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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):
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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 GeO2-BaF2-AlF3 glasses by performing differential scanning calorimetry (DSC), room temperature (RT) and high temperature (HR) XRD.

Experimental

The glass 60GeO2-25BaF2-15AlF3 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, Td.

Calorimetry

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

Dynamic heat treatments

Increase Td:
• The glass gradually crystallize.
• The glass transition region shifts towards high temperature.

Thermodynamics & Crystallization

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

Conclusions

• The crystals BaO-GeO2, GeF4, BaF2, and AlO3-BaO-2GeO3 are found to form with the increase of Td.
• As Td increases, the residual glass becomes strong and the connectivity of the network increases. Besides, ΔCp can be used as the thermodynamic fragility in our studied system.
• GeIV and germanate rings with GeIV might cause the nonlinear change of Tg.
• 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 Haastrup for XRD measurements and helpful discussion.

In-situ HT XRD patterns for the glass with Td=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.