the incomplete hydrolysis, the complex can simultaneously contain OR and OH groups. Thus



$$-\underset{\mathrm{OR}}{\overset{\mathrm{OH}}{\mathrm{Si}}}\leftarrow\underset{\mathrm{CH_3}}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}}-\mathrm{CH_3}$$

can be polymerized with ≡Si—OH



$$-\underset{\mathrm{OR}}{\overset{\mathrm{OH}}{\mathrm{Si}}}\leftarrow\underset{\mathrm{CH_3}}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}}-\mathrm{CH_3} + \equiv\mathrm{Si{-}OH} \rightleftharpoons \equiv\mathrm{Si{-}O}-\underset{\mathrm{OR}}{\overset{|}{\mathrm{Si}}}\leftarrow\underset{\mathrm{CH_3}}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}}-\mathrm{CH_3} + \mathrm{H_2O}$$

Because of the polarization caused by the S atom of DMSO to Si, the adjacent Si–OR, S–CH_3 and S = O bonds were weakened and broken at a certain temperature (see the dotted lines on the right side of the equation), and then the corresponding OR groups separated out. The MS curves of C_2H_5OH-system xerogels show two H_2O^+ (*m/z*, 18) peaks (Fig. 4) at 100 and 390°C, but the MS curves of the DMSO system show three H_2O^+ peaks (*m/z*, 18) (Fig. 2, at 100, 330 and 570°C). Among them, the peak at 100°C is the release of physically absorbed water on the surface of the xerogels. The small peaks at 330 and 570°C show that the condensation reaction of ≡ Si–OH can be extended by adding DMSO. The MS curves of DMSO in Fig. 2 show three positive-ion mass spectra peaks: SO^+ (*m/z*, 48), SO_2^+ (*m/z*, 64), and $[(CH_3)_2SO]^+$ (*m/z*, 78) at 210°C, which indicates that DMSO is volatilized at lower temperatures. Therefore it did not leave the samples and influence the sintering. The same results were found using DTA/GC and FTIR [3]. In addition, we also observed that the MS curves of both the C_2H_5OH and DMSO systems show CO_2^+ (*m/z*, 44) at 210 and 330°C, separately, and moreover, the intensity of CO_2^+ (*m/z*, 44) for the DMSO system is stronger than that for the C_2H_5OH system. This shows that most of the OR groups of the DMSO system tend to decompose completely before the conversion of xerogels to glasses, which decreases the release of gases during the transition from xerogels to glasses. Thus, this is beneficial for decreasing gas bubbles and preventing cracking of the samples.

4. Conclusions

The TG–DTA–MS results show that the thermal decomposition of the transition from xerogels to glasses for the system SiO_2–PbO–B_2O_3 with added DMSO proceeds in two steps: the first is at 210°C and its DTA curve shows a strong endothermic peak; the second is at about 348°C and the DTA shows a strong exothermic peak.

The MS results for DMSO-system xerogels show that the eight positive-ion mass spectra peaks at 210°C in the first step of the thermal decomposition were CH_3^+ (*m/z*, 15), H_2O^+ (*m/z*, 18), CH_3O^+ (*m/z*, 31), CO_2^+ (*m/z*, 44), $C_2H_5O^+$ (*m/z*, 45), SO^+ (*m/z*, 48), SO_2^+ (*m/z*, 64) and $[(CH_3)_2SO]^+$ (*m/z*, 78). The five positive-ion mass spectra peaks detected at 330°C in the second decomposition were CH_3^+ (*m/z*, 15), H_2O^+ (*m/z*, 18), CH_3O^+ (*m/z*, 31), CO_2^+ (*m/z*, 44) and $C_2H_5O^+$ (*m/z*, 45). But for the C_2H_5OH system, only the CH_3^+ (*m/z*, 15) peaks (180 and 300°C) and CO_2^+ (*m/z*, 44)

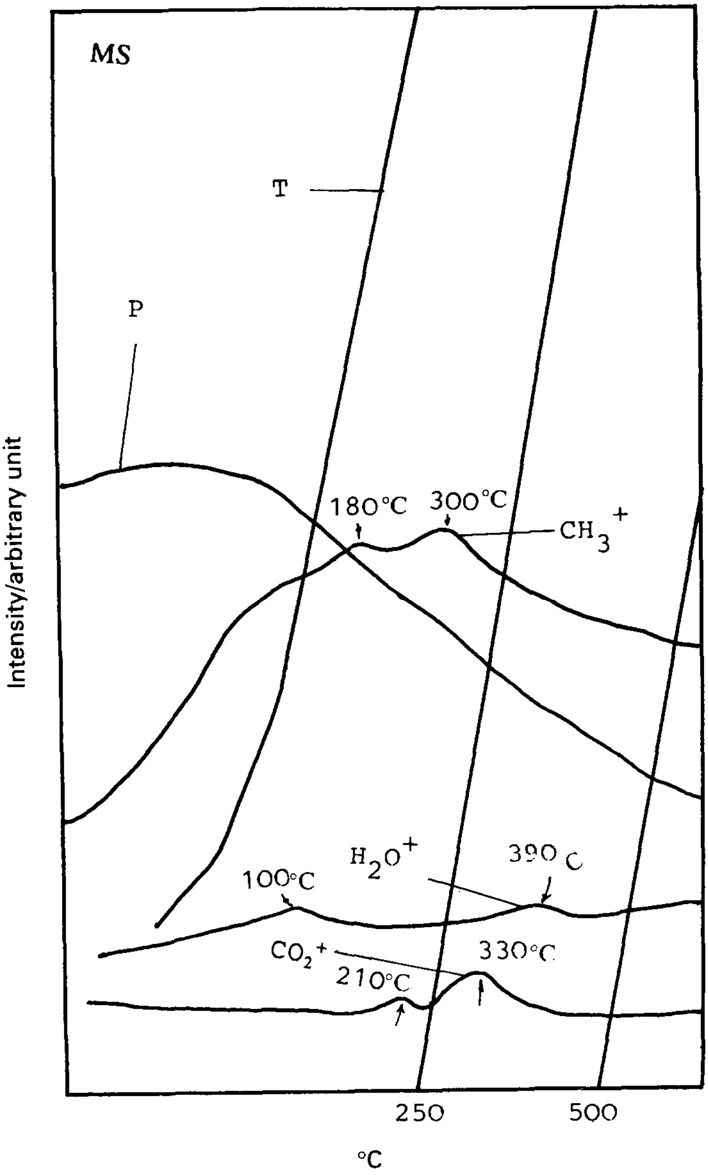


Fig. 4. Mass spectra for the C_2H_5OH-system xerogels.

peaks (210 and 330°C) were detected separately. This shows that adding DMSO is beneficial for decreasing gas bubbles in glasses and preventing cracking of the samples.

The polarization caused by the S atom of DMSO to Si should be one of the main factors for weakening and braking the adjacent bonds Si–OR, S–CH_3 and S=O at relatively low temperatures. Because the compounds containing S decompose at lower temperatures, adding DMSO did not affect the sintering processes of the xerogels. In fact, it enables the condensation reaction of $\equiv$Si–OH to develop at a higher temperature.

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