Temperature dependence and quantum efficiency of ultrabroad NIR photoluminescence from Ni^{2+} centers in nanocrystalline Ba-Al titanate glass ceramics

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Ultrabroad near-infrared (NIR) photoluminescence from Ni^{2+} -centers in nanocrystalline Ba-Al titanate glass ceramics was studied by temperature-dependent static and dynamic photoluminescence spectroscopy in the regime of 10 to 300 K. Photoluminescence covers the spectral range of about 1100 nm to >1600 nm with a typical bandwidth (FWHM) greater than 300 nm. For UV-LED excitation at 352 nm, an internal quantum efficiency of 65% is obtained. The excited state lifetime τ at room temperature is 39 μs . The stimulated emission cross section σ_{em} is $8.5 \times 10^{-20} \text{ cm}^2$, resulting in a practical figure of merit, $\sigma_{\text{em}} * \tau$, of $3.3 \times 10^{-24} \text{ cm}^2 \text{ s}$ at room temperature. These properties suggest suitability as a broadband gain medium for tunable lasers and optical amplifiers. © 2012 Optical Society of America

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3d transition metal ions such as Ni^{2+} , Co^{2+} , and Cr^{4+} doped into inorganic matrices have been a subject of interest for many years due to their broadband near-infrared (NIR) photoluminescence (PL). In such materials, NIR PL arises from d-d transitions and is hence strongly dependent on ligand field and coordination [1–5]. While various efforts have been undertaken to make use of this property in next-generation broadband optical amplifiers for telecommunication and other applications, especially with Co^{2+} and Cr^{4+} , any breakthrough has so far been prevented by difficulties in stabilizing the specific valence and coordination state in a suitable matrix material [1,2]. From a practical point of view, Ni^{2+} species seem the most promising choice to approach this problem. In an inorganic matrix, they may be present in three different coordination states, tetrahedral (fourfold, $^{\text{VI}}\text{Ni}^{2+}$), trigonal (fivefold, $^{\text{V}}\text{Ni}^{2+}$) and octahedral (sixfold, $^{\text{VI}}\text{Ni}^{2+}$). Only $^{\text{VI}}\text{Ni}^{2+}$ has been known to provide efficient NIR emission [3–5]. Consequently, $^{\text{VI}}\text{Ni}^{2+}$ -containing glass ceramics and single crystalline materials have drawn continuous attention over the last decade [3–5]. Of these two materials classes, glass ceramics, produced by controlled nucleation and crystallization of a suitable precursor glass, combine the advantages of glasses and crystalline materials: depending on viscosity and crystallization temperature of the precursor glass, they can be processed into optical fiber, and depending on the type of precipitated crystal species, high quantum efficiency (QE) can be obtained [6–8]. As a prerequisite, however, crystal precipitation must occur in sufficiently high number density to ensure very low crystallite size and, hence, high optical transparency. In this setting, the number of available matrix candidates has been limited to only a few systems, which typically rely on rare raw materials or exhibit major process limitations (such as high liquidus temperature and high dynamic fragility).

Recently, we reported on glasses of the type $30\text{TiO}_2\text{-}30\text{BaO-}30\text{SiO}_2\text{-}10\text{Al}_2\text{O}_3$ (TBSA, mol%) as a new matrix candidate [9]. In this system, nanocrystalline hol-

landite-type ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$, secondary BaTiO_3) Ba-Al titanates can be precipitated at high number density and crystal sizes of $\sim 30 \text{ nm} \pm 10 \text{ nm}$. Upon crystallization, added Ni^{2+} species undergo a coordination change from fivefold to sixfold due to incorporation into the crystalline environment. This was demonstrated to result in an intense NIR PL emission band spanning the spectral range of 1.0 to $1.6 \mu\text{m}$ with a full width at half maximum (FWHM) of $\sim 350 \text{ nm}$. Interestingly, it was shown that NIR PL can be induced with conventional near-UV (NUV) LEDs or other light sources and does not require laser excitation. In the present letter, we report on quantitative efficiency of photoemission from this material as a prerequisite for application as a gain medium in optical amplifiers. QE is obtained on the basis of low temperature static and dynamic PL spectroscopy, and stimulated emission cross section (σ_{em}) and figure of merit ($\sigma_{\text{em}}\tau$) are calculated.

A slab of $\sim 50 \text{ g}$ of TBSA precursor glass with a dopant concentration of 0.1 mol% (expressed as NiO) was prepared by conventional melting and quenching [9]. Melting was performed at 1550°C for 2 hrs in alumina crucibles under ambient atmosphere. The melt was then poured into a preheated graphite mould and annealed for 2 h at 500°C . Specimen of $15 \times 15 \times 2 \text{ mm}^3$ were cut from the obtained glass and polished to optical quality for spectroscopic analyses. Optimal conditions for transferring the precursor glass into a transparent nanocrystalline glass ceramic were found for annealing at 850°C for 2 h (ambient atmosphere) [9].

Temperature-dependent analyses (10 to 300 K) were performed in a closed-cycle liquid helium cryostat. Static excitation and emission spectra were recorded through optical windows with a high-resolution spectrofluorometer (Edinburgh Instruments FLSP 920) equipped with a 450 W steady-state xenon lamp and a pulsed 60 W Xe flashlamp as excitation sources. Decay curves were obtained by time-correlated single photon counting (TCSPC). A nitrogen-cooled NIR photomultiplier tube

(Hamamatsu R5509-72) was used for NIR PL detection with a response width of 800 ps. Excitation curves were corrected over the lamp intensity with a silicon photodiode. Emission curves were corrected over the spectral response of the NIR-PMT detector. The refractive index of the sample at 632 nm was measured on an ellipsometer (EL X-02C).

In Fig. 1(a), NIR PL and photoluminescence excitation (PLE) spectra of the Ni^{2+} -doped TBSA glass ceramic are illustrated as a function of temperature. Excitation spectra were obtained by monitoring PL at 1430 nm. The obtained PLE spectra consist of two bands and a shoulder with maxima at 352, 665, and 465 nm, respectively, which are readily assigned to spin-allowed ${}^3\text{T}_1({}^3\text{P}) \rightarrow {}^3\text{A}_2({}^3\text{F})$, ${}^3\text{T}_2({}^1\text{D}) \rightarrow {}^3\text{A}_2({}^3\text{F})$, and spin-forbidden ${}^3\text{T}_1({}^3\text{F}) \rightarrow {}^3\text{A}_2({}^3\text{F})$ transitions of Ni^{2+} ions on octahedral sites (${}^{\text{VI}}\text{Ni}^{2+}$). Position and shape of the excitation peaks remain unchanged with increasing temperature. The most intense excitation band [${}^3\text{T}_1({}^3\text{P}) \rightarrow {}^3\text{A}_2({}^3\text{F})$] spans the spectral range of 300 to 450 nm. It matches well emission from NUV LED chips (e.g., 350–420 nm). These can therefore be used as excitation sources. NIR PL spectra were recorded for monochromatic excitation at 352 nm. The resulting spectrum is dominated by a broad emission band (1100 to >1600 nm) which peaks at ~ 1430 nm. The width of this band (FWHM) exceeds 300 nm ($\sim 1545 \text{ cm}^{-1}$). NIR PL is ascribed to the spin-allowed relaxation of ${}^3\text{T}_{2g}({}^3\text{F}) \rightarrow {}^3\text{A}_{2g}({}^3\text{F})$ in ${}^{\text{VI}}\text{Ni}^{2+}$ and covers the complete telecommunication window (O–L bands, 1260–1625 nm). The intensity of the emission band decreases gradually with increasing temperature [Fig. 1(b)]. However, unlike the sharp intensity decrease that was previously observed in Ni^{2+} -doped silicate glass [10], the intensity at 300 K is still about 40% as strong as that at 10 K, indicating significantly less thermal quenching at room temperature. The shape of NIR PL spectra remains

Fig. 1. (Color online) (a) Temperature-dependent NIR PL and PLE spectra of Ni^{2+} -doped TBSA glass ceramic. (b) Variation of band intensity, position, and shape as a function of temperature. Lines in (b) are guides for the eye.

practically unaffected by temperature, but a notable blue-shift occurs with increasing temperature, namely from about 1500 nm at 10 K to 1430 nm at 300 K [Fig. 1(b)]. Similar behavior was found in a $\text{Ni}^{2+}:\text{LiGa}_5\text{O}_8$ glass ceramic by Suzuki *et al.* [4]. Secondary features such as a zero-phonon line and phononic side bands could not be detected in the observed band structure, even at temperatures down to 10 K. This indicates the strong vibronic interaction in this system.

Normalized NIR PL decay data are shown in Fig. 2(a) as a function of temperature, recording emission intensity at 1430 nm after excitation at 352 nm. None of the decay curves appear to follow a single exponential equation, what confirms the interaction of at least two distinct ${}^{\text{VI}}\text{Ni}^{2+}$ emission centers [9]. The effective excited state lifetime $\tau_{1/e}$ (the time after which the emission intensity did decay to $1/e$ of its initial value) at 10 K was found at about 60 μs . Its value decreases with increasing temperature. With 39 μs at room temperature, however, it is still about 65% as compared to the value at 10 K. The decrease of PL lifetime at high temperature is primarily caused by temperature-dependent nonradiative relaxation of ${}^3\text{T}_{2g}({}^3\text{F})$ to ${}^3\text{A}_{2g}({}^3\text{F})$. The obtained lifetime at 300 K under NUV excitation is much longer than that of crystalline $\text{Cr}^{4+}:\text{Mg}_2\text{SiO}_4$ (3.87 μs) excited with a Nd:YAG 1.064 μm laser [2] but shorter than what has been observed in $\text{Ni}^{2+}:\text{LiGa}_5\text{O}_8$ glass ceramic (583 μs) excited with a 970 nm laser diode [4].

Figure 2(b) depicts NIR PL lifetime and internal QE (η) of Ni^{2+} -doped TBSA glass ceramic as a function of temperature. Experimental data were fit to a parabolic function and extrapolated to 0 K. From this extrapolation, a lifetime of about 60 μs was estimated for a temperature of

Fig. 2. (Color online) (a) Temperature-dependent NIR PL decay curves of Ni^{2+} -doped TBSA glass ceramic. (b) Variation of effective lifetimes of the excited state ($\tau_{1/e}$) and calculated internal QE (η) as a function of temperature, showing experimental (dotted line) and fitted (solid line, parabolic fit of experimental data) data.

5 K. Internal η of the NIR PL process at temperature $T = x$ was then obtained from $\eta_{T=x} = (\tau_x/\tau_{5\text{ K}}) \times 100$, where τ_x is the experimental lifetime as obtained at temperature x and $\tau_{5\text{ K}}$ is the extrapolated lifetime at 5 K [5]. For ambient temperature ($x = 300\text{ K}$), a value of $\eta = 65\%$ was obtained. This value significantly exceeds the one which has been observed previously in most other materials, such as $\text{Ni}^{2+}:\text{MgAl}_2\text{O}_4$ ($\eta = 20\%$) [11] and $\text{Ni}^{2+}:\text{Mg}_2\text{SiO}_4$ crystal ($\eta \sim 3\%$) [12]. It is also bigger than that of a $\text{Ni}^{2+}:\text{LiGa}_5\text{O}_8$ glass ceramic ($\eta \sim 60\%$) [4]. While the observed QE is still smaller than what has been found for $\text{Ni}^{2+}:\text{MgO}$ single crystals ($\eta \sim 80\%$) [13], the latter are not suitable for optical fiber production and, hence, would target different applications.

The stimulated emission cross section σ_{em} can be estimated with the Füchtbauer–Ladenburg equation by assuming a Gaussian-shaped emission band of FWHM $\Delta\nu_{1/2}$:

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

where λ_0 is the wavelength at band center, n is the refractive index of the host material, τ is the emission lifetime, and η is the quantum efficiency. For a band center at 1430 nm, a value of $8.5 \times 10^{-20}\text{ cm}^2$ (300 K, $\eta = 65\%$, $\tau = 39\text{ }\mu\text{s}$, $n = 1.8 \pm 0.02$, and $\Delta\nu_{1/2} = 1545\text{ cm}^{-1}$) is obtained. The product of σ_{em} and τ is considered as a figure of merit when characterizing the potential of prospective laser materials. This is because it is proportional to the amplification gain and inverse laser oscillation threshold. So, the higher the value of $\sigma_{\text{em}} * \tau$, the more interesting would be potential application as laser gain medium [14]. In the present case, a value of $3.3 \times 10^{-24}\text{ cm}^2\text{ s}$ is obtained (300 K). This compares to typical data of glasses and glass ceramics that have been considered for similar applications, such as $\text{Ni}^{2+}:\text{LiGa}_5\text{O}_8$ glass ceramic ($3.7 \times 10^{-24}\text{ cm}^2\text{ s}$) [4], Pr^{3+} -doped chalcogenide glasses ($4.8 \times 10^{-24}\text{ cm}^2\text{ s}$) [15], and $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$ crystals ($1.4 \times 10^{-24}\text{ cm}^2\text{ s}$) [16], and Tm^{3+} -doped heavy metal oxide glasses ($\sim 9 \times 10^{-25}\text{ cm}^2\text{ s}$) [17]. The high value of $\sigma_{\text{em}} * \tau$ promises large amplification gain and low oscillation threshold, and hence suggests further studies with the objective of application of Ni^{2+} -doped TBSA glass ceramics as a broadband gain medium for tunable lasers and amplifiers.

In summary, we reported on highly efficient NIR PL from Ni^{2+} -doped nanocrystalline Ba-Al titanate glass

ceramics. The excited state lifetime of $^1\text{Ni}^{2+} [^3\text{T}_{2g}(^3\text{F})]$ was found at 60 μs at 10 K and 39 μs at 300 K, from which an internal QE of $\sim 65\%$ at room temperature was calculated. The stimulated emission cross section (σ_{em}) and figure of merit for an optical gain medium ($\sigma_{\text{em}} * \tau$) were found at $8.5 \times 10^{-20}\text{ cm}^2$ and $3.3 \times 10^{-24}\text{ cm}^2\text{ s}$, respectively.

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