



## 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

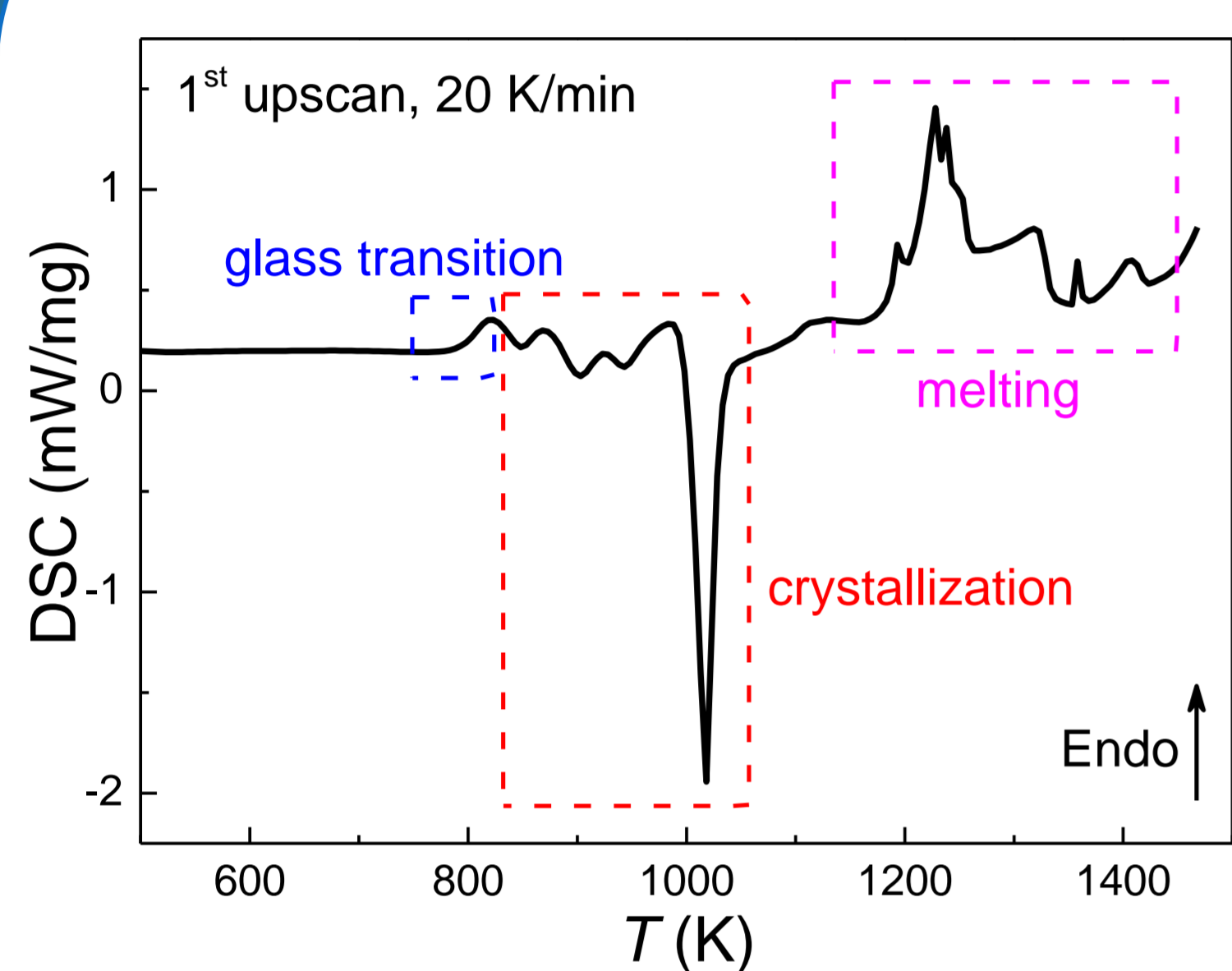


Fig. 1. DSC 1<sup>st</sup> upscan for the as-produced glass.

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

- Complex crystallization behaviors.
- Relatively low glass stability.

## Dynamic heat treatments

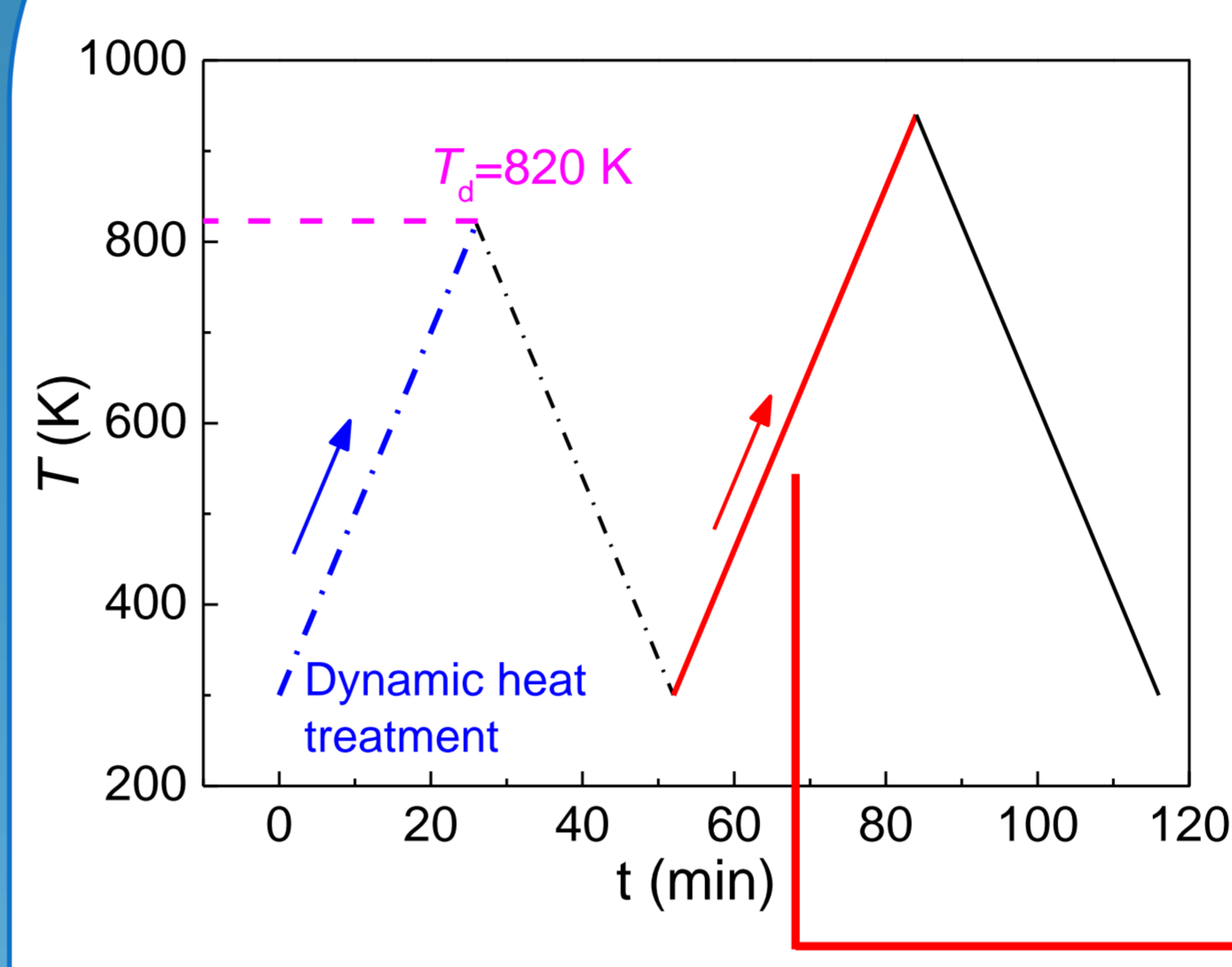


Fig. 2. Scheme diagram of dynamic heat treatment with  $T_d=820$  K.

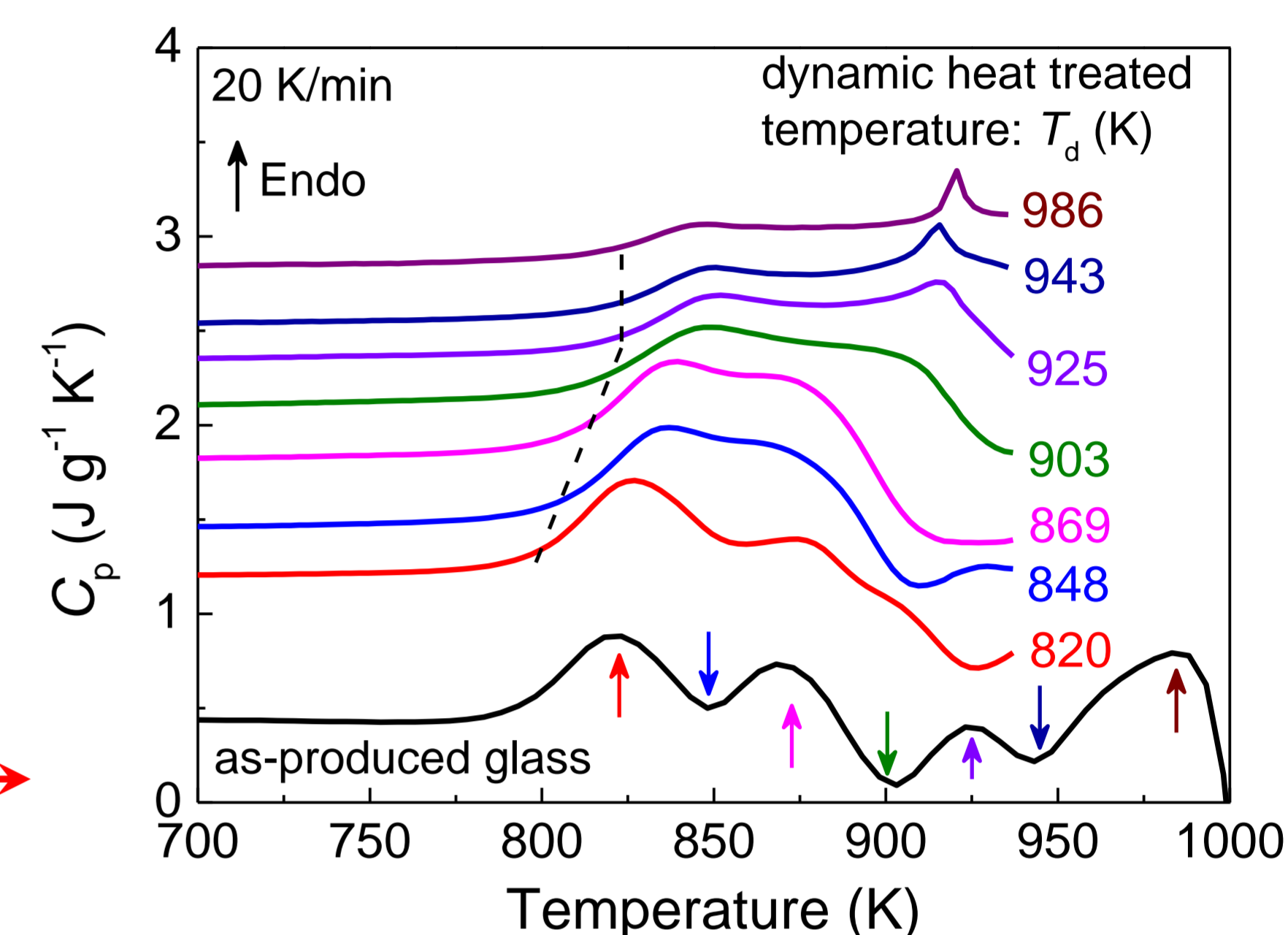


Fig. 3.  $C_p$  1<sup>st</sup> upscans for glasses with different  $T_d$ .

Increase  $T_d$ :

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

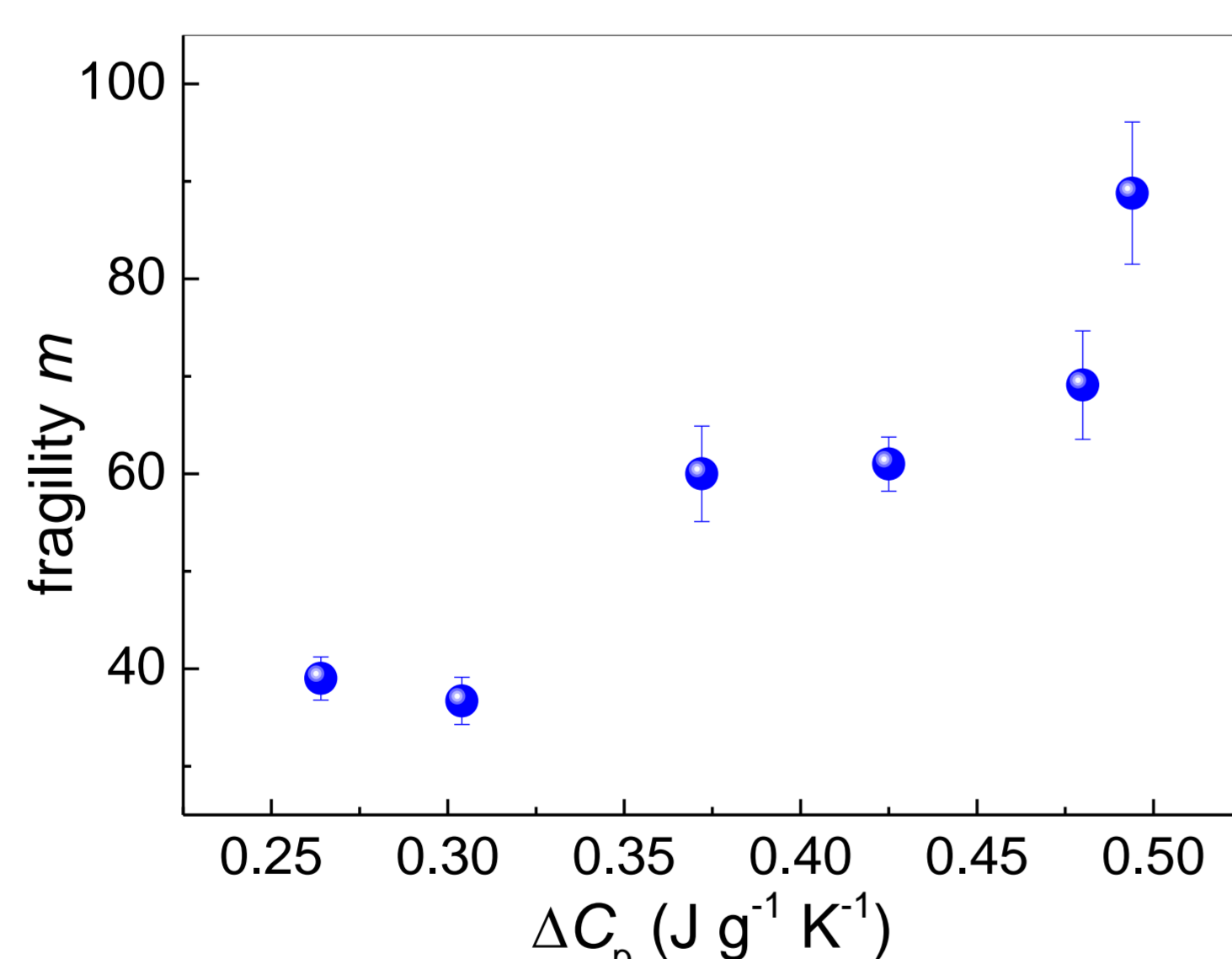
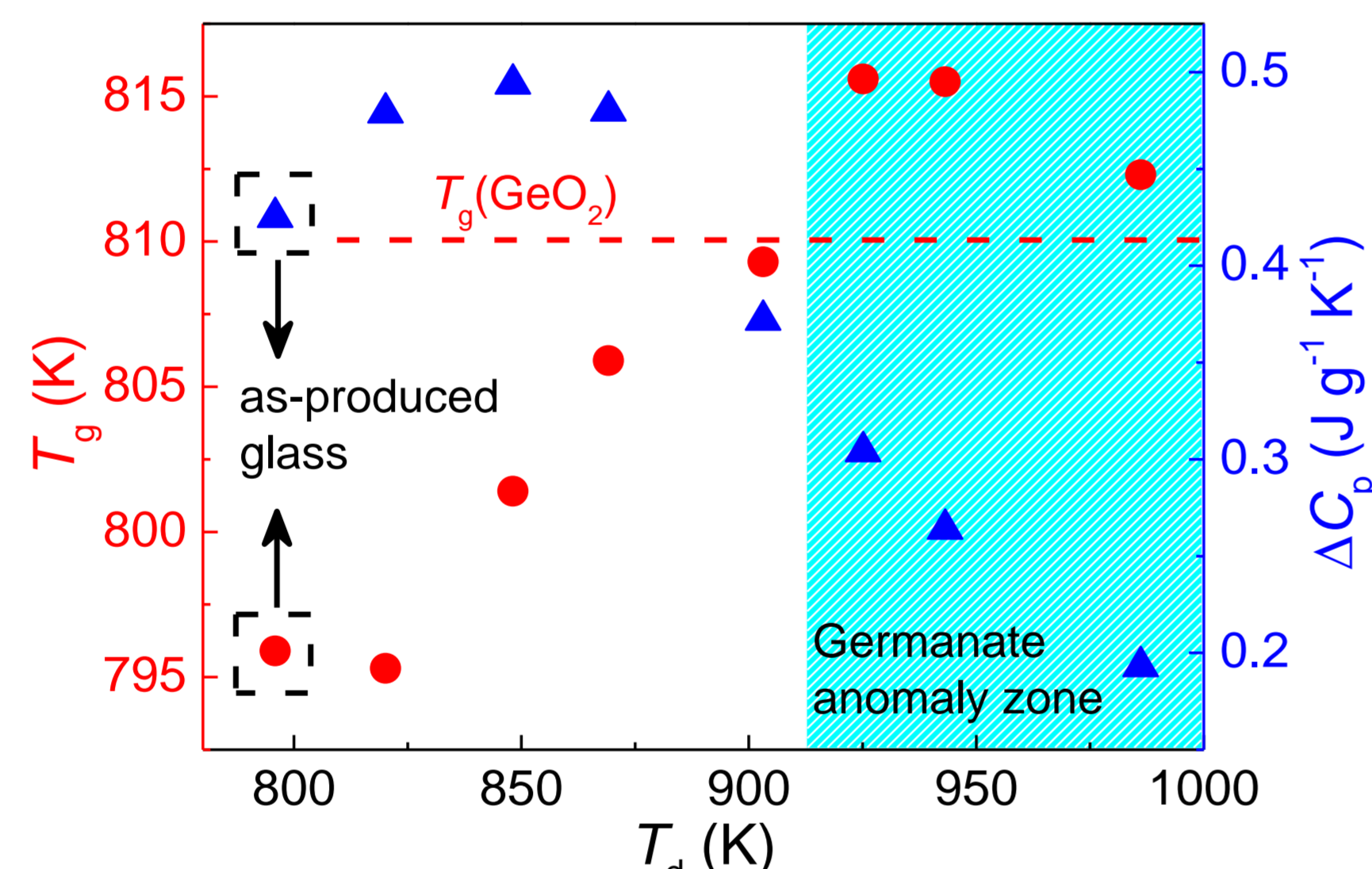
## Thermodynamics & Crystallization

$T_g$ : onset of the glass transition.

$\Delta C_p$ :  $C_p$  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  $\Delta C_p$  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.

$\Delta C_p$  can be seen as the thermodynamic fragility in studied system.

$T_d$ (K)	BaO-GeO <sub>2</sub>	GeF <sub>4</sub>	BaF <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> -BaO-2GeO <sub>2</sub>
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

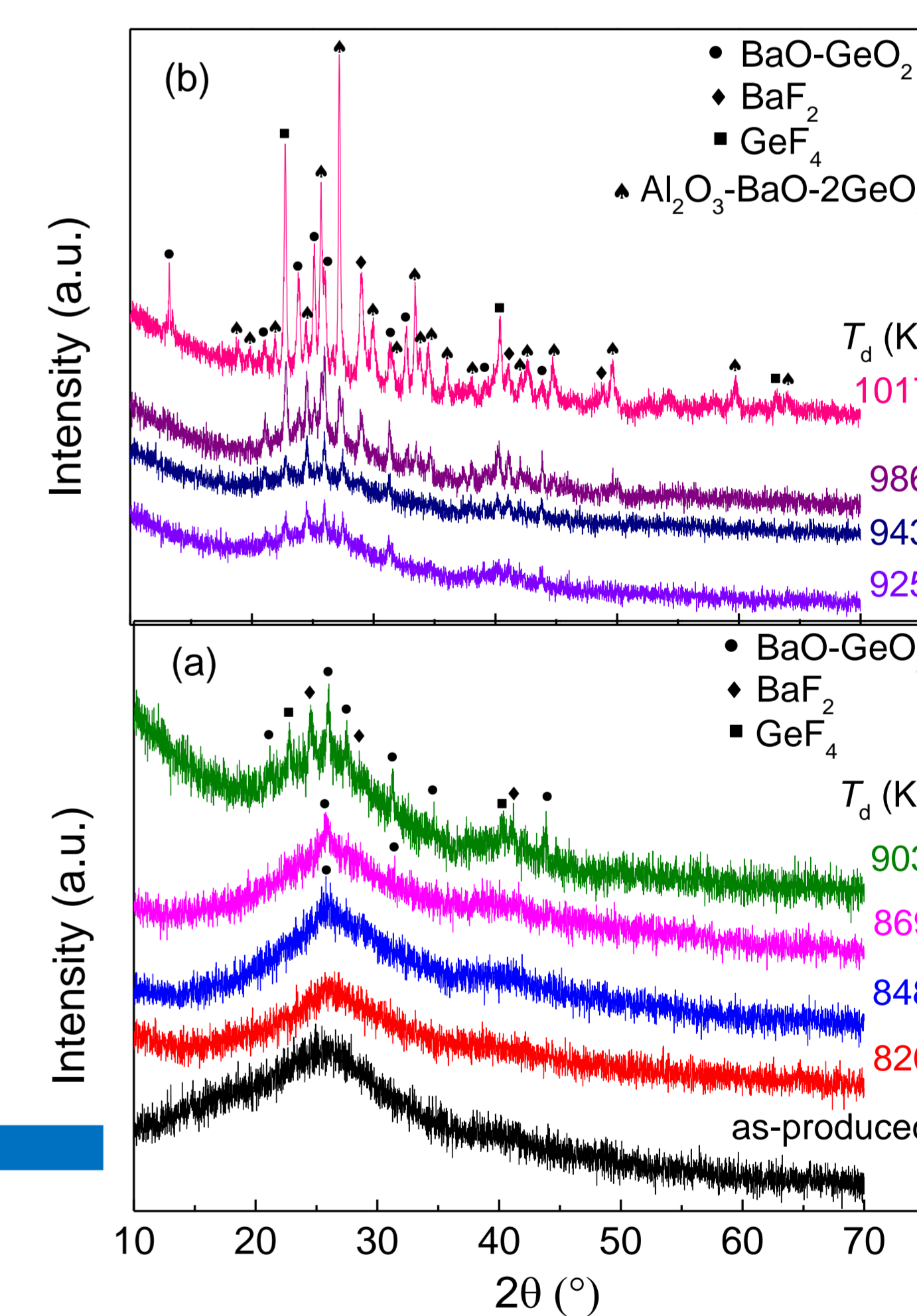
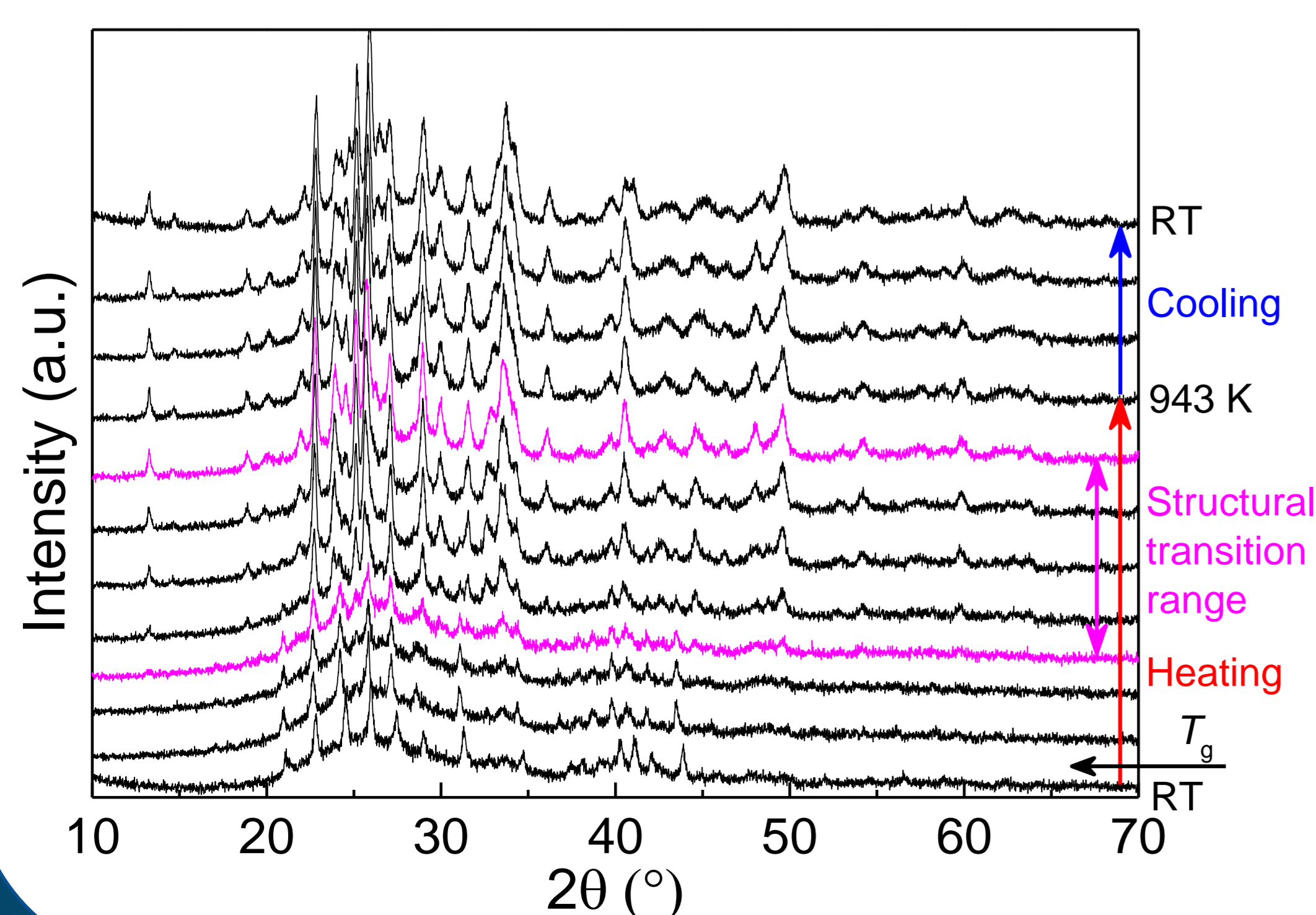


Fig. 4. RT XRD patterns for the glasses with different  $T_d$ .

## 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<sub>2</sub>, GeF<sub>4</sub>, BaF<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>-BaO-2GeO<sub>2</sub> 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,  $\Delta C_p$  can be used as the thermodynamic fragility in our studied system.
- Ge<sup>VI</sup> and germanate rings with Ge<sup>IV</sup> 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.