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Characterization of Phase Separation Processes in modifier-free binary Al_2O_3-SiO_2 glasses by Solid State NMR

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Introduction

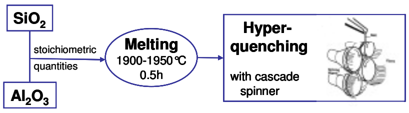
Many disordered materials used in technological applications are phase separated on the micro- or nanoscale. Prominent examples are bioactive glasses and glass ceramics which have applications in restorative surgery and as body implants. To optimize the chemical and mechanical properties of these biomaterials in an efficient manner, controlled crystallization of the initial glass ceramic composition can be induced by thermal treatment of glasses. We are interested in questions concerning structural ordering phenomena in the amorphous matrix before the crystallization takes place. To this end we chose 0.35 Al_2O_3 * 0.65 SiO_2 as a model system.

The structure of non-crystalline materials in the system Al_2O_3-SiO_2 has been a point of interest for many years [1,2]. The glass forming ability of silica melts with considerable amounts of alumina is low, but roller-quenching techniques and sol-gel methodology have made a preparation possible [3,4]. We are interested in the comparability of the micro-structures of these with different techniques obtained glasses. In a second step the base glasses were annealed at different temperatures below and above the glass transition.

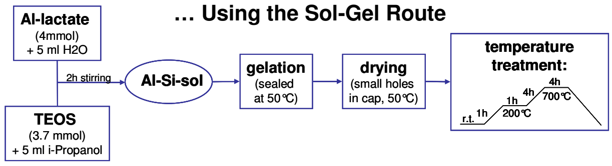
Synthesis of 0.35 Al_2O_3 * 0.65 SiO_2 …

… with Hyperquenching Techniques

The samples of the alumosilicate glass ceramic system have been provided by Dr. Y. Yue from Aalborg University.



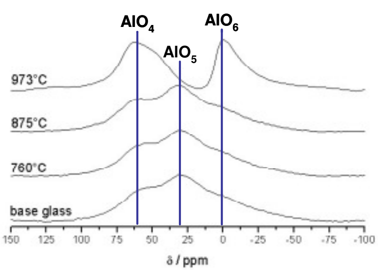
… Using the Sol-Gel Route



Parts of each base glass were annealed for 90 min. at different temperatures: 760℃, 875℃, 973℃ and 1075℃.

^{27}Al-NMR …

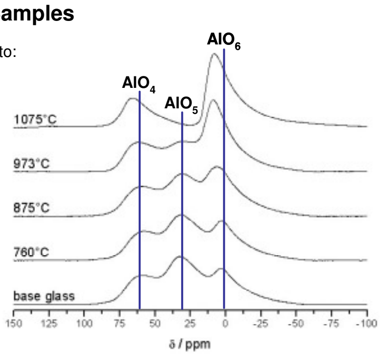
… of the Hyperquenched Samples



- Annealing up to 875℃:
  - constant AlO_4 content
  - constant AlO_5 content
  - constant AlO_6 content
- Annealing at 973℃:
  disappearance of AlO_5;
  crystallization to mullite

… of the Sol-Gel Derived Samples

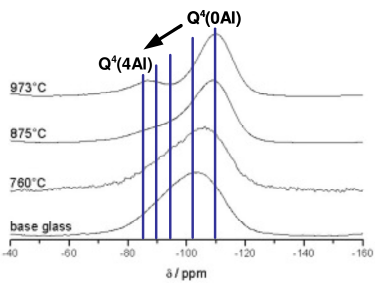
- Rising annealing temperature leads to:
  - increasing AlO_6 content
  - decreasing AlO_5 content
  - constant AlO_4 content
  - shift of AlO_6 to higher frequency
- Annealing at 1075℃:
  disappearance of AlO_5;
  crystallization to mullite ??



- The spectra of the hyperquenched samples show broader lines and not such a clear separation between the different groups like in the sol-gel derived samples.
- In the sol-gel samples the disappearance of the AlO_5 environment is a continuous process that is already visible at an annealing temperature of 875℃ and is completed at 1075℃, whereas in the hyperquenched samples this seems to happen suddenly between 875℃ and 973℃.

^{29}Si-NMR …

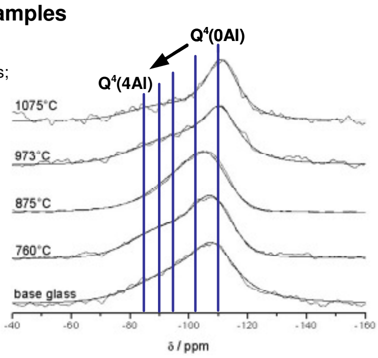
… of the Hyperquenched Samples



- Base glass:
  consists mainly of $Q^4(1Al)$ groups
- Increasing annealing temperature:
  - first formation of a shoulder on the left side
  - finally separation into two peaks
- Annealing at 973℃:
  large amount of $Q^4(0Al)$ and smaller one of $Q^4(4Al)$

… of the Sol-Gel Derived Samples

- Base glass:
  consists of a distribution of Q^4 groups; $Q^4(0Al)$ up to $Q^4(4Al)$
- Increasing annealing temperature:
  - shoulder becomes more pronounced
  - amount of $Q^4(0Al)$ increases
- Annealing at 1075℃:
  large amount of $Q^4(0Al)$ and smaller one of $Q^4(2Al)$ up to $Q^4(4Al)$



- As well in the hyperquenched as in the sol-gel derived samples a phase separation into silicon rich ($Q^4(0Al)$) and aluminum rich (Q^4(3 or 4 Al)) areas takes place with increasing annealing temperature.
- This process is in the hyperquenched system strongly pronounced, whereas it seems not yet completed in the sol-gel system when annealing at 1075℃.

Conclusions

- Alumosilicate glasses (0.35 Al_2O_3 * 0.65 SiO_2) obtained with hyperquenching techniques and via the sol-gel route were proven to have similar silicon and aluminum environments.
- Annealing the base glass at different temperatures below and above the phase transition leads in the sol-gel derived glasses to increasing AlO_6 environment and decreasing AlO_5 environment. Annealing at 1075℃ vanishes all five coordinated aluminum. In the hyperquenched system the AlO_5 environment disappears suddenly between 875℃ and 973℃.
- ^{29}Si-NMR shows phase separation into silicon rich and aluminum rich areas with increasing annealing temperature. This process is more pronounced in the hyperquenched system and seems to need higher annealing temperatures in the sol-gel system.

Literature

[1] Morikawa, H. et al.: J. Am. Ceram. Soc. **65** (1982) 78
[2] Risbud, S. et al.: J. Am. Ceram. Soc. **70** (1997) C10
[3] Schmücker, M. et al.: J. Non-Cryst. Solids **217** (1997) 99
[4] Eckert, H.: Prog. NMR Spectrosc. **24** (1992) 159

Acknowledgements

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