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Glass Transition and Crystallization in Oxyfluoride Germanate Glasses

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Introduction

- Oxyfluoride germanate glasses have great potential applications in the field of luminescence due to their low phonon energies, which can decrease the non-radiative transitions. Besides, the coexistence of oxygen and fluorine is expected to influence the crystallization behavior and glass structures. Furthermore, Ge can be in multi-fold coordination: 4, 5, and 6. The multiple Ge species can cause non-linear changes for thermodynamics, which is called germanate anomaly.
- We have explored the phase transition, the glass transition and crystallization behaviors in GeO_2-BaF_2-AlF_3 glasses by performing differential scanning calorimetry (DSC), room temperature (RT) and high temperature (HR) XRD.

Experimental

The glass $60GeO_2$–$25BaF_2$–$15AlF_3$ was synthesized using the conventional melt-quenching method. The dynamic heat treatments were performed by DSC for some of the glasses. The dynamic heat treatments were non-isothermal with different target temperatures, T_d.

Calorimetry

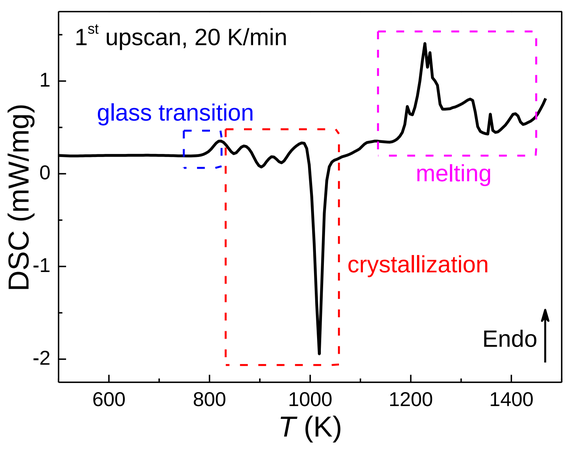


Fig. 1. DSC 1st upscan for the as-produced glass.

The first crystallization peak appears prior to the end of the glass transition.

- Complex crystallization behaviors.
- Relatively low glass stability.

Dynamic heat treatments

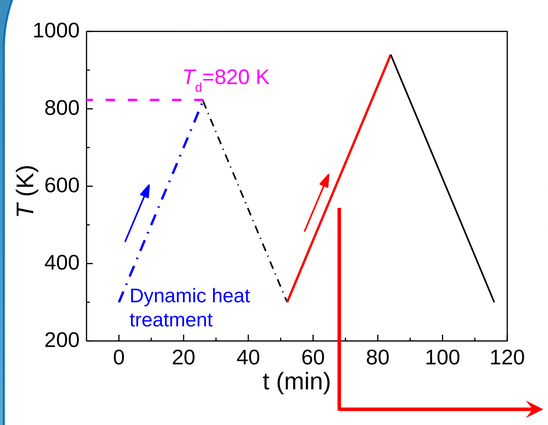


Fig. 2. Scheme diagram of dynamic heat treatment with T_d=820 K.

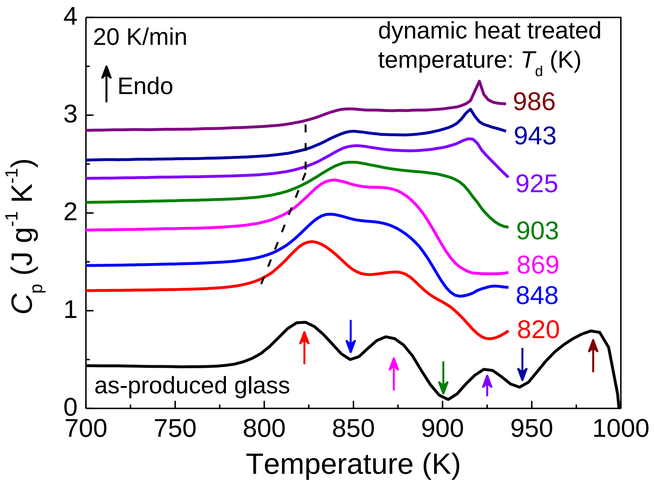


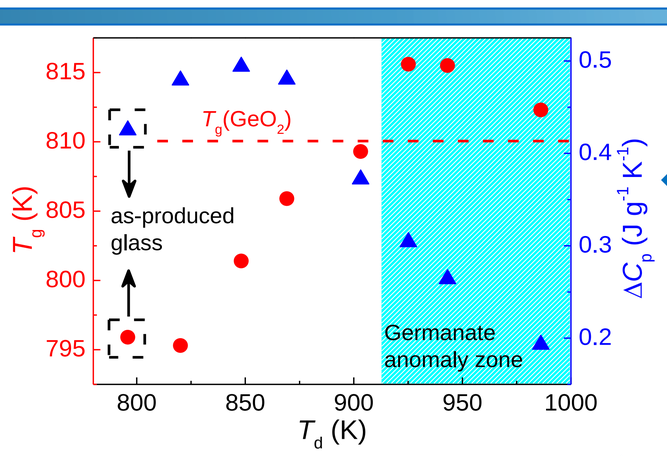
Fig. 3. C_p 1st upscans for glasses with different T_d.

Increase T_d:
- The glass gradually crystallize.
- The glass transition region shifts towards high temperature.

Thermodynamics & Crystallization

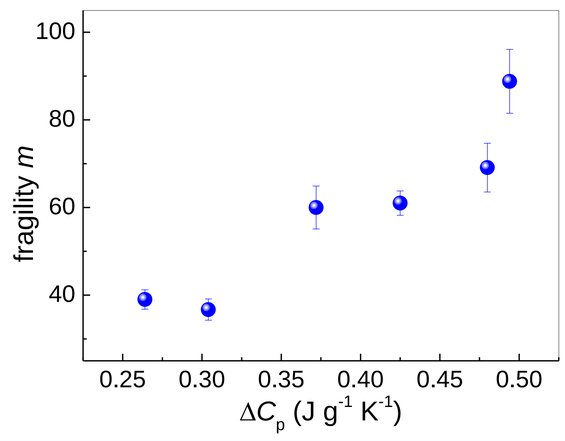
T_g: onset of the glass transition.

ΔC_p: C_p difference between glass C_p and liquid C_p at T_g.



Liquid fragility index m:

$$m = \left.\frac{\partial log\eta}{\partial T_g/T}\right|_{T=T_g} = \frac{\partial \log(\frac{1}{q_c})}{\partial \frac{T_g}{T_f}}$$



Increase T_d:
Glass transition temperature (T_g) exhibits a non-linear change. The ΔC_p starts to decrease from T_d=869 K. The non-linear change of T_g with T_d is similar as that with composition, indicating the possible existence of germanate anomaly zone.

ΔC_p can be seen as the thermodynamic fragility in studied system.

T_d (K)	BaO-GeO_2	GeF_4	BaF_2	Al_2O_3-BaO-$2GeO_2$
820				
848	X			
869	X			
903	X	X	X	
925	X	X	X	
943	X	X	X	
986	X	X	X	X
1017	X	X	X	X

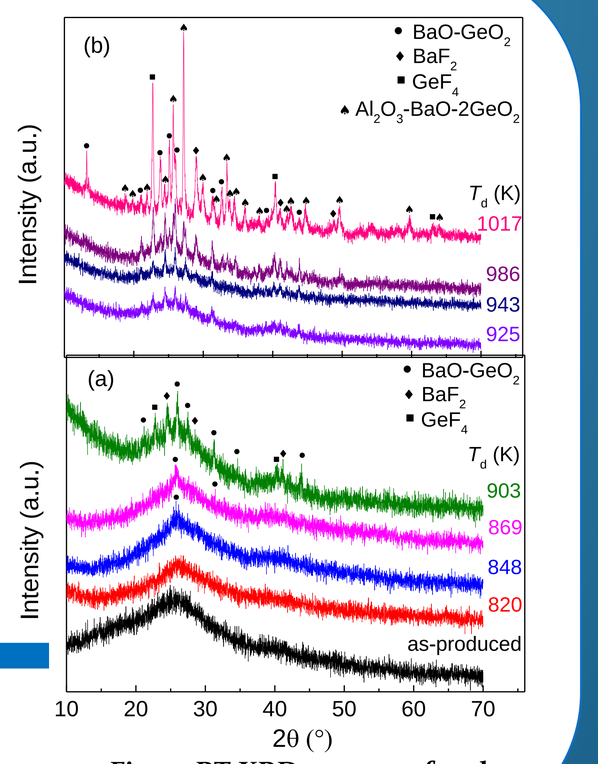
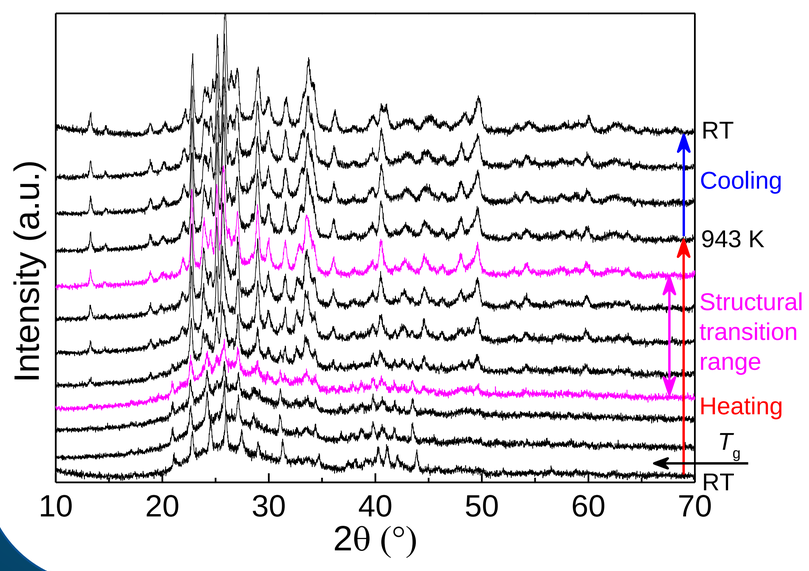


Fig. 4. RT XRD patterns for the glasses with different T_d.

In-situ HT XRD patterns for the glass with T_d=943 K



Some structural changes occur in the temperature range of 900-940 K. Furthermore, the new structure retains when cooled down to room temperature.

Conclusions

- The crystals BaO-GeO_2, GeF_4, BaF_2, and Al_2O_3-BaO-$2GeO_2$ are found to form with the increase of T_d.
- As T_d increases, the residual glass becomes strong and the connectivity of the network increases. Besides, ΔC_p can be used as the thermodynamic fragility in our studied system.
- Ge^{VI} and germanate rings with Ge^{IV} might cause the nonlinear change of T_g.
- Further neutron scattering measurements would give great help for exploring the structural transformation.

Acknowledgement

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