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Infra-red transmitting glass-ceramics of the As–Ge–Se system nucleated by zirconium selenide

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The aim of this study was to produce an infra-red transmitting chalcogenide glass-ceramic nucleated by an appropriate nucleant. In order to crystallize chalcogenide glasses in a controlled manner a preliminary series of experiments, in which the metals of group IVB of the periodic table of elements were used as nucleants, showed that zirconium is an effective additive. Studies of glass compositions $x\mathrm{ZrSe_2}-(100-x)[\mathrm{As_{0.1}Ge_{0.3}Se_{0.6}}]$ indicated that for values of x 0.25 and 0.50 mol%, glass-ceramics with high thermomechanical properties were produced. By heat treating at 400° C for 15 h, the glass $As_{0.1}Ge_{0.3}Se_{0.6}$ with 0.25 mol% $ZrSe_2$ was transformed into a glass-ceramic with a fracture toughness of 0.848 MN $m^{-3/2}$, a sag point of 530° C and satisfactory infra-red transmission. X-ray diffraction analysis revealed that the precipitated crystal phase was germanium selenide ($GeSe_2$). The parasite absorption band with a maximum around 800 cm^{-1} generally present in the infra-red spectra was eliminated by adding 0.1 wt% metallic zirconium. The infra-red transmision and thermomechanical properties for glass-ceramics of compositions with 0.50 mol% $ZrSe_2$ were poorer than for those with 0.25 mol% $ZrSe_2$, for the same heat treatment condtions. The kinetics and activation energies of crystallization were studied by means of electron microscopy. The mechanism of controlled crystallization proceeds by the precipitation of crystalline $GeSe_2$ on the $ZrSe_2$ nuclei formed by heat treatment of the initial chalcogenide glass supersaturated in $ZrSe_2$.

1. Introduction

It is well-known that chalcogenide glasses with weak bonds between larger atoms are good infra-red (i.r.) transmitting materials. To enlarge their domain of application it is necessary to increase their softening temperature and mechanical strength. Since 1960 an increasing number of compositions have been reported [1–14]. Attempts to improve the mechanical properties and increase the sag-point are often undertaken simply by changing compositions. At present there are few chalcogenide glasses which have softening temperatures above 500° C. However, if these glasses could be converted into glass-ceramics of small grain size, using an appropriate nucleant and heat-treatment cycle for controlled crystallization, it should be possible to increase the softening temperature with little effect on the infra-red transmission properties. The purpose of this study was to produce an As–Ge–Se system glass-ceramic with improved thermomechanical properties and with infra-red transmitting properties comparable to those of the glass before the controlled crystallization.

The problems associated with the controlled crystallization of oxide glasses have already been extensively studied whereas little work has been conducted in the field of non-oxide glasses. For

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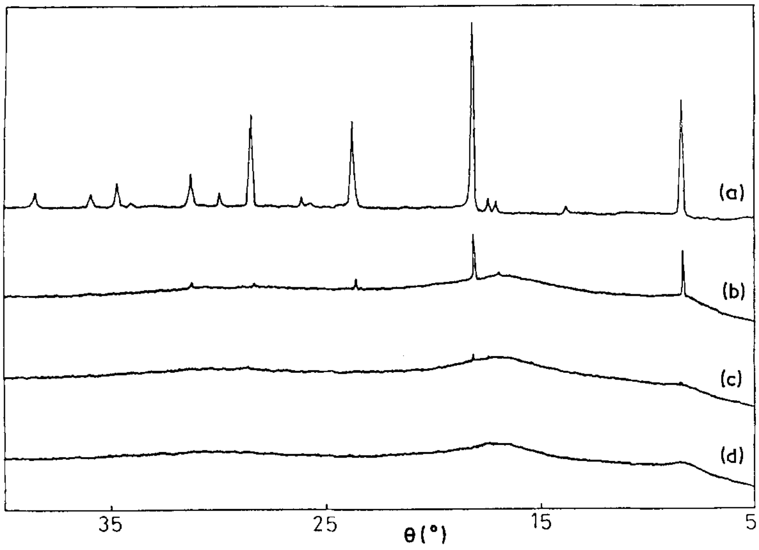

Figure 1 X-ray diffraction spectra: (a) synthesized $ZrSe_2$, (b) glasses with 10 mol% $ZrSe_2$, (c) glass with 1 mol% $ZrSe_2$ and (d) glass with 0.5 mol% $ZrSe_2$ before heat treatment.

this reason research on the controlled crystallization of chalcogenide glasses is also important from a fundamental stand-point.

2. Experimental procedure

2.1. Composition

For the present investigation, on the basis of the earlier studies [6, 9], a chalcogenide glass of composition $As_{0.1}Ge_{0.3}Se_{0.6}$ was selected firstly because it has a sufficiently high sag-point (420° C) and a good infra-red transmittance to about 12 μm, and secondly because of its relatively low rate of divitrification. Without nucleant this glass does not present volume crystallization. In the preliminary experiments zirconium was selected as nucleant due to its high field strength.

A series of compositions $x\mathrm{ZrSe_2}-(100-x)$ $[As_{0.1}Ge_{0.3}Se_{0.6}]$ was selected with $x = 0.25$, 0.5, 1, 5, or 10 mol%. Compositions with $x \geqslant 1$ mol%, obtained by melting and crystallizing rapidly during quenching in air, are unsuitable for infrared transmission. X-ray diffraction spectra of chalcogenide glasses with different $ZrSe_2$ contents and of synthesized $ZrSe_2$ are shown in Fig. 1. It is obvious that the crystalline phase in these glasses is zirconium selenide. Infra-red transmission is bound to the formation of large $ZrSe_2$ crystals. Further investigation was therefore concentrated on compositions with $x = 0.25$ and 0.50 mol%.

2.2. Preparation

Glass samples were prepared by melting the appropriate amounts of the elements in evacuated sealed silica glass ampoules of 30 ml volume at 850° C for 24 h, placing them in a rocking furnace to ensure adequate mixing, and then quenching the melts in air. The glasses were synthesized from high-purity starting materials to minimize parasite absorption due to oxide impurities. Annealing and heat treating for controlled crystallization were carried out in a horizontal furnace at selected temperatures. After cooling to room temperature the ampoules were carefully broken to extract the glass. The glass samples were examined by optical microscopy and X-ray diffraction analysis.

2.3. Mechanical properties

2.3.1. Fracture toughness and fracture surface energy.

The fracture toughnesses, K_{IC}, of the glasses and the resulting glass-ceramics were determined by a three-point loading technique according to the notched beam test [15]. A three-point bending jig with a 28 mm span between the outer knife edges was used on an Instron universal testing machine, model 1196, operating at room temperature. Five specimens were used on average for each toughness measurement.

The fracture surface energy, γ, was calculated from the formula:

$$\gamma = \frac{K_{IC}^2}{2E}, \qquad (1)$$

where E is the Young's modulus, equal to 1.75×10^{10} Nm^{-2} [16].

2.3.2. Microhardness

The microhardnesses of the glasses and the resulting glass-ceramics were measured using the Vickers diamond pyramid test. More than ten indentations were made for each specimen with a 15 sec loading time at a maximum load of 25 or 50 g.

2.4. Sag-point

The sag-point provides an estimate of the temperature at which a glass deforms under its own weight. In the present work, the method of Savage and Nielsen [2] was used, with 12 mm x 1 mm x 1 mm samples. The temperature of the furnace was increased at the rate of 2 to 3° C min^{-1} until the glass sample started to sag under its own weight. The corresponding temperature was measured by means of a thermocouple adjacent to the specimen.

2.5. Thermal expansion

The thermal expansions of the glasses and glass-ceramics were measured using an electronic dilatometer DI 10 model 2. This consisted of a fused silica specimen holder and a linear variable differential transformer (LVDT) which produced an electrical signal proportional to the displacement of the core. Samples 14 mm in length were used. The transformation temperature, T_g, and the diatometric softening temperature, T_D, were also determined from the trace.

2.6. Infra-red transmission

Samples of approximately 3 mm in thickness were polished on both sides using cerium oxide powder. Infra-red transmission spectra of the glasses and glass-ceramics were recorded on a Perkin–Elmer 517 spectrometer.

2.7. Electron microscopy

Electron microscopy studies were carried out using single-stage carbon replicas. Crystal size measurements were obtained from statistics compiled from several electron micrographs.

2.8. X-ray diffraction

The identification of glass formation or crystallized phases was made using an X-ray diffractometer with CoKα radiation.

3. Results and discussion

3.1. Mechanical properties

3.1.1. Fracture toughness and fracture surface energy

The fracture toughness data of glasses and glass-ceramics are shown in Table I. As can be seen, there is nearly a 3.5 times increase in fracture toughness and a 12 times increase in fracture surface energy for glass with addition of 0.25 mol% $ZrSe_2$ after heat treatment at 400° C for 15 h. Further extended heat treatment does not result in a further increase of the fracture toughness. However, for a glass with 0.50 mol% $ZrSe_2$ the maximum fracture toughness is obtained after heat treatment for 24 h. This is evidently less than that of glass nucleated by 0.25 mol% $ZrSe_2$. The effective increase of fracture toughness is probably due to superposed, entangled germanium selenide crystals in orthohombic form. The existence of large crystals does not favour the formation of a microstructure with high fracture toughness, which is why glass with a higher content of $ZrSe_2$ (0.50 mol%) has a fracture toughness less than that of glass with 0.25 Mol% $ZrSe_2$. As will be shown later, in glasses with 0.50 mol% $ZrSe_2$ even air-quenched precipitation of tetragonal $ZrSe_2$ crystals occurs, leading to the formation of large $GeSe_2$ crystals.

3.1.2. Microhardness

Microhardness measurements were performed on

TABLE I Fracture toughness and fracture energy of glasses and glass-ceramics

Sample number	$ZrSe_2$ content (mol%)	Heat treatment temperature (°C)	Duration of heat treatment (h)	Fracture toughness, K_{IC} ($\text{MN m}^{-3/2}$)	Fracture energy (N m^{-1})
1	0	–	–	0.286	2.4
2	0.25	–	–	0.246	1.7
3	0.25	400	15	0.848	20.6
4	0.25	400	24	0.845	20.4
5	0.50	–	–	0.289	2.5
6	0.50	400	15	0.308	2.7
7	0.50	400	24	0.762	16.6

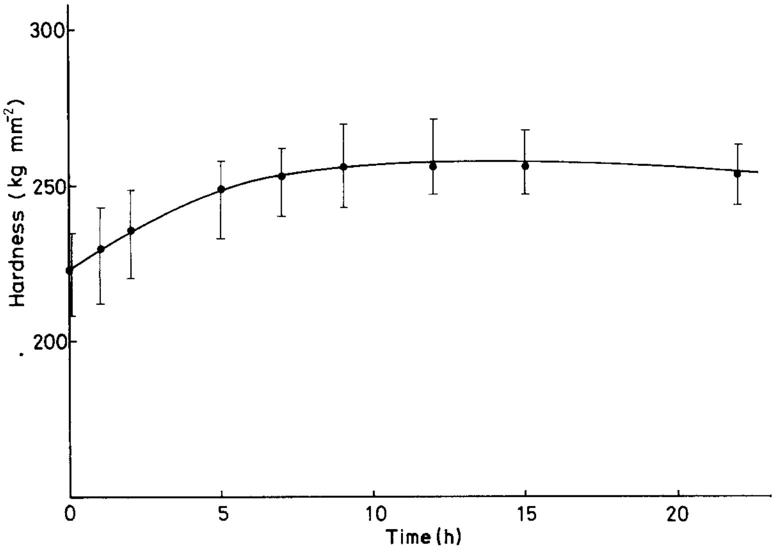

Figure 2 Vickers microhardness as a function of heat treatment time.

glasses before and after various heat treatments. Fig. 2 shows the results of hardness measurements on glasses and glass-ceramics, subjected to heat treatments for up to 24 h at 400° C. Two observations can be made:

(a) The microhardness reaches a maximum after heat treatment for 12 h at 400° C. As expected the increase is due to the formation of $GeSe_2$ microcrystals, clearly revealed by electron microscopy.

(b) After heat treatment for 12 h at 400° C the microhardness remains almost constant, which means that it is no longer affected by crystal size. On the contrary, after heat treatment for 15 h the microhardness of chalcogenide glass-ceramics shows a tendency to decrease.

3.2. Sag-point and dilatometric softening temperature

Since, in the glass As–Ge–Se arsenic and germanium form strong covalent bonds with selenium the system has a relatively high softening temperature. Before heat treatment the sag-point is not sensitive to the addition of 0.25 and 0.50 mol% $ZrSe_2$ in the composition (see Table II). The sag-point of glasses remains practically constant around 420° C. After heat treatment at 400° C the sag-point is increased to 530° C, i.e., the controlled crystallization gains 110° C in softening temperature. The increase of sag-point is due to the formation of $GeSe_2$ crystals.

The transformation temperatures, T_g, and dilatometric softening points, T_D, of glasses of different compositions before and after heat treatment are indicated in Table III. As might be expected, the base glass and glasses containing from 0.25 to 0.50 mol% $ZrSe_2$ have almost the same transformation temperature. Because of differences in crystallinity, the T_D values show different trends. Generally, the higher the degree of crystallinity, the higher the T_D value.

When the thermal expansion runs were conduc-

TABLE II Sag-point of glasses and glass-ceramics

Sample number	$ZrSe_2$ content (mol%)	Heat treatment temperature (°C)	Duration of heat treatment (h)	Sag-point (°C)
1	0	–	–	420
2	0.25	–	–	422
3	0.25	400	15	530
4	0.25	400	24	532
5	0.50	–	–	424
6	0.50	400	15	531
7	0.50	400	24	532

TABLE III Transformation and dilatometric softening temperatures of glasses and glass-ceramics

Sample number	$ZrSe_2$ content, x (mol%) and heat treatment	Transformation temperature (°C)	Dilatometric softening temperature (°C)
1	$x = 0$, glass of basic composition; without heat treatment	353	381
2	$x = 0.25$; without heat treatment	352	380
3	$x = 0.25$, after 15 h of heat treatment at 400° C (1st scan)	347	446
4	$x = 0.25$; after 15 h of heat treatment at 400° C (2nd scan)	330	473
5	$x = 0.25$; after 15 h of heat treatment at 400° C (3rd scan)	331	473
6	$x = 0.25$; after 24 h of heat treatment at 400° C	340	452
7	$x = 0.50$; without heat treatment	352	381
8	$x = 0.50$; after 15 h of heat treatment at 400° C	351	387
9	$x = 0.50$; after 24 h of heat treatment at 400° C	352	440

ted on glasses with 0.25 mol% $ZrSe_2$ preheated at 400° C for 15 h, a plateau at the dilatometric softening point was observed after the first scan (Fig. 3). This effect can be caused by the equilibrium of continuous crystallization of $GeSe_2$ and the softening of the glass phase. After the second scan, because almost the maximum degree of crystallinity has been attained, there is no further change in T_g or T_D. A temperature range of almost 60° C between the dilatometric softening temperature and the sag-point is observed so that the glass may not be considered as very "short".

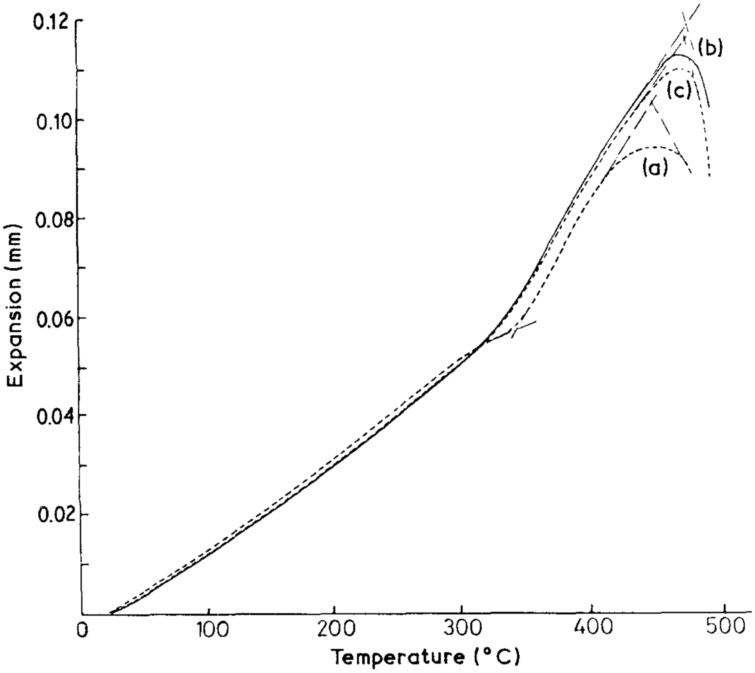

Figure 3 Expansion curve of $As_{0.1}Ge_{0.3}Se_{0.6}$ glass with 0.25 mol% $ZrSe_2$ pre-treated at 400° C for 15 h (a) 1st scan, (b) 2nd scan and (c) 3rd scan.

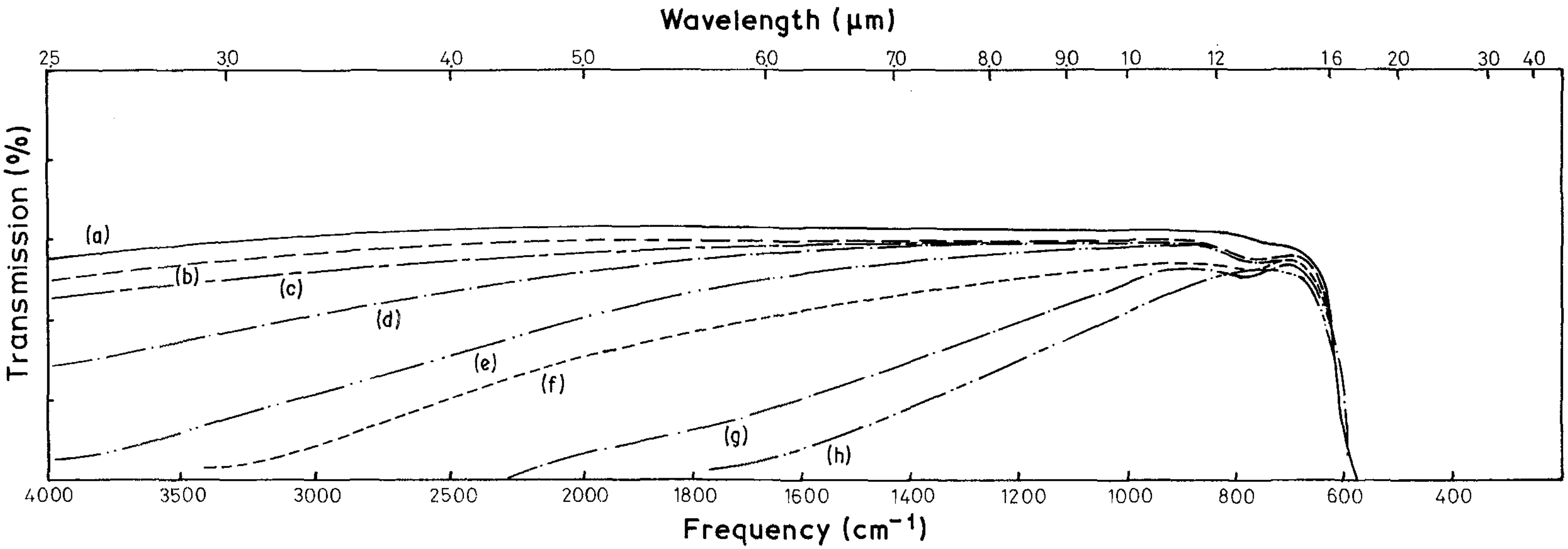

Figure 4 Infra-red transmission spectra for $As_{0.1}Ge_{0.3}Sc_{0.6}$ glass with 0.25 mol% $ZrSe_2$, heat treated at 400° C for (a) 0 h, (b) 2 h, (c) 5 h, (d) 7 h, (e) 9 h, (f) 12 h, (g) 15 h and (h) 24 h and then air-quenched. Thickness of samples: 3 mm.

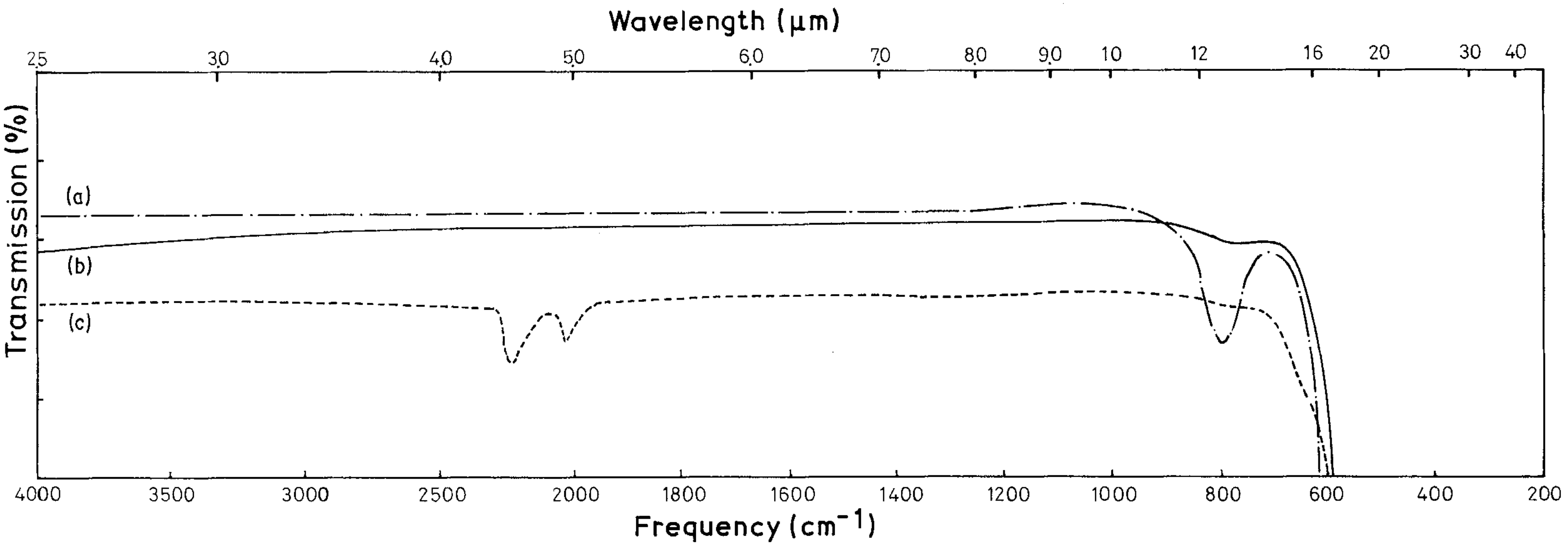

Figure 5 Infra-red transmission spectra for $As_{0.1}Ge_{0.3}Se_{0.6}$ glass (a) without addition, (b) with addition of 0.1 wt% metallic zirconium and (c) with addition of 0.3×10^{-2} wt% paraffin. Thickness of samples: 3 mm.

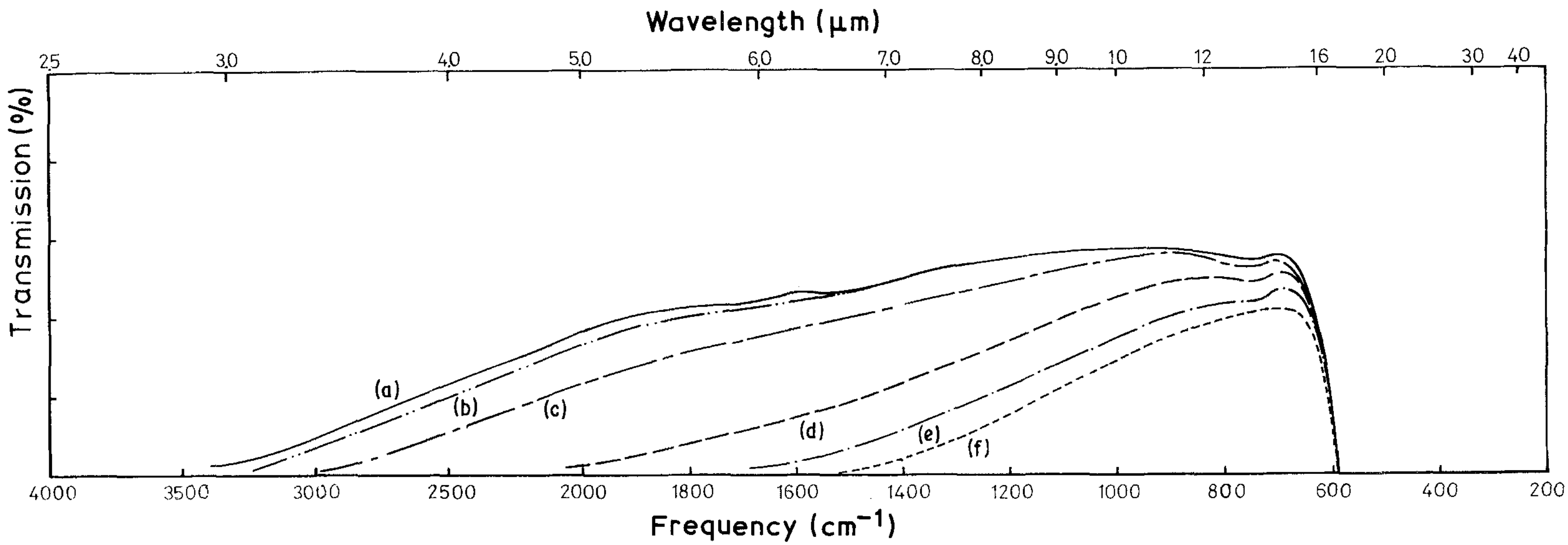

Figure 6 Infra-red transmission spectra for $As_{0.1}Ge_{0.3}Se_{0.6}$ glass with 0.50 mol% $ZrSe_2$ addition, heat treated at 400° C for (a) 0 h, (b) 5 h, (c) 10 h, (d) 15 h, (e) 20 h and (f) 24 h and then air-quenched. Thickness of samples: 3 mm.

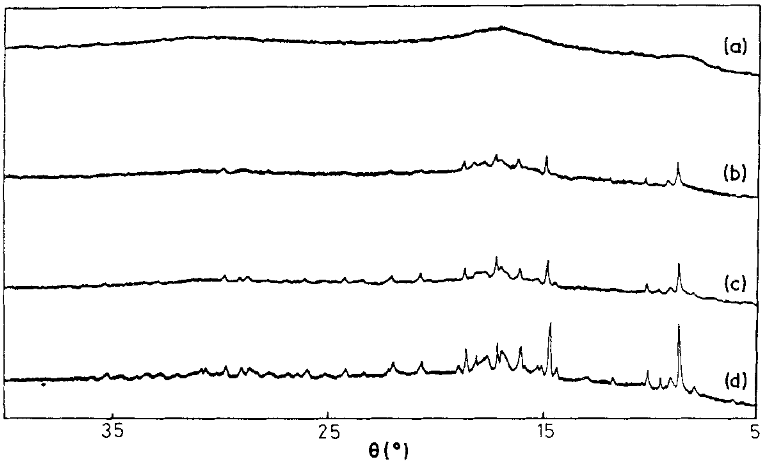

Figure 7 X-ray diffraction spectra for $As_{0.1}Ge_{0.3}Se_{0.6}$ glass with 0.25 mol% $ZrSe_2$ addition, heat treated at 400° C for (a) 5 h, (b) 15 h, (c) 24 h and (d) 74 h.

3.3. Infra-red transmission

Fig. 4 shows the infra-red transmission spectra of $As_{0.1}Ge_{0.3}Se_{0.6}$ glass-ceramics containing 0.25 mol% $ZrSe_2$ as a function of the heat treatment time at 400° C. The glass samples of 3 mm thickness without heat treatment have an i.r. transmission of 62% for wavelengths between 8 and 16 μm. On the short wavelength side, for the glasses after various times of heat treatment, the i.r. transmission spectra show an approximately linear decrease. It is evident that the region of gradually decreasing transmission is due to light scattering from the particles of crystal phase $ZeSe_2$ and particularly $GeSe_2$. It should perhaps be emphasized that the degree of scattering is strongly dependent on crystal size and the maximum scattering occurs for a crystal size of the same order of magnitude as the radiation wavelength. For crystal sizes much smaller than the wavelength of the incident radiation, scattering increases with crystal size and is inversely proportional to the fourth power of wavelength. Experimentally, according to our crystal-size measurements and i.r. transmission spectra studies, a particle size less than 1.1 μm is recommended to obtain a satisfactory i.r. transmission between wavelengths of 8 and 16 μm.

The parasite absorption band with a maximum around 800 cm^{-1}, probably due to the Ge–O stretching mode, was remarkably diminished by adding 0.1 wt% metallic zirconium retaining oxygen. Fig. 5 shows the i.r. transmission spectrum of basic glass $As_{0.1}Ge_{0.3}Se_{0.6}$ and those of glasses to which has been added 0.1 wt% metallic zirconium of 0.3×10^{-2} wt% paraffin, After the addition of paraffin the parasite absorption band at 800 cm^{-1} disappeared almost completely, but new impurity bands were observed at around 2250

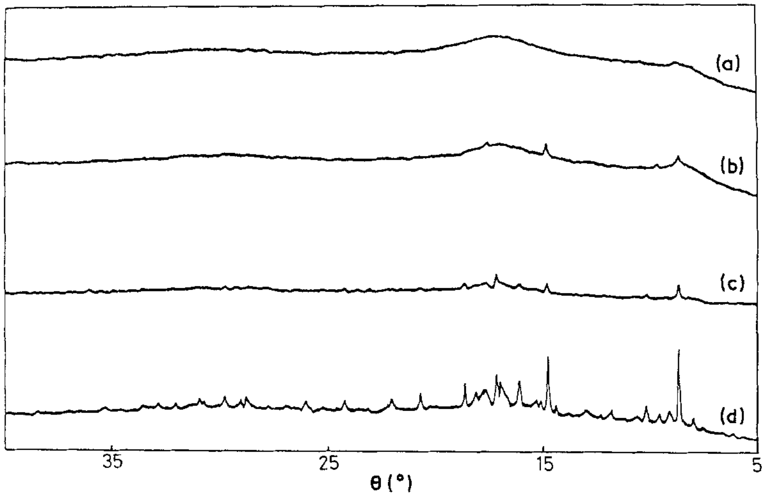

Figure 8 X-ray diffraction spectra for $As_{0.1}Ge_{0.3}Se_{0.6}$ glass with 0.50 mol% $ZrSe_2$ addition, heat treated at 400° C for (a) 5 h, (b) 15 h, (c) 24 h and (d) 64 h.

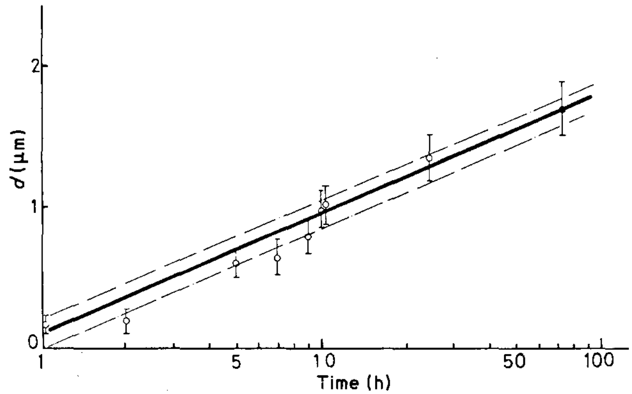

Figure 9 Crystal size, d, plotted against logarithm of heat-treatment time.

and 2000 cm^{-1} due to carbon and H_2Se, and the overall transmission diminished. On the contrary, the addition of 0.1 wt% metallic zirconium has no particular effect on i.r. transmission; at the same time, it is observed that the parasite absorption band at 800 cm^{-1} almost disappears and, on the long wave side, i.r. transmission is maintained up to a wavelength of 16 μm.

As noted earlier, i.r. transperency loss on the short wavelength side occurs as a function of heat-treatment time. According to Fig. 4, after heat treatment for 12 to 15 h, the i.r. transmission of glass-ceramics in the 8 to 16 μm region still reaches 52.0 to 49.5%.

Infra-red transmission of glass-ceramics with 0.50 mol% $ZrSe_2$ (Fig. 6) is poorer than that of glass-ceramics with 0.25 mol% $ZrSe_2$ for the same heat treatment conditions.

3.4. Kinetics and the mechanism of crystallization

The method of heat treatment at a fixed tempera-

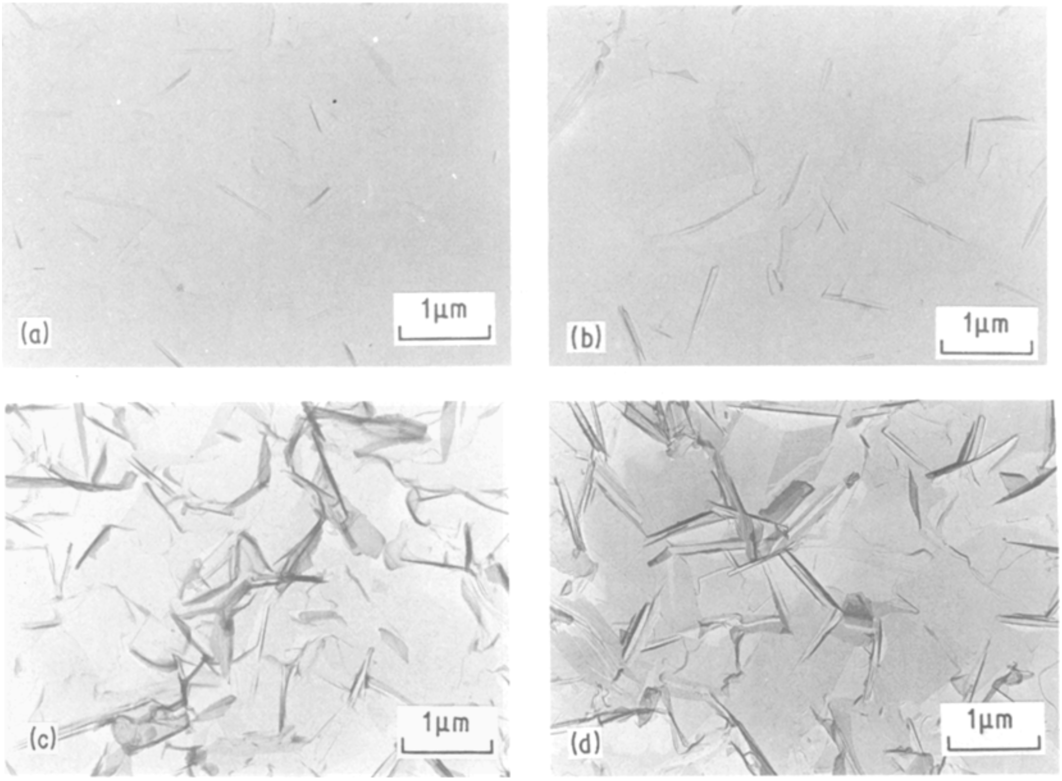

Figure 10 Electron micrographs of glass-ceramics formed by controlled crystallization of glasses with 0.25 mol% $ZrSe_2$ addition, heat treated at 400° C for (a) 7 h, (b) 12 h, (c) 15 h and (d) 24 h.

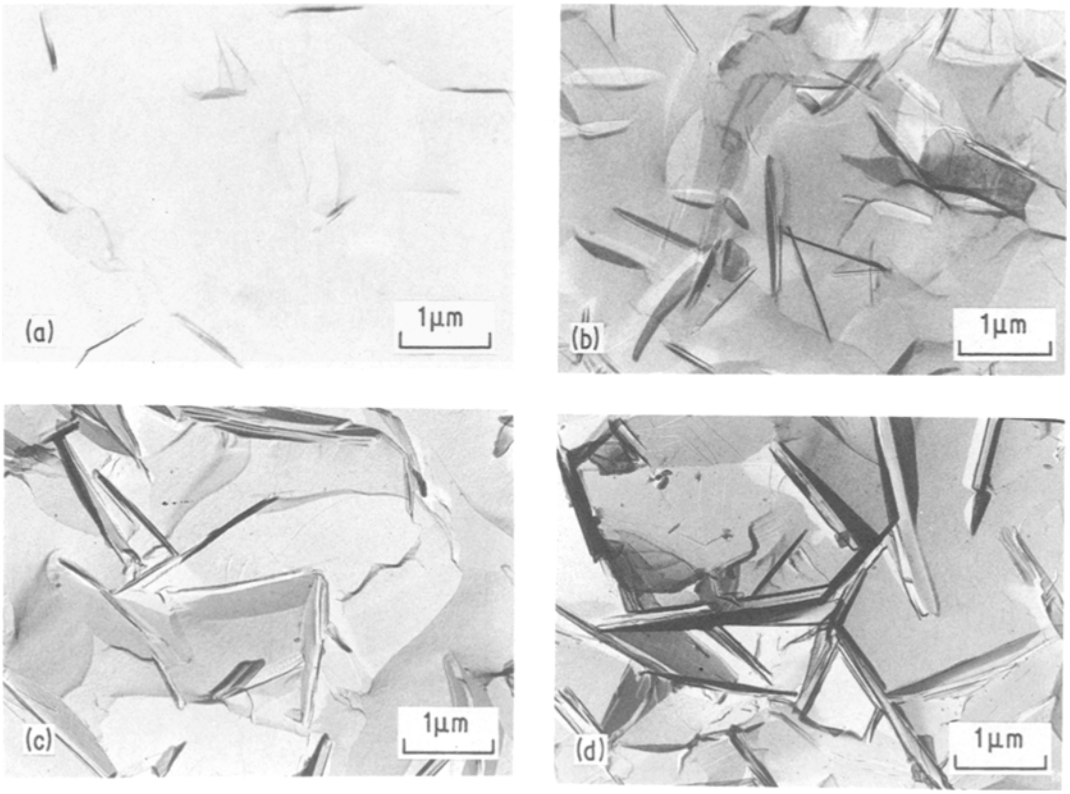

Figure 11 Electron micrographs of glass-ceramics formed by controlled crystallization of glasses with 0.50 mol% $ZrSe_2$ addition, heat treated at 400° C for (a) 5 h, (b) 10 h, (c) 15 h and (d) 24 h.

ture (400° C) for a selected time, followed by quenching in air, has been used to investigate the kinetics of the catalysed crystallization of As–Ge–Se glasses nucleated by $ZrSe_2$.

By changing the time of heat treatment, glass-ceramics of various crystallinities and of differing crystal sizes were obtained. X-ray diffraction studies of the crystallized glasses showed that the crystalline phase consists only of the germanium selenide (Figs 7 and 8).

As shown in Fig. 9, the plot of microcrystal size against the logarithm of heat-treatment time is more or less a linear dependence. Fig. 10 shows a series of electron micrographs of crystallized glasses nucleated by 0.25 mol% $ZrSe_2$ and heat treatment at 400° C for between 7 and 24 h. It should be mentioned that when the glass has been heat-treated for between 12 and 15 h an evident increase of crystallinity is observed. As is well-known, the size of the microcrystals plays an important role, particularly as far as the mechanical and optical properties of glass-ceramics are concerned. As a rule, the mechanical strength and i.r. transmission decrease with increasing size of microcrystals. In this case, when the size of the microcrystals is about 1 μm the maximum strength and i.r. transmission of 50% (thickness 3 mm) are obtained. However, as shown in Fig. 11, the crystal size of the crystallized glass nucleated by 0.50 mol% $ZrSe_2$ and heat-treated at 400° C, even for 15 h, is much more than 1 μm and so, consequently, the i.r. transparency loss becomes very important.

X-ray diffraction studies of the crystalline phase under different temperature conditions (360, 380, 400 and 420° C) for 24 h demonstrated the exclusive formation of germanium selenide.

Electron microscopy studies of crystal size growth as a function of heat treatment tempera-tire have been used to determine the activation energy of crystallization. At an atomic level, the process necessary for crystal growth is the jumping of an atom from one side of the boundary to the other which is similar to a diffusional jump across the boundary; consequently, the tempera-

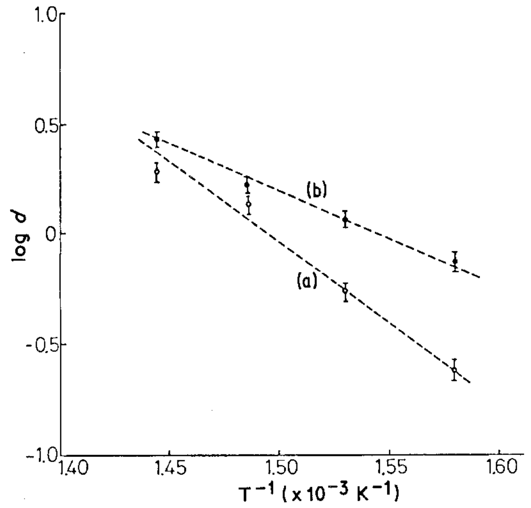

Figure 12 Arrhenius plots of crystal-size growth for the temperature range from 360 to 420° C (a) with 0.25 mol% $ZrSe_2$ addition and (b) with 0.50 mol% $ZrSe_2$ addition.

ture dependence is similar in form to that of diffusion dependence:

$$d = d_0 \exp(-E_c/RT), \qquad (2)$$

where d is the crystal diameter at temperature T (in K), d_0 is the initial crystal diameter and E_c is the experimental activation energy of crystallization. It can be seen that when $\log d$ is plotted against T^{-1} a straight line is obtained.

Fig. 12 shows the Arrhenius plots of crystal growth for the temperature range from 360 to 420° C. The values of the activation energies of crystallization obtained for glasses with $ZrSe_2$ contents of 0.25 and 0.50 mol% are 33.6 and 19.6 kcal mol^{-1}, respectively; these values are much smaller than the activation energy of chalcogenide glass of the same composition without nucleant ($\simeq$ 45 kcal mol^{-1}).

The lowering of the activation energy of crystallization explains why the catalysed crystallization takes place at a temperature much lower than that of crystallization without nucleant. The variations in free energy during the crystallization process with and without $ZrSe_2$ nucleant are shown schematically in Fig. 13.

The activation energy of homogeneous nucleation and crystal growth of $GeSe_2$ without nucleant, E_1, is much higher than that of the formation of $ZrSe_2$ nuclei, E_2, and the subsequent heterogeneous nucleation and crystal growth of $GeSe_2$ on these substrates, E_3.

As noted, 0.25 mol% $ZrSe_2$ is sufficient to produce an As–Ge–Se system glass-ceramic of high mechanical strength and increased sag-point. The discussion of the mechanism of the crystallization process is therefore of great interest, especially from the view-point of the controlled crystallization of chalcogenide glasses.

The melting of glasses was performed at 850° C the melts being quenched in air. Because of the low solubility of $ZrSe_2$ in the As–Ge–Se system, glasses obtained by rapid cooling are supersaturated in $ZrSe_2$ so that precipitation of $ZrSe_2$ crystals in glass is observed even for the addition of 0.50 mol% of $ZrSe_2$; consequently, the crystal phase which first appears in glass and acts as a nucleation catalyst is presumed to be the tetragonal $ZrSe_2$.

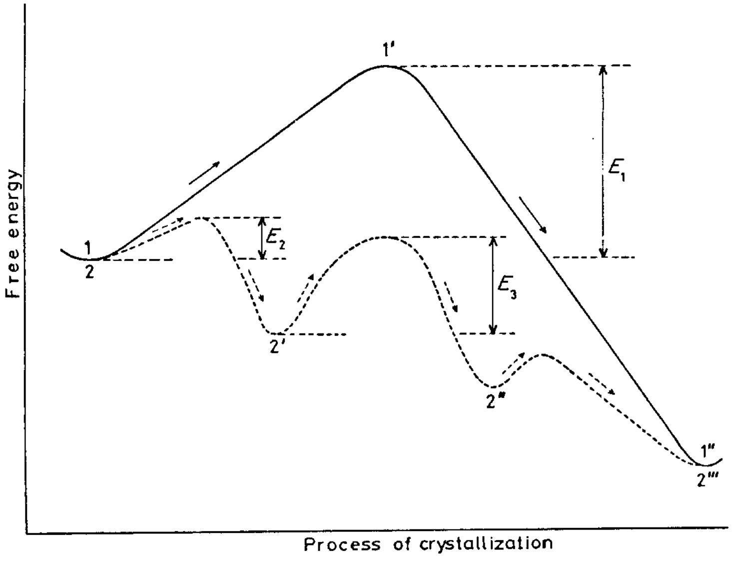

Figure 13 Variation in free energy during the crystallization process of the As–Ge–Se system glass: (1) initial glass without nucleant → (1') homogeneous nucleation and crystal growth of $GeSe_2$ → (1'') formation of crystal phase $GeSe_2$; (2) initial glass with nucleant $ZrSe_2$ addition → (2') formation of $ZrSe_2$-based nucleation substrates → (2'') precipitation of crystal phase $GeSe_2$ on $ZrSe_2$ heterogeneous nucleation and crystal growth of $GeSe_2$ → (2''') $GeSe_2$ based glass-ceramic.

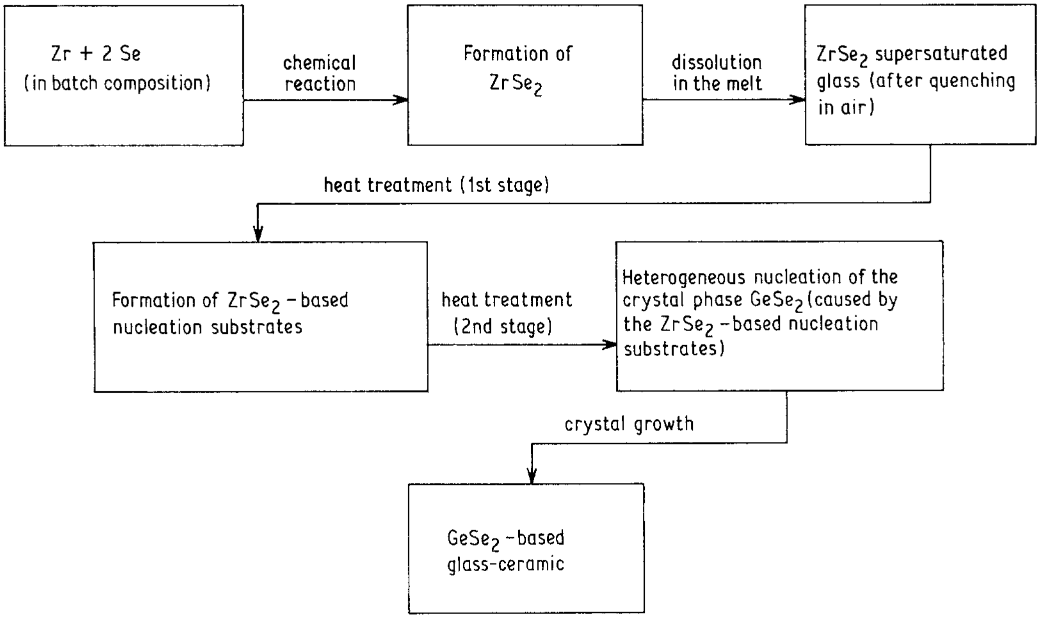

Figure 14 Possible mechanism of the glass-ceramic process.

It may be suggested that this primary precipitation provides an interface favourable to the subsequent nucleation and growth of the $GeSe_2$ crystals during heat treatment.

The possible mechanism of the glass-ceramic process is shown schematically in Fig. 14.

Conclusions

A new chacogenide glass-ceramic with good thermomechanical properties and capable of transmitting in the infra-red region at wavelengths between 8 and 16 μm was produced by crystallizing an As–Ge–Se system glass nucleated by $ZrSe_2$. The controlled crystallization process raised the sag-point from 420° C to 530° C. At the same time, the fracture toughness was increased by more than three times from $0.246\,MN\,m^{-3/2}$ to $0.848\,MN\,m^{-3/2}$ with only a loss of about 10% in the i.r. transmission at wavelengths of 8 to 16 μm.

The optimum thermomechanical properties and infra-red transmission were obtained for an $As_{0.1}Ge_{0.3}Se_{0.6}$ glass nucleated by 0.25 mol% $ZrSe_2$ and heat treated at 400° C for about 15 h.

The study of the kinetics of the crystallization suggests a two-step process with $ZrSe_2$ substrates precipitated in the first stage catalysing the heterogeneous nucleation of the final, crystalline $GeSe_2$ phase.

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