

## Crystallization studies on $\text{Cu}_x\text{Ge}_{15}\text{Te}_{85-x}$ glasses

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 2755

(<http://iopscience.iop.org/0953-8984/8/16/004>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.208

The article was downloaded on 13/05/2010 at 16:32

Please note that [terms and conditions apply](#).

## Crystallization studies on $\text{Cu}_x\text{Ge}_{15}\text{Te}_{85-x}$ glasses

K Ramesh†, S Asokan‡§, K S Sangunni† and E S R Gopal†||

† Department of Physics, Indian Institute of Science, Bangalore 560012, India

‡ Department of Instrumentation, Indian Institute of Science, Bangalore 560012 India

Received 20 July 1995, in final form 26 February 1996

**Abstract.** Differential scanning calorimetric (DSC) studies have been carried out in an attempt to explain the composition dependence of the thermal crystallization behaviour of  $\text{Cu}_x\text{Ge}_{15}\text{Te}_{85-x}$  glasses. It is seen that these glasses exhibit a single glass transition and single-stage crystallization on heating. The glass transition temperature, crystallization temperature and the activation energy for crystallization are each found to exhibit an anomaly at around the composition  $x = 5$ . The anomalies observed in the thermal properties at  $x = 5$  can be associated with rigidity percolation.

### 1. Introduction

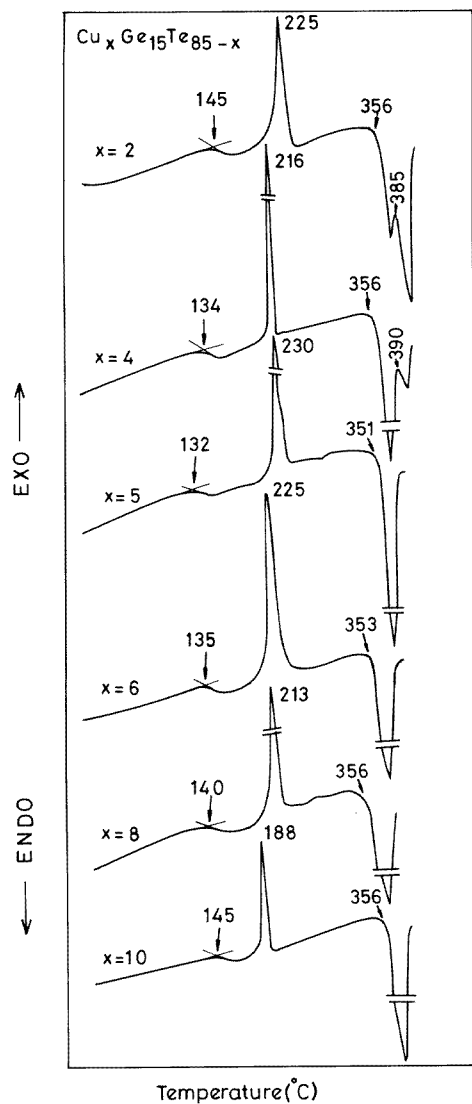
In the Cu–Ge–Te system, the bulk glass formation is centred at around 20 at.% of Ge (13–23) and homogeneous glasses can be obtained by progressively replacing Te by Cu, up to 10 at.% [1]. On the basis of the thermal crystallization studies on  $\text{Cu}_3\text{Ge}_{20}\text{Te}_{77}$  glass undertaken earlier, it is proposed that the addition of copper to the GeTe system increases the ability to crystallize and decreases the glass-forming tendency of the Ge–Te system [1, 2]. It is also suggested that the increase in Cu or Ge content in Cu–Ge–Te glasses results in the progressive replacement of weak van der Waals bonds between the Te chains by covalent bonds, thereby strengthening the glass structure, which results in increases in density, microhardness, etc [1]. In the present work differential scanning calorimetric studies have been undertaken on  $\text{Cu}_x\text{Ge}_{15}\text{Te}_{85-x}$  glasses, in an effort to achieve an understanding of the crystallization behaviour of these glasses and also the variation of the thermal parameters such as the glass transition temperature, the crystallization temperature, the glass-forming ability and the activation energy for crystallization with Cu concentration.

### 2. Experimental procedure

The melt-quenching technique was adopted to prepare bulk  $\text{Cu}_x\text{Ge}_{15}\text{Te}_{85-x}$  glasses in the composition range  $2 < x < 10$  (at.%). Appropriate amounts of the constituent elements were sealed in evacuated ( $10^{-6}$  Torr) quartz ampoules. The ampoules were heated to 1050 °C in a horizontal rotary furnace for 48 hours. Ampoules containing the melt were rotated continuously at 10 rpm to ensure homogeneity of the melt and were subsequently quenched in a NaOH + ice-water mixture. The amorphous nature of the samples was

§ E-mail: sasokan@isu.iisc.ernet.in.

|| Also at: National Physical Laboratory, New Delhi, India.



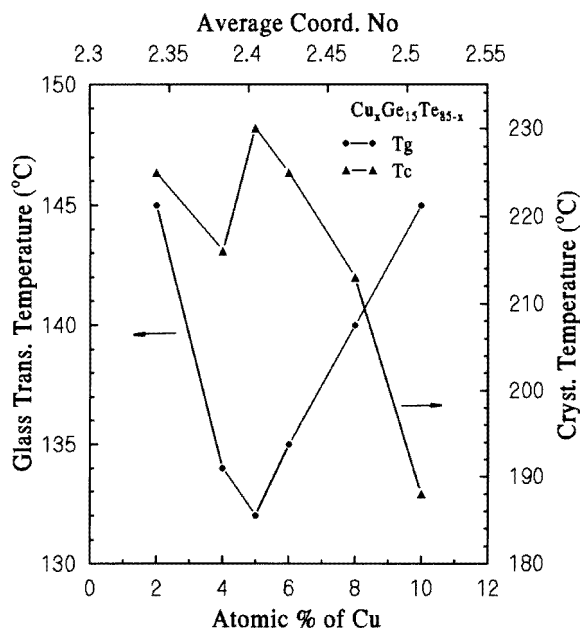
**Figure 1.** Differential scanning calorimetric thermograms of  $\text{Cu}_x\text{Ge}_{15}\text{Te}_{85-x}$  glasses for the heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ .

confirmed via x-ray diffraction. DSC studies were undertaken on a Stanton–Redcroft DSC-1500 Differential Scanning Calorimeter. About 20 mg of the sample compounds were used in the DSC runs, with alumina as the reference material. The activation energy for the thermal crystallization was estimated for all of the glasses, using Kissinger's method. The samples were isothermally annealed at the crystallization temperature for about 72 hours and x-ray diffraction studies were undertaken on a Philips powder diffractometer.

### 3. Results and discussion

#### 3.1. DSC studies

Figure 1 shows the differential scanning calorimetric traces taken at  $10\text{ }^\circ\text{C min}^{-1}$ , indicating that all of the  $\text{Cu}_x\text{Ge}_{15}\text{Te}_{85-x}$  glasses ( $2 < x < 10$ ) exhibit a single glass transition and



**Figure 2.** The variation of the glass transition and crystallization temperatures of  $\text{Cu}_x\text{Ge}_{15}\text{Te}_{85-x}$  glasses with composition and average coordination number.

single-stage crystallization on heating.

Figure 2 shows the composition dependence of the glass transition temperature ( $T_g$ ) and crystallization temperature ( $T_c$ ) of  $\text{Cu}_x\text{Ge}_{15}\text{Te}_{85-x}$  samples. It can be seen from figure 2 that the glass transition temperature exhibits a minimum and the crystallization temperature a local maximum at around the composition  $x = 5$ .

The DSC experiments were also conducted on all of the glasses at different heating rates, to evaluate the activation energy for crystallization. Figure 3 shows the differential scanning calorimetric traces for a representative  $\text{Cu}_5\text{Ge}_{15}\text{Te}_{80}$  glass at different heating rates. The Kissinger plot [3] of the variation of  $\log(\beta/T_c^2)$  versus  $(1000/T_c)$ , for  $\text{Cu}_5\text{Ge}_{15}\text{Te}_{80}$  glass, is shown in figure 4. The activation energy for the thermal crystallization of the  $\text{Cu}_5\text{Ge}_{15}\text{Te}_{80}$  sample was estimated to be 0.91 eV. For the other samples, the activation energy lies in the range 0.7–1.0 eV.

The separation between the glass transition and crystallization temperatures can be taken

**Table 1.** The thermal parameters of  $\text{Cu}_x\text{Ge}_{15}\text{Te}_{85-x}$  glasses.

Cu (at.%)	$T_g$ (°C)	$T_c$ (°C)	$E_c$ (eV)	$K_{gl}$
2	145	225	0.991	0.563
4	134	216	0.792	0.543
5	132	230	0.919	0.700
6	135	225	0.826	0.643
8	140	213	0.784	0.465
10	145	188	0.721	0.239

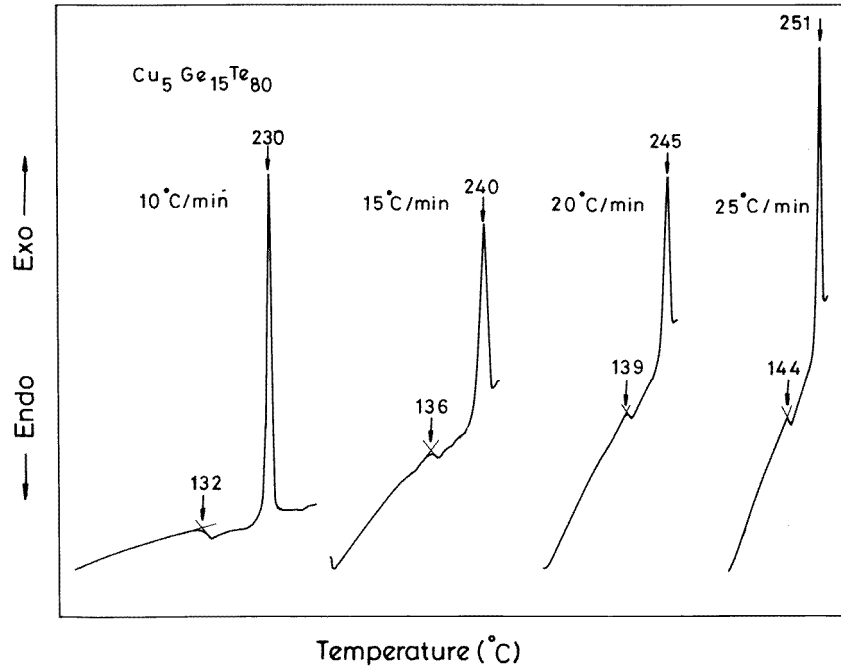


Figure 3. DSC traces of  $\text{Cu}_5\text{Ge}_{15}\text{Te}_{80}$  glass for different heating rates.

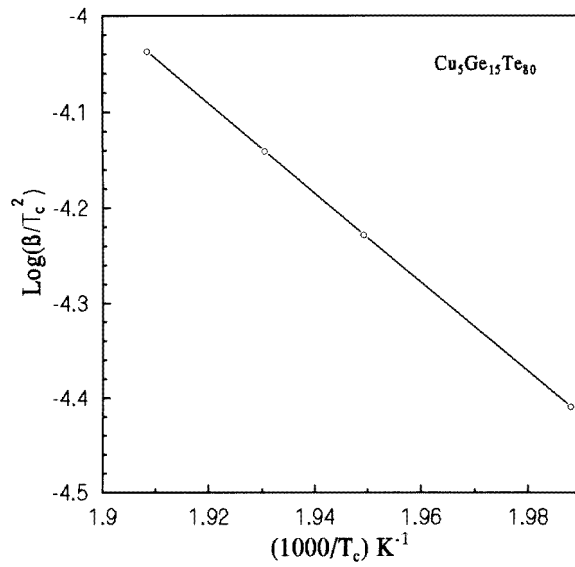
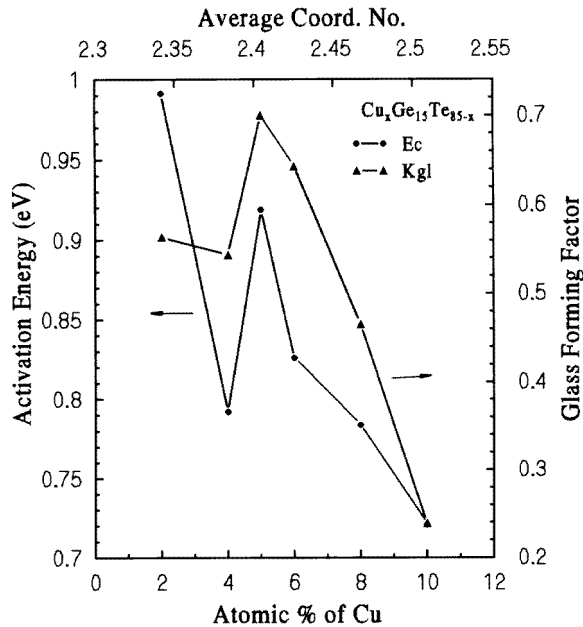


Figure 4. A Kissinger plot showing the variation of  $\log(\beta/T_c^2)$  versus  $(1000/T_c)$  for  $\text{Cu}_5\text{Ge}_{15}\text{Te}_{80}$  glass.

to be indicative of the glass-forming ability of the material. The glass formation factor of a material is given by [4, 5]

$$K_{gl} = \frac{(T_c - T_g)}{(T_m - T_c)} \quad (1)$$

where  $T_m$  is the peak melting temperature. If  $K_{gl} \leq 0.1$ , the glass is usually difficult to prepare. Good glass formers normally have values of  $K_{gl} \geq 0.4$ . From table 1 it is seen that the glass-forming ability is less for high-copper-content glasses.



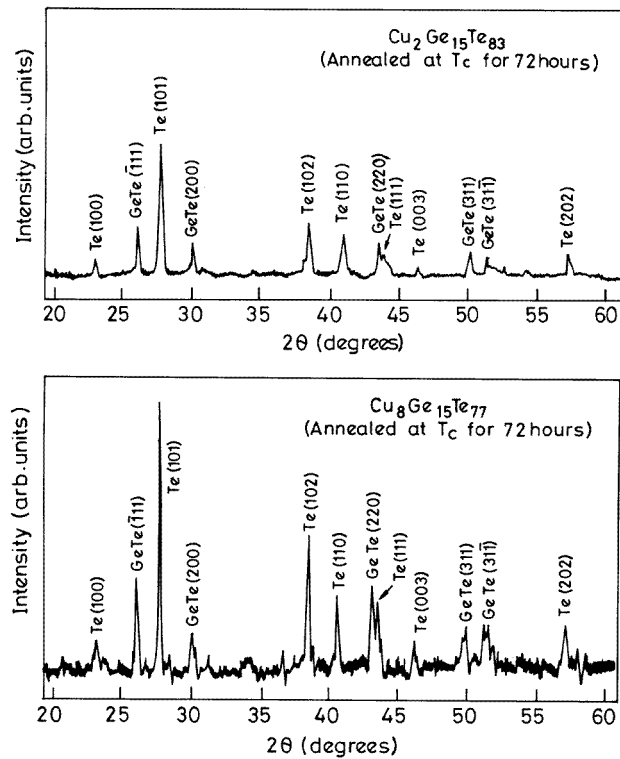
**Figure 5.** The variations of the crystallization activation energy and glass-forming factor of  $\text{Cu}_x\text{Ge}_{15}\text{Te}_{85-x}$  glasses with composition and average coordination number.

The variations of the activation energy for crystallization and the glass-forming factor of  $\text{Cu}_x\text{Ge}_{15}\text{Te}_{85-x}$  glasses with composition are shown in figure 5. It is seen from figure 5 that the activation energy for crystallization and the glass-forming ability of  $\text{Cu}_x\text{Ge}_{15}\text{Te}_{85-x}$  glasses each exhibit a maximum at around the composition 5 at.% Cu.

Table 1 collects together various thermal parameters, namely  $T_g$ ,  $T_c$ ,  $E_c$  and  $K_{gl}$ , of Cu-Ge-Te glasses of different compositions. In table 1, peak temperatures are indicated for  $T_c$ , and the tangent of the baseline and the endotherm is taken as  $T_g$ .

### 3.2. X-ray investigations

The x-ray diffraction studies on glasses annealed at the end of the crystallization reaction yield interesting results. Figure 6 shows the x-ray diffraction patterns of two representative  $\text{Cu}_2\text{Ge}_{15}\text{Te}_{83}$  and  $\text{Cu}_8\text{Ge}_{15}\text{Te}_{77}$  samples annealed at the respective crystallization temperatures for about 72 hours. It can be seen from figure 6 that the diffraction patterns of crystallized  $\text{Cu}_x\text{Ge}_{15}\text{Te}_{85-x}$  samples are fully indexable with hexagonal Te [6] and rhombohedral  $\alpha$ -GeTe [7] phases.



**Figure 6.** The x-ray diffraction patterns of  $\text{Cu}_2\text{Ge}_{15}\text{Te}_{83}$  and  $\text{Cu}_8\text{Ge}_{15}\text{Te}_{77}$  glasses annealed at the crystallization temperature for 72 hours.

We have not been able to identify elemental Cu or compounds of copper with Te or Ge, namely  $\text{Cu}_2\text{Te}$  [8],  $\text{CuTe}$  [9],  $\text{CuGe}$  [10],  $\text{Cu}_3\text{Ge}$  [11], etc, in the crystallized  $\text{Cu}_x\text{Ge}_{15}\text{Te}_{85-x}$  samples. It is known that Cu in Cu–Ge–Te is fourfold coordinated like Ge. Furthermore, the atomic radii of Cu and Ge are comparable (1.28 and 1.22 Å respectively). The electronegativities of Cu and Ge are also of the same order (1.8 and 1.9 respectively). It is therefore likely that the available copper randomly substitutes for Ge in the Ge–Te phase during crystallization and does not form any Cu–Te or Cu–Ge phase.

### 3.3. Rigidity percolation and the composition dependence of thermal parameters

In chalcogenide network glasses, there is a critical average coordination of atoms (known as the rigidity percolation threshold) at which the structural rigidity of the material undergoes a transformation. Theoretical investigations based on the network constraints proposed by Phillips and Thorpe [12, 13] suggest that the rigidity percolation occurs at the average coordination  $Z_{av} = 2.4$ . In some glassy systems, if the effect of medium-range order is included in the constraint theory, the percolation threshold shifts to  $Z_{av} = 2.67$  [14]. There is also a recent idea that the rigidity percolation occurs at  $Z_{av} = 2.4$  and the chemical ordering threshold occurs at  $Z_{av} = 2.67$  [15, 16]. The rigidity percolation and chemical ordering effects can be identified from unusual variations in the physical properties in different glassy systems, exhibited at these thresholds. From the property anomalies exhibited, it has been

concluded earlier that rigidity percolation occurs in binary chalcogenide glassy systems such as Ge–Te [18], Si–Te [19], Ge–Se [20], Ge–S [18], Si–Se [18], and As–Te [21], at  $Z_{av} = 2.4$ . Similarly, it has been found that certain ternary glassy systems, like As–Se–Te [22] and Al–As–Te [23], also show the rigidity transformation at  $Z_{av} = 2.4$ . In Ge–As–Se, Ge–Sb–Se, and Ge–In–Se glasses [15–17] anomalies have been noticed at both  $Z_{av} = 2.4$  and  $Z_{av} = 2.67$ . It has been suggested that the anomalies observed at  $Z_{av} = 2.4$  are due to rigidity percolation and that the effects seen at  $Z_{av} = 2.67$  occur because of the chemical ordering effect [15–17]. However, in ternary systems such as Ge–As–Te [24] and Si–As–Te [25], the rigidity percolation transition is said to occur at around  $Z_{av} = 2.6$ .

Generally in chalcogenide network glasses, germanium is fourfold coordinated and Te is twofold coordinated [26]. Earlier investigations suggest that Cu in Cu–Ge–Te glasses is fourfold coordinated [26]. The average coordination derived using the coordination numbers mentioned above, for the glasses  $Cu_xGe_{15}Te_{85-x}$ , using the formula [27]

$$Z_{av} = \frac{Z_{Cu}(x) + Z_{Ge}(15) + Z_{Te}(85 - x)}{100} \quad (2)$$

and for the composition  $Cu_5Ge_{15}Te_{80}$  at which anomalies in thermal properties are observed turns out to be 2.4. This suggests that in Cu–Ge–Te the rigidity percolation occurs at  $Z_{av} = 2.4$ , and the anomalies exhibited in the glass transition temperature, the crystallization temperature, the activation energy for crystallization and the glass-forming ability may be associated with the rigidity percolation. This observation is also supported by high-pressure resistivity measurements which reveal anomalies in properties such as the conductivity activation energy at different pressures, for the  $x = 5$  composition [28].

Due to the glass-forming region of the Cu–Ge–Te system being restricted [1], it has not been possible to investigate compositions for which  $Z_{av}$  is above 2.55. Hence, the possibility of the occurrence of any effect at  $Z_{av} = 2.67$  in Cu–Ge–Te glasses has not been probed in the present study.

#### 4. Conclusions

Bulk, melt-quenched  $Cu_xGe_{15}Te_{85-x}$  glasses are found to exhibit a single glass transition and single-stage crystallization on heating. X-ray diffraction studies on  $Cu_xGe_{15}Te_{85-x}$  samples annealed at the crystallization temperature for 72 hours indicate that they crystallize into hexagonal Te and rhombohedral GeTe phases. It is likely that the available Cu randomly replaces Ge in the crystallized material. The composition dependences of the glass transition temperature, the crystallization temperature, the activation energy for crystallization and the glass-forming ability of  $Cu_xGe_{15}Te_{85-x}$  glasses are found to exhibit unusual variations at around the composition  $x = 5$ . The anomalies observed in the thermal properties at  $x = 5$  can be associated with the rigidity percolation.

#### References

- [1] Borisova Z U 1985 *Glassy Semiconductors* (New York: Plenum) p 436
- [2] Ligeró R A, Casa-Ruiz M, Trujillo M P, Orozco A and Jimenez-Garay R 1994 *Phys. Chem. Glasses* **35** 115
- [3] Kissinger H E 1956 *J. Res. NBS* **57** 217
- [4] Hurby A 1972 *Czech. J. Phys.* **B 22** 1187
- [5] Thornburg D D 1974 *Mater. Res. Bull.* **9** 1481
- [6] Wyckoff R W G 1958 *Crystal Structures* vol 1, 2nd edn (New York: Index Science) p 1196
- [7] Schubert K and Fricke H 1953 *Z. Metallk.* **44** 457
- [8] Nowontny H 1954 *Z. Metallk.* **37** 371



- [9] Anderko and Schubert K 1954 *Z. Metallk.* **45** 371
- [10] Aalushko I 1981 *Russ. Met.* **94** 1981
- [11] Nowonty H and Bachmayer MH 1950 *Chemie* **81** 669
- [12] Phillips J C 1985 *Phys. Rev. B* **31** 8157
- [13] Phillips J C and Thorpe M F 1985 *Solid State Commun.* **53** 699
- [14] Tanaka K 1989 *Phys. Rev. B* **39** 1270
- [15] Sudha M and Giridhar A 1993 *J. Non-Cryst. Solids* **152** 42
- [16] Sudha M and Giridhar A 1992 *J. Non-Cryst. Solids* **143** 52
- [17] Sudha M and Giridhar A 1993 *J. Non-Cryst. Solids* **162** 294
- [18] Asokan S, Parthasarathy G and Gopal E S R 1988 *Phil. Mag.* **57** 49
- [19] Asokan S, Parthasarathy G and Gopal E S R 1987 *Phys. Rev. B* **35** 8269
- [20] Asokan S, Prasad M V N, Parthasarathy G and Gopal E S R 1989 *Phys. Rev. Lett.* **62** 808
- [21] Titus S S K, Asokan S and Gopal E S R 1992 *Solid State Commun.* **83** 745
- [22] Titus S S K, Asokan S and Gopal E S R 1992 *High Press. Res.* **10** 629
- [23] Murugavel S, Acharya K V and Asokan S 1995 *J. Non-Cryst. Solids* **191** 327
- [24] Srinivasan A, Ramesh K, Madhusoodanan K N and Gopal E S R 1992 *Phil. Mag.* **65** 249
- [25] Srinivasan A, Ramesh K, Madhusoodanan K N and Gopal E S R 1992 *Phys. Status Solidi b* **170** K83
- [26] Casa-Ruiz M, Vazquez J, Ligerio R A and Jimenez-Garay R 1993 *J. Mater. Sci.* **28** 1037
- [27] Gopal E S R, Srinivasan A and Asokan S 1993 *Indian J. Pure Appl. Phys.* **31** 211.
- [28] Ramesh K, Asokan S, Sangunni K S and Gopal E S R 1996 *Phys. Chem. Glasses* at press