Broadband 1400 nm emission from Ni$^{2+}$ in zinc—alumino—silicate glass

Takenobu Suzuki$^a$ and Yasutake Ohishi
Toyota Technological Institute, 2-12-1, Hisakata, Tempaku-ku, Nagoya 468-8511, Japan

(Received 19 January 2004; accepted 18 March 2004; published online 29 April 2004)

Broadband near-infrared emission from Ni$^{2+}$ in zinc—alumino—silicate glass was observed at room temperature. The emission band had a peak at $\sim$1400 nm with a bandwidth more than 300 nm, and covered the $O$, $E$, $S$, $C$, and $L$ bands (1260–1625 nm). The emission lifetime was more than 200 $\mu$s even at room temperature. The observed near-infrared emission could be attributed to the $3A_{2g}(3F) \rightarrow 3T_{1g}(3F)$ transition of Ni$^{2+}$ in octahedral sites. This nickel-doped glass can be expected as an amplification medium for tunable lasers and broadband optical amplifiers for the wavelength division multiplexing transmission system applications. © 2004 American Institute of Physics. [DOI: 10.1063/1.1741027]

The demand to increase the transmission capacity of wavelength division multiplexing (WDM) system is indispensable due to the rapid development of telecommunications. Considerable effort has been devoted to materials and design for optical fibers, waveguide devices, and optical fiber amplifiers to revolutionize the telecommunication systems. Specifically, many attempts have been made to broaden and flatten gain spectra of optical fiber amplifiers, such as Er-doped fiber amplifiers (EDFAs),$^1$ tellurite-based EDFA,$^2$ Tm-doped fiber amplifiers,$^3$ and fiber Raman amplifiers (FRAs).$^4$

However, the expansion of the optical amplification bandwidth due to one rare-earth ion is limited, because the bandwidth of the $4f \rightarrow 4f$ optical transition is narrow by nature. Though, FRAs can realize broadband amplification, they require multiwavelength pumping schemes and have low gain efficiency. Broadband FRAs have complex structures and require high-power consumption. If ultrabroadband amplification is realized with high gain efficiency by the single wavelength pumping, the drastic evolution could be expected to occur in the WDM technology.

Broadband tunable lasers, such as Ti$^{3+}$:Al$_2$O$_3$,$^5$ Cr$^{4+}$ :YAG,$^6$ Cr$^{3+}$ :LiCAF (Ref. 7) were realized by using transition metals as active ions. If transition metals were active in glasses, ultrabroadband optical amplifiers could be realized. Cr$^{4+}$ doped in glasses has been extensively investigated so far.$^8$–$^{10}$ As chromium ions can easily take multivalent states, such as Cr$^{3+}$, Cr$^{4+}$, and Cr$^{6+}$, the strict valence control is required to obtain Cr$^{4+}$. In contrast, nickel takes the divalent state in almost all hosts, as divalent nickel is extremely stable. There would be no serious need to control the valence state of nickel doped in glasses to obtain Ni$^{2+}$.

There has been no comprehensive investigation about emission from nickel-doped glasses, to our knowledge, though it has been known that the Ni$^{2+}$ ion shows a broad emission band around 1.3 $\mu$m in MgO at room temperature.$^{11}$ We have obtained an efficient broadband emission in the near-infrared region from Ni$^{2+}$ doped in zinc—alumino—silicate glass at room temperature. We report the characteristics of broadband near-infrared emission from a nickel-doped zinc—alumino—silicate glass in this letter.

A ZnO–Al$_2$O$_3$–SiO$_2$ system glass was used as a host of Ni$^{2+}$. Sample glasses were prepared by a conventional casting method. The nickel content doped in the glass was 0.1 wt %, Raw materials of reagent grade were mixed thoroughly and melted in a Pt–Rh crucible in an O$_2$ atmosphere at 1600 $^\circ$C for 2 h in an electric furnace. The melts were poured onto an annealed steel plate and slowly cooled down to room temperature. The sample was polished to optical quality before subjecting it to the optical measurements. The sample thickness was about 4 mm. Absorption spectra were recorded by using a double-beam spectrophotometer (Perkin–Elmer Lambda 900). The nickel-doped glass sample was excited with a 976 nm laser diode (Sumitomo Electric) in the emission measurements. Emission from the sample was dispersed by a single monochromator (blaze, 1.0 $\mu$m; grating, 600 grooves/mm; resolution, 3 nm) and detected by an InGaAs photodiode (Hamamatsu Photonics, 65852-11). Emission decay curves were obtained by a photomultiplier (Hamamatsu Photonics, H5170-75) as a detector and accumulated using an oscilloscope (Yokogawa, DL-1620). The temperature of the glass was changed from 5 K to 300 K using a cryostat (Daikin) in the emission spectra and decay curve measurements. Refractive indices of the glass were measured by a prism-coupler method.

Optical absorption spectra of the glasses were shown in

![Graph](image-url)
Fig. 1. The difference spectrum of absorptions between the nickel-doped and nondoped glasses were also shown in Fig. 1. A broadband near-infrared absorption band centered at 1400 nm and a visible band centered at 600 nm in the difference spectrum could be attributed to the $^3A_2^o \rightarrow T_{2g}^o$ and $^3A_2^o \rightarrow T_{1g}^o$ transitions of Ni$^{2+}$ in octahedral sites. Although it was reported that the intensity of an absorption band due to Ni$^{2+}$ in tetrahedral sites is about 10–100 times larger than that in octahedral sites,12 there were no clear absorption bands derived from Ni$^{2+}$ in tetrahedral sites. It is considered that almost all the Ni$^{2+}$ ions in the glass would occupy octahedral sites. The Racah parameter $B$ and crystal field strength parameter $Dq$ of octahedral Ni$^{2+}$ (Ref. 13) in the glass estimated from absorption spectra were $B=652$ cm$^{-1}$ and $Dq=932$ cm$^{-1}$.

The temperature dependence of emission spectra of the glass was shown in Fig. 2. The full width of half maximums (FWHMs) of the spectra were wider than 300 nm in wavelength. The Ni$^{2+}$ emission covered the $O$, $E$, $S$, $C$, and $L$ bands (1260–1625 nm). The intensity decreased with an increase in temperature. The intensity at 5 K was about ten times as large as that at 300 K. In contrast, the shape of the emission hardly changed with temperature. There were no structural features, such as the zero-phonon line, in the shape of the emission. The peak of the emission shifted to lower wavelengths with an increase in temperature from 1380 nm at 5 K to 1420 nm at 300 K.

The emission decay curves at several temperatures are shown in Fig. 3. The emission decay curves had strong nonexponential characteristics at each temperature so that the average lifetimes were obtained by using $\tau = \int t I(t) dt / \int I(t) dt$. Multiple site effects of Ni$^{2+}$ and nonradiative multipolar interactions among Ni$^{2+}$ are considered the origins of the nonexponential decay. The mechanisms for the nonexponential emission decay are under investigation.

Figure 4 shows the temperature dependence of the observed emission lifetimes. The lifetime decreased gradually with an increase in temperature. It was 440 $\mu$s at 5 K and as long as 240 $\mu$s at 300 K. This is a rather long lifetime of the emission from Ni$^{2+}$ doped in glasses at room temperature. The obtained lifetime of nickel-doped glass at 300 K is comparable to that of practical tunable laser crystals, such as 220 $\mu$s for Cr$^{3+}$ in BeAl$_2$O$_4$ (Ref. 14) and much longer than 3.6 $\mu$s for Cr$^{4+}$ in Mg$_2$SiO$_4$.15 The internal fluorescence quantum efficiency ($\eta$) defined as $\tau_{500K}/\tau_{5K}$ of the transition was obtained as 0.55. The stimulated emission cross section $\sigma$ as a function of wavelength to a first approximation coincides with the spontaneous emission spectrum, which is expressed by the following formula:

$$\sigma(\lambda) = \frac{\lambda^2 g(\lambda) \eta}{8 \pi n^2 \tau},$$

where $\lambda$ is wavelength, $g(\lambda)$ is the normalized spontaneous emission shape function, $n$ is the host refractive index, and $\tau$ is the emission lifetime. By assuming a Gaussian-shaped emission band, $\sigma$ at the band center can be estimated by the following formula:

$$\sigma = \frac{\lambda_0^2 \eta}{4 \pi n^2 \tau} \times \left( \frac{\ln 2}{\pi} \right)^{1/2} \frac{1}{\Delta \nu_{1/2}},$$

where $\lambda_0$ is the band center wavelength and $\Delta \nu_{1/2}$ is the FWHM of the emission. We can obtain $\sigma=1.3 \times 10^{-20}$ cm$^2$, with $\lambda_0=1380$ nm, $\eta=0.55$, $n=1.59$, $\tau=240$ $\mu$s, and $\Delta \nu_{1/2}=1650$ cm$^{-1}$. The calculated $\eta$ and hence the $\sigma$ must be considered as upper limits. The product of the lifetime and the stimulated emission cross section, $\sigma \tau$, is an important parameter to characterize laser materials, because the laser threshold is proportional to $(\sigma \tau)^{-1}$. The $\sigma \tau$ product of the Ni$^{2+}$ in the present zinc–alumino–silicate glass was $3.1 \times 10^{-24}$ s cm$^{-2}$ and more than two times that of Ti$^{3+}$:Al$_2$O$_3$ ($\sigma \tau=1.4 \times 10^{-24}$ s cm$^{-2}$).16 It suggests that this Ni$^{2+}$-doped zinc–alumino–silicate glass is a promising amplification material.

In summary, we observed the broadband near-infrared emission from Ni$^{2+}$-doped zinc–alumino–silicate glass. The

**FIG. 2.** Temperature dependence of near-infrared emission of nickel-doped glass.

**FIG. 3.** Normalized emission decay curves of near-infrared emission of the nickel-doped glass.

**FIG. 4.** Temperature dependence of lifetime of near-infrared emission of the nickel-doped glass.
observed lifetime was 240 \( \mu s \) even at room temperature. The possibility of using 980 nm as a pump source suggests that the present glass could be a candidate for a broadband fiber amplifier and tunable laser covering from the \( O \) to \( L \) bands.

The authors would like to thank Koichi Hoshino for his helpful discussion. This work was partly supported by the Nippon Sheet Glass Foundation for Materials Science and Engineering and the Ministry of Education, Culture, Sports, Science, and Technology as a part of studies of the Private University High-Tech Center Program.