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Glass Transition and Crystallization in Oxyfluoride Germanate Glasses

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Publication date:
2017

Document Version
Publisher's PDF, also known as Version of record

[Link to publication from Aalborg University](#)

Citation for published version (APA):

Liu, H., Hu, Y., Jørgensen, J-E., & Yue, Y. (2017). *Glass Transition and Crystallization in Oxyfluoride Germanate Glasses*. Poster presented at Materials for Energy Applications through Neutron and X-Ray Eyes, Göteborg, Sweden.

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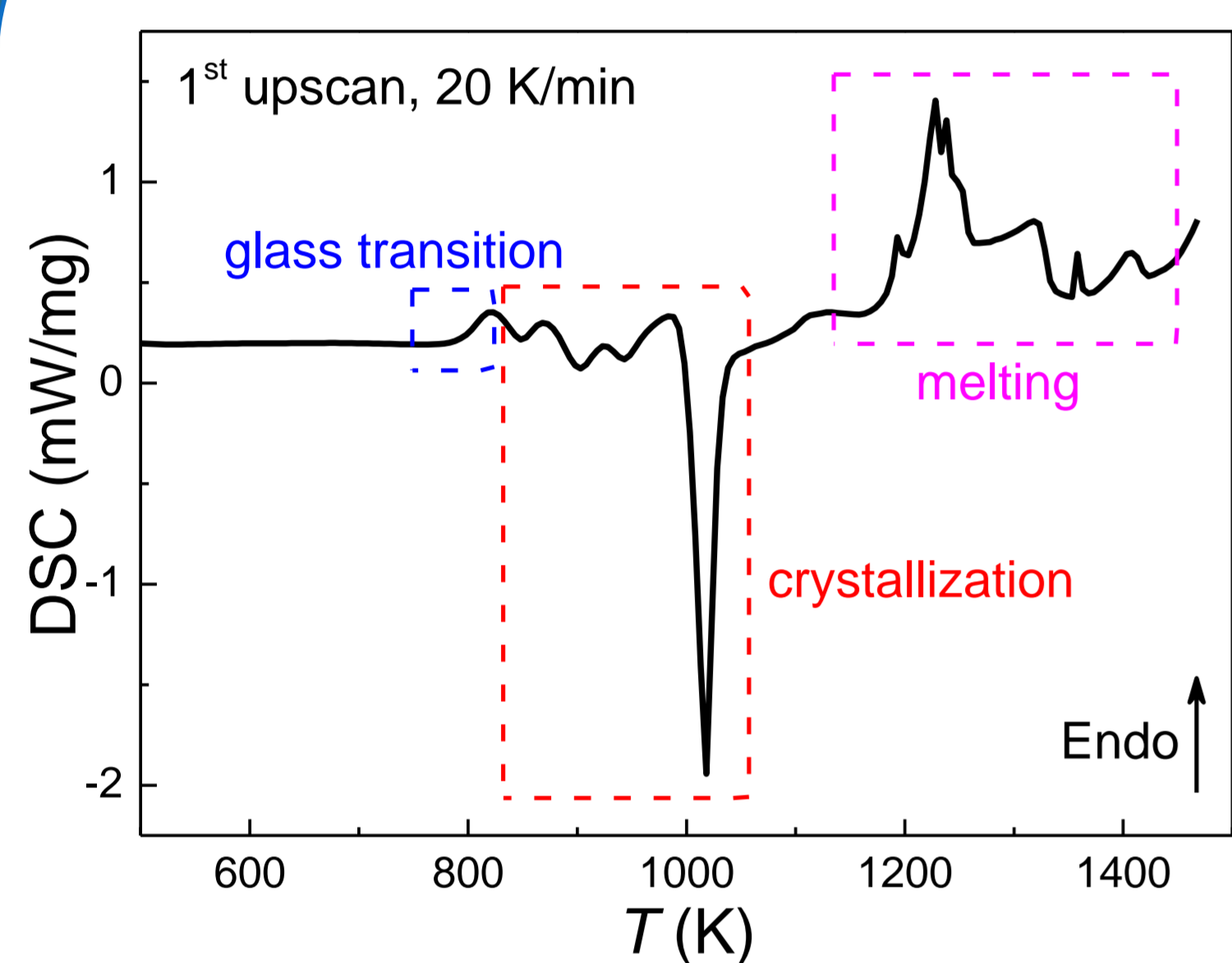
Introduction

- 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 $\text{GeO}_2\text{-BaF}_2\text{-AlF}_3$ glasses by performing differential scanning calorimetry (DSC), room temperature (RT) and high temperature (HR) XRD.

Experimental

The glass $60\text{GeO}_2\text{-}25\text{BaF}_2\text{-}15\text{AlF}_3$ 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 .

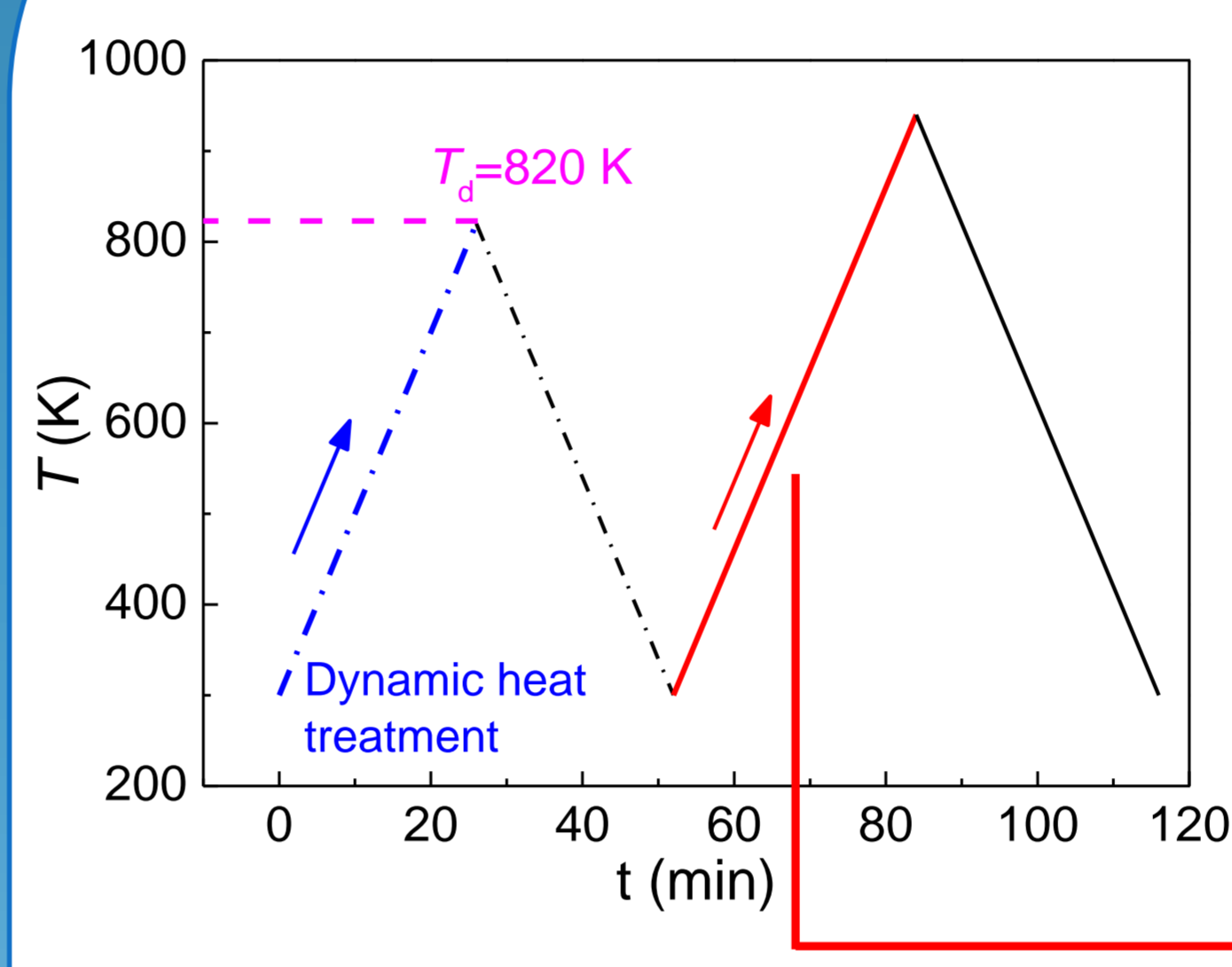
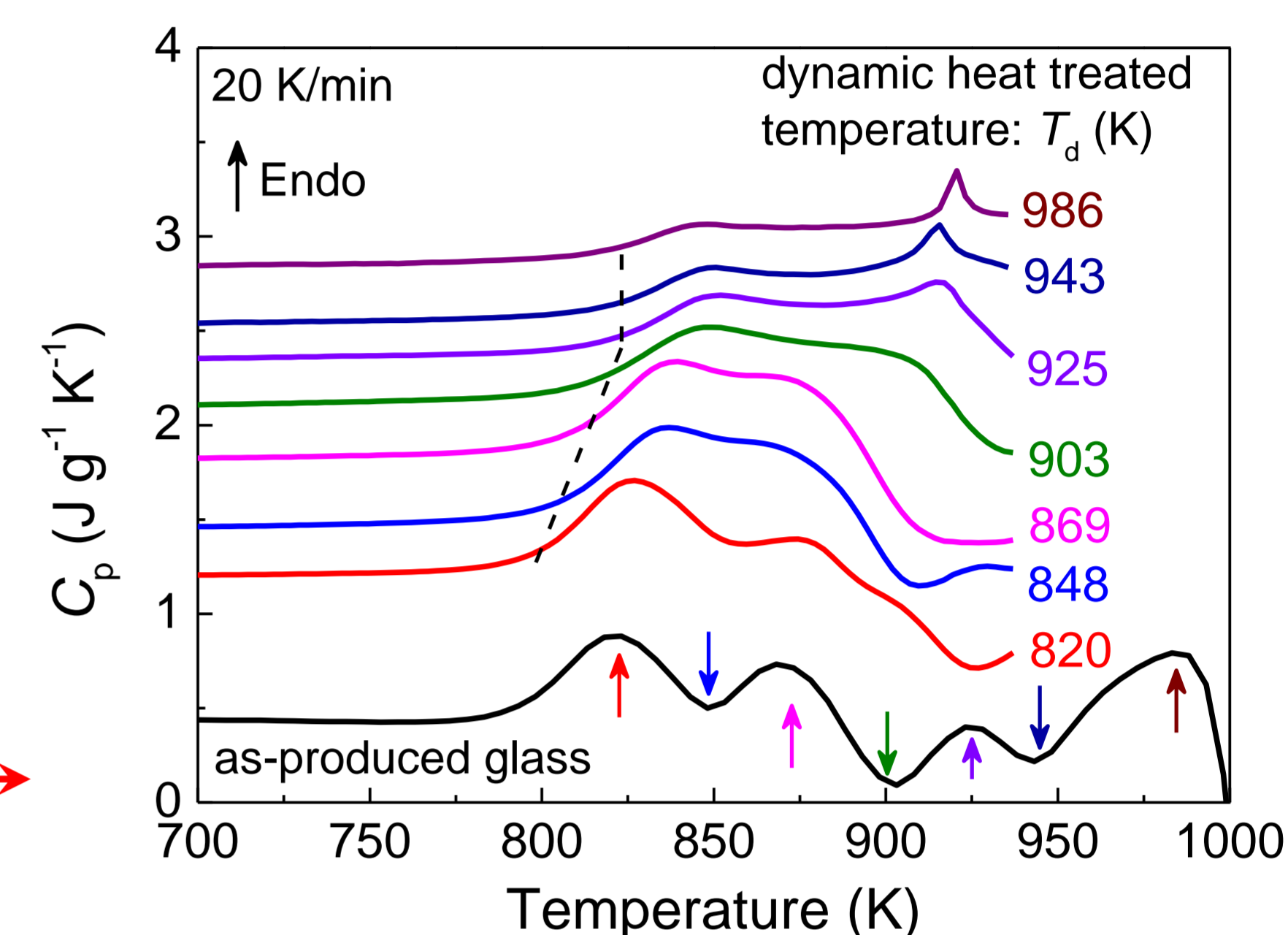
Calorimetry


 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.

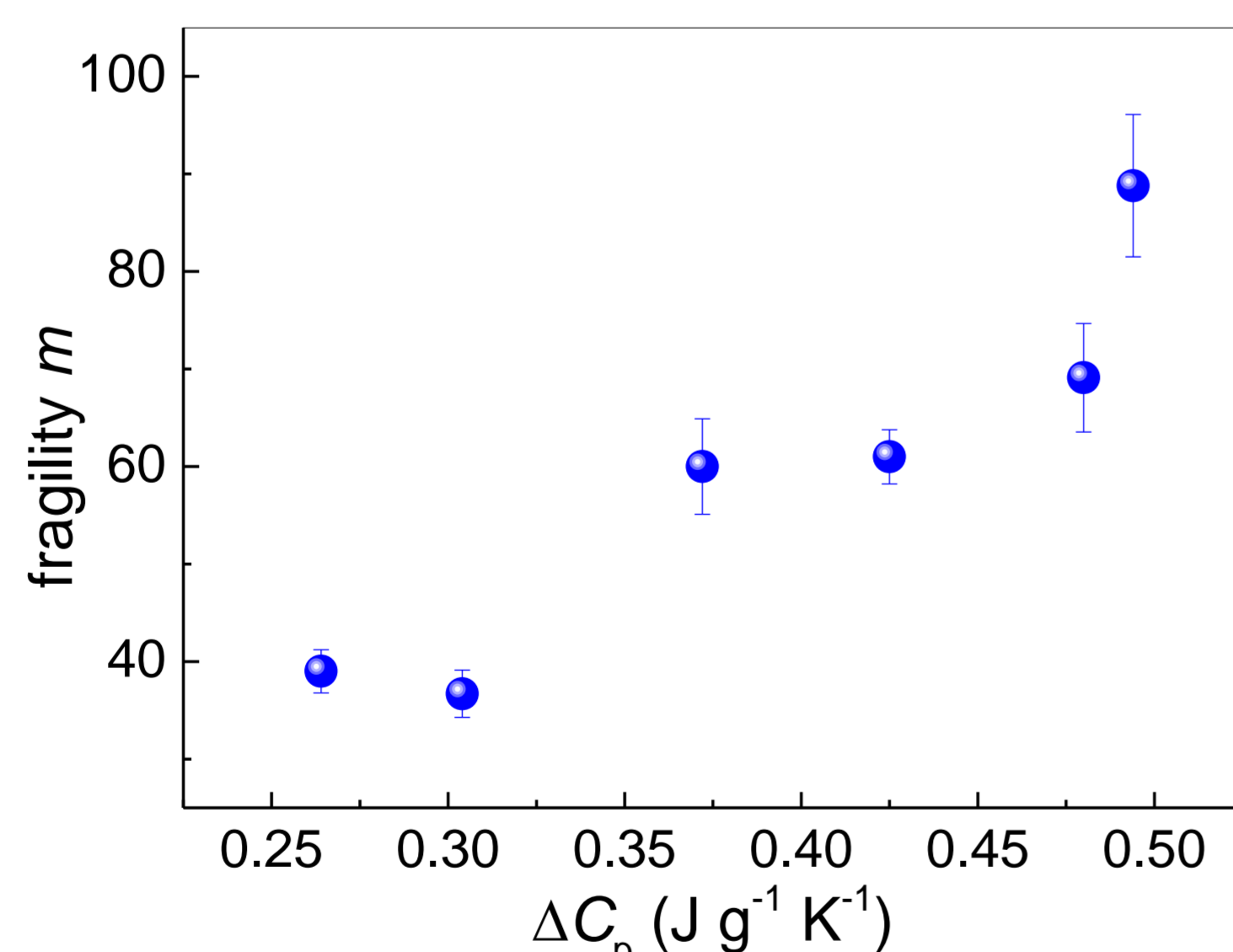
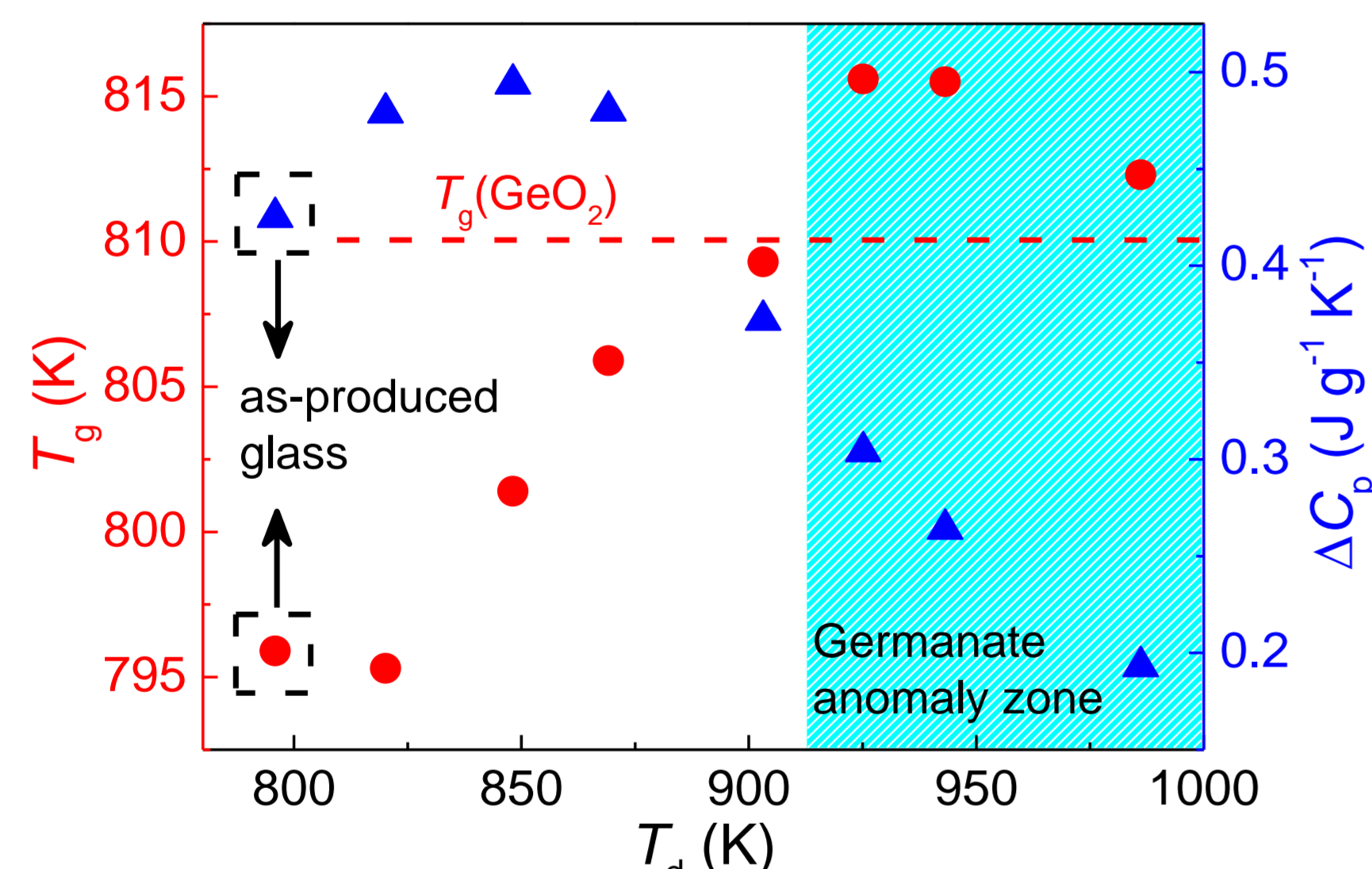
Thermodynamics & Crystallization

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 :

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

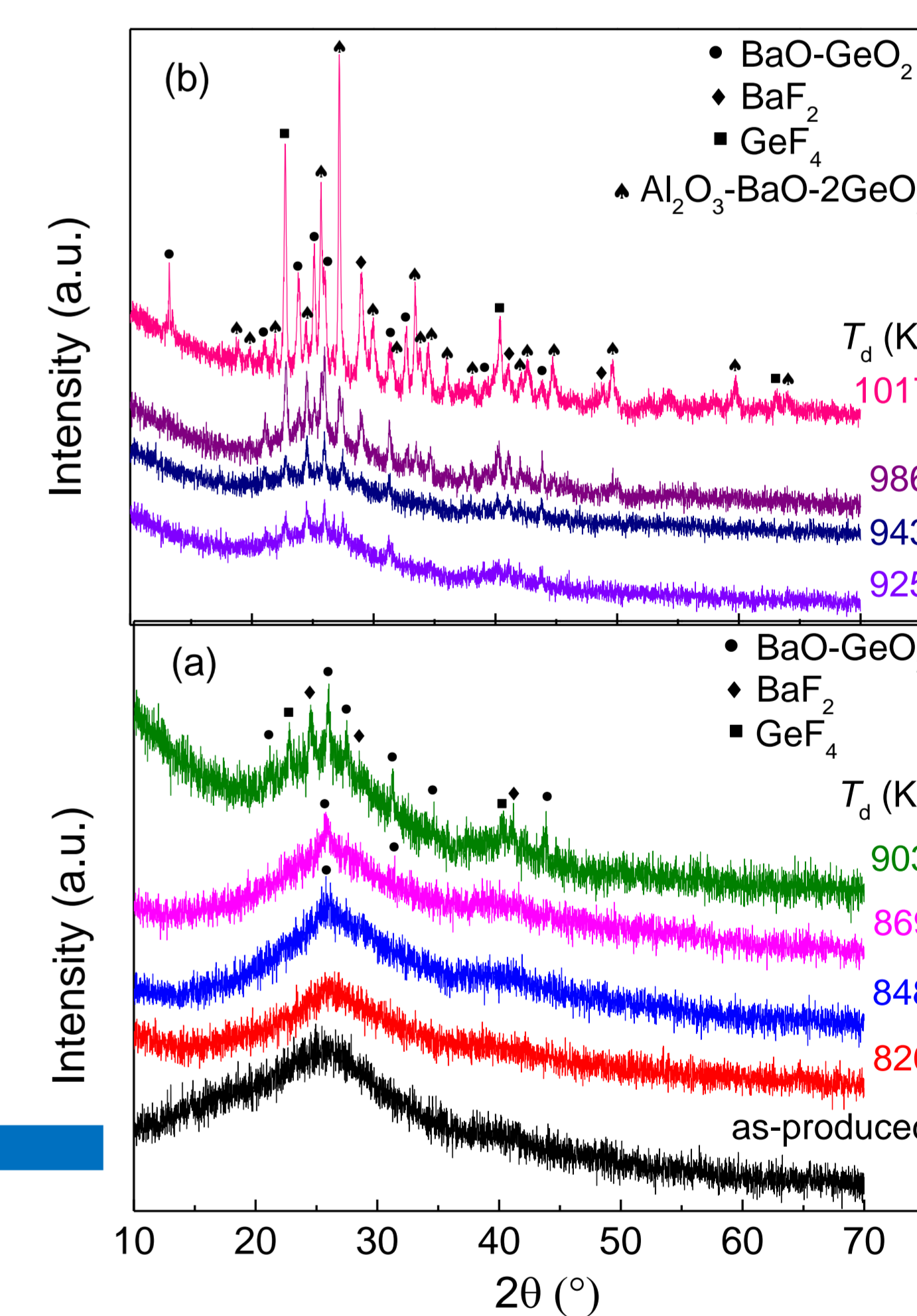


Increase T_d :

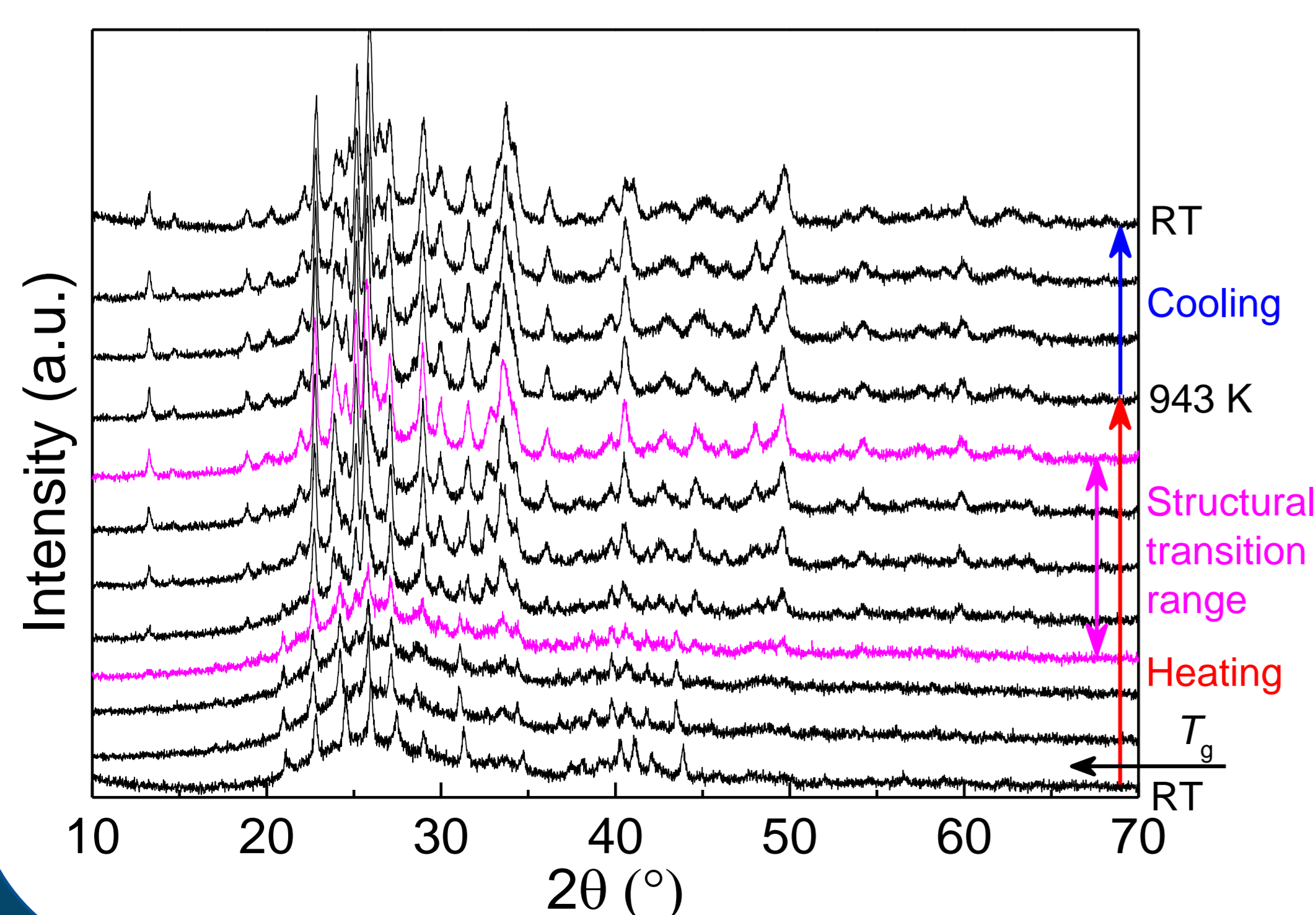
Glass transition temperature (T_g) exhibits a non-linear change. The ΔC_p starts to decrease from $T_d=869$ K. The non-linear change of T_g with T_d is similar as that with composition, indicating the possible existence of germanate anomaly zone.

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

T_d (K)	BaO-GeO ₂	GeF ₄	BaF ₂	Al ₂ O 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-GeO₂, GeF₄, BaF₂, and Al₂O₃-BaO-2GeO₂ 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

We thank Ang Zhao for glass preparation, Rasmus R. Petersen and Sonja Hastrup for XRD measurements and helpful discussion.