Chromium(IV) ions containing novel silicate glasses

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Abstract

Luminescence of approximately 1.3 μm is required in photonics for lasers operating in the near infrared (NIR) region. Luminescent characteristics suitable for this application are exhibited by Cr(IV), but the achievement of chromium in the oxidation state IV in silicate glass appeared to be a rather difficult task. This paper presents our novel approach based on an ion implantation of oxygen ions into specially designed sodium-silicate glasses containing Cr(III) and provides a description of the possible processes involved.

Keywords:
Chromium(IV) Silicate glass Luminescence

1. Introduction

Silicate glasses as photonic materials have many advantages mainly because of their excellent compatibility with commonly used optical fibres, which, along with the feasibility of changing the final properties in a wide range of possible varieties of compositions and its low cost, make them highly suitable as host media for laser-active ions.

Chromium ions are used as active ions for tuneable solid-state lasers in the near infrared (NIR) region, for which they are becoming a matter of special interest. While the Cr(III) ions can operate in the region between 700 and 1000 nm, Cr(IV) ions have been reported as an interesting dopant able to achieve laser emission in the range of 1200–1600 nm [1–4]. However, although the Cr(III) valence state is common and stable, the existence and stability of the Cr(IV) is rather elusive. Murata et al. [4] suggested that for aluminate, gallate and alumino-silicate glasses, the active centres responsible for the 1350 nm luminescence originated from the oxygen-excess defects (OED) around the chromium ions. Thus the Cr(IV) would not be an unstable intermediate state in the Cr(III)–Cr(VI) redox equilibrium, and the formation of such a rather unusual oxidation state of chromium seems to be associated with a mechanism other than redox equilibrium.

OED are found essentially in glass, in each in a different amount. The formation of silicate glasses can be envisaged by the reaction between a metal oxide (e.g. Na2O, CaO) and the acid oxide (e.g. SiO2). The obtained glasses can then be characterised e.g. in terms of their optical basicity, which in fact refers to the basicity (from the point of view of the Lewis theory of acids and bases [5]) of terminal non-bridging oxygen (NBO) atoms in the glass matrix. Hence the higher the basicity of the glass, the higher the partial negative charges on the NBOs. The term ‘optical basicity’ is used as a characteristic constant for the oxygen bonds in the glass and in fact illustrates the ability of the NBOs to induce a partial positive charge on the surrounding cations [6]. The high-optical-basicity of a glass also corresponds to a high relative proportion of the NBO to the bridging oxygen atoms (BO, which contribute to acidity). Consequently, the enhancement of the NBO in the silicate glass network leads to the formation of OED according to [4]. Moreover, highly basic glasses are required for the luminescence of the chromium ion in the region of 1.3 μm, reported as typical for Cr(IV) in the literature [1–4].

It arises from the considerations above that a glass with a rather high-optical-basicity, which would (on the basis of its character) offer a high amount of OED, is required in order to obtain and stabilise Cr(IV).

This paper will report on an entirely new approach of how to form and stabilise Cr(IV) in the silicate glass. Our process is based on the introduction of oxygen cations into the specially formed Cr(III)-containing silicate glasses via ion implantation.

2. Experimental details

The composition of the sodium–calcium–silicate glasses is set in such a way that it yields rather high-optical-basicity glasses and is based on those already developed in our laboratory and reported in [7]. Optical basicities were calculated according to [8]. The formed glasses were doped with Cr2O3 to the concentration of 0.5 or 0.1 at.% of Cr(III) (G5, G1, respectively). A reference sample of the un-doped glass (labelled as RG) was also prepared. The
batches were melted for 4 h in a Pt crucible at 1500 °C in an oxidation atmosphere. After the melting the homogeneous melt was cast into a stainless steel mould to obtain glass bars. The glass bars were then subsequently cooled in a two-step process to relax stresses introduced during the glass forming; the first cooling was immediately after the forming of hot glass bars for 1 h at 520 °C and then slowly cooled down to the room temperature. The second cooling step occurred for 48 h also at 520 °C for further hardening of the glass bars. Finally, the bulk glass was cut into 2–3 mm thick rectangular parallelepipeds and polished to optical quality prior to their use in further experiments.

Ion implantation with keV–MeV ions produce well localised layers of nearly any composition up to the depths of several μm. For these reasons the ion implantation is an indispensable tool for material research and industry [9]. Low energy implantations, with ion energies up several hundreds keV are usually accomplished on commercially available devices. For higher ion energies, up to several MeV, small accelerators are used. The ion beam line at new Tandetron 4130MC accelerator with an implantation device was used for implantation of glasses.

The energy of O⁺ implanted ions was 601 keV and at fluence 7·10¹⁴ ions/cm² using low current about 20 nA/cm². The beam entry port located at the chamber backside is provided with an assembly of four Faraday cups (each with secondary electron suppression) for scanned beam intensity measurement. A digital current integrator measures the output from the Faraday cups. The mean projected range, Rp, and range straggling, ΔRp, calculated by the SRIM code were 1.08 and 0.5 μm, respectively.

3. Measurements

The IR absorption spectra of the glasses were collected using a FTIR spectrometer, NICOLET 740, DSP 680 in the range of 11,500–1000 cm⁻¹. The transmittance spectra were collected in the region from 450 to 2000 nm at room temperature by using tungsten lamp and one grating monochromator MDR 23 with resolution 1.3 nm/mm in the range of 450–1000 nm and 2.6 nm/mm in the range 1000–2000 nm, respectively. Light transmitted through the sample was detected by a pyrometer, whose electrical signal was amplified by the lock-in amplifier PAR 5206. Reference frequency of the chopper was 30 Hz. The photoluminescence spectra were measured in the spectral region from 900 to 1500 nm at 300 K using the 808 nm continuous wave output of a semiconductor laser. Special arrangement of photoluminescence excitation was used to suppress laser scattered light.

The chemical compositions of the melted glasses as well as those of the surface layers of the treated substrates were measured by Electron Microprobe Analysis (EMA) using a CAMECA SX-100 electron microprobe. These analyses were carried out in wavelength dispersive spectrometers with diameters of 4 or 2 μm and an accelerating potential of 20 kV. A beam current of 2 nA was measured on a Faraday cup. A counting time of 10 s was used for all the elements. SiO₂ [Si Kα], Al₂O₃ [Al Kα], diopside [Ca Kα], albite [Na Kα], willemite [Zn Kα], leucite [K Kα] and chromium oxide [Cr Kα] were used as standards. The charge-up between the electron beam and the non-conducting glasses was avoided by a thin graphite layer (for concentration profiles from the polished edge) or a thin gold layer (for Back Scatter Electron (BSE) pictures of surfaces) deposited on the substrates.

4. Results and discussion

4.1. Glass

The EMA measurements confirmed very good agreement of the melted-bulk-glass composition with the respective batch compositions differing only in the content of sodium oxide, Na₂O. Even though ca 2 at.% of sodium oxide evaporated from the batch, it did not affect the resulting values of optical basicity being calculated for the glass batch (0.5720) and for the bulk glass using real composition (0.5709) significantly; see Table 1.

IR absorption spectroscopy was used to characterise the suitability of the used glasses for the sought wavelength range. The first absorption edge was found at 3600 cm⁻¹ (corresponding to a wavelength of 2800 nm) regardless of the concentration of chromium ions observed, because similar spectra were obtained for all the glasses (see Fig. 1A). Transmission spectra (see Fig. 1B) taken in the region 500–2000 nm showed the only absorption band in the region from 533 to 818 nm (typical for presence of Cr³⁺). According to the spectra, we may state that our novel glasses are suitable for utilisation in optics in the range of NIR wavelengths.

4.2. Implantation

Ion beam analytical methods can not determine the oxygen increase in silica glass because of a small amount of implanted oxy-

### Table 1

<table>
<thead>
<tr>
<th>at.%</th>
<th>Batch properties</th>
<th>Glass properties</th>
</tr>
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<tbody>
<tr>
<td>Cr⁺⁺</td>
<td>Na⁺</td>
<td>Basicity</td>
</tr>
<tr>
<td>G5</td>
<td>0.5</td>
<td>24.6</td>
</tr>
<tr>
<td>G1</td>
<td>0.1</td>
<td>25</td>
</tr>
<tr>
<td>RG</td>
<td>0</td>
<td>24.6</td>
</tr>
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Fig. 1A. The IR absorption spectra of the bulk glasses (examples).

Fig. 1B. The transmission spectra of the bulk glasses (examples).
gen comparing to high oxygen content in the glass substrate. We can provide a simulation of the mean range of implanted ions using SRIM software [10]. The range of implanted O\(^+\) ions at energy 601 keV depends on the structure and density of used glass. Here is an example simulation for the low-density glass (silica) SiO\(_2\) with the density 2.19 g/cm\(^3\) and for high-density glass GZ6 with the density 2.497 g/cm\(^3\). The depth profiles of O\(^+\) ions at energy 601 keV are presented in Fig. 2A (mean range is 1.2 \(\mu m\) for SiO\(_2\)) and in Fig. 2B (mean range of ions is 1.05 \(\mu m\) for GZ6 glass). Statistical parameters of ion depth distribution are included in the Fig. 2A and B.

Photoluminescence spectra in near IR region showed broad bands with maximum at 1050 nm for each prepared glass (see below Fig. 3A and B). This emission band was attributed to octahedrally coordinated Cr (III).

Fig. 3A and B shows the emission spectra (\(\lambda_{exc} = 808\) nm) of G1 and G5 before and after the implantation (IM). Obviously, the emission band with its maximum at 1.05 \(\mu m\) is present in every sample, which is a typical emission feature of octahedrally coordinated Cr(III) [2]. The post-implanted G5 (IM G5 in Fig. 3A) shows a significant decrease in the intensity of the 1.05 \(\mu m\) band, which may indicate oxidation of Cr(III). As neither Cr(VI) nor Cr(V) exhibit any luminescence in this spectral region, it is impossible to judge which oxidation state of chromium this might be. Nevertheless, there is an indication of a slight luminescence at ca 1230 nm, which could be attributed to Cr(IV).

An entirely different situation is illustrated in Fig. 3B, where a similar decrease in the intensity of the 1050 nm band is clearly accompanied by the emergence of a new distinctive strong band centred at 1300 nm, which is clear evidence of the presence of the desired Cr(IV). In other words, the oxygen implantation triggered the formation of a new optical centre attributed to tetrahedrally coordinate Cr\(^{4+}\) ions (according to [2]).

The observed effects, i.e. a lower intensity of the Cr(III) bands, or the appearance of new bands, must be caused by the incorporation of positively charged oxygen ions into the glass network and hence a significant enhancement of the OED in the silicate glass network. The results obtained indicate that it is likely that Cr(IV) centres are formed by OED around Cr(III).

How could such an oxidation have occurred?

(I) When oxygen ions enter a glass surface, they interact with the silicate network and cause a localised surplus of oxygen (thus increasing the local concentration of OED). The surplus of oxygen causes a depolymerisation of the silica network and consequently also an increase of NBO. Subsequently, the total negative partial charge of all the oxygen atoms around the Cr(III) grows, and thus chromium ions need to adapt, as a reaction to which they gather a higher positive partial charge and their final oxidation state manifests itself as Cr(IV).
(II) Positively charged oxygen ions exhibit a very strong oxidation power. When they are incorporated into a glass and come into contact with the chromium ions, they are able to overcome the energy barrier needed for separating an electron, gather an electron from the Cr(III) valence shell and consequently oxidise the Cr(III) to Cr(IV).

A likely mechanism of processes (i) and (ii) is indicated by Equation A. However, several accompanying processes, such as the cracking of oxygen bridges between Si(IV) atoms, stronger oxidation of chromium ions, etc. (see Eqs. (B and C)), are also likely to occur. They are merely those extreme mechanisms, and many of their various combinations can be expected.

\[
\text{O}^+ + \text{Cr(III)} \rightarrow \text{O}_2^+ + \text{Cr(IV)} \quad (A)
\]

\[
\text{O}^+ + \text{Cr(III)} \rightarrow \text{O}_2^+ + \text{Cr(V)/Cr(VI)} \quad (B)
\]

\[
\text{O}^+ + -\text{Si(O}_2^+)\text{O-} + \text{Si(O}_2^+)\text{O-} \rightarrow 2 -\text{Si(O}_2^+)\text{O-} \quad (C)
\]

According to [4] the occurrence of Cr\textsuperscript{4+} was always accompanied by presence of the OEDs. The OEDs are there characterised as superoxides or even peroxides centres, i.e., the centres possessing lower negative charge than that which could be expected for the same amount of oxygen ions (e.g., compare O\textsuperscript{2–} with 2O\textsuperscript{2–}). Thus it is easy to foresee that the OEDs will have in fact oxidising properties.

In our samples, the implantation of O\textsuperscript{2–} ions in thin surface layer (see Fig. 2A and B) caused either presence of high oxidation power possessing O\textsuperscript{2–} ions either rather high amount of OEDs centres, both having ability to oxidise Cr\textsuperscript{3+} to higher oxidation states.

5. Conclusion

We have proved that ion implantation is a powerful tool that may affect the silicate glass network in such a way that it would exhibit entirely different behaviour. In this special case, the ion implantation of oxygen cations into specially designed silicate glasses made the Cr(III) behave like Cr(IV) and thus exhibit the desired luminescence at 1300 nm. The possible explanations of this effect have also been presented. The intensity and shape of the characteristic Cr(IV) emission band did not change even after 10 h of annealing at 200 °C therefore we can foresee that the oxidation state Cr\textsuperscript{4+} is in our glasses quite stable.

These encouraging results form the basis for a more detailed study of the effects of the implantation of oxidising ions into Cr(III)-containing glasses, where the occurrence of Cr(V) and Cr(VI) in the implanted samples will be examined.

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References