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An infrared spectroscopic investigation of glasses in the system K_2O–P_2O_5–GeO_2

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There is considerable practical and theoretical interest in new vitreous materials in multivariant combination with GeO_2. Glasses containing GeO_2 and P_2O_5 are promising as new media with novel optical constants.

In a previous study [1] we determined the glass-forming region in the system K_2O–P_2O_5–GeO_2. The glasses were prepared in a Pt crucible at 1300–1350 °C and refined for 3 h, the resultant glasses were then annealed at 320–350 °C for 5 h.

The samples for infrared measurement (wave number range 1500–400 cm^{-1}) were prepared by dispersing the glass powder in KBr powder. The mixture containing about 5 wt % glass was cold-pressed into discs 2–3 mm thick and 38 mm in diameter. The spectra were obtained on a Perkin–Elmer 180 infrared spectrometer and are shown in Fig. 1. The compositions of the glasses and the measured wave numbers are listed in Table I.

The spectrum of the glass with the composition $25K_2O{\cdot}75GeO_2$ contains an intense band A with frequency 840 cm^{-1}, a band B with frequency 575 cm^{-1} and shoulder at 475 cm^{-1}. When P_2O_5 is added to the glasses instead of K_2O, the spectra of the glasses contain narrow bands of moderate intensity, band C with frequency 1120–1100 cm^{-1} and band D with frequency 1250–1120 cm^{-1}.

Band A, observed in the spectra of K_2O–GeO_2 glasses, is due to the antisymmetric stretching vibration of the Ge–O–Ge bonds and band B to

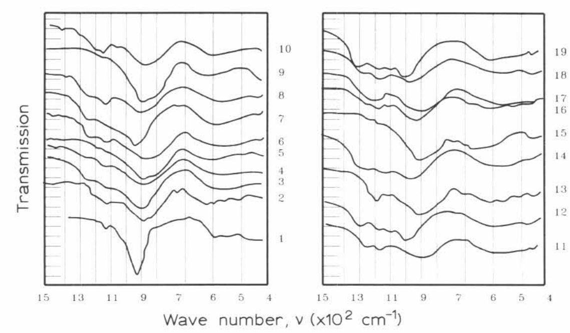

Figure 1 Infrared spectra of glasses in the system K_2O–P_2O_5–GeO_2.

deformation vibration [2–5]. Band A is shifted towards lower frequencies and broadened as the K_2O content of the glass is increased.

When P_2O_5 is added to the glass, the band between 900 and 800 cm^{-1} becomes narrower and shifts towards higher frequencies. This is even more pronounced in glasses 3, 7, 12 and 19, in which $K_2O{:}P_2O_5 = 1$. Here the position and width of band A practically coincide with the corresponding values in pure vitreous GeO_2 [6–14]. From these data it can be inferred that P_2O_5 forms its own lattice in the glass independently of GeO_2 (owing to the absence of bands intermediate between those of P–O–P and P–O 1120–1100 cm^{-1}, and Ge–O–Ge, 900–800 cm^{-1}). Since the bands of the Ge–O–Ge bonds shift towards higher frequencies and become

TABLE I The composition of the glasses and the wave numbers of their infrared peaks

	Glass composition (mol %)			Wave numbers, cm^{-1}					
Glass no.	K_2O	P_2O_5	GeO_2	D	C	E	A	F	B
1			100	1155	1100	1000	900	640	580
2	14.3		85.7	1180	1100		845		595 480
3	7.15	7.15	85.7	1200	1100		880		550
4	13.5	4.50	82.0	1210	1100	1020	840		550
5	25.0		75.0	1150	1100		840		575 475
6	18.75	6.25	75.0	1200	1100	1020	830		560
7	12.5	12.5	75.0	1200	1100	1050	915		550
8	23.1	7.70	69.0	1210	1100	950	840		540
9	33.3		66.7	1100	1100		840		560
10	27.7	5.60	66.7	1250	1100	1000	840		560
11	22.2	11.1	66.7	1200	1100		830		560 480
12	16.65	16.65	66.7	1230	1100	1030	915	680	540 485
13	32.1	3.60	64.3	1170	1115	1010	850	660	560 480
14	21.4	14.3	64.3	1190	1100		870		560 480
15	40.0		60.0	1150	1100		840	630	580 470
16	35.0	5.0	60.0	1190	1100	1030	850	620	555 470
17	30.0	10.0	60.0	1120	1120	1000	820	630	570 465
18	25.0	15.0	60.0	1200	1100	1030	870		570
19	20.0	20.0	60.0	1230	1115	1030	920		570

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narrower as the P_2O_5 content of the glass increases, it can be postulated that P_2O_5 combines with K_2O more actively than GeO_2. When $K_2O{:}P_2O_5 = 1$ all of the potassium oxide is combined with P_2O_5, because in these glasses the band due to Ge–O–Ge bonds coincides with the band due to Ge–O–Ge bonds in pure GeO_2 glass.

A similar phenomenon occurs in glasses of the system Na_2O–B_2O_3–SiO_2, where addition of B_2O_3 leads to transference of Na_2O from the SiO_2 to the B_2O_3 [15, 16].

Upon further increasing the P_2O_5 content of the glass there is a marked change in the intensity and width of band B. This shows the influence of P_2O_5 on GeO_2 when there is insufficient K_2O. Apparently, the P_2O_5 combines with the GeO_2.

The composition dependence of the structure of potassium phosphogermanate glass can be represented as follows. In two-component potassium germanate glass the K_2O is combined with GeO_2. Addition of small amounts of P_2O_5 leads to transference of K_2O from GeO_2 to P_2O_5. This glass consists of two parts: potassium germanate ($pK_2O{\cdot}nGeO_2$) and potassium phosphate ($gK_2O{\cdot}mP_2O_5$). Upon further increasing the P_2O_5 content and attainment of the ratio $K_2O{:}P_2O_5 = 1$ the glass consists of $(GeO_2)_n$ and potassium phosphate ($gK_2O{\cdot}mP_2O_5$) sectors. Further increasing the P_2O_5 content leads to combination of P_2O_5 with GeO_2 ($nGeO_2{\cdot}mP_2O_5$). This glass consists of potassium phosphate and phosphogermanate sectors.

Using a molecular model of the structure of inorganic glasses we have shown that, in glasses of the system K_2O–P_2O_5–GeO_2, $(GeO_2)_n$ and $(P_2O_5)_m$ molecules are present, which upon addition of K_2O are converted to compounds of the type $pK_2O{\cdot}nGeO_2$ and $gK_2O{\cdot}mP_2O_5$, and finally compounds of type $nGeO_2{\cdot}mP_2O_5$, where n, m, p and g are small integers.

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