Fundamental research on twofold phase formation of apatite solid-solutions and leucite in glass-ceramics

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Abstract In this study the phase formation of apatites in the multi-component SiO_2-Al_2O_3-Na_2O-K_2O-CaO/SrO-P_2O_5-F system was investigated. Based on a special composition CaO was partially and completely substituted by SrO. Room and high temperature X-ray diffraction (RT- and HT-XRD) and scanning electron microscopy (SEM) were used to characterize the phase formation. The results of this study showed a formation of two different apatite solid-solutions, $Sr_{7.3}Ca_{2.7}(PO_4)_6F_2$ and $Sr_6Ca_4(PO_4)_6F_2$ and Sr-apatite $Sr_5(PO_4)_3F$. Leucite formation is based on surface crystallization. The conclusion is a twofold volume and surface nucleation and crystallization mechanism.

Introduction

Studying the nucleation and crystallization mechanisms of glass-ceramics with a complex chemical composition is one of the most important prerequisites for the development of new, tailor-made materials. The volume crystallization of fluorapatite is initiated by primary crystal phase formation prior to the main crystal precipitation in leucite-fluorapatite glass-ceramics. Fluorapatite crystallization is known to precipitate at 800 °C [1-4]. Hill et al. [5] investigated the influence of strontium substitution in fluorapatite glass-ceramics. Leucite-fluorapatite glass-ceramics are used for a wide range of indications as is shown by the translucent biomaterials used in restorative dentistry. Five glass compositions with different CaO/SrO contents were examined in this study. The main focus was placed on phase formation as a function of temperature.

Experimental

Using the multicomponent system with the following composition in wt.% as the starting point: 54.6 SiO_2, 14.2 Al_2O_3, 8.4 Na_2O, 10.7 K_2O, 5.0 CaO, 0.9 ZrO_2, 0.2 TiO_2, 4.0 P_2O_5, 0.2 Li_2O, 0.3 B_2O_3, 0.8 CeO_2 and 0.7 F, CaO was systematically replaced by SrO (Table 1).

	glass 1 / wt. %	glass 2 / wt. %	glass 3 / wt. %	glass 4 / wt. %	glass 5 / wt. %
CaO	5.0	3.7	2.4	1.2	0.0
SrO	0.0	2.3	4.5	7.0	8.8

Table 1 *CaO- and SrO-contents of the base glasses*

The relationship of all the additional components to each other was maintained. For the investigation of the phase formation by high temperature X-ray diffraction we used powder samples. However, since the detection of the apatite phases was not possible because of the surface crystallization of leucite during the measurement, the apatite formation had to be investigated on heat treated powder compact samples by means of room temperature X-ray diffraction. The room and high temperature X-ray diffraction analysis (Bruker AXS D 5005) was conducted in 2Θ angle range between 10° and 60° with a step size of 0.014° and a measuring time of 0.5 s per scan (Cu Kα radiation). Additionally, the structure and crystal morphology of selected samples were examined by scanning electron microscope (LEO DSM 962). The nucleation and crystallization mechanisms of glass 1 (Table 1) had already been very thoroughly examined by the international research group TC7 (Technical Committee 7) of the ICG International Committee for Glass).

Results

The high temperature X-ray diffraction analysis of glasses 1 and 5 showed the start of surface crystallization of leucite at temperatures between 800 and 850 °C (Fig. 1). Additionally, the formation of different primary phases was observed. Glass 1 showed α-$NaCaPO_4$ between room temperature and approximately 600 °C and β-$NaCaPO_4$ between approximately 600 and 1000 °C (Fig. 1). Glass 5, which contains SrO instead of CaO, showed only a primary crystal phase of $NaSrPO_4$ between room temperature and approximately 1000 °C (Fig. 1). Glasses 2-4, which contained different CaO/SrO ratios, showed $NaSrPO_4$ s.s. as the primary phase between room temperature and 1000 °C (Fig. 1). This also demostrates that

spontaneous crystallization from the melt took place as early as in the quenching process during the cooling of the glass. The start of apatite formation in glass 1 was evident from approximately 800 °C and in glass 5 from approximately 700°C (Fig. 1). The fact that an apatite solid-solution of $Sr_{7.3}Ca_{2.7}(PO_4)_6F_2$ and $Sr_6Ca_4(PO_4)_6F_2$, occurred from approximately 800 °C in glass-ceramics based on glasses 2-4 with the simultaneous presence of CaO and SrO is noteworthy (Fig. 1).

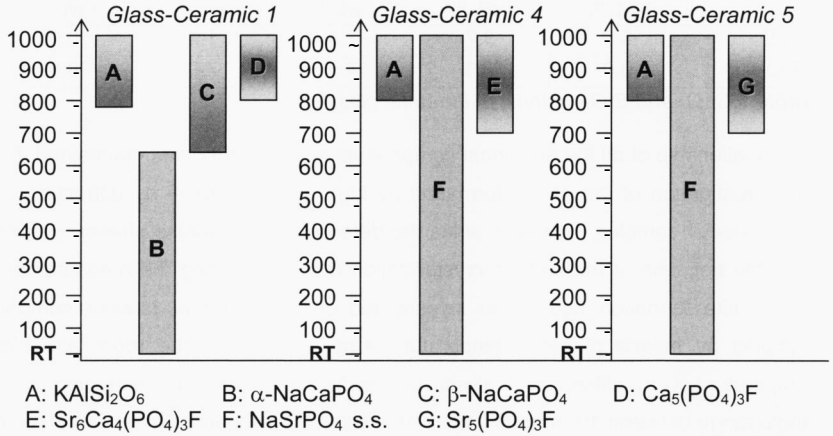

Figure 1 *Schemes of the room and high temperature X-ray diffraction results of the different phase formation processes (Glass-Ceramic 1, 4 and 5).*

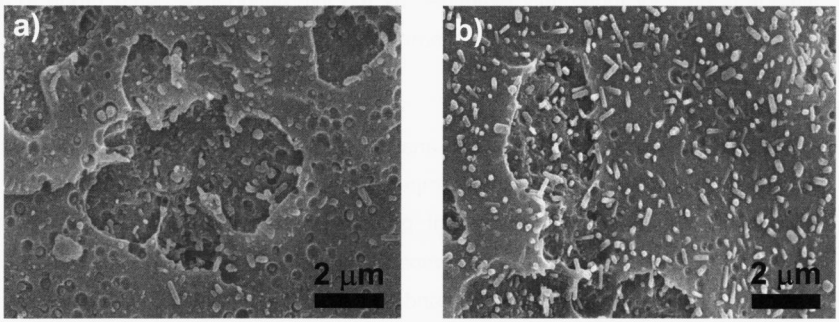

Figure 2a-b *Microstructures of heat treated powder compacts (etched fracture surface 3% HF, 10sec.) a) Glass-Ceramic 4 after heat treatment (1000°C / 1h) b) Glass-Ceramic 5 after heat treatment (1000°C / 1h)*

The needle-like formation of apatite crystals in all glass-ceramics at temperatures above 750 °C was proven on heat treated powder compact samples by SEM images (Figs 2a-b) and also by RT-XRD.

Discussion

The solid state reactions and the phase formation associated with them are the result of complex nucleation and crystallization mechanisms in this multicomponent glass-ceramics. The surface crystallization of leucite was combined with the volume crystallization of apatite. Two separate reactions took place. It was possible to produce glass-ceramics, with $Ca_5(PO_4)_3F$ or $Sr_5(PO_4)_3F$, or apatite solid-solutions of $Sr_6Ca_4(PO_4)_6F_2$ or $Sr_{7.3}Ca_{2.7}(PO_4)_6F_2$. The different solid solution formations may be attributed to the fact that the bivalent alkaline-earth ions Ca^{2+} and Sr^{2+} build up in different quantity ratios in the amorphous phosphate phase separation during the cooling process.

Conclusion

As shown by the results of this investigation, we succeeded in transferring the findings regarding the fluorapatite formation in CaO-rich glass-ceramics to the phase formation of apatite and apatite solid solutions in SrO-poor and SrO-rich glass-ceramics. The main differences in phase formation occur during the primary phases. SrO-poor glass-ceramics showed α-, β-$NaCaPO_4$ and SrO-rich glass-ceramics $NaSrPO_4$ as the primary phase.

Acknowledgements

The authors would like to thank N. Unkelbach (University of applied Science Höhr-Grenzhausen, D) for experimental studies (part of diploma degree) and Mr. W. Keutschegger (Ivoclar Vivadent AG, FL) for the SEM and X-ray diffraction studies.

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