Enhanced room-temperature emission in Cr$^{4+}$ ions containing alumino-silicate glasses

C. Batchelor, W. J. Chung, S. Shen, and A. Jha

The Institute for Materials Research, Houldsworth Building, Clarendon Road, University of Leeds, Leeds, LS2 9JT, United Kingdom

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The Bi$_2$O$_3$ modified alumino-silicate glasses, when excited at 800 nm exhibited a broadband emission of Cr$^{4+}$ in the range of 1.2 to $\sim$1.6 $\mu$m at room temperature. The mean lifetime of (1$^E$ $\rightarrow$ 3$^T_1$) transition in Cr$^{4+}$-doped glass at RT was as long as $\sim$426 $\mu$s, enabling the realization of both tunable lasers and broadband fiber amplifiers. The Cr$^{4+}$ emission at RT also showed the dependency on the excitation wavelength and site distribution within the chosen glass host. A photoinduced charge transfer process from the Cr$^{3+}$ ion into Cr$^{4+}$ ion appears to be responsible for the excitation of Cr$^{4+}$. © 2003 American Institute of Physics. [DOI: 10.1063/1.1581374]

It is well known that the Cr$^{4+}$ ions, when excited with a visible source at 514 nm or 800 nm, can generate near infrared emission at 1.2~1.6 $\mu$m in crystals, as observed in the forsterite (MgSiO$_3$) crystal. Such transition-metal ion-doped crystals are classed as “the host for vibronic lasers.” But because of a rapid growth of the wavelength division multiplexing network systems, Cr$^{4+}$-doped glasses and crystals have drawn attention for development as a tunable laser source and broadband amplifiers in the 1100- to 1600-nm region. In response to the need for lasers and amplifiers, it is necessary to identify an optimum glass host for fiber fabrication. Chromium ions are likely to exist in the stable form of 3$^+$ valence state and are hardly found in tetravalent coordination state in normal glasses. The aluminate, alumino-silicate, and gallate glasses have been widely studied for obtaining the 4$^+$ oxidation state of Cr ions. As the interaction between the 3$d^2$ electrons and the vibrational modes of the lattice is responsible for the broad emission of the Cr$^{4+}$ ion, the alumino-silicate, aluminate, and gallate hosts suffer from poor emission intensity and comparatively short lifetimes of the fluorescence of the order of 50~100 $\mu$s at room temperature. Broadband amplifiers and tunable lasers are required to have high quantum efficiency, large emission cross section, and long lifetimes of the metastable state.

In this investigation, we have prepared alumino-silicate glasses (SiO$_2$–Al$_2$O$_3$–Li$_2$O–TiO$_2$–ZnO) modified with metal oxides (Bi$_2$O$_3$) and found no clear absorption bands due to the Cr$^{4+}$ ions. However, we have observed strong broad emission and excessively long lifetime of Cr$^{4+}$ at RT compared to the silicate, aluminate, and alumino-silicate hosts studied previously. The measured lifetimes are comparable with the rare-earth ion-doped glasses that are used for fiber amplifiers, for example, Pr-doped and Nd-doped fluoride glasses. The mechanism of the excitation of and emission from Cr$^{4+}$ ions is discussed.

The nominal composition of the alumino-silicate glasses was based on the lithium–aluminosilicate (LAS-type) glasses having 51 SiO$_2$, 25.5 Al$_2$O$_3$, 18 Li$_2$O, 5.5 ZnO, and 0.01 Cr$_2$O$_3$ (in mol %). In metal-ion modified glasses, 1 mol % of Bi$_2$O$_3$ was added to replace 1 mol % of Li$_2$O. High-purity starting materials (99.99+% ) were weighed and well mixed prior to the melting. The prepared batches were melted in a platinum crucible for 3 h at 1600°C in air and allowed to cool to room temperature after homogenization. Absorption spectra of the optically polished samples were characterized by UV-VIS-NIR spectrophotometry (Perkin Elmer, Lambda 19). A single-mode Ar-ion laser (Coherent, Innova 90) and a Ti:sapphire laser (Schwartz Electro Optics, Titan CWBB) were chosen for excitation. Visible and infrared fluorescence were collected using a scanning spectrometer (Edinburgh Instruments, FS920). The photomultiplier tube and InGaAs devices were two different types of detectors used to measure emission in the visible and infrared ranges, respectively. A lock-in amplifier with mechanical chopper was used to measure the steady-state spectra. The lifetimes were measured with a fast-current amplifier (<1 MHz, Femto Inc.) and a digital oscilloscope (Tektronics, TDS3012). The sample was placed in a cryostat sample chamber (Oxford Instruments, Optistat$^{(TM)}$) for low-temperature experiments.

As can be seen in Fig. 1, the UV absorption edge of the glass has been redshifted with the addition of a metal-oxide.
(Bi2O3) modifier. The characteristic absorption bands due to the Cr6+ (360 nm) and Cr3+ around 500–700 nm were reported in the glass without a modifier.5,14 It is, thus, evident that the Cr ions after melting exist in two stable forms: the Cr3+ and/or Cr6+ state in the present glass system. A strong visible absorption band due to 3A2→3T1 transitions of Cr4+ normally occurs at ~620 nm in most aluminate glasses with weak absorption near 900 nm due to 3A2→1T2.3–9,15 However, no clear evidence for such absorption bands was found in the compositions investigated herein, and is exemplified in Fig. 1(b). The comparison of absorption spectra in Fig. 1 implies that the Cr3+ valence state either did not form, or if formed, the absorption bands might be obscured by the absorption edge due to the presence of Bi2O3.16

The measured emission spectra of the glasses with argon-ion laser (~514 nm) are shown in Fig. 2(a). A broad emission band from 700–1200 nm was observed in the glass without Bi2O3 modifier, which is almost identical to the emission data reported for the silicate glasses prepared in oxidizing atmospheres.4,6 Such an emission is characterized as the typical emission of the vibronically broadened Cr3+:4T2→4A2 transition, which occupy low-field sites.4

Glasses with modifier oxides, however, exhibit a large emission, with a broadband in the 1000-1600-nm range, which resembles a typical emission of Cr4+:1E or 3T2→3A2 observed in forsterite8 and other aluminate glasses.4–9 Although there appears to be no direct evidence for the presence of Cr4+ states in the glass from the absorption spectrum, the emission data in Fig. 2 confirm the presence of the Cr4+ state in the glass. Emission bands in the 600- to 800-nm range are due to the Cr3+ ions occupying high crystal-field sites.4,6,14

It is interesting to find that a large part of the emission due to the Cr3+ has been shifted from the low-field sites to high-field sites with the addition of a modifier. Moreover, the Cr4+ ions also show significantly stronger emission than the Cr3+ ions. These results strongly indicate that the Cr3+ ions at low-field sites play an important role in determining the Cr4+-ion emission via a charge or an energy transfer process, discussed subsequently.

Unlike previous investigations,2,5–8 the emission from Cr4+ ions was also measured with the excitation source at 800 nm, both at the RT and 77 K [see Fig. 2(b)]. As shown in the Fig. 2, larger than 230 nm full width at half-maximum was observed, which spans the 1300- to 1500-nm telecommunications wavelengths and will be able to complement the performance of Er-ion- and Tm-ion-doped devices. The lifetime measured at RT is shown in Fig. 3. The fluorescence characteristics showed an almost linear exponential decay behavior in the 1/e2 intensity range, beyond which it deviated from linearity, implying that an alternative mechanism must contribute to the overall decay, rather than the pure electronic transition. The mean lifetime of ~426 µs at 1320 nm was obtained by using \( \tau_m = \int \phi(t)dt/\int \phi(t)dt \). The 800-nm pumping scheme offers a potential advantage of using high-power semiconductor lasers, which are commercially available. Therefore, the broad emission with excitation source at 800 nm, as well as the long lifetimes in the present Cr4+-doped glass, provides a significant opportunity to realize the broadband fiber and planar lasers and amplifiers. The integrated intensity at RT was ~0.37 times that at 77 K, and is comparatively larger than the hosts reported in the literature.2,5–8 The results are promising, leaving a further scope for improvement to higher values than 0.37 at RT.

It should be also noticed that the peak emission has shifted from ~1200 nm in Fig. 2(a) to ~1300 nm in Fig. 2(b) with the change in excitation wavelength from 514 to 800 nm. Moreover, there is a shoulder on the emission at ~1400 nm. From the Tanabe–Sugano diagram for an ion with 3d2 electron configuration,12 the electronic-vibrational states of 3T2 and 1E cross each other at a certain crystal-field parameter, and the 3T2 state lies below the 1E level at low crystal-field sites. The line shape of Cr4+ is therefore determined by the spin–orbit interactions of two levels and their site distribution.7,15 It is believed that the strong emission at ~1200 nm is due to the Cr4+ ions occupying the high-field sites, however the Cr4+ ions at low-field sites are responsible for the broad emission up to 1600 nm.2,7,15,18 Transitions from the mixed energy levels of 3T2-1E were attributed to the emissions of Cr4+ in alumino-silicate glasses, rather than from the single energy level of 3T2.18 A peak shift with the change in the excitation wavelength occurs, resulting in a significant reduction in intensity at ~1200 nm, which implies that fewer Cr4+ ions at the high-field sites are excited for the eyes.
by 800-nm pump than when the 514-nm source was used, suggesting that both the Cr$^{3+}$ excitation and emission spectra are dependent on the site distribution of ions in the glass host. The emission band at $\sim$1400 nm implies that there may be sites for Cr$^{4+}$ ions, which are preferentially at lower crystal-field site than those sites responsible for the emission centered at $\sim$1300 nm.

It was previously shown by Murata and co-workers$^{8,9}$ that the oxygen-excess defects in aluminate and gallate glasses contribute to the formation of Cr$^{4+}$ ions from Cr$^{3+}$ state. However, in this investigation, the addition of Bi$_2$O$_3$ in the LAS glass can also provide an excess of oxygen (O$^{2-}$) in the glass when it decomposes via the reaction: Bi$_2$O$_3$ = 2BiO$^-$ + (1/2)O$_2$. The decomposed oxygen available as O$^{2-}$ is likely to be available for determining the redox states of Cr$^{3+}$ and/or Cr$^{4+}$ during melting; consequently, the Cr$^{4+}$-states form in the glass. In view of a conspicuous absence of Cr$^{4+}$-ion absorption band in the present investigation, compared to previous reports,$^{4,9-15}$ we propose that the Cr$^{4+}$ ions formed via redox reaction is only present in much smaller quantities than 0.01 mol % of total Cr$^{3+}$ ions in the glass, which may also explain the reason for a weaker absorption intensity of Cr$^{4+}$ ions at RT. In general, Cr$^{4+}$-doped aluminate and gallate glasses showed much shorter lifetimes less than $\sim$100 $\mu$s$^{2,8,7,10,11}$ whereas the prolonged lifetime ($\sim$426 $\mu$s) has been observed in the present glass. The observed lifetime implies that the mechanism for the excitation of Cr$^{4+}$ ions may be different from those reported previously.$^{4-9,15}$

It is evident from Fig. 1 that the presence of modifier metal ions, for example, Bi$^{3+}$, shifts the short-wavelength cutoff edge to longer wavelengths, which overlaps with the Cr$^{3+}$ absorption peak. It should also be noted that the glass (a) in Fig. 1 does not show any emission of Cr$^{4+}$ when excited at 514 or 800 nm. Since the Cr$^{4+}$ emission is only seen in the presence of Bi$_2$O$_3$ in the glass, the formation of Cr$^{4+}$ state must be related to the oxidation of Cr$^{3+}$ ions occupying low crystal-field sites. The efficient energy transfer from the Cr$^{3+}$ ion to the pre-existing Cr$^{4+}$ ion is also possible and may be responsible for the extended lifetime of Cr$^{4+}$. However, the energy transfer cannot be completely explained with the experimental results presented herein, by considering the likely concentrations of Cr$^{4+}$ ions depicted by the absorption band in Fig. 1(b) and the disappearance of the emission due to the Cr$^{3+}$ occupying the low-field sites in Fig. 2(a).

It should be emphasized that, in spite of the low concentrations of the pre-existing Cr$^{4+}$ ions in the glass modified with Bi$_2$O$_3$, the emission of the Cr$^{4+}$ ions is dominant when they are pumped with either 514 or 800 nm. It supports the reason that it is the pump excitation at 514$\sim$800 nm which promotes the oxidation process of Cr$^{3+}$ to the Cr$^{4+}$ state. Bismuth oxide must be involved in the charge-transfer process of chromium ions by lowering the charge-transfer band. The lowered electronic edge due to the bismuth oxide has been also found in Bi$_2$SiO$_5$ crystals.$^{19}$ The correspondence of electronic edge with the absorption band of Cr$^{3+}$ in the LAS glasses could facilitate the following charge transfer: Bi$^{3+}$ + Cr$^{3+}$ = Cr$^{4+}$ + Bi$^{2+}$, involving an electron from the Bi-ion site to the vicinal Cr$^{3+}$ site. Such a mechanism does not involve any ionic motion or a major change in the local phonon structure. The oxidation of Cr$^{3+}$ ions occupying a nearby Bi$^{3+}$ site during the excitation appears to be responsible for the disappearance of the emission of Cr$^{3+}$ and the prolonged lifetime of Cr$^{4+}$ metastable states. The Cr$^{6+}$ states present in the glass also appear to contribute to the redox reaction: Cr$^{6+}$ + 2Bi$^{2+}$ = Cr$^{4+}$ + 2Bi$^{3+}$, which is important for the recovery of the Bi$^{3+}$ state.

In summary, we observed the broadband emission of Cr$^{4+}$ level [(1$E$ or $T_2$)$\rightarrow$3$A_2$] with the addition of Bi$_2$O$_3$ in the aluminate-silicate glasses. The observed lifetime was $\sim$426 $\mu$s at RT using the 800-nm excitation wavelength. The possibility of using 800 nm as a pump source, as well as the enhanced lifetime at RT, suggests that the present glass could be a potential candidate for a broadband fiber amplifier covering a 1.2- to $\sim$1.5-$\mu$m telecommunications window. The Cr$^{4+}$ ions can be formed with the addition of Bi$_2$O$_3$, but in small concentrations in the LAS glass. It is the charge transfer between the Cr$^{3+}$ ions and Bi$^{3+}$ ions that is responsible for the broadband emission of Cr$^{4+}$ and its extended lifetime.

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