

Presentation abstract within the DFG Research Training Group for
Micro-, meso- and macroporous nonmetallic Materials

Structure and properties of anisotropic glasses and glass-ceramics

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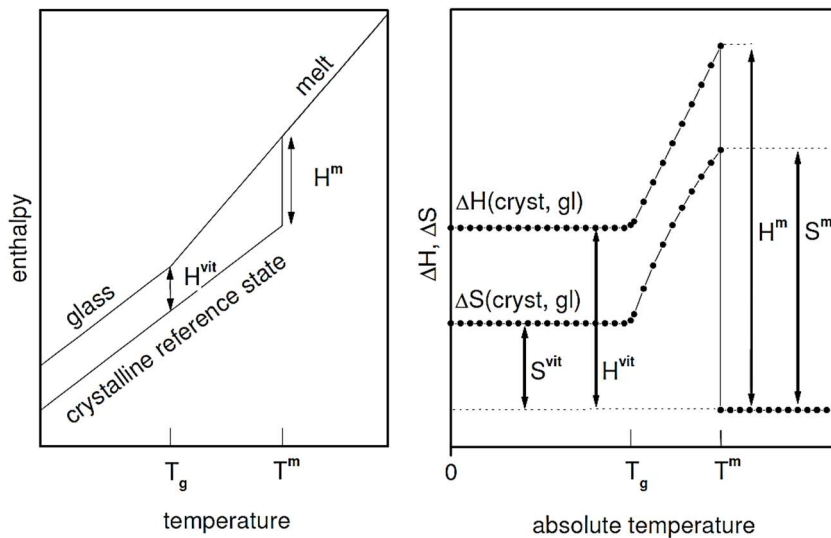
Basically, the presentation will give insights into the development of anisotropic glasses and glass-ceramics, the latter ranging in their physical characteristics, as a composite material, between glasses and ceramics. These materials are usually derived from glasses as initial material. And to be more precise in describing „what a glass is“, the following definitions are applied:

Ideally, glass is a homogeneous and *isotropic* material. In everyday use, the term "glass" is not clear or often restricted. One may designate an object (e.g. a wine glass) or a certain chemical composition (e.g. window glass or lead crystal glass) as glass. In the scientific sense, the term "glass" describes a state of aggregation, which, in analogy to the terms gas, liquid, crystalline solid, is *completely independent of a chemical composition*. This state is achieved by avoiding crystallization, i.e. the formation of a long-range order. Hence, in the physical sense, a *glass* or the *glassy state* refers to a non-equilibrium state of matter.

Philip W. Anderson, one of the 1977 Nobel Prize winners in Physics, made the following statement in 1995: "*The deepest and most important unsolved problem in condensed matter science is probably the theory of the nature of glass and the glass transition.*" We are, more than 25 years later, still unable to fully solve this problem. From a scientific point of view, it is also worthwhile to take a closer look at the phenomenon of the glass state and the glass transition.

Viscosity represents the most important kinetic property of a glass melt. Kinetics determine whether crystallization or glass formation occurs when a liquid cools. If the melt is super cooled, this super cooling and further temperature reduction and thus increase in viscosity take place so quickly that no crystal nuclei can form or nuclei that have already formed cannot continue to grow. This is how you get to the glass transition region; the liquid is no longer in internal equilibrium. And compared to a crystalline material, a glass has a short-range order as the crystalline counterpart but no long-range order.

Nevertheless, glass shows a mid-range order which is not depicted in crystalline materials. By describing a glass and the respective crystalline counterpart (or the derived glass-ceramic) a thermodynamic concept can be applied which relies on the enthalpy differences between these two states. The right image below shows the enthalpy and entropy difference between glass and the crystalline reference state. Below T_g (and with taking advantage of the *Simon-approximation*) constant values of H_{vit} and S_{vit} remain until $T = 0$ K. Between T_g and T_m the values increase to H_m and S_m respectively. At T_g , the heat capacity (= slope of the enthalpy curve) increases by the value $\Delta c_p = c_p(\text{liq}) - c_p(\text{gl})$.



This leads to a very stringent and useful description of the glass / the glassy state on basis of the crystalline reference state.

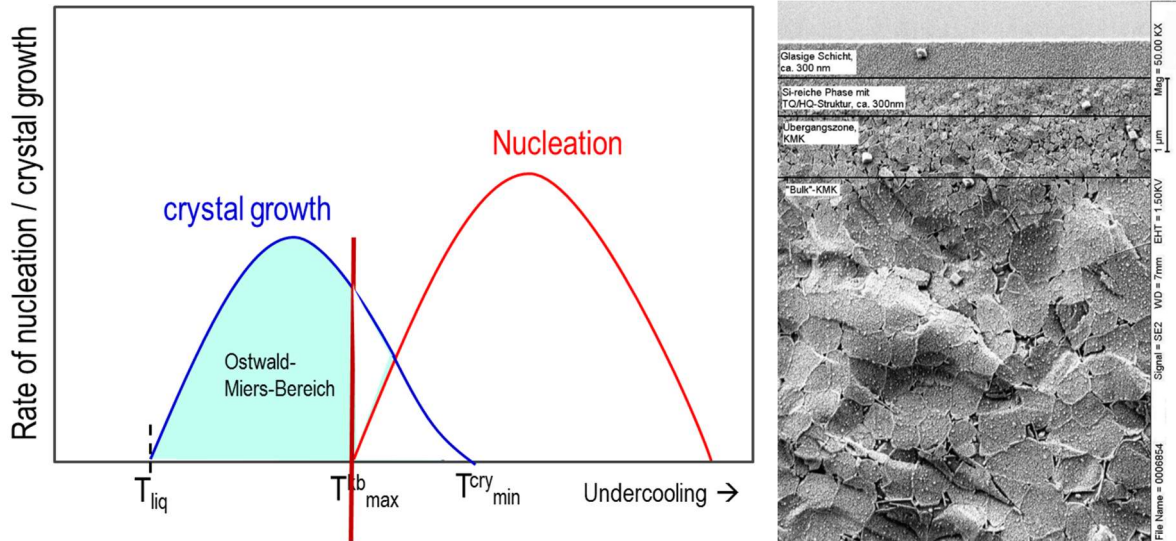
Now, the *undesired* crystallization of a melt is called "devitrification". However, if one manages to allow crystallization to take place partially and in a controlled manner in a glass melt, one can obtain a material consisting of a glass phase and a crystalline phase with fundamentally new properties. These glass-ceramics are materials that are produced usually from glass melts through controlled, controlled crystallization. Glass-ceramics therefore consist of a glassy and one or more crystalline phases. Controlled crystallization leads to a composite material with generally fundamentally different properties than the corresponding starting glass.

Compared to glasses of the same chemistry, glass-ceramics are often characterized by higher thermal and mechanical resistance as a result of a more rigid crystalline structure. When manufactured appropriately, glass ceramics differ from ceramic materials of comparable composition in that they are free of pores. To a certain extent, it is therefore possible to combine the advantages of glass (manufacturing method and shape) and traditional ceramics (thermal and mechanical resistance). The properties of glass ceramics are influenced both by the type and content of the crystal phase(s) and the residual glass phase contained in them. There are therefore several degrees of freedom in setting the properties of a glass ceramic.

The topic of the actual research is that glass-ceramics (like glasses) can show intrinsic and extrinsic gradients. Glass-ceramics (usually in contrast to glasses) can exhibit anisotropy if the crystal phase is aligned in a preferred direction (thermal conductivity, electrical and optical properties).

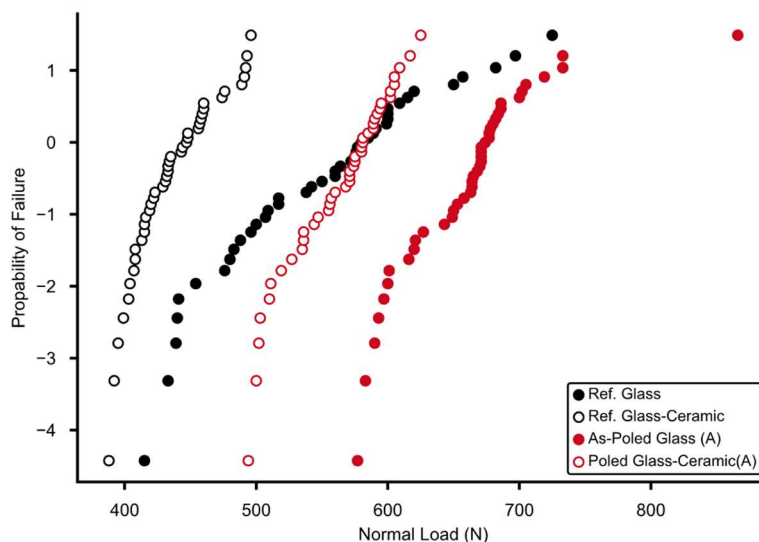
Hence, there are basically two options to bring a glass or a glass-ceramic into an anisotropic state. One is influencing the glass-ceramic in its crystallization in that way that different phases are crystallized in different regions in the material. The other option is to induce the anisotropy already in the glass itself.

For the first option, controlling the nucleation and crystal growth rate, sketched below, differently in different areas of the material is necessary. This can be achieved e.g. by controlled diffusion processes via T-t control. This enables different structures and a highly anisotropic material can be derived as shown in the right SEM image.



The material shown right enables e.g. a high-strength base material with a highly polish-able surface, suitable as substrates for photolithographic processes.

For initial glasses we investigated ways to apply a thermal poling process to glasses by using carbon electrodes as blocking electrodes for the surrounding atmosphere. This leads to a complex charge compensation process and the need to maintain stoichiometric relations. Oxygen anions can migrate towards the anode or electrons discharge into the the anode and polymerization of the network and the formation of oxygen tri-cluster occur. This in turn leads to a highly anisotropic glass, enabling functionalization and different applications later on. Especially mechanical properties are increased significantly, showing below improvements in breakage probability of ca. 25 – 50 % due to compressive stresses induced.



The final description of the system of glass and ceramic phases in terms of their thermodynamic, mechanical and other properties then is again accomplished by applying the thermodynamic approach of H_{vit} and S_{vit} presented in the beginning of this abstract.