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# Comparative study of the crystallization behavior within the $Na_2O-Y_2O_3-ZrO_2-SiO_2$ system during heating and cooling

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Phase formation in glasses from the system  $Na_2O-Y_2O_3$ —SiO<sub>2</sub> with different concentrations of  $ZrO_2$  were studied concerning phase formation and crystallization behavior. The compositions were near the stoichiometry of  $NaYSi_2O_6$ . A comparison of microstructure and phase content after instant crystallization during slow cooling and after subsequent thermal annealing is given. The phases as well as the microstructure differ depending on thermal history. During cooling, predominantly a phase with apatite structure ( $NaY_9Si_6O_{26}$ ) precipitates and the residual glassy phase is enriched in  $ZrO_2$ . The composition of the glassy phase was quantified and an enrichment of  $ZrO_2$  of slightly above five mol% was measured.  $ZrO_2$  concentrations >5 mol% lead to the precipitation of  $Y_2O_3$  enriched  $ZrO_2$ . A fast cooling of the melt results in glass formation without instant crystallization. Subsequent heating at temperatures below 1000 °C leads to the precipitation of an unknown phase whereas at higher temperatures  $NaYSi_2O_6$  crystallizes. Two-step heating in terms of nucleation and crystal growth were performed and small  $ZrO_2$ -particles have been formed homogenously within the sample volume. Those particles do not trigger volume crystallization within the glasses and surface crystallization is the predominant crystallization mechanism.

# 1. Introduction

Glasses within the system Na<sub>2</sub>O-Y<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> are of great scientific interest because of their good sodium ion conductivity and their possible application as solid electrolyte.1,2 Especially sodium-rich glasses and glassceramics show the often desired high sodium conductivity.<sup>3</sup> The glass formation range within the ternary Na<sub>2</sub>O-Y<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system is evaluated by two different studies, as summarized in Fig. 1. In ref. 2, it was reported that the glass formation is limited by the maximum Y<sub>2</sub>O<sub>3</sub>-concentration of 9 mol%. In contradiction, ref. 4 reports a maximum Y<sub>2</sub>O<sub>3</sub> concentration of around 15 mol%. The discrepancies cannot fully be explained by the synthesis temperatures or synthesis routes because in both studies, an almost identical experimental setup was used for the melting of the glasses. Independent from those investigations, it is known that other glass systems such as the Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> enable much higher Y<sub>2</sub>O<sub>3</sub>concentrations. Hence, additions of Al<sub>2</sub>O<sub>3</sub> should enlarge the glass formation range. Such glass-ceramics focus on the However, the general crystallization behavior within the ternary system  $Na_2O-Y_2O_3-SiO_2$  is scarcely described in literature.

The common technology to produce glass-ceramics is usually to quench a glass melt and to re-heat it to a

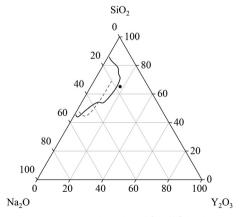


Fig. 1 Glass formation range in units of [mol%] in the system Na<sub>2</sub>O-Y<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> reported in ref. 4 (solid line) and ref. 2 (dashed line). The dot depicts the starting composition for the investigations within this manuscript.

precipitation of yttrium aluminium garnet (YAG) crystals (mostly doped with Ce<sup>3+</sup>) for white light emission.<sup>6,7</sup>

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temperature slightly above  $T_{\rm g}$  in order to achieve nucleation and then in a second step to a higher temperature to allow crystal growth. Another strategy, however, is to slowly cool the glass and to achieve nucleation and crystal growth upon cooling. The phases formed during these different types of temperature-time schedules might be different and the formed microstructure, too. In this paper, glass-ceramics prepared by both concepts are reported on and compared with each other.

In order to prepare such compact materials, the crystallization behavior has to be studied with respect to phase formation. Furthermore, the effect of additives on the formation of volume crystals has to be investigated. One of the most popular oxidic nucleation agents is ZrO2, which is able to trigger volume crystallization in various glass systems.8 It should be noted that in some glass compositions, such as Li<sub>2</sub>O·2 SiO<sub>2</sub> minor concentrations of ZrO<sub>2</sub> (≤2 mol%) show the opposite effect, i.e. act as nucleation inhibitors.9,10

This work focuses on the glass formation in the range of high Y<sub>2</sub>O<sub>3</sub> concentrations, near the border between glass formation and instant crystallization during cooling. The compositions within this manuscript are based on a stoichiometric disilicate with the composition NaYSi<sub>2</sub>O<sub>6</sub>. This stoichiometry is also depicted in Fig. 1 and serves as starting point for the investigations. Furthermore, the effect of different concentrations of ZrO2 on the glass stability and crystallization behavior is investigated.

# 2. Materials and methods

Samples with the compositions summarized in Table 1 were melted in Pt crucibles using an electric furnace with MoSi<sub>2</sub> heating elements. The sample Zr0 possesses the same stoichiometry as crystalline NaYSi2O6. If ZrO2 is added, the molar ratios Na2O:Y2O3:SiO2 were kept constant. Reagent grade raw materials (Na<sub>2</sub>CO<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>) were thoroughly mixed and afterwards heated to a temperature of 1650 to 1680 °C for several hours in order to obtain a homogenous melt. Afterwards, two different cooling regimes were used. In a first regime, samples were cooled from the melting temperature of 1650 or 1680 °C down to 800 °C with a rate of 1 K min<sup>-1</sup>. Afterwards, the furnace was switched off in order to allow a slow cooling of the sample down to room temperature. This procedure was used to achieve instant crystallization during cooling. Some of the compositions were re-melted at 1650 to 1680 °C and afterwards cast in a steel

Table 1 Batch compositions of the melted glasses in units of [mol%]

Sample name	Na <sub>2</sub> O	$Y_2O_3$	$SiO_2$	$ZrO_2$
Zr0	16.67	16.67	66.67	_
Zr5	15.83	15.83	63.33	5
Zr7	15.5	15.5	62	7
Zr9	15.17	15.17	60.67	9
Zr11	14.83	14.83	59.33	11

mould, which was then transferred into a muffle furnace preheated to a temperature in the range from 750 to 780 °C, which is slightly above the respective glass transition temperatures. Directly afterwards, the pre-heated furnace was switched off to allow cooling to room temperature with a rate of around 1 to 2 K min<sup>-1</sup>. After removal from the cold furnace, those samples are amorphous and were used for reheating in order to achieve nucleation and crystallization.

These heat treatments were performed in a muffle furnace using a heating rate of 5 K min<sup>-1</sup> and a temperature accuracy of ±5 K. The supplied temperatures were in the range from 850 and 1150 °C kept for 5 h. Differential scanning calorimetry (DSC) was performed with a Linseis DSC Pt 1600. For this purpose, the glass samples were crushed using a steel mortar and subsequently sieved to a size fraction of 400 to 500 µm. This comparatively large grain size was chosen to predominantly observe volume effects. Afterwards, 60 mg of the crushed and sieved glass were given into a corundum crucible, which was heated with a rate of 10 K min<sup>-1</sup>.

The phase content was determined via X-ray diffraction (XRD) using a Bruker D8 Advance ( $\theta/\theta$ -geometry) and Nifiltered Cu Kα radiation. Measurements were performed in a  $2\theta$ -range from 10 to 60°.

The microstructure and composition of the appearing phases was studied via scanning electron microscopy (SEM) in combination with elemental analyses (energy dispersive X-ray spectroscopy, EDXS). Therefore, a ZEISS Supra 55 VP in combination with a Bruker EDXS system were used. From elemental distribution maps, smaller regions of interest belonging to solely one phase were defined and afterwards quantified. This procedure was used to determine the composition of different crystalline or amorphous phases.

# Results and discussion

#### 3.1 Crystallization upon cooling

The stoichiometric sodium-yttrium-disilicate composition (composition Zr0 in Table 1) served as starting point for the investigations. From the glass formation ranges shown in Fig. 1, it can be seen that this composition is marginally outside the published glass formation range. However, the descriptions of the glass formation range vary in literature and the maximum concentration of Y<sub>2</sub>O<sub>3</sub> in such glasses is not yet clear. During melting of the composition Zr0, a solid layer has formed at the top of the liquid. Very high melting temperatures of 1680 °C kept for several hours lead to the disappearance of this layer and hence enabled the preparation of clear glasses.

If the melts are slowly cooled to room temperature, instant crystallization occurs. In order to investigate the crystallization and phase formation during slow cooling, the melts were cooled from 1680 to 800 °C using a rate of 1 K min<sup>-1</sup>. At 800 °C, the furnace was switched off and the samples were allowed to cool to room temperature with a rate of around 1 to 2 K min<sup>-1</sup>. Fig. 2 shows SEM micrographs of compositions with different ZrO<sub>2</sub>-concentrations after slow

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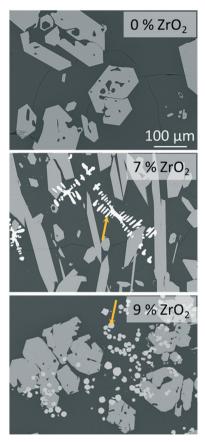


Fig. 2 SEM micrographs (backscattered electrons) of samples ZrO, Zr7, and Zr9 after slow cooling to room temperature at identical magnifications. The arrows point at ZrO<sub>2</sub> precipitates.

cooling. In sample Zr0, solely one crystalline phase is observed, whereas in the samples Zr7 and Zr9, a second phase precipitates. In Fig. 2, this latter phase is marked with arrows. In the case of sample Zr7, it precipitates in dendritic morphology with crystal sizes above 100 µm as known from other ZrO2-containing materials obtained via cooling of a melt, such as fused-cast refractories.11 In Zr9, a different morphology is observed. Dendrites were not found within this sample but spheres with diameters below around 20 μm. The sample Zr5 is not shown in Fig. 2 because it is similar to Zr0, i.e., only one phase appears. The compositions of the residual glassy phase and the crystalline phases are determined via EDXS on samples, where two crystalline phases are observed under the supplied conditions.

The mol% compositions of the respective phases are summarized in Table 2. From those results, it can be seen that the phases have, within the limits of error of EDXS, the same composition which does not depend on the ZrO2-concentration. The glassy phase contains around 5.2 to 5.3 mol% ZrO<sub>2</sub>. The main crystalline phase is enriched in Na, Si, and Y. It also contains some ZrO2. This phase should be the NaY9Si6O26 with apatite structure and the space group  $P6_3/m$  (176).<sup>12</sup>

As reported in literature, the phase NaY<sub>9</sub>Si<sub>6</sub>O<sub>26</sub> also appears the stoichiometric compound NaYSi<sub>2</sub>O<sub>6</sub>

Table 2 Quantification results from EDXS of samples with different ZrO<sub>2</sub>-concentrations (in mol%) after slow cooling

	Sample	Na <sub>2</sub> O	$SiO_2$	$Y_2O_3$	$ZrO_2$
Glassy phase	Zr7	22.8	67.5	4.4	5.3
• •	Zr9	22.0	68.5	4.2	5.3
	Zr11	22.5	67.3	5.0	5.2
Main crystal phase	Zr7	5.5	56.8	33.7	3.9
•	Zr9	5.2	57.4	33.5	3.9
	Zr11	5.6	56.6	35.6	2.3
Secondary crystal phase	Zr7	0.1	2.3	15.9	81.7
	Zr9	0.0	1.9	15.1	82.9
	Zr11	0.1	2.0	17.4	80.5

incongruently. 13 The measured composition is not exactly equal the stoichiometry of NaY<sub>9</sub>Si<sub>6</sub>O<sub>26</sub>, especially the Y-concentration is too low. However, also ZrO2 seems to be incorporated into the phase which changes the whole stoichiometry. It remains unclear, at which particular position, Zr<sup>4+</sup> is incorporated. Reports in the literature about the formation of a solid solution, where quadrivalent ions are incorporated, also give no clear evidence on the incorporation.<sup>14</sup>

In this phase, Y3+ occurs at two different sites; one of them is only occupied by Y3+ which has a coordination number of 7 (in the following denoted as Y2-sites) and, while at the other site with the coordination number of 9, 75% are occupied by Y3+ (denoted as Y1-sites) the other 25% by Na+ (denoted as Na-sites). According to the EDXS analyses, the empirical composition of the crystalline phase is as follows: 3.1 Na, 15.8 Si, 18.8 Y, 1.1 Zr, and 61.2 O (at%), which correlates with a phase with a stoichiometry of around Na<sub>1.3</sub>Y<sub>8.0</sub>Si<sub>6.7</sub>Zr<sub>0.5</sub>O<sub>26</sub>. Since Zr<sup>4+</sup> has a similar ionic radius as Y<sup>3+</sup>, (72 and 90 pm, respectively<sup>15</sup>), it should hence be assumed that Zr<sup>4+</sup> occupies Y<sup>3+</sup> sites, which of the two above described sites, however, remains unclear.

The basic composition in Kröger-Vink notation is as follows:

Zr4+ should occupy Y3+ sites in a concentration according to the measured chemical composition. The accuracy of the used quantification method, especially taking the measuring errors for light elements like oxygen or sodium into account, implicates that the phase should be NaY<sub>9</sub>Si<sub>6</sub>O<sub>26</sub> in which Zr<sup>4+</sup> is incorporated at Y<sup>3+</sup> sites.

NaY<sub>9</sub>Si<sub>6</sub>O<sub>26</sub> has a very high melting temperature. Similar compositions are reported in ref. 13 to have melting points at around 1800 °C, or even higher. This also explains the different glass formation ranges reported in literature. At very high temperatures during synthesis (and a long melting time), residual crystalline phases should completely be dissolved and hence no longer act as seeds during subsequent cooling. This is observed, if the melts are casted and hence cooled rapidly.

The secondary phase which appears bright in the micrographs of Zr7 and Zr9 in Fig. 2 contains ZrO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub>.

From the high Y<sub>2</sub>O<sub>3</sub>-concentration it can be concluded that cubic ZrO2 should have formed. According to the literature, Y<sup>3+</sup> occupies Zr<sup>4+</sup> sites; the charge is balanced by O<sup>2-</sup> vacancies, which stabilizes the cubic phase down to room temperature. This is well-known from literature. As seen in the micrograph of sample Zr9, numerous ZrO<sub>2</sub> crystals are embedded in the NaY<sub>9</sub>Si<sub>6</sub>O<sub>26</sub> phase (see Fig. 2); hence the ZrO<sub>2</sub> phase must have formed first and in a later stage, i.e., at lower temperatures, NaY<sub>9</sub>Si<sub>6</sub>O<sub>26</sub> was crystallized. Nevertheless, there are also ZrO2 crystals surrounded by the glass phase and hence not obviously embedded in NaY<sub>9</sub>Si<sub>6</sub>O<sub>26</sub> crystals. It might, however, be possible that the NaY<sub>9</sub>Si<sub>6</sub>O<sub>26</sub> crystals have contact to the ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>)-phase outside the cutplane visualized in the SEM-micrographs. There are also numerous ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) crystals which do not have contact to the NaY<sub>9</sub>Si<sub>6</sub>O<sub>26</sub> phase.

The results from quantification are supported by the respective XRD patterns displayed in Fig. 3. In the pattern of Zr5, solely the NaY<sub>9</sub>Si<sub>6</sub>O<sub>26</sub> phase is identified, other phases are not detected within the limits of XRD. By contrast, in the patterns Zr7, Zr9, and Zr11, additionally XRD peaks attributable to cubic ZrO2 occur. The intensity of those peaks increases with increasing ZrO2 concentration. In the sample with 5 mol% ZrO2, cubic zirconia was not detected and hence ZrO<sub>2</sub> is solely incorporated in the glass phase and the previously described. NaY<sub>9</sub>Si<sub>6</sub>O<sub>26</sub> phase as concentrations of the ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) and the NaY<sub>9</sub>Si<sub>6</sub>O<sub>26</sub> crystals as well as of the glassy phase do not depend on the ZrO2 concentration of the respective samples. The ZrO2 concentration of the glass phase is always in the range from 5.2 to 5.3 mol% which seems to be the solubility limit applying a low cooling rate. This is also supported by the

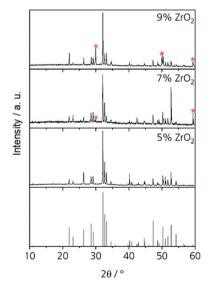


Fig. 3 XRD patterns of Zr5, Zr7, Zr9 and Zr11 after slow cooling to room temperature. The theoretic pattern at the bottom belongs to NaY<sub>9</sub>Si<sub>6</sub>O<sub>26</sub> (JCPDS no. 00-035-0404). The peaks of cubic zirconia (JCPDS no. 01-077-2112) are marked with red stars.

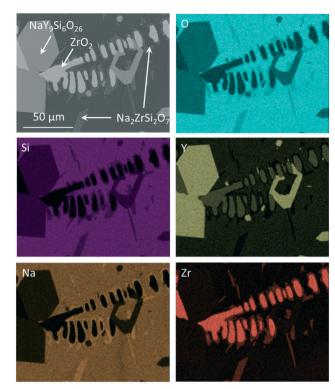


Fig. 4 EDXS elemental analysis of Zr7 after slow cooling to room temperature and subsequent reheating to 1100 °C for 10 h.

observation, that ZrO<sub>2</sub> crystals are not observed in the sample Zr5.

If the slowly cooled samples, in which ZrO<sub>2</sub> and NaY<sub>9</sub>Si<sub>6</sub>O<sub>26</sub> have already been precipitated, are reheated to a temperature of 1100 °C for 10 h, it can be seen that further crystallization takes place within the sample volume (Fig. 4). In the micrograph (see Fig. 4) altogether four different phases occur. The NaY<sub>9</sub>Si<sub>6</sub>O<sub>26</sub> and the ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) crystals, a glassy phase and additionally a crystalline phase enriched in ZrO<sub>2</sub> and Na2O. The latter phase grows preferably on the ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) crystals, however, some of these crystals also grow on NaY<sub>9</sub>Si<sub>6</sub>O<sub>26</sub>. EDXS elemental mappings are displayed in Fig. 4. The composition of the new phase, which surrounds the ZrO<sub>2</sub> crystals was quantified via EDXS. The quantification led to the conclusion that this crystal phase is Na<sub>2</sub>ZrSi<sub>2</sub>O<sub>7</sub>.

# 3.2 Crystallization of the quenched glass upon heating

First heat treatments of the quenched glasses were performed on an amorphous sample with the composition Zr0 after casting on a metal mould. After heat treatments for 5 h at different temperatures in the range from 850 to 1150 °C, at least two crystalline phases can be detected by powder XRD. The respective diffractograms are displayed in Fig. 5. At 850 °C, crystallization can already be detected but the amorphous hump is also clearly visible. After thermal treatment at 900 and 950 °C, numerous sharp diffraction peaks occur; both diffractograms are almost identical. However, the crystalline phase or phases could not be identified. After crystallizing at

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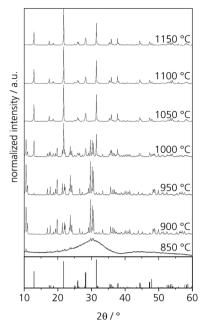


Fig. 5 XRD patterns of glass ZrO after heat treatments for 5 h at different temperatures. The theoretical peaks displayed at the bottom are attributed to NaYSi<sub>2</sub>O<sub>6</sub> (calculated from ICSD 171255, ref. 16).

1000 °C, the formation of NaYSi<sub>2</sub>O<sub>6</sub> crystals is detected. It should be noted that the composition of the sample Zr0 is the same as that of the crystal. Thermal treatment at temperatures in the range from 1050 to 1150 °C results in the sole crystallization of NaYSi<sub>2</sub>O<sub>6</sub>.

In order to characterize the unknown phase, a glass specimen was heat treated at 850 °C for 5 h. This glass shows surface crystallization. However, the surface layer does not adhere to the bulk glass and flaked off from the glass easily. The crystalline layer was studied via EDXS and showed the same composition as the base glass. Hence, the unknown phase might be a different polymorph of NaYSi<sub>2</sub>O<sub>6</sub>.

From the cooling experiments, it can be concluded that long-term heat treatments below the melting point lead to a ZrO<sub>2</sub> concentration of around 5.2 to 5.3 mol% in the glass matrix. Higher ZrO<sub>2</sub> concentrations lead to the precipitation of cubic ZrO<sub>2</sub>-crystals containing high concentrations of Y<sub>2</sub>O<sub>3</sub>. Hence, in addition to the cooling experiments, the crystallization behavior was also studied upon heating of glass samples with the compositions Zr7 and Zr9.

In Fig. 6, the results from DSC of the stoichiometric glass Zr0 are illustrated together with Zr7 and Zr9. Glass Zr0 has a glass transition temperature of 761 °C, which increases to 799 and 794 °C for the glasses Zr7 and Zr9, respectively. The decrease of  $T_g$  from Zr7 to Zr9 might be due to the occurrence of phase separation. With increasing ZrO2 concentration, droplets enriched in ZrO2 can be formed, which consequently decrease the ZrO2 concentration in the residual glass phase. This results in a decrease of  $T_g$ . The formation of droplets with a size of around 5 nm enriched in ZrO<sub>2</sub> has already been reported for the Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> system.<sup>17</sup> For all the three glasses, the same grain size

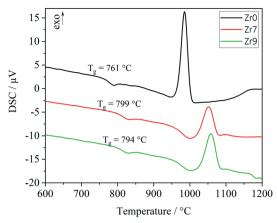


Fig. 6 DSC curves of powder samples with a grain size of 400-500 um.

fraction was used for DSC. Hence, also the exothermal crystallization peaks can be compared with each other. In the case of Zr0, a sharp peak with high intensity was measured. The onset is at 957 °C and the maximum is at 985 °C. An increase of the ZrO2 concentration leads to a shift of the crystallization peaks to higher temperatures. The onsets of the crystallization peaks are at 1013 and 1029 °C, while the maxima are at 1052 and 1058 °C for the glasses Zr7 and Zr9, respectively. The DSC curves of Zr7 and Zr9 are similar with respect to the shape of the crystallization peaks and the respective temperatures. However, there is a significant difference in comparison to the sample Zr0. The glass transition temperature shows a huge increase of 38 K between Zr0 and Zr7 and the crystallization temperatures increase by 56 K (onset) and 67 K (maximum), respectively. Also, the glass stability, illustrated by the difference between crystallization temperature (onset) and  $T_g$ , increases from Zr0 (197 K) to Zr7 (215 K) and Zr9 (226 K).

The exothermal crystallization peaks in Fig. 6 change their shapes from an intense and narrow signal (Zr0) to a broad and not as intense peak (Zr7 and Zr9), which should be due to a change of the crystallization mechanism from surface to volume crystallization or due to a decrease of the crystal growth velocity with increasing ZrO<sub>2</sub> concentration.

For a more detailed study of the crystallization behavior, two step heat treatments of the samples with the compositions Zr0 and Zr7 were performed. The samples were first heated to a temperature in the range of 800 to 820 °C for 20 h in order to achieve nucleation and subsequently to 1000 or 1150 °C for 1 h to allow crystal growth. In the glass without ZrO2, nucleation solely occurred at the surface and hence crystallization starts from the surface (upper micrograph of Fig. 7), which leads to numerous cracks within the volume of the material. Volume crystallization was not observed. By contrast, in sample Zr7, volume crystals can be found after thermal treatment (lower micrograph of Fig. 7). However, the number density is not very high and hence, very huge crystals with diameters of more than 100 μm appear. It should be noted that the glass stability parameter of the Zr0

800 °C, 20 h + 1000 °C, 1 h 10 µm 820 °C, 20 h + 1000 °C, 1 h 100 µm

Fig. 7 SEM micrographs of glasses Zr0 and Zr7 after two-step heat treatments at 820 °C for 20 h and 1000 °C for 1 h.

sample is somewhat lower than those of the samples Zr5 and Zr9. Nevertheless, the latter nucleates in the volume while the sample Zr0 does not. Hence ZrO2 acts as nucleation agent in the studied system despite of the higher glass stability parameter.

The elemental distribution of Zr7 after a two-step heat treatment is shown in Fig. 8. There, tiny Y<sub>2</sub>O<sub>3</sub>-enriched ZrO<sub>2</sub> crystals can be seen, which are precipitated homogenously in

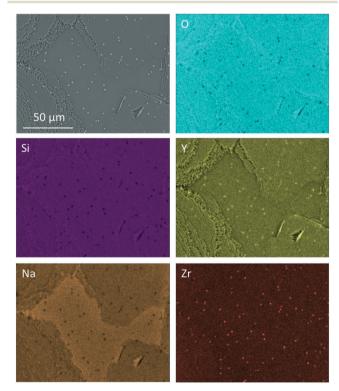


Fig. 8 EDXS elemental mapping of sample Zr7 after a two-step heat treatment at 820 °C for 20 h followed by 1000 °C for 1 h.

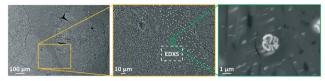


Fig. 9 SEM micrographs of sample Zr9 after a two-step heat treatment at 820 °C for 20 h and 1150 °C for 1 h. The dashed areas in the left micrograph mark large crystals and the framed area in the middle micrograph was used for an EDXS elemental analysis displayed in Fig. 10.

the volume (see bright dots in the Y- and Zr-mappings). Those crystals are much smaller than the ZrO<sub>2</sub> precipitations, which can be found after slow cooling.

Increasing the ZrO<sub>2</sub>-conentration to 9 mol% (sample Zr9) does not improve the nucleation behavior of the glasses. In Fig. 9, SEM micrographs of sample Zr9 are shown after nucleation and crystallization. The number density of crystals is still very low and comparable to sample Zr7. The micrographs show a sample with the composition Zr9, heat treated at higher temperatures (820 °C for 20 h + 1150 °C for 1 h) and it can be seen that a large number of bright spots is enriched in between the larger crystals (see micrograph in the middle of Fig. 9). The right micrograph of Fig. 9 shows such a bright particle in more detail.

Fig. 10 shows an EDXS elemental analysis, where it is seen that the bright spots are ZrO<sub>2</sub> crystals enriched in Y<sub>2</sub>O<sub>3</sub>. Zirconia crystals are found all over the sample. Quantifications within Fig. 10 lead to the following

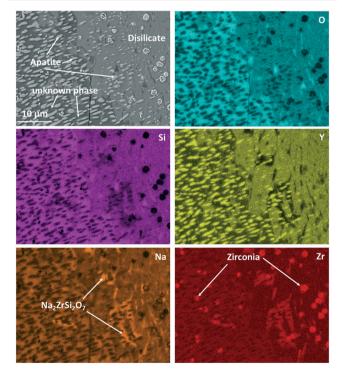


Fig. 10 EDXS elemental mapping of Zr9 after a two-step heat treatment at 820 °C for 20 h + 1150 °C for 1 h. The mapping was recorded in the area of Fig. 9 marked with "EDXS".

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conclusions concerning the appearing crystalline phases and their growth:

The main phase in Fig. 10, which is visible in the left half of the micrograph, is apatite, NaY<sub>9</sub>Si<sub>6</sub>O<sub>26</sub>. This phase is embedded in another crystalline phase (see below), which, however, could not clearly be identified and in the following is denoted as "unknown phase". The apatite crystals have an elongated morphology and surprisingly are all oriented with their long axis, probably the crystallographic (0001)-axis in the same direction. This is assumed because apatite crystals of different composition, (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F), however, of the same space group show needle to rod-like shape when crystallized from homogeneous glass and the elongated direction is that of the crystallographic (0001)-axis. 18,19 There are two possibilities to explain this: the first is that the apatite crystal grows up on a precursor crystal, i.e., the particular apatite crystal has a definite orientation relation to the precursor crystal. The second possible reason is that the apatite phase shows a dendritic growth and the bright crystalline spots in Fig. 10 are attributed to one dendrite which is cut in such a manner that the main branch of the dendrite is not in the cut plane. It should be noted that dendritic growth of calcium apatite has already been reported in ref. 20 and 21. The major crystalline phase in the right half of Fig. 10 is NaYSi<sub>2</sub>O<sub>6</sub>. However, this phase is only the main phase within the displayed micrograph. An overview of the microstructure is given in Fig. 9, where it is also seen that the NaYSi<sub>2</sub>O<sub>6</sub> phase only appears in between the large crystals and is hence only a minor phase. In the volume fraction, where this phase is detected, the ZrO<sub>2</sub>-crystals are larger. An explanation might be that during heating, the ZrO2 crystals precipitate inside the glass. Some of the crystals lead to the formation of volume crystals. The apatite crystals as well as the unknown phase seem to grow at first, which leads to an enrichment of ZrO<sub>2</sub> in the residual material. There, the zirconia crystals can grow to a larger size. In a later stage, the NaYSi<sub>2</sub>O<sub>6</sub> phase forms and the residual glassy phase also crystallizes. There, Na<sub>2</sub>O is enriched and Na<sub>2</sub>ZrSi<sub>2</sub>O<sub>7</sub> is additionally formed.

This was also proven by XRD. However, different from the composition without zirconia, which forms solely the NaYSi<sub>2</sub>O<sub>6</sub> phase at high temperatures (see Fig. 5), in the composition with 9 mol% ZrO2 the unknown phase also precipitates in a large amount. This phase is marked in the micrograph in Fig. 10. The "unknown phase" is seen on the left side. Its composition was measured to be around: 61.7 O, 8.6 Na, 22.8 Si, 4.4 Y, 2.4 Zr (in at%) which is attributed to an empirical formula Na<sub>0.84</sub>Y<sub>0.44</sub>Zr<sub>0.24</sub>Si<sub>2.21</sub>O<sub>6</sub>. The phase is assumed to be a polymorph of NaYSi2O6 in which some Y3+ has been substituted by Zr<sup>4+</sup>.

# Conclusions

Quenching of melts in the system Na<sub>2</sub>O/Y<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> with ZrO<sub>2</sub> additions and subsequent thermal treatment resulted in phase compositions and microstructures fairly different from those obtained during slow cooling of melts with the same composition. Slow cooling results in the formation of NaY<sub>9</sub>Si<sub>6</sub>O<sub>26</sub> crystals with apatite structure and for ZrO<sub>2</sub>concentrations >5 mol% also of yttrium stabilized cubic zirconia. During reheating of the slow cooled glasses, zirconia crystals serve as starting points for the formation of Na<sub>2</sub>ZrSi<sub>2</sub>O<sub>7</sub>. If the material is prepared via melt quench technique, and if ZrO2 is given in concentrations above 5 mol%, homogenously distributed small ZrO2 crystals are precipitated. Furthermore, glasses are obtained from which NaYSi<sub>2</sub>O<sub>6</sub> precipitates at high temperatures. At crystallization temperatures below around 1000 °C, a phase forms, which could not be identified, but is assumed to be a polymorph of NaYSi<sub>2</sub>O<sub>6</sub> in which a part of Y<sup>3+</sup> is substituted by Zr<sup>4+</sup>. It also precipitates at higher temperatures in the case of a sample with a ZrO<sub>2</sub> concentration of 9 mol%. For a more detailed characterization of the crystallization processes within this glass system, the unknown phase has to be characterized in future experiments.

# Conflicts of interest

There are no conflicts of interest to declare.

### References

- 1 J. Schilm, D. Wagner, C. Heubner, U. Langklotz, C. W. Lee, H. S. Kang, J. W. Park and M. Kusnezoff, J. Eur. Ceram. Soc., 2021, 41, 4876-4883.
- 2 M. Alexander and B. Riley, Solid State Ionics, 1986, 18-19, 478-482.
- 3 T. Okura, K. Kawada, N. Yoshida, H. Monma and K. Yamashita, Solid State Ionics, 2012, 225, 367-370.
- 4 P. W. Angel and R. E. Hann, J. Am. Ceram. Soc., 1992, 75, 3278-3282.
- 5 M. J. Hyatt and D. E. Day, J. Am. Ceram. Soc., 1987, 70, C-283-C-287.
- 6 S. Alahraché, M. Deschamps, J. Lambert, M. R. Suchomel, D. De Sousa Meneses, G. Matzen, D. Massiot, E. Véron and M. Allix, J. Phys. Chem. C, 2011, 115, 20499-20506.
- 7 A. Keshavarzi, W. Wisniewski and C. Rüssel, CrystEngComm, 2012, 14, 6904.
- 8 W. Höland, V. Rheinberger and M. Schweiger, Philos. Trans. R. Soc., A, 2003, 361, 575-589.
- K. Thieme and C. Rüssel, J. Mater. Sci., 2015, 50, 1488-1499.
- 10 H. R. Fernandes, D. U. Tulyaganov and J. M. F. Ferreira, J. Mater. Sci., 2013, 48, 765-773.
- 11 W. Wisniewski, C. Thieme and C. Rüssel, J. Eur. Ceram. Soc., 2019, 39, 2186-2198.
- 12 R. P. Gunawardane, R. A. Howie and F. P. Glasser, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 1982, 38, 1564-1566.
- 13 F. C. Lee, J. Marr and F. P. Glasser, Ceram. Int., 1981, 7, 43-47.
- 14 J. R. Tolchard, P. R. Slater and M. S. Islam, Adv. Funct. Mater., 2007, 17, 2564-2571.

- 15 R. D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr., 1976, 32, 751–767.
- 16 D. M. Többens, V. Kahlenberg and R. Kaindl, *Inorg. Chem.*, 2005, 44, 9554–9560.
- 17 T. Höche, M. Mäder, S. Bhattacharyya, G. S. Henderson, T. Gemming, R. Wurth and C. Rüssel, *CrystEngComm*, 2011, 13, 2550–2556.
- 18 C. Moisescu, C. Jana and C. Rüssel, *J. Non-Cryst. Solids*, 1999, 248, 169–175.
- 19 W. Wisniewski, R. de Kloe and C. Rüssel, *CrystEngComm*, 2015, 17, 2969–2973.
- 20 J. J. Shyu and J. M. Wu, J. Mater. Sci., 1994, 29, 3167-3171.
- 21 J.-J. Shyu and J.-M. Wu, J. Am. Ceram. Soc., 1991, 74, 1532–1540.