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Optical absorption and photoluminescence properties of chromium in different host glasses

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ABSTRACT

The optical absorption, excitation and fluorescence spectra, and emission lifetimes of chromium (III) were investigated in a wide variety of oxide glasses (aluminosilicate, aluminate and phosphate). For all glasses, weak crystal field strengths were deduced from the absorption spectra. The effect of the glass matrix and the Cr^{3+} concentration on the fluorescence properties of Cr^{3+} ions were investigated. An increased fluorescence intensity of $Cr^{3+}$was found for glasses of low optical basicity, the spectral position of the Cr^{3+} absorption and emission, however, was hardly influenced by the glass composition. The optical absorption spectra of the chromium doped aluminosilicate and aluminate glasses showed the presence of Cr^{VI}, while in phosphate glasses most chromium occurred as Cr^{3+} ions. Furthermore, for the glass with the lowest basicity, the Cr^{3+}concentration was optimized in order to achieve maximum fluorescence emission intensity.

1. Introduction

Since many years, technological applications have generated increasing interest in the studies of different glass compositions doped with transition-metal ions due to their interesting optical and spectroscopic properties [1–8]. Among the transition metal ions, chromium is especially interesting due to its broad and intense absorption and emission spectra. The Cr^{3+} ion with a $3d^3$ configuration is one of the most frequently studied and most efficient activators in optical materials and may act as sensitizer for flash lamp pumped laser materials due to its broad and strong absorption in the visible range and its fluorescence emission in the near infrared region [4–12]. In contrast to rare earth ions, the spectroscopic properties of transition metal ions such as Cr^{3+} strongly depend on the glass matrix. Furthermore chromium may exist in different oxidation states which have different optical properties and are incorporated differently in a glass matrix. Cr^{3+} may act as a network modifier while Cr^{VI} acts as network former with $CrO_4{}^{2-}$ structural units. Its structural role depends on the modifier-former properties, the size of the ions and their crystal field strengths [2,13–15]. The control of the valency state of chromium ions in glasses is indispensable for the development of tunable glass lasers. In silicate and borate glasses, the redox couple Cr^{3+}–Cr^{VI} can coexist in varying ratios depending on the glass composition and condition of melting, while in phosphate glasses only trace quantities of Cr^{VI} may occur [16].

This report describes systematical investigations of the optical properties of chromium ions in different host glasses such as aluminosilicate, aluminate and phosphate glasses. For this, one phosphate glass composition which is similar to the commercially available laser glass KigreQ$_x$ (NaKLaAP) was chosen. This composition is supplemented by newly developed phosphate compositions of different optical basicities. For the aluminosilicate glasses, a composition which should be advantageous for laser applications (LiAS [17]) is supplemented by other aluminosilicate glasses of different optical basicities and an aluminate glass. For all these compositions, the effect of the glass matrix on the absorption and fluorescence properties of Cr^{3+} ions was investigated.

2. Experimental procedures

The glasses were prepared from reagent grade raw materials. The raw materials used were SiO_2 (Sipur A1, BremthalerQuarzitwerk, Germany), $(NH_4)_2HPO_4$ (LaborchemieApolda, Germany), Al_2O_3 (Pengda Munich, Germany), $Al(OH)_3$ (Sumitomo Ltd, Germany) in case of the phosphate glasses, MgO (Merck, Germany), ZnO (Heubach, Germany), Li_2CO_3 (Sigma-Aldrich, USA), La_2O_3 (LaborchemieApolda, Germany), $BaCO_3$ (Reachim, USSR), K_2CO_3 (Merck, Germany), Na_2CO_3 (Merck, Germany), $CaCO_3$ (Merck, Germany) and Cr_2O_3 (Merck, Germany). The chemical compositions of the glasses (in mol%) are summarized in Table 1.

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Table 1
M compositions (mol%), transition temperature T_g, refractive index n_d, theoretical optical basicities and density of all studied glasses doped with 10^{19} Cr^{3+}/cm^3.

Composition	LiMgLaAP	LiZnLaAP	BaLaAP	KNaLaAP	LiAS	BaAS	LaAS	BaLaAS	Aluminate
SiO_2	–	–	–	–	60	55	70	50	4.8
P_2O_5	69	65	61	61	–	–	–	–	–
Al_2O_3	05	05	05	09	22	10	15	05	32.4
La_2O_3	09	09	09	09	–	–	15	05	–
Li_2O	10	15	–	–	18	–	–	–	–
ZnO	–	06	–	–	–	–	–	–	–
MgO	07	–	–	–	–	–	–	–	9.1
K_2O	–	–	–	06	–	–	–	–	–
Na_2O	–	–	–	15	–	–	–	–	–
BaO	–	–	25	–	–	35	–	40	6.6
CaO	–	–	–	–	–	–	–	–	47.1
T_g (°C)	450	450	500	480	790	760	780	785	780
n_d ± 0.001	1.549	1.557	1.582	1.537	1.533	1.676	1.662	1.620	1.660
Λ_{th}	0.472	0.473	0.499	0.507	0.557	0.635	0.641	0.710	0.779
$\rho \pm 0.001$ (g/cm^3)	2.800	2.889	3.336	2.892	2.441	4.228	3.569	4.239	3.176

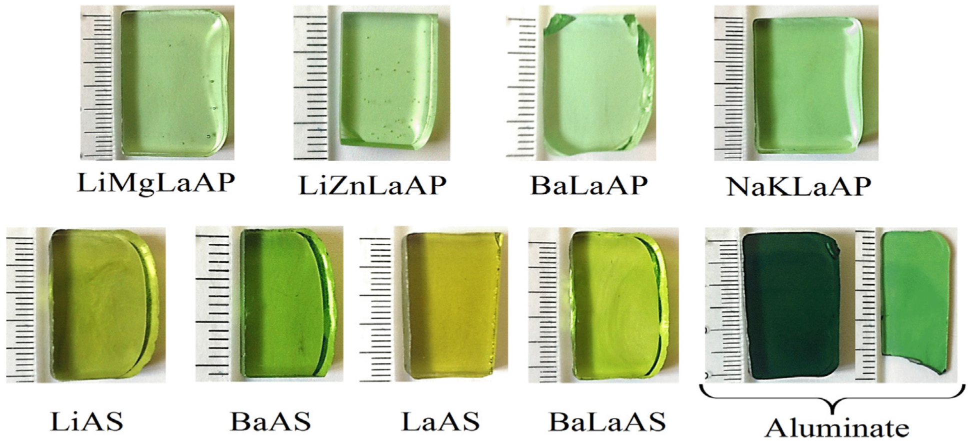

Fig. 1. All prepared glass samples doped with 10^{19} chromium ions per cm^3 (thickness 5 mm). For the aluminate glass an additional sample of only 1 mm thickness is shown.

The glasses were prepared by using the melt quenching technique. The aluminosilicate and aluminate glasses were melted in a platinum crucible at a temperature of 1600 °C. Then, the samples were cast into a copper mold and subsequently transferred into an annealing furnace, preheated to temperatures in the range of 700–850 °C depending on the glass transition temperature T_g of the respective glasses. The phosphate glasses were melted in a quartz crucible at 1250 °C, casted into a graphite mold and transferred to an annealing furnace preheated to a temperature between 500 and 525 °C. Subsequently, the annealing furnace was switched off and all samples were slowly cooled down to room temperature (cooling rate: approximately 3 K min^{-1}). The glass samples were cut and polished for spectroscopic measurements. Fig. 1 shows the images of the prepared glasses. The densities were measured using a helium pycnometer (AccuPyc 1330, Micromeritics GmbH, Germany). The standard deviation of these measurements was less than ± 0.0015 g/cm^3. Furthermore, the glass transition temperature (T_g) was determined by using DTA measurements (DTA-50, Shimadzu, Japan). The diffraction patterns were recorded using a D5000 diffractometer (Siemens, Germany). The *UV–vis-NIR* absorption spectra were recorded at room temperature using polished samples with a thickness of 1 mm (UV-3101PC, Shimadzu, Japan). The same samples were used to investigate the fluorescence spectra. For these studies, a fluorescence spectrometer (RF-5301PC, Shimadzu, Japan) was used. Excitation spectra were recorded at an emission wavelength of 820 nm, while emission spectra were obtained using an excitation wavelength of 640 nm. Fluorescence lifetimes of Cr^{3+} doped phosphate glasses were determined using a self-made setup as described in Ref. [18] with an excitation wavelength of 640 nm. The optical basicity values of the glass compositions were calculated as described in Ref [19] by using the averaged partial basicity values of Duffy (1), Duffy (2) and Lebouteiller and Courtine given in Ref. [20].

3. Results and discussion

3.1. XRD analyses

Fig. 2 shows the X-ray diffraction pattern of the different host glasses. The absence of well-defined sharp diffraction peaks indicates the nonexistence of any crystalline phase and confirms the amorphous nature of the prepared samples.

3.2. Absorption spectra

The optical absorption spectra observed at room temperature for aluminosilicate and aluminate glasses doped with 10^{19} $Cr^{3+/VI}/cm^3$ are shown in Fig. 3(a). The spectra exhibit two broad bands with high intensities located at approximately 200 nm (50,000 cm^{-1}) and 370 nm (27,027 cm^{-1}). Additionally, a band with very low intensity near 650 nm (15,384 cm^{-1}) is observed. The two broad bands are assigned to the charge transfer (CT) transition ($\pi \rightarrow d$) of the Cr^{VI} ions in these host glasses [21,22]. The