Optical properties of transparent Li$_2$O–Ga$_2$O$_3$–SiO$_2$ glass-ceramics embedding Ni-doped nanocrystals

Takenobu Suzuki, Ganapathy Senthil Murugan, and Yasutake Ohishi

Department of Future Industry-oriented Basic Science and Materials, Toyota Technological Institute, 2-12-1, Hisakata, Tempaku-ku, Nagoya 468-8511, Japan

(Received 12 October 2004; accepted 9 February 2005; published online 21 March 2005)

Transparent Li$_2$O–Ga$_2$O$_3$–SiO$_2$ (LGS) glass-ceramics embedding Ni: LiGa$_5$O$_8$ nanocrystals were fabricated. An intense emission centered around 1300 nm with the width of more than 300 nm was observed by 976 nm photoexcitation of the glass-ceramics. The lifetime was more than 900 μs at 5 K and 500 μs at 300 K. The emission could be attributed to the $^3T_{2g}(^2D) \rightarrow ^3A_{1g}(^2F)$ transition of Ni$^2+$ in distorted octahedral sites in LiGa$_5$O$_8$. The product of stimulated emission cross section and lifetime for the emission was about $3.7 \times 10^{-24}$ cm$^2$s and was a sufficiently practical value. © 2005 American Institute of Physics, [DOI: 10.1063/1.1891272]

The demand to increase the transmission capacity of wavelength division multiplexing (WDM) system is indispensable due to the rapid development of the optical telecommunication. Considerable effort has been devoted on materials for optical fiber amplifiers to revolutionize the telecommunication systems.

Broadband tunable lasers were realized by using transition metals as active ions such as Ti$^{3+}$: sapphire and Cr$^{4+}$: Mg$_2$SiO$_4$. If transition metals were active in glasses, ultrabroadband optical amplifiers could be realized. Cr$^{4+}$ doped in glasses have been extensively investigated. 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 the hosts, as the divalent nickel is extremely stable. There would be no serious need to control the valence state of nickel doped in glasses to obtain Ni$^{2+}$.

Transition metal-doped glasses are not applicable to gain media for lasers and optical amplifiers, since nonradiative decay processes dominate the relaxations of the excited states of transition metals and the quantum efficiency of transition metals is very low in glasses, though they can have sufficiently large quantum efficiency in single crystals. However, it is difficult to obtain single crystal fibers. In contrast, glasses can be easily obtained as large size bulk and they can be used as fiber and waveguide materials.

Glass-ceramics are of interest as hosts for transition metals, since they have the advantage of both crystalline and glassy properties. Glass-ceramics possess mechanical properties like glasses as high ability to be drawn into fibers. If the sizes of crystals in glass-ceramics are far less than the wavelength of interest, light scattering caused by the crystals would be negligible. Furthermore, if transition metal ions are successfully included in crystalline phase in glass-ceramics, the quantum efficiency of the broadband emissions could become high like in single crystals. In addition, glass-ceramics can be fabricated on a massive scale. It is thought that transition metal-doped glass-ceramics have a great potential for broadband optical amplification media if transition metals are successfully incorporated into the crystalline phase.

Recently, spectroscopic investigations of the Ni-doped glass-ceramics have been reported. We have also reported the fabrication of Ni-doped transparent zinc–alumino-silicate (ZAS) glass-ceramics with relatively high quantum efficiency. As improvement of the quantum efficiency is an important issue to realize Ni-doped glass-ceramics applicable to optical amplifiers and lasers. We have researched Ni-doped glass ceramics with higher quantum efficiency.

Transparent glass-ceramics embedding LiGa$_5$O$_8$ nanocrystals are very attractive as a matrix for Ni doping, since the quantum efficiency of near-infrared emission from Ni: LiGa$_5$O$_8$ was almost 100% up to 350 K. If the Ni is incorporated into the LiGa$_5$O$_8$ nanocrystals in glasses, transparent glass-ceramics with high quantum efficiency can be synthesized.

We have obtained a new Ni-doped Li$_2$O–Ga$_2$O$_3$–SiO$_2$ (LGS) glass-ceramics with larger quantum efficiency than Ni-doped ZAS glass-ceramics. In this letter, we will present the structural and optical properties of Ni-doped LGS glass-ceramics embedding Ni: LiGa$_5$O$_8$ and the potential of the glass-ceramics as a broadband optical amplification or tunable laser medium.

Glasses of the 30 g batch were prepared from reagent grade Li$_2$CO$_3$, Ga$_2$O$_3$, SiO$_2$, and NiO. The concentration of NiO was 0.1 mol %. The raw materials were mixed thoroughly and melted in a Pt–Rh crucible for 2 h at 1600 °C in the ambient atmosphere. The melt was poured onto a heated steel plate and cooled down to room temperature.

X-ray diffraction (XRD) measurements were carried out using Mo $K\alpha$ radiation to identify crystalline phases and the average sizes of the crystals in the sample. The samples were cut to the thickness of 4 mm and were polished to optical quality before subjecting them to the optical measurements. Absorption spectra were recorded by using a double-beam spectrophotometer (Perkin-Elmer Lambda 900). The glass samples were excited with a 976 nm laser diode electrically modulated ten pulses per second in the emission measurements. Emission from the samples was dispersed by a single monochromator (blaze, 1.0 μm; grating, 600 grooves/mm; resolution, 3 nm) and detected by a photomultiplier. Emission decay curves were obtained by the photomultiplier.

---

$^{a}$Present address: 2-12-1, Hisakata, Tempaku-ku, Nagoya 468-8511, Japan; electronic mail: takenobu@toyota-ti.ac.jp
The absorption spectrum of the as-quenched glass resembles the absorption spectra of Ni$^{2+}$ ions in octahedral sites in other materials, and especially in LiGa$_5$O$_8$. The broad absorption bands centered at 1055, 627, and 380 nm in the postannealed glass-ceramic could be attributed to the spin-allowed $^3A_2g(^1F) \rightarrow ^3T_{2g}(^3F)$, $^3A_2g(^1F) \rightarrow ^3T_{1g}(^1F)$, and $^3A_2g(^1F) \rightarrow ^3T_{1s}(^1P)$ transitions of Ni$^{2+}$ in octahedral sites, respectively. The weak absorption bands centered at 770 and 450 nm were attributed to the spin-forbidden $^3A_2g(^3F) \rightarrow ^3E_{1s}(^1D)$ and $^3A_2g(^3F) \rightarrow ^3T_{2g}(^1D)$ transitions, respectively. The Racah parameter $B$ and $C$, and crystal field strength parameter $D_q$ of octahedral Ni$^{2+}$ (Ref. 12) in the glass-ceramic estimated by fitting to the absorption peaks were $B=95$ cm$^{-1}$, $C=315$ cm$^{-2}$, and $D_q=948$ cm$^{-1}$. These values are considerably agreed well with $B=900$ cm$^{-1}$, $C=315$ cm$^{-2}$, and $D_q=977$ cm$^{-1}$ of Ni:LiGa$_5$O$_8$ at 70 K. This suggests that the nanocrystals precipitated by annealing are LiGa$_5$O$_8$ incorporating Ni. Absorption peaks and crystal field parameters of octahedral Ni$^{2+}$ in LGS glass-ceramic and LiGa$_5$O$_8$ single crystal are shown in Table I.

Emission spectra of the glass-ceramic measured at 5, 100, 200, and 300 K are shown in Fig. 3. The emission could be attributed to the transition from the $^3T_{2g}(^1F)$ excited state to the $^3A_2g$ ground state of Ni$^{2+}$ ions in octahedral sites. The FWHM of the spectra were greater than 300 nm in wavelength. The Ni$^{2+}$ emission covered the O–C band (1260–1560 nm). The intensity decreased with increase in temperature. The intensity at 5 K was about 4 times as large as that at 300 K. Structural features such as the zero-phonon line and phonon sidebands were not clearly seen in the emission spectra even at 5 K. The peak of the emission were shifted to shorter wavelengths with increase in temperature from 1360 nm at 5 K to 1300 nm at 300 K.
The emission decay curves had strong nonexponential characteristics at each temperature so that the average lifetimes were obtained by using \( \tau = \frac{1}{\ln 2} \frac{dt}{dI(t)/dt} \). Figure 4 shows the temperature dependence of the observed emission lifetimes. The emission lifetime decreased gradually with increase in temperature. It was 974 \( \mu s \) at 5 K and as long as 583 \( \mu s \) at 300 K, while the emission lifetime of LiGa\(_2\)O\(_4\) doped with 0.1 mol % NiO polycrystalline powder was observed as 1640 \( \mu s \) at room temperature. The lifetime at 300 K was 0.6 times as long as that at 5 K, while the intensity decreased by a factor of 4. The discrepancy between the lifetime and intensity decrease with temperature also happens in case Ni-doped ZAS glass-ceramics.\(^6\) Vibration in matrix glassy phase may contribute this phenomenon so that the size of crystalline phase is small (\( \sim 5 \) nm). Smaller lifetime of glass-ceramics than LiGa\(_2\)O\(_4\) polycrystalline would be caused by concentration quenching so that Ni\(^{2+}\) ions should be condensed in crystalline phase. The emission lifetime of LGS is greater than that of ZAS previously reported in Ref. 6 and a practical tunable laser ceramic, rare-earth ions such as the \( 3\text{P}_2 \rightarrow 3\text{F}_2 \) transition of \( \text{Tm}^{3+} \) doped in heavy oxide glass. Ni-doped Li\(_2\)O–Ga\(_2\)O\(_3\)–SiO\(_2\) glass ceramics are promising materials for tunable lasers and broadband optical amplifiers for the wavelength division multiplexing transmission systems.

In summary, we synthesized transparent Li\(_2\)O–Ga\(_2\)O\(_3\)–SiO\(_2\) glass-ceramics embedding Ni: LiGa\(_2\)O\(_4\) nanocrystals. A near-infrared emission centered at about 1300 nm with the width of more than 300 nm was observed by 976 nm photoexcitation of the glass-ceramics at room temperature. The emission lifetime was 974 \( \mu s \) at 5 K and 583 \( \mu s \) at 300 K. The observed near-infrared emission could be attributed to the \( 3\text{P}_2 \rightarrow 3\text{F}_2 \) transition of Ni\(^{2+}\) in octahedral sites in LiGa\(_2\)O\(_4\) crystalline phase. The quantum efficiency of the emission calculated from lifetime measurements was 0.60. The value was greater than that of ZAS glass-ceramics. The figure of merit \( \left( \sigma \tau \right) \) of the emission as a transition for a laser or amplification was about 3.7 \( \times 10^{-24} \) cm\(^2\) s which is greater than those of the \( 3\text{P}_2 \rightarrow 3\text{F}_2 \) transition of Ni doped in transparent ZAS glass-ceramic.

This work was partly supported by Izumi Science and Technology Foundation, Nippon Sheet Glass Foundation for Materials Science and Engineering, and the Ministry of Education, Culture, Sports, Science and Technology as part of studies of the Private University High-Tech Center Program.

---


---

FIG. 4. Temperature dependence of lifetime of near-infrared emission of Ni-doped LGS glass ceramic.