

Luminescent ZnO-Al₂O₃-SiO₂ glasses and glass ceramics

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Abstract. Glasses in the composition range in mol% 35-50 ZnO – 10-15 Al₂O₃ – 40-55 SiO₂ were prepared, undoped and doped with 1×10^{19} and 1×10^{20} Sm³⁺ per cm³ glass as luminescent species for the visible region, especially for blue and red emission.

Phase separation occurs in glass samples with high SiO₂ content. SiO₂-rich droplets in a Zn²⁺- Al³⁺-enriched matrix were formed. Sm³⁺ ions prefer the Zn²⁺-Al³⁺-rich glass matrix.

By thermal treatment glass samples were transformed into glass ceramics with the main crystal phases: Zn₂SiO₄ (willemite), ZnAl₂O₄ (gahnite) and SiO₂-mixed crystals. XRD, SEM and TEM measurements were carried out. The luminescent Sm³⁺ ions are concentrated in the glass matrix.

Photoluminescence excitation and emission spectra were recorded in the UV-VIS-region and the time resolved emission behavior was measured by excitation with a N₂-laser at 337 nm.

The glasses and glass ceramics have interesting chemical and physical properties, high T_g around 700°C, low coefficient of thermal expansion ~ 4 ppm/K, and high chemical stability.

Introduction

Glasses and ceramics find various applications in different technical and optical fields because of their wide spread of physical-chemical properties. On the basis of the system ZnO-Al₂O₃-SiO₂ glasses with high T_g around 700°C, low thermal expansion coefficient around 4 ppm/K, and high chemical stability can be prepared. Glass-ceramics with the crystal phases Zn₂SiO₄ (willemite), ZnAl₂O₄ (gahnite) and high quartz can be obtained by thermal treatment [1-3].

Crystalline Zn₂SiO₄ doped with small amounts of Mn²⁺ is a well known green-emitting lamp and cathode-ray phosphor [4]. The use of fluorescence measurement techniques is expanding rapidly.

In this work, the luminescent behavior of Sm³⁺, with 4f⁵ electronic configuration which provides strong emission in the visible range (orange-red), has been studied in glasses and glass ceramics with high ZnO content by different methods.

Experimental

Glasses in the composition range in mol% 35-50 ZnO – 10-15 Al₂O₃ – 40-55 SiO₂ undoped and doped with 1×10^{19} and 1×10^{20} Sm³⁺ per cm³ (~0.1 and 1.0 wt%) were prepared. Mixtures (200 g) of high purity raw materials (Fe < 1ppm) were melted in Pt crucibles at 1550°C for 2h. The melts were fritted in water and remelted in Pt crucible for 2h. Then the melts were poured in moulds or quenched on copper plates to avoid phase separation. After annealing from 750°C with 3-5 K/min the glasses were cut, ground and polished to produce samples for different measurements. The optical absorption spectra (190-3200 nm) were recorded with sample thicknesses of 2 and 10 mm with an error < 1 %. Fluorescence excitation and emission spectra were recorded (200-900 nm) with an intensity error < 5 %. The fluorescence decay curves were measured with a special experimental setup after excitation at 337 nm with a short N₂-laser pulse [5]. The refractive indices were measured with an error $\Delta n \pm 2 \times 10^{-5}$. The density of the glass was determined using Archimedes' principle, error ± 0.002 . DTA, dilatometer and viscometer measurements were carried out to obtain

values for the thermal properties. X-ray diffraction (XRD), and electron microscopy (SEM, TEM, with EDX and WDX) measurements were used to characterize the crystallization behavior.

Results and discussion

Normally glasses and glass ceramics were investigated with high SiO₂, higher Al₂O₃, lower ZnO content, and with addition of other components, especially nucleating agents, like TiO₂ or ZrO₂, e.g. to get transparent glass ceramics based on spinel composition with gahnite (ZnAl₂O₄) as main crystalline phase [2, 3]. In this work the main crystal phase should be willemite (Zn₂SiO₄). Surprisingly it was possible to obtain bulk glasses up to very high ZnO content, 50 mol%, and low SiO₂ content, 40 mol%. The phase diagram of the binary ZnO-SiO₂ system shows stable phase separation in the melt, $T > 1700^{\circ}\text{C}$, up to ~ 40 mol% ZnO, and an eutectic composition, 50 mol% ZnO – 50 SiO₂, with $T_1 \sim 1430^{\circ}\text{C}$ [6]. Glasses ZAS1 and ZAS4 provided phase separation by normal cooling (Fig. 6a) and were homogenous by quenching. All other compositions (Table 1) yielded homogenous glasses with high $T_g \sim 700^{\circ}\text{C}$ and low thermal expansion coefficients, ~ 4 ppm/K. Glass ceramics with lower TEC values (nearly 0!) were also obtained in special cases.

The refractive indices increase with increasing ZnO content from 1.61 to 1.67, and decrease with increasing Al₂O₃ content. The changes in the Abbe number are only small.

Table 1: Composition (in mol%) and properties measured on the undoped glasses

Glass	ZnO	Al ₂ O ₃	SiO ₂	$T_g \pm 5$ [°C]	density [g/cm ³]	refractive index (546nm)	Abbe number ± 1	TEC ± 0.1 [ppm/K]
ZAS1	35	10	55	705	3.24	1.6135	51	3.6
ZAS4	40	10	50	700	3.42	1.6331	50	3.9
ZAS5A	45	10	45	690	3.53	1.6630	47	3.8
ZAS5B	42.5	12.5	45	700	3.47	1.6426	49	4.0
ZAS5C	40	15	45	700	3.41	1.6367	50	3.8
ZAS6	50	10	40	690	3.64	1.6681	47	3.9

The homogenous glass samples have high UV transmission with an UV-edge around 230 nm. The Sm³⁺-doping causes weak narrow absorption bands due to f-f-electronic transitions. The strongest band has the maximum at 402 nm (Fig. 1). The optical absorption spectra correlate with the fluorescence excitation spectra (Fig. 2). The glass samples are colorless or weak yellow in the case of 10^{20} Sm³⁺/cm³ doping.

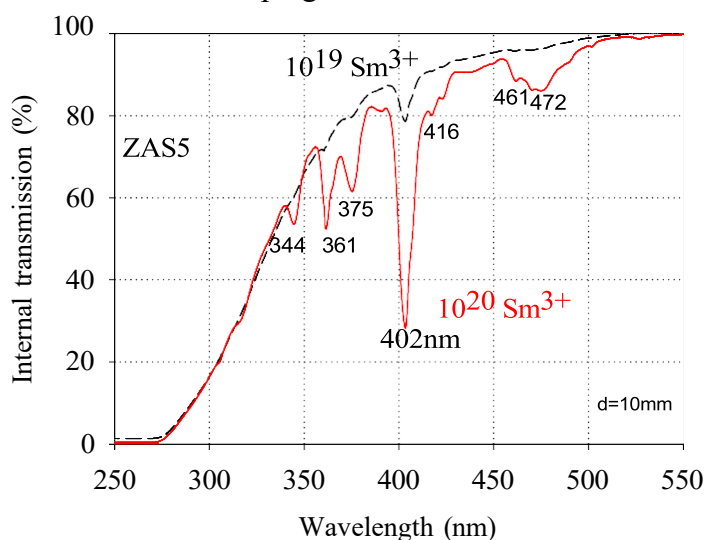


Fig. 1: Optical transmission spectra in the UV-Vis region demonstrated at glass samples ZAS5 doped with 10^{19} and 10^{20} Sm³⁺ per cm³ (~ 0.1 and 1.0 wt% Sm₂O₃) with sample thickness 10 mm.

The optical absorption intensity increases linear with the doped Sm³⁺ concentration, but the fluorescence intensity shows concentration quenching effect at 10^{20} Sm³⁺ per cm³. Fluorescence emission bands at ~ 560 , 600 and 650 nm were measured after excitation at ~ 400 nm. Lifetimes with $\tau_e \sim 2.2$ ms for 10^{19}

Sm³⁺/cm³ and 1.8 ms for 10^{20} Sm³⁺/cm³ were determined (Fig. 4).

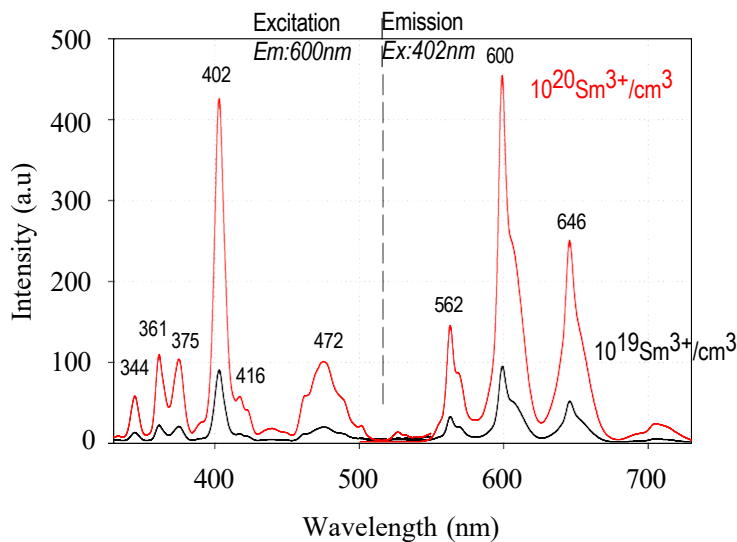


Fig. 2: Fluorescence excitation and emission spectra typical for all glass samples doped with 10^{19} and 10^{20} $\text{Sm}^{3+}/\text{cm}^3$ with lifetimes $\tau_e \sim 2.2$ and 1.8 ms, demonstrated with ZAS5 samples. Effect of concentration quenching at higher Sm^{3+} doping can be recognized.

Very interesting is the strong increase of fluorescence intensity which could be obtained by special thermal treatment and lead to phase separation or a translucent glass ceramic.

The fluorescence intensity of the phase separated glasses and the translucent

glass ceramic were much higher due to accumulation of the Sm^{3+} in the glass matrix and amplification by scattering effects of small SiO_2 -rich droplets or small crystals (Fig. 3). The translucent glass ceramic was obtained by two step thermal treatment, at 750°C for 10 hours and at 850°C for 5 hours.

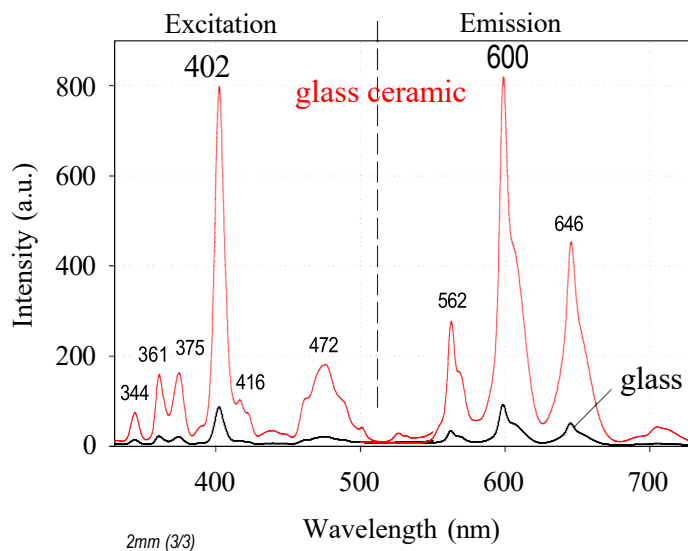


Fig.3: Fluorescence excitation and emission spectra of glass and translucent glass ceramic sample with the same composition, ZAS5 / 10^{19} $\text{Sm}^{3+}/\text{cm}^3$.

It was possible, to get with lower Sm^{3+} -doping ($10^{19}/\text{cm}^3$) a much higher fluorescence intensity than with higher Sm^{3+} -doping ($10^{20}/\text{cm}^3$).

The effect of fluorescence amplification by translucent crystallization was much lower at higher Sm^{3+} doping due to concentration quenching.

In the opposite, a strong decrease of the fluorescence intensity was found in all opaque glass ceramic samples which had only a small glass phase and a lot of large crystals. In these cases, it is not possible to excite the Sm^{3+} ions in the glassy volume, and additionally, concentration quenching exists.

Thermal treatment was carried out with all undoped and doped glass samples to study the crystallization behavior. Exothermic peaks were detected in the DTA curves around 950 , 1050 and 1120°C . At first, all samples were treated for 3 hours at these temperatures, and the crystal phases formed were analyzed with different methods. The main crystal phase was Zn_2SiO_4 (willemite and other modifications) with a needle-like form and strong birefringence. With increasing temperature of thermal treatment, and increasing Al_2O_3 content additionally ZnAl_2O_4 (gahnite) and high quartz mixed crystals were found (Fig. 5). The crystallization tendency increases with the ZnO and Al_2O_3 content. The Sm^{3+} -ions are accumulated in the glassy phase. It was not possible to detect samarium in the SiO_2 -droplet phase of glass samples with phase separation or in the various crystal phases. The Sm^{3+} ion (radius ~ 1.0 Å) is in comparison with Mn^{2+} ($r \sim 0.66$ Å) too large for incorporation in the Zn_2SiO_4 , ZnAl_2O_4 or SiO_2 crystal phases with much smaller ionic radii (Zn^{2+} : $r \sim 0.60$ Å CN4 and 0.74 Å at CN 6; Al^{3+} : 0.39 Å at CN 4 and 0.54 Å at CN 6) [7].

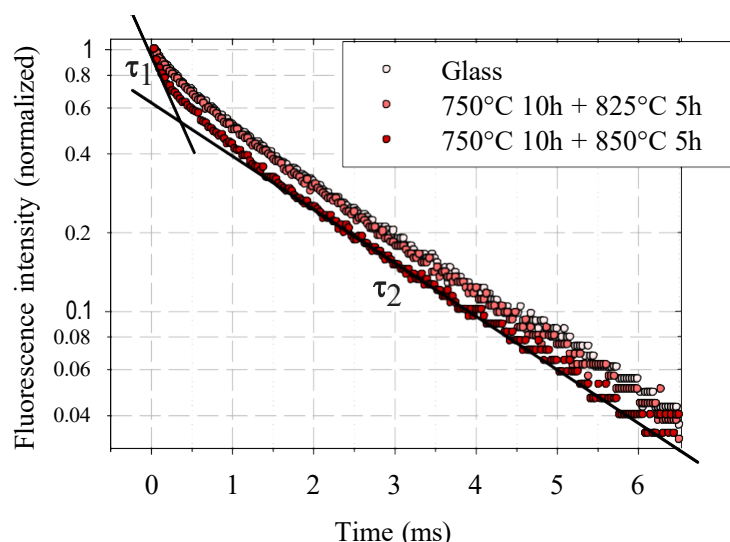


Fig. 4: Fluorescence decay curves of glass and ceramic samples, ZAS5B/ 10^{20} Sm^{3+} per cm^3 with fitted lifetimes.

The fluorescence decay ($\log I_F$) behavior is not single exponentially with time. Two different lifetimes, $\tau_1 \sim 0.5$ ms and $\tau_2 \sim 2.2$ ms, can be fitted. The origin could be two different local structures of the Sm^{3+} ions.

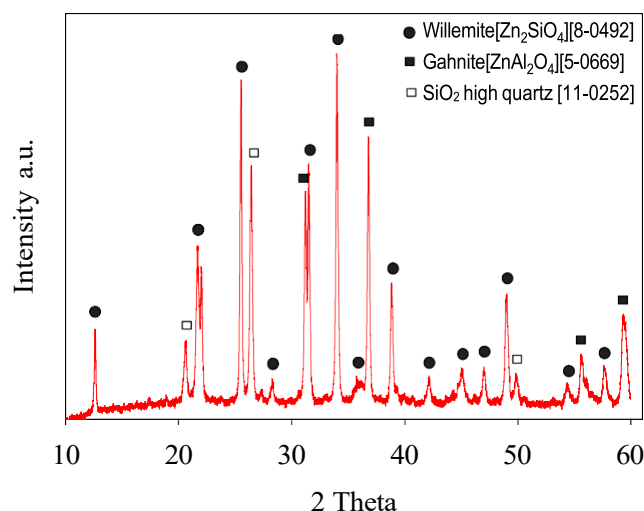


Fig. 5: XRD pattern of glass sample ZAS1 with 10^{20} Sm^{3+} per cm^3 after thermal treatment: 3 hours at 1120°C .

The sample is nearly completely crystallized. The SEM and TEM images of the same samples are demonstrated at Figs. 6 b and c.

EDX analyses have shown that the white crystals are Zn_2SiO_4 (Fig. 6b), and the small cubic crystals mainly ZnAl_2O_4 , but SiO_2 mixed crystals could not be excluded too (Fig. 6c). The glassy phase between the crystals is only very small. The Sm^{3+} fluorescence of these strongly crystallized samples is only very low.

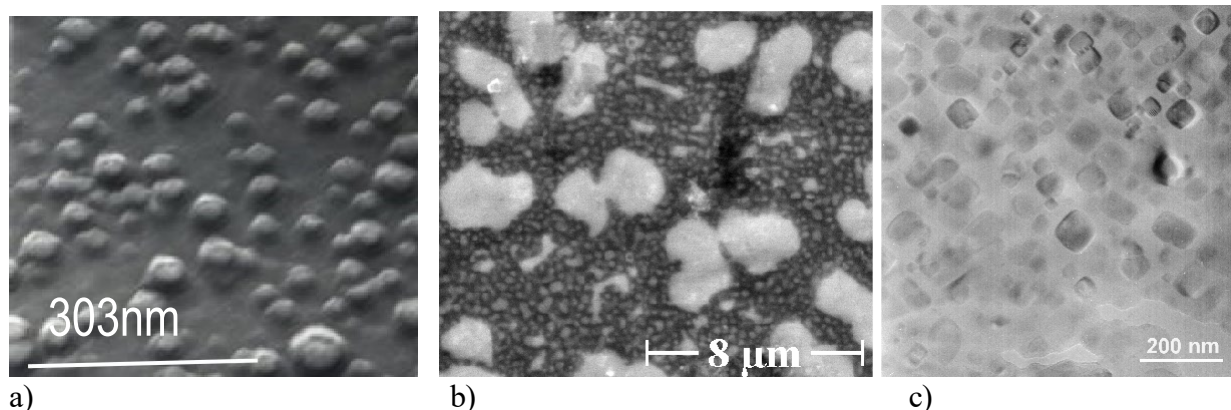


Fig. 6: TEM and SEM micrographs of ZAS1/ 10^{20} Sm^{3+} cm^{-3} samples

a) After normal cooling: phase separation with SiO_2 rich droplets

b) and c): Quenched samples after thermal treatment at 1120°C for 3 hours.

It is known that ions with d^{10} electronic configuration like Zn^{2+} , Cu^+ , Ag^+ , etc. show an intense and broad absorption band in the ultraviolet region which can also show luminescence [4]. In this work, all undoped glasses, which had very high UV transmission, <250 nm, and the prepared glass ceramics were measured by luminescence excitation and emission spectroscopy. Typical spectra are given in Fig. 7. All samples have shown blue luminescence emission with excitation in the UV

around 250 nm. Significant differences were found between glasses and glass ceramics with the same composition. The glass samples provide broad emission with maxima around 370 and 485 nm. The glass ceramic samples show much higher blue emission with a maximum at 370 nm.

The Zn^{2+} ions are fourfold coordinated in Zn_2SiO_4 and in ZnAl_2O_4 . It could be assumed that the emission at 370 nm is due to electronic transitions in fourfold coordinated Zn^{2+} in the glass ceramics and emission maximum at 485 nm of the glass samples is caused by six fold coordinated Zn^{2+} ions. The emission maximum at 370 nm is much lower. That would mean that Zn^{2+} ions can be coordinated with 4 to 6 oxygens in the glasses and act as both network former and modifier.

So, it is possible to obtain stable glass formation in this ternary system up to high ZnO and low SiO_2 content. Glasses and glass ceramics have shown also blue luminescence emission by UV lamp excitation with the Hg-line at 254 nm. Strong afterglow could be observed with the glass ceramic samples. The nature of this effect is not clear.

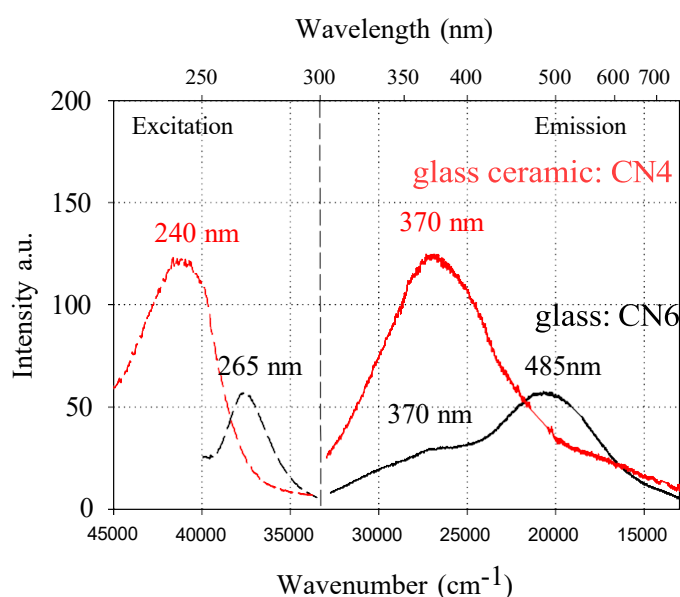


Fig. 7: Luminescence excitation and emission spectra of undoped glass and glass ceramic samples, demonstrated with samples ZAS4 (40ZnO-10Al₂O₃-50 SiO₂) as glass and glass ceramic with Zn_2SiO_4 crystal phase.

Summary

Stable glasses in the composition range in mol% 35-50 ZnO – 10-15 Al₂O₃ – 40-55 SiO₂ were prepared, undoped and doped with 1×10^{19} and 1×10^{20} Sm³⁺ per cm³ glass as luminescent species for the visible region, especially for blue (undoped) and orange-red (with Sm³⁺) emission.

Phase separation occurs in glass samples with high SiO₂ content. SiO₂-rich droplets in a Zn²⁺- Al³⁺-enriched matrix were formed. Sm³⁺ ions prefer accumulation in the Zn²⁺-Al³⁺-rich glass matrix.

By thermal treatment glass samples were transformed into glass ceramics with the main crystal phases: Zn_2SiO_4 (willemite), ZnAl_2O_4 (gahnite) and SiO₂-mixed crystals. XRD, SEM and TEM measurements were carried out. The luminescent Sm³⁺ ions are concentrated in the glass matrix.

The glasses and glass ceramics have interesting chemical and physical properties, high T_g around 700°C, low thermal expansion coefficient, TEC < 4 ppm/K, and high chemical stability.

The refractive indices, n_e , increase with increasing ZnO content from 1.61 to 1.67, and decrease with increasing Al₂O₃ content. The changes in the Abbe number are only small, $v_e \sim 49 \pm 2$.

The undoped glass samples with high purity have very high UV transmission, edge < 250 nm, and provide blue emission with a maximum at 485 nm by UV excitation due to electron transitions of Zn^{2+} with d^{10} configuration. It is assumed that the Zn^{2+} ions are six fold and fourfold coordinated with oxygen in these glasses.

The undoped glass ceramic samples show much higher blue emission with a maximum at 370 nm due to fourfold coordination with oxygen in the crystal phases Zn_2SiO_4 (willemite) and ZnAl_2O_4 (gahnite).

The Sm^{3+} ions could neither be accumulated in the crystal phases nor in the SiO_2 droplets of phase separated glasses. They are too large. They prefer the Zn-Al-rich glass phases.

A large fluorescence amplification effect could be obtained with low Sm^{3+} -doping by phase separation of glass samples, or formation of translucent glass ceramics. The origin of this unusual increase of the fluorescence intensity is of complex nature. Main reasons should be the increase of Sm^{3+} content in the matrix phase and scattering effects.

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