

# Raman spectroscopic investigation of the structure and crystallization of binary alkali germanate glasses

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Raman spectra have been measured on bulk  $\text{GeO}_2$  glass and the alkali germanate glasses of composition  $\text{M}_2\text{O} \cdot x\text{GeO}_2$  where  $\text{M} = \text{K}, \text{Na}, \text{Li}$ , and  $x$  varies from 19 to 1, as well as on crystallized glasses. The low alkali content glasses ( $x \geq 3$ ) retain a completely polymerized structure of germania polyhedra. Addition of small amounts of alkali oxide to  $\text{GeO}_2$  glass does not break the  $\text{Ge}-\text{O}-\text{Ge}$  bridging bonds and creates higher co-ordination of germanium atoms. Further addition of alkali oxide eventually breaks up some of the  $\text{Ge}-\text{O}-\text{Ge}$  bonds to create  $\text{Ge}-\text{O}^-$  non-bridging oxygens. In the K- and Na-glasses a small number of non-bridging oxygens already exist at  $x = 4.5$ , while in the Li-glasses they do not exist even at  $x = 4$ . The structures of the low alkali content glasses start to disappear at  $x$  between 4 and 3 and they disappear almost completely at  $x = 2$ . At  $x$  between 2 and 1, glass structures become analogous to the silicate glass structures. At  $x = 2$ , the glass consists of disordered  $(\text{Ge}_2\text{O}_5)_n$  sheet-like structures and at  $x = 1$  disordered  $(\text{GeO}_3)_n$  chain structures.

## 1. Introduction

In certain aspects, the structures of alkali germanate glasses should be analogous to alkali silicate glasses. However, there is one essential difference. Germanium can take on both four and six co-ordination, whereas silicon appears only in four-fold co-ordination except at extremely high pressures. For alkali silicate glasses [1-3], addition of alkali oxide to  $\text{SiO}_2$  glass breaks  $\text{Si}-\text{O}-\text{Si}$  bridging bonds creating non-bridging oxygens. The number of non-bridging oxygens increases continuously with increasing alkali oxide content.

At the disilicate composition all the  $[\text{SiO}_4]$  tetrahedra have one non-bridging oxygen on average. Further addition of alkali oxide creates tetrahedra with two non-bridging oxygens, and at the metasilicate composition all the  $[\text{SiO}_4]$  tetrahedra have two non-bridging oxygens. On the other hand a different structural model has been postulated for alkali germanate glasses [4, 5]. Addition of alkali oxide to  $\text{GeO}_2$  glass converts some

of the germanium from four to six co-ordination without breaking  $\text{Ge}-\text{O}-\text{Ge}$  bridging bonds. The number of such six co-ordinated germanium increases until the alkali oxide content is about 15 to 20 mol %. Further addition of alkali oxide results in breaking  $\text{Ge}-\text{O}-\text{Ge}$  bonds and converting six co-ordinated germanium back to four co-ordination. The structural model was based on the characteristic variation of physical properties with composition, such as density [5], refractive index [5], viscosity [6], thermal expansion [6], internal friction [7], and velocity of sound propagation [7]. All these properties exhibit a maximum at alkali oxide concentrations between 15 and 20 mol %.

A pronounced difference exists in the crystalline phases occurring in the systems. In the alkali germanate systems there are compounds such as  $\text{M}_2\text{Ge}_8\text{O}_{17}$ ,  $\text{M}_2\text{Ge}_7\text{O}_{15}$ ,  $\text{M}_2\text{Ge}_6\text{O}_{13}$ ,  $\text{M}_4\text{Ge}_9\text{O}_{20}$ , and  $\text{M}_2\text{Ge}_4\text{O}_9$  ( $\text{M}$  is alkali metal ion) [8-25]. These compounds consist of both four and six co-ordinated germanium but with no non-bridging

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oxygens ( $K_2Ge_8O_{17}$  has also five co-ordinated germanium). Similar compounds are not found in the alkali silicate system. At high alkali oxide concentrations, both systems become more similar to each other.

Raman spectroscopy has been demonstrated to be a useful technique for the structural characterization of glasses. Systematic changes in Raman spectra with composition, and with crystallization, and comparison of glass spectra with crystal spectra are used to deduce structural information [1, 3, 26, 27].

Raman spectra of potassium, sodium and lithium germanate glasses were measured in the composition range between germanium dioxide and the meta-germanate. The glasses were crystallized at subsolidus temperatures, and the crystallized phases were characterized by Raman spectroscopy and X-ray diffraction. The structures of germanate glasses were deduced from systematic variations of the glass spectra with composition and by comparison of the glass and the crystal spectra as well as the results of crystallization study.

Infra-red [28] and Raman [29] spectra of alkali germanate glasses have been reported.

## 2. Experimental details

### 2.1. Preparation of glasses

Alkali germanate glasses were prepared of composition  $M_2O \cdot xGeO_2$  where M is potassium, sodium, and lithium, and  $x$  varies from 19 to 1, 19 to 1.5, and 19 to 4, respectively. The starting chemicals were Fisher reagent grade alkali carbonates and Eagle-Picher Industries and Alfa Inorganic Ventron electronic grade  $GeO_2$  powder (quartz form). For the potassium and sodium germanate glasses, 5 to 10 g batches were well mixed and melted in Pt-crucibles in a SiC glo-bar furnace at temperatures between 1075 and 1225° C for 3 to 4 h. Glass rods of approximately 1 mm diameter were drawn from the melts. The  $K_2O \cdot GeO_2$  melt and the  $Na_2O \cdot 1.5 GeO_2$  melt were quenched by pressing the melt between a graphite block and a stainless steel block. For the lithium germanate glasses, 1 to 1.3 g batches were ground with pestel and mortar and heated at 100 to 1250° C for about 3 h in one-end-open Pt-tubes (5 mm diameter and 2 cm long). The tubes were sealed, reheated at about 1200° C for ½ h, quenched in water, and annealed at about 370° C for 1 h.  $GeO_2$  glass was prepared by fusing  $GeO_2$  powder by hydrogen torch in a graphite boat.

### 2.2. Preparation of Crystals

Glasses, in rod or scrap, were crystallized at subsolidus temperatures in an electric furnace. Potassium and sodium metagermanate were crystallized from the melt. Rutile structure  $GeO_2$  was crystallized hydrothermally from quartz  $GeO_2$  powder at 620° C under a pressure of 1 kbar.

### 2.3. Raman spectroscopic measurements

Raman spectra of the glasses were measured on a Spex model 1401 double-grating spectrometer at a scattering angle of 90°. The excitation source was 488 nm (20 492  $cm^{-1}$ ) line of a Spectra-Physics model 164 Ar-ion laser. The detailed measurement procedures and the Raman scattering geometry were described elsewhere [26, 27]. Both parallel ( $xx$ ) and crossed polarized ( $xy$ ) spectra were measured on glasses. Crossed polarized spectra were of low intensity and they were recorded within a 4 to 5 times higher gain than that for the parallel polarized spectra. Raman spectra of crystals were measured in an unpolarized mode. All the spectra were recorded at a 50  $cm^{-1} min^{-1}$  scanning speed with a spectral slit width of 3  $cm^{-1}$  for all the glasses and 2  $cm^{-1}$  for all the crystals.

## 3. Results

### 3.1. Raman spectra of bulk glasses

Parallel polarized ( $xx$ ) spectra of potassium, sodium, and lithium germanate glasses and crossed polarized ( $xy$ ) spectra of potassium germanate glasses are shown in Fig. 1. In this paper, parallel polarized ( $xx$ ) spectra are presented most of the time. If no polarization is given, parallel polarisation may be assumed.

Over the whole composition range, the spectra of potassium glasses are similar to those of sodium glasses except that the former exhibit more detailed features in the frequency region between 200 and 700  $cm^{-1}$ , while the lithium glass spectra are somewhat different.

For the purposes of description and discussion, it is useful to divide the spectra into three regions, the high-frequency region from 700 to 1000  $cm^{-1}$ , the middle-frequency from 200 to 700  $cm^{-1}$  and the low-frequency region below 200  $cm^{-1}$ .

Spectra of the high-frequency region (700 to 1000  $cm^{-1}$ ) are of most interest. At low alkali concentrations ( $x \geq 4$ ), the intensity of two or three bands in the high-frequency region increases slightly with increasing alkali concentrations, but

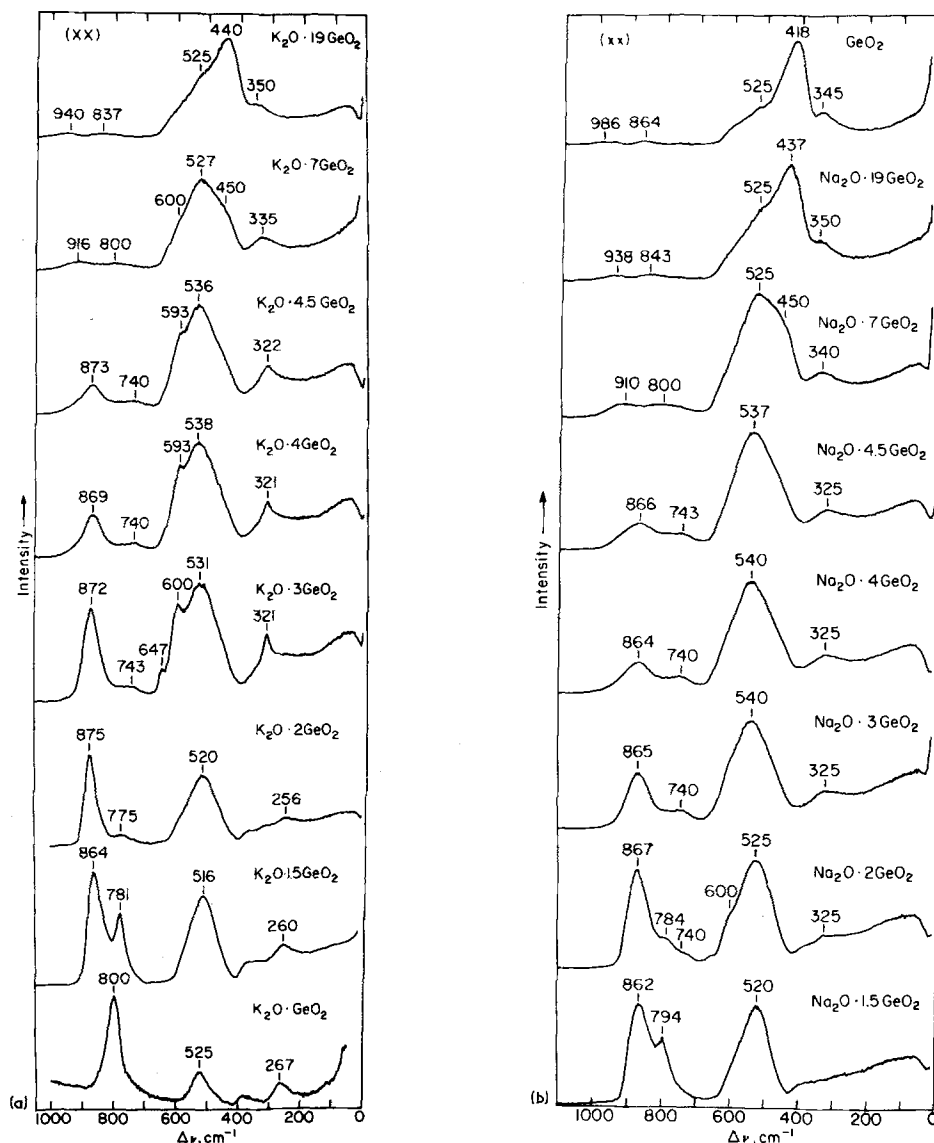


Figure 1 (a) to (c) Parallel polarized (xx) Raman spectra of (a)  $K_2O \cdot xGeO_2$  glasses, (b)  $Na_2O \cdot xGeO_2$  glasses and (c)  $Li_2O \cdot xGeO_2$  glasses. (d) Crossed polarised (xy) Raman spectra of  $K_2O \cdot xGeO_2$  glasses. The  $420\text{ cm}^{-1}$  band of  $GeO_2$  glass is probably spill-over from the intense polarized  $418\text{ cm}^{-1}$  band.

they are still weak compared with intense bands in the middle-frequency region.

The spectra of the high-frequency region are shown in expanded scale in Fig. 2. In the potassium and the sodium germanate series, there are two bands whose frequencies decrease and the intensity of the higher frequency band increases compared with that of the lower frequency band with increasing alkali concentrations. On the other hand, the lithium glass spectra become distinct from the others as the alkali concentration increases and the three overlapping bands appear at  $x$  between 7 and 4.

The frequency of the highest frequency band of the potassium and the sodium germanate series is plotted against the alkali content in Fig. 3. In both series the frequency decreases by about  $120\text{ cm}^{-1}$  as the alkali content increases from 0 to 22 mol % ( $x = 4.5$ ) and it becomes almost constant at higher alkali concentrations. The frequency is always slightly higher for the potassium germanate glasses than for the sodium germanate glasses. The intensity of this band increases drastically at  $x$  below 4 and becomes the characteristic band of the digermanate glass at  $x = 2$ , where the band is almost completely polarized. At  $x$  between 4.5 and

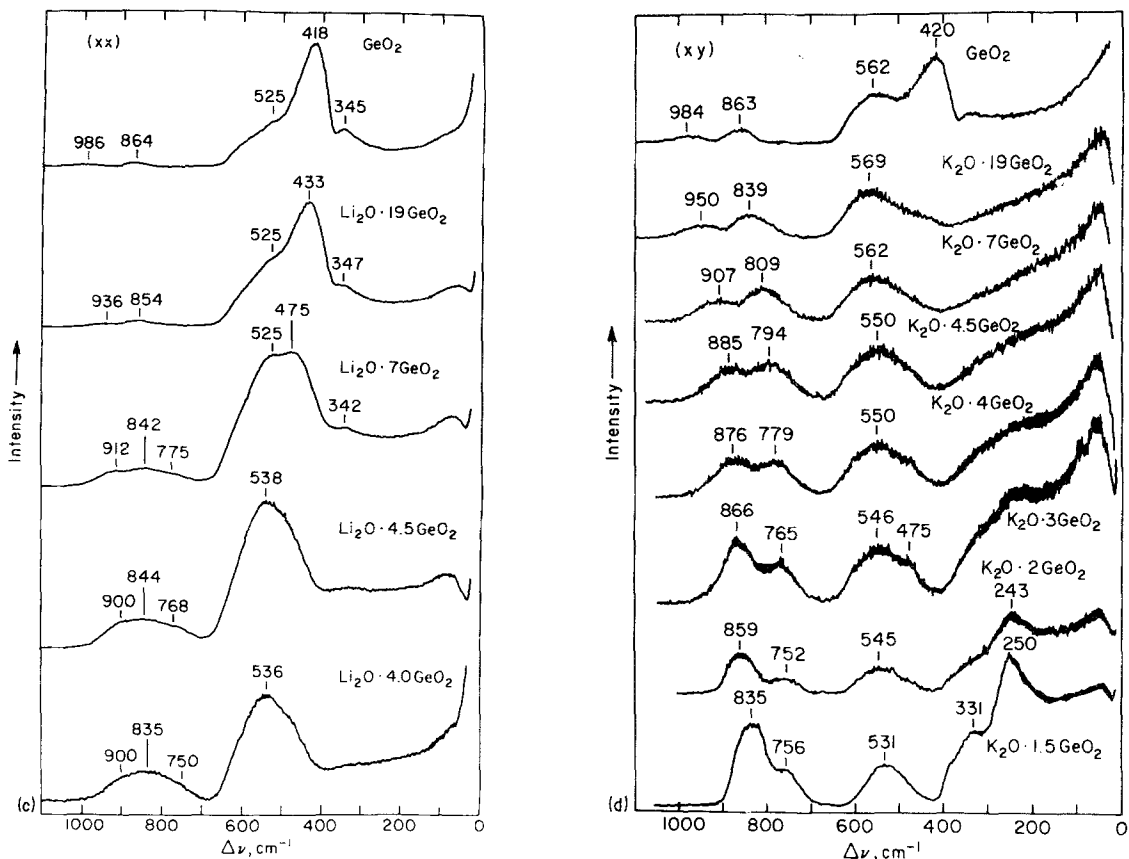


Figure 1 continued

3, the band is more intense for the potassium germanate glasses than the sodium germanate glasses.

At  $x$  between 2 and 1, the spectra of the potassium and sodium germanate glasses become very similar to the alkali silicate glass spectra. At  $x = 2$  the highest frequency band at about  $870 \text{ cm}^{-1}$  is

very intense and also a small band appears at about  $780 \text{ cm}^{-1}$ . These two bands correspond to the  $1000 \text{ cm}^{-1}$  band and  $950 \text{ cm}^{-1}$  band of the alkali silicate glass spectra [1–3]. The intensity of the  $780 \text{ cm}^{-1}$  band increases while that of the  $870 \text{ cm}^{-1}$  band decreases with the increasing alkali

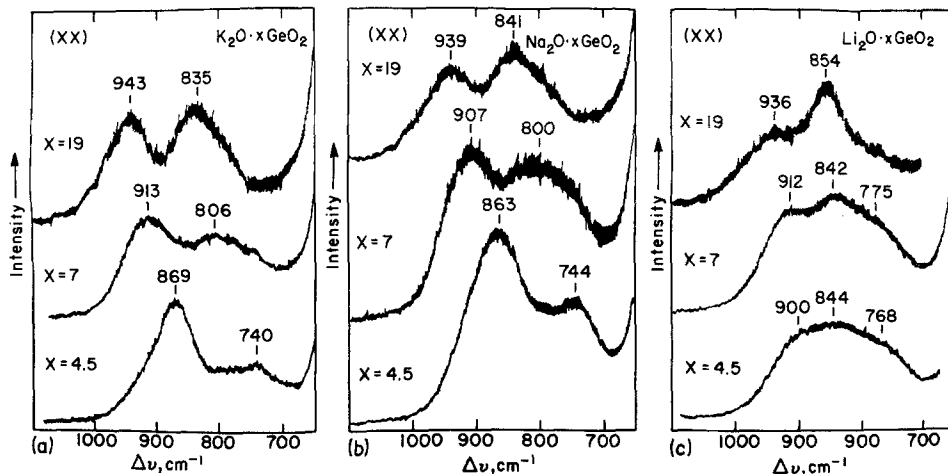


Figure 2 Raman spectra of the low alkali content glasses in the high-frequency region in an expanded scale. (a)  $\text{K}_2\text{O} \cdot x\text{GeO}_2$  glasses. (b)  $\text{Na}_2\text{O} \cdot x\text{GeO}_2$  glasses. (c)  $\text{Li}_2\text{O} \cdot x\text{GeO}_2$  glasses.

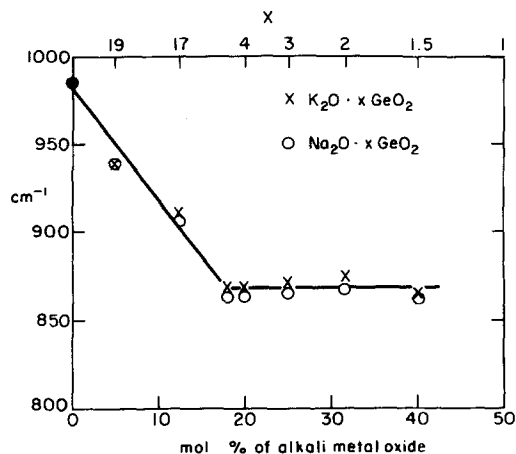


Figure 3 Variation of frequency of the highest frequency band for the series of potassium and sodium germanium glasses.

content, and finally at  $x = 1$  the band at  $800 \text{ cm}^{-1}$  is the only feature in this region. The lower frequency band shifts from  $780$  to  $800 \text{ cm}^{-1}$  as the alkali content increases from  $x = 2$  to  $x = 1$ , while the  $870 \text{ cm}^{-1}$  band shifts to lower frequencies. The band width at half height of the  $870 \text{ cm}^{-1}$  band of the  $\text{Na}_2\text{O} \cdot 2\text{GeO}_2$  glass spectrum ( $78 \text{ cm}^{-1}$ ) is wider than that of the  $\text{K}_2\text{O} \cdot 2\text{GeO}_2$  glass spectrum ( $48 \text{ cm}^{-1}$ ). The band width of the  $870 \text{ cm}^{-1}$  band of the  $\text{K}_2\text{O} \cdot x\text{GeO}_2$  glass spectra is  $54 \text{ cm}^{-1}$  at  $x = 3$ ,  $48 \text{ cm}^{-1}$  at  $x = 2$ , and  $61 \text{ cm}^{-1}$  at  $x = 1.5$ . There is a minimum at  $x$  around 2. For the alkali silicate glasses, the band width of the disilicate composition decreases in the order of  $\text{Li} > \text{Na} > \text{K}$ -silicate glass, and it shows a minimum at  $x = 1.8$  for Na- and K silicate glasses [1, 2].

Spectra of the middle-frequency region ( $200$  to  $700 \text{ cm}^{-1}$ ) consist of an intense band located between  $400$  and  $650 \text{ cm}^{-1}$  and weak band between  $250$  and  $350 \text{ cm}^{-1}$ . At  $x > 4$ , the intense band is the dominant feature. By addition of alkali oxide, the intense band of the  $\text{GeO}_2$  glass spectrum at  $418 \text{ cm}^{-1}$  shifts to higher frequencies and decreases intensity, at the same time the band at  $525$  to  $540 \text{ cm}^{-1}$  increases in intensity and becomes a dominant band at  $x$  around 4.5. In addition to these bands, a band or a shoulder appears at about  $600 \text{ cm}^{-1}$  accompanied by a small band at  $320$  to  $325 \text{ cm}^{-1}$  in the potassium and sodium germanate glass spectra at  $x$  between 7 and 2. They are not observed in the lithium germanate glass spectra. These features are most pronounced in the  $\text{K}_2\text{O} \cdot 3\text{GeO}_2$  glass spectrum but disappear at

$x = 2$ . They are still observed together with a weak shoulder at  $740 \text{ cm}^{-1}$  in the  $\text{Na}_2\text{O} \cdot 2\text{GeO}_2$  glass spectrum.

Spectra of the low-frequency region ( $0$  to  $200 \text{ cm}^{-1}$ ) consist of a broad continuum terminating at about  $50 \text{ cm}^{-1}$ . The spectra do not change much with the alkali content throughout the three series. The broad band at about  $50 \text{ cm}^{-1}$  is common to all glasses. It has been studied in detail in vitreous  $\text{SiO}_2$ ,  $\text{GeO}_2$  and  $\text{B}_2\text{O}_3$  [30–32]. It was shown that the band is due to a temperature-weighted density of states arising from low-lying optic modes.

### 3.2. Crystallization of glasses

Crystallized phases from the glasses at various temperatures were identified by both Raman spectroscopy and X-ray powder diffraction. Crystallized  $\text{K}_2\text{O} \cdot x\text{GeO}_2$  with  $x \leq 3$  is very hygroscopic and phase identification was done only by Raman spectroscopy. The results are tabulated in Tables I to III.

Crystallization of glass at subsolidus temperatures is very often non-equilibrium and biased by the structure of the parent glasses. Crystallization of quartz and cristobalite forms of  $\text{GeO}_2$  from the low alkali content glasses is a typical example. Owing to the non-equilibrium crystallization, particularly for the sodium and potassium germanate systems, more than one phase appeared even at the stoichiometric compositions. Potassium enneagermanate ( $\text{K}_4\text{Ge}_9\text{O}_{20}$ ) and sodium tetragermanate ( $\text{Na}_2\text{Ge}_4\text{O}_9$ ) crystallized metastably in wide composition ranges which cross over the composition of the stable phase,  $\text{K}_2\text{Ge}_4\text{O}_9$ , and  $\text{Na}_4\text{Ge}_9\text{O}_{20}$ , respectively. Another interesting result is the metastable crystallization of sodium digermanate. Sodium digermanate ( $\text{Na}_2\text{Ge}_2\text{O}_5$ ) is probably a metastable phase at all temperatures, and it only crystallized at  $490^\circ \text{C}$  with other stable and metastable phases.

Lithium germanate glasses, in contrast with the others, tend to crystallize into stable phases.

The trace of rutile  $\text{GeO}_2$  and  $\text{Li}_2\text{Ge}_7\text{O}_{15}$  found in the crystallized glasses at  $780^\circ \text{C}$  of  $\text{Li}_2\text{O} \cdot 7\text{GeO}_2$  and  $\text{Li}_2\text{O} \cdot 4\text{GeO}_2$ , respectively, may be due to slight differences in the actual glass compositions from the nominal compositions.

The results of crystallization experiments are particularly interesting when the Raman spectra of the crystallized glasses are compared with the glass spectra in the next section.

TABLE I Crystallization products of potassium germanate glasses

Conditions	Composition of glass					
	$K_2O \cdot 19GeO_2$	$K_2O \cdot 7GeO_2$ [ $K_2Ge_7O_{15}$ ]	$K_2O \cdot 4.5GeO_2$ [ $K_4Ge_9O_{20}$ ]	$K_2O \cdot 3GeO_4$	$K_2O \cdot 2GeO_2$ [ $K_2Ge_2O_5$ ]	$K_2O \cdot 1.5GeO_2$
810° C	Quartz <sup>1</sup>	$K_2Ge_7O_{15}$ <sup>4</sup>	$K_2Ge_4O_9$ <sup>6</sup>			
12 h	Rutile (s) <sup>2</sup>	$K_2Ge_4O_9$ (s)	$K_2Ge_7O_{15}$ (t)			
700° C	$K_2Ge_7O_{15}$ (s)			$K_2Ge_4O_9$ $K_2Ge_2O_5$	$K_2Ge_2O_5$ <sup>7</sup>	$K_2Ge_2O_5$ $K_2Ge_2O_5$ <sup>8</sup>
16 h						
600° C	Quartz	$K_4Ge_9O_{20}$ <sup>5</sup>	$K_4Ge_9O_{20}$ (s)	$K_2Ge_4O_9$ $K_4Ge_9O_{20}$ (s)		
22 h	Crist (s) <sup>3</sup>	$K_2Ge_4O_9$ (t)				
	$K_2Ge_7O_{15}$	$K_4Ge_9O_{20}$ (t)				

(t) trace; (s), small amount; Quartz,  $\alpha$ -Quartz form  $GeO_2$ ; Crist, Cristobalite form  $GeO_2$ ; Rutile, Rutile form  $GeO_2$ .

<sup>1</sup> Quartz  $GeO_2$ . A stable phase above 1033° C [33]. The crystal structure is known  $P3_221$ ;  $a = 4.987$ , and  $c = 5.652$  Å [34].

<sup>2</sup> Rutile  $GeO_2$ . A stable phase below 1033° C [33]. The crystal is known  $P4_2/mnm$ ;  $a = 4.395$  and  $c = 2.860$  Å [35].

<sup>3</sup> Cristobalite  $GeO_2$ . Probably metastable at all temperatures [36].

<sup>4</sup>  $K_2Ge_7O_{15}$  or  $K_2Ge_8O_{17}$ .  $K_2Ge_8O_{17}$  is reported as a stable phase in [10], but X-ray diffraction pattern is almost identical to that of  $K_2Ge_8O_{17}$  in [24, 25].  $K_2Ge_8O_{17}$  has five-fold co-ordinated Ge atoms in addition to four and six co-ordination.  $Pnam$ ;  $a = 13.37$ ,  $b = 13.37$ , and  $c = 8.85$  Å [24, 25].

<sup>5</sup>  $K_4Ge_9O_{20}$ . Probably metastable at all temperatures [10, 16] isotypical to  $Na_4Ge_9O_{20}$  [16].

<sup>6</sup>  $K_2Ge_4O_9$ . Probably a stable phase [10], the X-ray diffraction pattern of  $3K_2O \cdot 11GeO_2$  in [10] is identical to that of single-crystal  $K_2Ge_4O_9$  in [15]. The crystal structure is known and it has both four- and six-fold co-ordinated Ge atoms  $P\bar{3}c1$ ;  $a = 11.84$  and  $c = 9.80$  Å [23].

<sup>7</sup>  $K_2Ge_2O_5$ . A stable phase [10].

<sup>8</sup>  $K_2Ge_2O_5$ . Probably a stable phase. " $10K_2O \cdot 11GeO_2$  (?)” in [10] is probably  $K_2Ge_2O_5$ . No X-ray data are available.

TABLE II Crystallization products of sodium germanate glasses

Conditions	Composition of glass	$\text{Na}_2\text{O} \cdot 0.19\text{GeO}_2$	$\text{Na}_2\text{O} \cdot 0.7\text{GeO}_2$ [ $\text{Na}_2\text{Ge}_7\text{O}_{15}$ ]	$\text{Na}_2\text{O} \cdot 0.4 \cdot 5\text{GeO}_2$ [ $\text{Na}_4\text{Ge}_9\text{O}_{20}$ ]	$\text{Na}_2\text{O} \cdot 0.3\text{GeO}_2$	$\text{Na}_2 \cdot 2\text{GeO}_2$ [ $\text{Na}_2\text{Ge}_2\text{O}_5$ ]
890° C						
17 h						
730° C						
17 h	Quartz $\text{Na}_4\text{Ge}_9\text{O}_{20}$ (s) Rutile (t)		Quartz $\text{Na}_4\text{Ge}_9\text{O}_{20}$	$\text{Na}_4\text{Ge}_9\text{O}_{20}$ <sup>1</sup>	$\text{Na}_4\text{Ge}_9\text{O}_{20}$ $\text{Na}_2\text{GeO}_3$ (t)	$\text{Na}_2\text{GeO}_3$ <sup>4</sup> $\text{Na}_4\text{Ge}_9\text{O}_{20}$
600° C						
22 h	Quartz $\text{Na}_4\text{Ge}_9\text{O}_{20}$ (s) $\text{Na}_2\text{GeO}_4\text{O}_9$ (t) Glass		Quartz $\text{Na}_4\text{Ge}_9\text{O}_{20}$ $\text{Na}_2\text{Ge}_4\text{O}_9$ Glass	$\text{Na}_4\text{Ge}_9\text{O}_{20}$ $\text{Na}_2\text{Ge}_4\text{O}_9$ Glass	$\text{Na}_4\text{Ge}_9\text{O}_{20}$ $\text{Na}_2\text{Ge}_4\text{O}_9$ Glass	$\text{Na}_2\text{Ge}_4\text{O}_9$ $\text{Na}_2\text{GeO}_3$ $\text{Na}_4\text{Ge}_9\text{O}_{20}$
490° C						
41 h						

(t) trace; (s), small amount; Quartz,  $\alpha$ -Quartz form  $\text{GeO}_2$ ; Rutile, Rutile form  $\text{GeO}_2$ .

<sup>1</sup>  $\text{Na}_4\text{Ge}_9\text{O}_{20}$ . A stable phase [9, 16]. The crystal structure is known and it has both four- and six-fold co-ordinated Ge atoms  $14_1/a$ ;  $a = 14.98$  and  $c = 7.384$  Å [13] isotypical to  $\text{K}_4\text{Ge}_9\text{O}_{20}$  [16].

<sup>2</sup>  $\text{Na}_2\text{Ge}_4\text{O}_9$ . Probably metastable at all temperatures [9, 16]. Isostructural to  $\text{K}_2\text{Ge}_4\text{O}_9$  [14, 16].

<sup>3</sup>  $\text{Na}_2\text{Ge}_2\text{O}_5$ . Probably metastable at all temperatures. It is reported as a stable phase in [11], but non-existence of this phase is reported in [9].

<sup>4</sup>  $\text{Na}_2\text{GeO}_3$ . A stable phase [9]. The crystal structure is known and has  $(\text{GeO}_3)_2$  repeated chains.  $Cmc2_1$ ;  $a = 10.85$ ,  $b = 6.225$ ,  $c = 4.930$  Å [22].

TABLE III Crystallization product of lithium germanate glasses

Conditions	Composition of glass			
	$\text{Li}_2\text{O} \cdot 0.19\text{GeO}_2$	$\text{Li}_2\text{O} \cdot 0.7\text{GeO}_2$ [ $\text{Li}_2\text{Ge}_7\text{O}_{15}$ ]	$\text{Li}_2\text{O} \cdot 0.45\text{GeO}_2$ [ $\text{Li}_4\text{Ge}_9\text{O}_{20}$ ] <sup>2</sup>	$\text{Li}_2\text{O} \cdot 0.4\text{GeO}_2$ [ $\text{Li}_2\text{Ge}_4\text{O}_9$ ]
780° C 21 h	Quartz $\text{Li}_2\text{Ge}_7\text{O}_{15}$ Rutile (t)	$\text{Li}_2\text{Ge}_7\text{O}_{15}$ <sup>1</sup> Rutile (t)	$\text{Li}_2\text{Ge}_4\text{O}_9$ $\text{Li}_2\text{Ge}_7\text{O}_{15}$ (s)	$\text{Li}_2\text{Ge}_4\text{O}_9$ <sup>3</sup> $\text{Li}_2\text{Ge}_7\text{O}_{15}$ (t)
600° C 22 h	$\text{Li}_2\text{Ge}_7\text{O}_{15}$ Glass	$\text{Li}_2\text{Ge}_7\text{O}_{15}$ Rutile (t)	$\text{Li}_2\text{Ge}_4\text{O}_9$ $\text{Li}_2\text{Ge}_7\text{O}_{15}$ (s)	$\text{Li}_2\text{Ge}_4\text{O}_9$

(t) trace; (s), small amount; Quartz,  $\alpha$ -Quartz form  $\text{GeO}_2$ ; Rutile, Rutile form  $\text{GeO}_2$ .

<sup>1</sup>  $\text{Li}_2\text{Ge}_7\text{O}_{15}$ . A stable phase [8, 17]. The crystal structure is known and it has both four- and six-fold co-ordinated Ge atoms  $Pbcn$ ;  $a = 7.36$ ,  $b = 16.76$  and  $c = 9.69$  Å [20].

<sup>2</sup>  $\text{Li}_4\text{Ge}_9\text{O}_{20}$ . It is reported to crystallize from melt [17]. The crystal structure is known and it has both four- and six-fold co-ordinated Ge atoms  $C_2$ ;  $a = 12.43$ ,  $b = 8.00$ ,  $c = 7.49$  Å and  $\beta = 91.0^\circ$  [21] but the structure is quite different from  $\text{Na}_4\text{Ge}_9\text{O}_{20}$  [13].

<sup>3</sup>  $\text{Li}_2\text{Ge}_4\text{O}_9$ . It is not in the phase diagram of [8], but reported to crystallize from both glass and melt [17]. The crystal structure is known and it has both four- and six-fold co-ordinated Ge atoms  $Pcca$ ;  $a = 9.29$ ,  $b = 4.64$  and  $c = 15.76$  Å [19], but the structure is different from  $\text{K}_2\text{Ge}_4\text{O}_9$  [23].

There is substantial confusion in the literature [8–25] concerning the identities of crystalline phases and their thermodynamic stabilities. However, no attempt was made to establish the correct phase diagrams in this study and there remain many uncertainties (see footnotes to the tables).

### 3.3. Comparison of glass and crystal spectra

The Raman spectra of  $\text{GeO}_2$  glass and  $\text{K}_2\text{O} \cdot x\text{GeO}_2$  glasses are compared in Figs. 4 and 5 and the Raman spectra of other related crystals are shown in Fig. 6.

Short-range structures of glasses frequently resemble those of crystals, and vibrational spectra of glasses are often similar to crystal spectra, although fine features of crystal spectra are lost in glass spectra. Bands due to the low-lying optic modes of crystals become a continuum band in the low frequency range of glass spectra.

#### 3.3.1. The $\text{GeO}_2$ composition

There is a pronounced resemblance between the  $\text{GeO}_2$  glass spectrum and the spectrum of quartz-structure  $\text{GeO}_2$  crystal (Fig 4). The two very weak and broad bands of the glass spectrum at 986 and 864  $\text{cm}^{-1}$  correspond to the two groups of very weak bands of the crystal at around 970 and 870  $\text{cm}^{-1}$ . The most intense band of the glass spectrum at 418  $\text{cm}^{-1}$  corresponds to the most intense band of the crystal at 445  $\text{cm}^{-1}$ , and the broad shoulder between 500 and 600  $\text{cm}^{-1}$  in the glass spectrum corresponds to the weak bands of the crystal at 519, 585 and 597  $\text{cm}^{-1}$ . Several sharp bands of the crystal spectrum at frequencies below 300  $\text{cm}^{-1}$  become a continuum band in the glass spectrum. On the other hand, the spectrum of rutile-structure  $\text{GeO}_2$  (Fig. 6a), which has a very intense band at about 700  $\text{cm}^{-1}$ , has no resemblance to the glass spectrum at all.

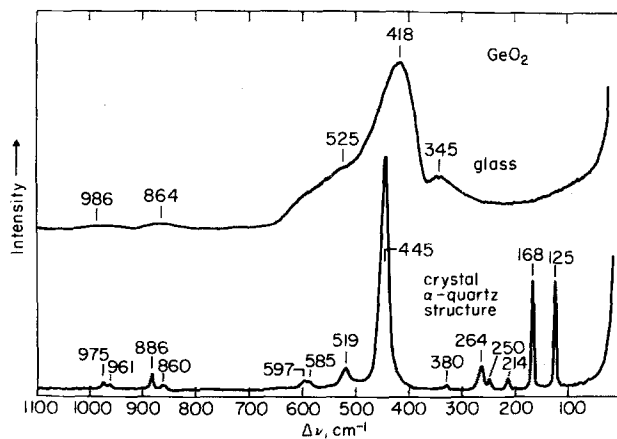
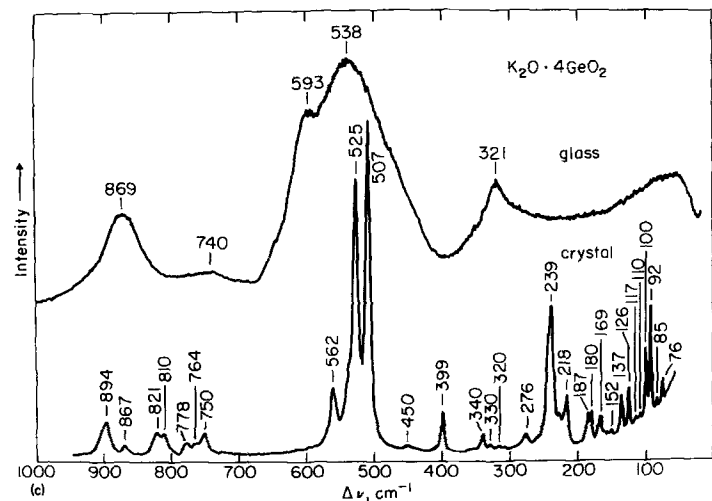
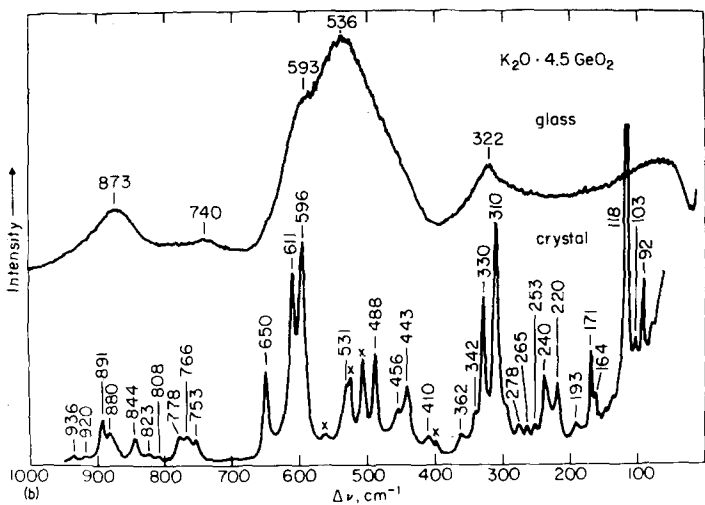
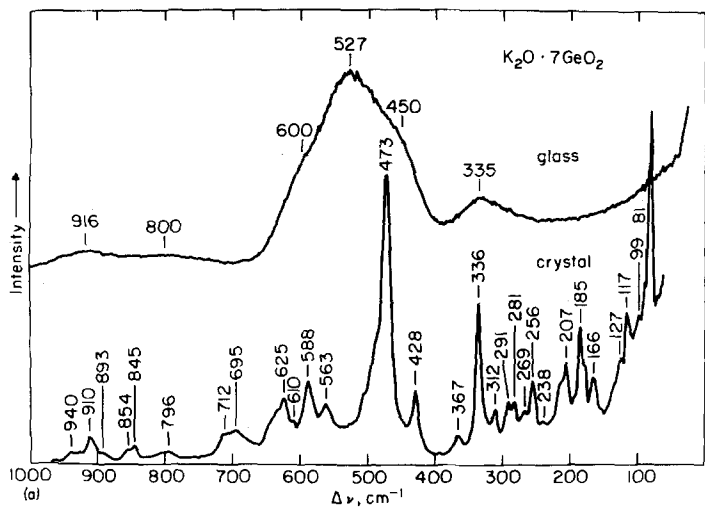


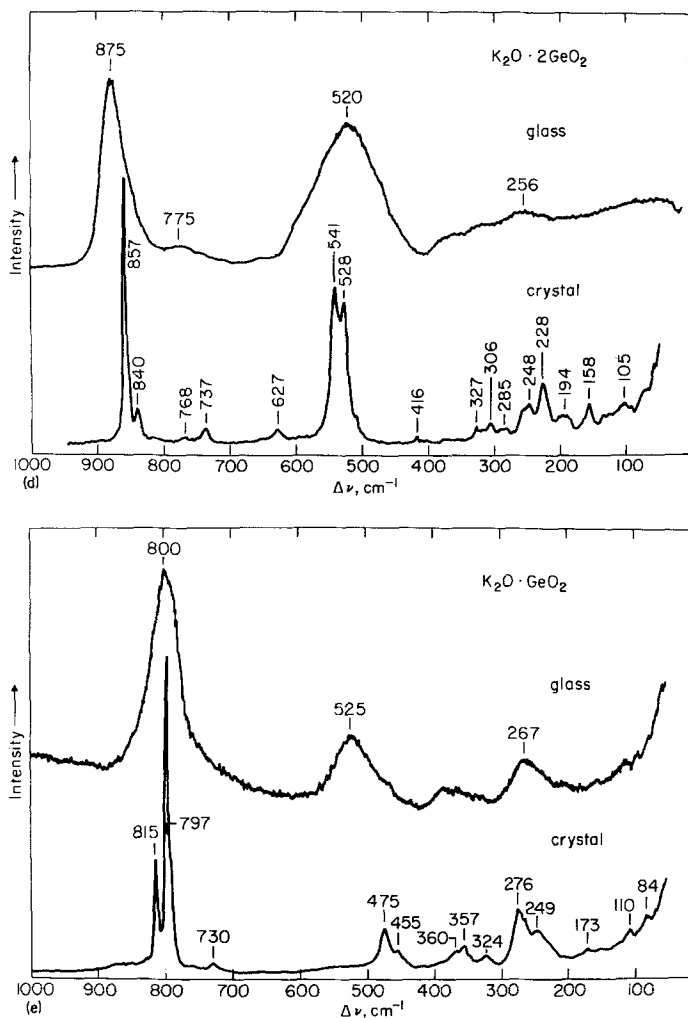
Figure 4 Comparison of spectrum of  $\text{GeO}_2$  glass and alpha-quartz structure  $\text{GeO}_2$  crystal.





**Figure 5** Comparison of spectra of  $K_2O \cdot xGeO_2$  glasses and spectra of crystals. (a) Comparison of spectrum of  $K_2O \cdot 7GeO_2$  glass with glass crystallized at  $600^\circ C$ . Essentially  $K_2Ge_7O_{15}$ ; traces of  $K_2Ge_4O_9$  and  $K_4Ge_9O_{20}$  are not detected by Raman. (b) Comparison of spectrum of  $K_2O \cdot 4.5GeO_2$  glasses with glass crystallized at  $600^\circ C$ . Mainly  $K_4Ge_9O_{20}$ . The bands marked x are due to  $K_2Ge_4O_9$ . (c) Comparison of spectrum of  $K_2O \cdot 4GeO_2$  glass with glass crystallized at  $810^\circ C$ . Spectrum is due to  $K_2Ge_2O_5$ . (e) Comparison of spectrum of  $K_2O \cdot GeO_2$  glass with  $K_2GeO_3$  crystal crystallized from the  $K_2O \cdot GeO_2$  melt.

Figure 5 continued.



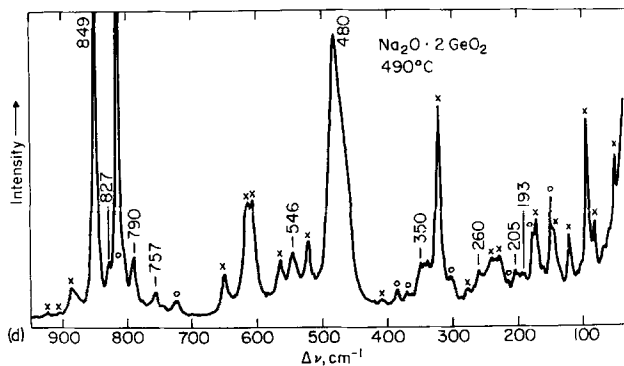
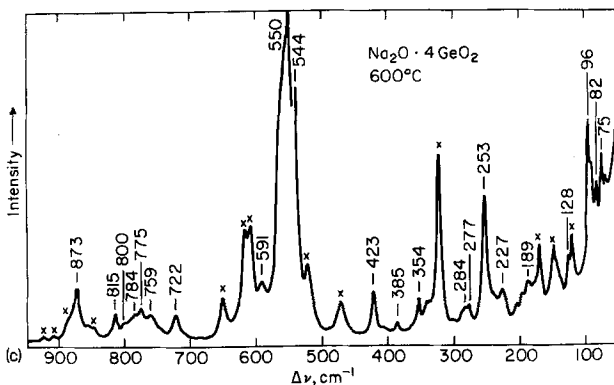
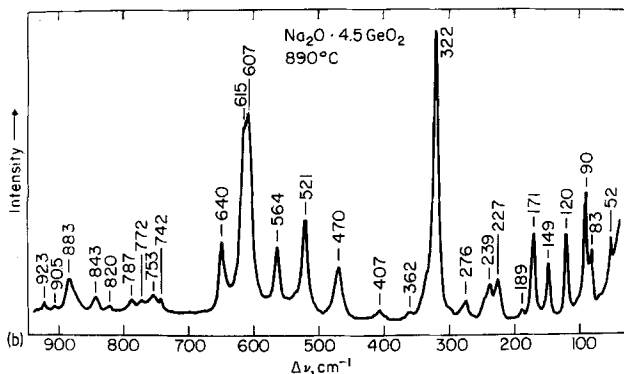
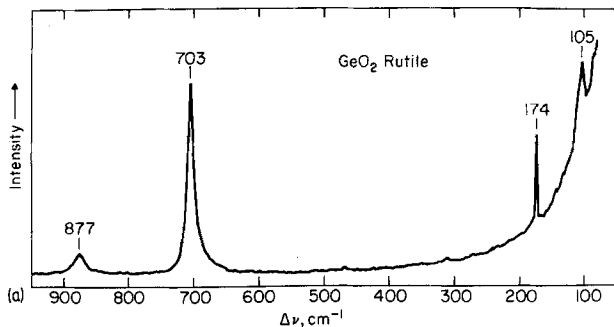
Symmetry assignments of the Raman bands of both rutile and quartz form  $GeO_2$  crystals have been made by Scott [37].

### 3.3.2. Low alkali oxide concentration region, $x \geq 3$

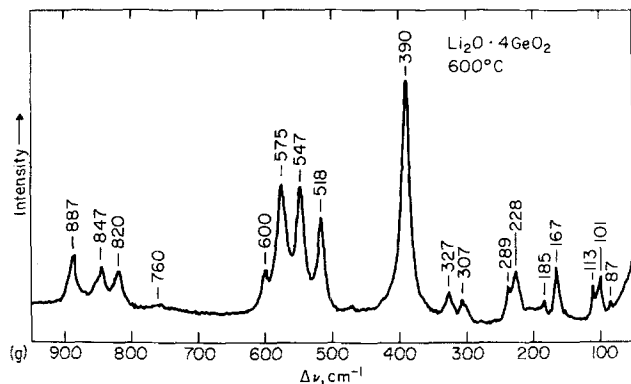
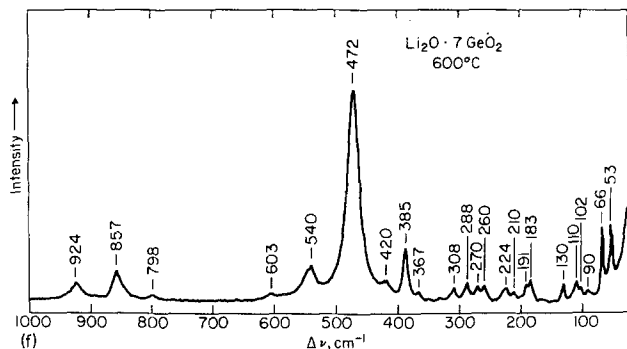
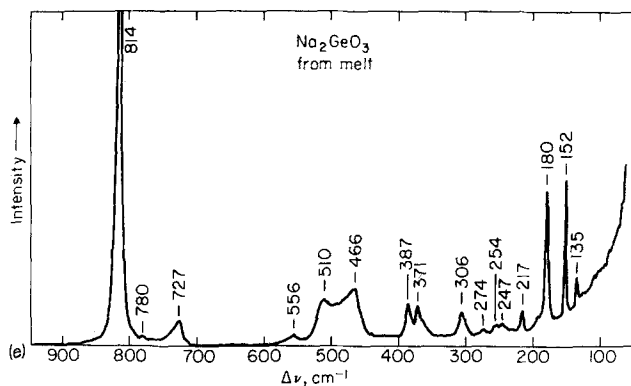
Several crystalline phases occur in this composition range in contrast with the silicate systems. However, none of the crystal spectra match with the glass spectra even at the stoichiometric compositions, although some general features are somewhat similar. The intense bands in the middle frequency region of the glass spectra consist of more than one broad band, but the frequency ranges of the bands occurring in the corresponding crystal spectra do not match with all the bands in the glass spectra. The glass spectra rather seem to comprise overlapped bands due to more than one structural units which may be found in the crystals.

Take the  $K_2O \cdot 4GeO_2$  composition as an example (Fig. 5c). The three bands at 507, 525, and 562 cm<sup>-1</sup> in the crystalline  $K_2Ge_4O_9$  spectrum correspond to the most intense band at 538 cm<sup>-1</sup> in the glass spectrum, but there are no bands in the crystal spectrum matching with the bands at 593 and 321 cm<sup>-1</sup> in the glass spectrum. These bands seem to match with the two groups of the bands at 611 and 596 cm<sup>-1</sup>, and at 330 and 310 cm<sup>-1</sup> in the crystalline  $K_4Ge_9O_{20}$  spectrum. It suggests that the  $K_2O \cdot 4GeO_2$  glass contains structures similar to the crystalline  $K_2Ge_4O_9$ , as well as the structures similar to crystalline  $K_4Ge_9O_{20}$ . Thus, metastable crystallization of the  $K_4Ge_9O_{20}$  crystal from the  $K_2O \cdot 4GeO_2$  glass is not so surprising.

In the potassium and sodium glass spectra of  $x = 4.5$  and 4, the intensity of the band at about 870 cm<sup>-1</sup> is appreciably greater than that of the group of bands around 870 cm<sup>-1</sup> in the crystal



**Figure 6** Raman spectra of other related crystals. (a) Rutile-structure  $\text{GeO}_2$  (b)  $\text{Na}_4\text{Ge}_9\text{O}_{20}$  crystallized from the  $\text{Na}_2\text{O} \cdot 4.5\text{GeO}_2$  glass at  $890^\circ\text{C}$ . (c)  $\text{Na}_2\text{Ge}_4\text{O}_9$  crystallized from the  $\text{Na}_2\text{O} \cdot 4\text{GeO}_2$  glass at  $600^\circ\text{C}$ . The bands marked x are due to  $\text{Na}_4\text{Ge}_9\text{O}_{20}$ . (d)  $\text{Na}_2\text{Ge}_2\text{O}_5$  crystallized from the  $\text{Na}_2\text{O} \cdot 2\text{GeO}_2$  glass at  $490^\circ\text{C}$ . The bands marked x and o are due to  $\text{Na}_4\text{Ge}_9\text{O}_{20}$  and  $\text{Na}_2\text{Ge}_3\text{O}_6$ , respectively. (e)  $\text{Na}_2\text{Ge}_3\text{O}_6$  crystallized from the  $\text{Na}_2\text{O} \cdot \text{GeO}_2$  melt. (f)  $\text{Li}_2\text{Ge}_7\text{O}_{15}$  crystallized from the  $\text{Li}_2\text{O} \cdot 7\text{GeO}_2$  glass at  $600^\circ\text{C}$ . (g)  $\text{Li}_2\text{Ge}_4\text{O}_9$  crystallized from  $\text{Li}_2\text{O} \cdot 4\text{GeO}_2$  glass at  $600^\circ\text{C}$ .



spectra. This is probably due to the existence of a small number of non-bridging oxygens in these glasses. There are no non-bridging oxygens in the crystals.

### 3.3.3. High alkali oxide concentration region, $x \geq 2$

The Raman spectra of both digermanate ( $x = 2$ ) and metagermanate ( $x = 1$ ) crystals are quite different from those of the low alkali content crystals, and they have a very intense high-frequency band. They are analogous to the spectra of alkali di- and metasilicate crystals [1, 2]. There is a pronounced resemblance between the glass and the

crystal spectrum at both the di- and the metagermanate compositions, as is also the case for the alkali silicate systems [1, 2]. Thus, by analogy to the alkali silicate glasses, the intense band of the digermanate glass spectrum at about  $850 \text{ cm}^{-1}$  is attributed to the stretching mode of  $\text{Ge}-\text{O}^-$  (non-bridging oxygen) of  $(\text{Ge}_2\text{O}_5)_n$  structure and the intense band of the metagermanate glass at about  $800 \text{ cm}^{-1}$  to the stretching mode of  $\text{Ge}-\text{O}^-$  of  $(\text{GeO}_3)_n$  chain structure.

There are extra features observed in the  $\text{Na}_2\text{O} \cdot 2\text{GeO}_2$  glass spectrum. Weak but still noticeable bands or shoulders at  $740$ ,  $600$  and  $325 \text{ cm}^{-1}$  probably indicate that the glass still contains in

small part some structure similar to the crystalline  $\text{Na}_4\text{Ge}_9\text{O}_{20}$ . This is interesting because  $\text{Na}_2\text{Ge}_2\text{O}_5$  crystal is probably metastable at all temperatures and it crystallizes from the glass only at low temperatures with  $\text{Na}_4\text{Ge}_9\text{O}_{20}$  and  $\text{Na}_2\text{GeO}_3$ , which are presumably the stable phases.

#### 4. Discussion and conclusions

The results of the present study in general agree with the structural model based on physical property measurements [4, 5]. The structures of low alkali content glasses are unique to the germanates, while the structures of high alkali content glasses are analogous to those of the silicate glasses.

##### 4.1. $\text{GeO}_2$ glass

The pronounced similarity between the glass spectrum and the  $\text{GeO}_2$ -quartz crystal spectrum, and metastable crystallization of quartz-form  $\text{GeO}_2$  from the glass indicate that  $\text{GeO}_2$  glass consists of  $\text{GeO}_4$  tetrahedra which are probably arranged in short-range structures similar to the structure of quartz form crystalline  $\text{GeO}_2$ . The short-range structures similar to those in the cristobalite form of crystalline  $\text{GeO}_2$  may possibly exist but the Raman spectrum of the crystal was not available for comparison. The low intensity of the high-frequency bands of both the glass spectrum and the quartz form crystal spectrum seems to be characteristic of the spectra of polymerized complex ions without non-bridging oxygens. The high-frequency bands are probably due to antisymmetrical Ge—O—Ge stretching modes which give rise to strong infra-red absorption bands but weak Raman scatterings. Germanium dioxide glass and quartz form crystal have strong infra-red absorption bands in the high-frequency region [5]. Materials such as  $\text{SiO}_2$  glass [32, 38],  $\text{SiO}_2$  crystalline polymorphs [39–44], and  $\text{B}_2\text{O}_3$  glass [44–47] exhibit weak Raman scatterings but strong infra-red absorption in the high-frequency region: 1000 to 1200  $\text{cm}^{-1}$  for  $\text{SiO}_2$  and 1200 to 1600  $\text{cm}^{-1}$  for  $\text{B}_2\text{O}_3$ .

##### 4.2. Low alkali content glasses, $x \geq 3$

Comparisons of glass and crystal spectra indicate that the structures of the glasses in this composition range are more complex than that of  $\text{GeO}_2$  glass and consist of more than one structure even at the stoichiometric compositions. The glass spectra seem to be comprised of overlapping bands

of the different vibrating structural units. This is perhaps one of the reasons why more than one phase crystallizes metastably from the glasses even at the stoichiometric compositions. There is no evidence that the glasses are actually phase separated, although the possibility cannot be ruled out entirely.

There is only indirect spectroscopic evidence for the existence of six or five co-ordinated germanium atoms either in the crystals or in the glasses. Frequencies of the bands in the high-frequency region decrease as the alkali content increases. This may be due to decreases of the average force constants of Ge—O—Ge stretching modes by increasing the higher co-ordinated germanium atoms.

Low intensities of the high-frequency bands of the glass spectra at  $x \geq 7$  indicates absence of non-bridging oxygens in these glasses. This is somewhat analogous to alkali borate glasses, where the co-ordination number of boron changes from 3 to 4 by addition of alkali oxide to  $\text{B}_2\text{O}_3$  glass without forming non-bridging oxygens, and the high-frequency Raman bands 1200 to 1600  $\text{cm}^{-1}$  are weak [45, 46].

On the other hand, the appearance of the 870  $\text{cm}^{-1}$  band in the glass spectra indicates formation of non-bridging oxygens. The band at about 870  $\text{cm}^{-1}$  in the spectra of the potassium and sodium glasses of  $x = 4.5$  and  $x = 4$  is more intense than the bands in the same frequency region of the corresponding crystal spectrum. These crystals do not have non-bridging oxygens.

The 870  $\text{cm}^{-1}$  band increases in intensity drastically without significant frequency shift by further increase of the alkali content and becomes the characteristic band of the digermanate glass spectrum at  $x = 2$ . Therefore, this band is attributed to the Ge—O<sup>-</sup> (non-bridging oxygen) stretchings or one of the stretching modes of the  $[\text{GeO}_4]$  tetrahedron with one non-bridging oxygen. Thus, in the potassium and the sodium glasses of  $x = 4.5$  and  $x = 4$  a small number of non-bridging oxygens are already formed, while in the lithium glass spectra the 870  $\text{cm}^{-1}$  band does not appear even at  $x = 4$ . The alkali germanate crystals of  $x \geq 4$  have both 4 and 6 (sometimes also 5) co-ordinated germanium atoms and the number of the latter increases without forming non-bridging oxygens as the alkali content increases [13, 19–21, 23–25]. In consequence, the crystals have the highest density at  $x = 4$  for the

potassium and the sodium germanate system [16, 18] and at  $x = 4.5$  for the lithium germanate system [17, 48]. For the glasses, on the other hand, the composition at which the maximum density occurs depends very much on the alkali oxides [5]. It shifts to lower alkali concentrations in the following sequence: at  $x$  about 4 for the lithium glass, at  $x = 5.7$  to 4.5 for the sodium glass and at  $x = 9$  to 6 for the potassium glass. Formation of non-bridging oxygens in the potassium and the sodium glasses of  $x \geq 4$  is probably responsible for the shift of the maximum to lower alkali concentrations than for the crystals.

#### 4.3. High alkali content glasses, $1 \leq x \leq 2$

In the digermanate glass ( $x = 2$ ), germanium atoms are tetrahedrally co-ordinated by oxygens and three corners of the tetrahedron are shared with three other tetrahedra leaving one non-bridging oxygen to form  $(\text{Ge}_2\text{O}_5)_n$  ( $n$  is not a defined number here). It gives rise to the characteristic high-frequency Raman band at about  $870 \text{ cm}^{-1}$  similar to the  $1000 \text{ cm}^{-1}$  band of the silicate glasses. The width of the  $870 \text{ cm}^{-1}$  band at half height of the potassium ( $48 \text{ cm}^{-1}$ ) and the sodium ( $78 \text{ cm}^{-1}$ ) digermanate glass is almost equal to the band width of the corresponding disilicate glass ( $50$  and  $70 \text{ cm}^{-1}$ , respectively). The band width is correlated with disorder of the Si-O and the Ge-O network [1-3]. Thus, the Ge-O network in the sodium digermanate glass is more disordered than that of the potassium glass. The potassium digermanate glass consists solely of disordered  $(\text{Ge}_2\text{O}_5)_n$  structures, but the sodium digermanate glass still contains the low alkali content glass structure in a small portion.

With a further increase of alkali content the number of the  $[\text{GeO}_4]$  tetrahedra of two non-bridging oxygens increases and intensity of the  $780 \text{ cm}^{-1}$  increases relative to that of the  $870 \text{ cm}^{-1}$  band. Finally, at  $x = 1$ , the glass is composed of disordered  $(\text{GeO}_3)_n$  chain structures which gives rise to an intense band at  $800 \text{ cm}^{-1}$ .

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