Broadband Infrared Luminescence of Ni^{2+} in Petalite-Type Transparent Glass Ceramics *

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Transparent Ni^{2+}-doped magnesium aluminosilicate glass ceramics are prepared. The formation of petalite-type crystallites in the glass ceramics is confirmed by x-ray diffraction. Broadband infrared luminescence centred at around 1235 nm with full width at half maximum (FWHM) of about 300 nm is observed from the Ni^{2+}-doped glass ceramics. The observed infrared emission could be attributed to the $^3T_2(F) \rightarrow {}^3A_2(F)$ transition of octahedral Ni^{2+} ions in petalite-type crystallites. The product of the fluorescence lifetime and the stimulated emission cross sections is 1.2×10^{-24} cm^2s.

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Rare-earth (RE) ion (e.g. Er^{3+}, Pr^{3+}, Tm^{3+}) doped fibre amplifiers, which have been widely used in the present optical communication systems, have allowed transmission of large data volumes using a number of channels at different wavelengths through dense wavelength division multiplexing (DWDM). However, the gain bandwidth of these amplifiers is often less than 100 nm because the *f–f* transitions between $4f$ orbits of RE ions are confined in the inner-shell, which are insensitive to local environment. Due to the rapid increase of information traffic, there exists urgent demand for fibre amplifiers to broaden the gain spectrum in the telecommunication window. Unlike RE ions, transition metal (TM) ions (e.g. Cr^{4+} and Ni^{2+}) exhibit broadband emission in the near-infrared region (NIR) over the telecoms windows. TM doped glasses can be easily drawn into fibres, whereas unfortunately TM ions have been found to exhibit weak or no luminescence owing to strong nonradiative relaxation of excited states via lattice vibrations in glasses.

In the past decades, transparent glass ceramics (TGCs) have received great attention as hosts for TM ions because they combine the advantage of crystalline hosts with the relative ease of the manufacturing of glass.[1−3] Chromium ion doped TGCs for potential applications of tunable lasers and luminescent solar concentrators have been extensively studied.[4−7] Although Cr^{3+} and Cr^{4+} doped transparent glass ceramics exhibit broadband emission in the NIR, it is not easy to control the valence state of chromium ions in glasses or glass ceramics, and no optical gain has been achieved to date. In contrast, nickel ions usually exist as a divalent state in glasses and glass ceramics, and the emission from Ni^{2+} doped transparent glass ceramics locates closer to 1.3 μm, which shows the minimum wavelength dispersion of the silica fibre. Recently, great interest has been focused on the possibility of nickel ions incorporated as active ions in TGCs for tunable lasers and broadband optical fibre amplifiers.[8−11]

We have obtained a novel Ni^{2+}-doped magnesium aluminosilicate TGC with broadband emission in NIR. In this Letter, we present characteristics of the Ni^{2+}-doped magnesium aluminosilicate glass ceramics.

Glass samples with composition of 49.1SiO_2-19.7Al_2O_3-21.9MgO-6.1TiO_2-3.2ZrO_2 (in mol%) and doped with various concentrations of NiO were prepared by the conventional melting method. Analytical reagents of MgO, SiO_2, Al_2O_3, TiO_2, ZrO_2 and NiO were selected as raw materials. TiO_2 and ZrO_2 were added as nucleating agents. About 30 g batch materials were mixed completely and melted in a corundum crucible at 1580°C for 2 h in air. The melt was cast onto a heated stainless steel plate and then cooled down to room temperature. The glass samples were cut to the thickness of 3 mm and were polished to optical quality before subjecting to optical measurements. We carried out two-stage heat treatments in isothermal conditions in the temperature interval from 790 to 875°C. As a result, the transparent Ni^{2+}-doped magnesium aluminosilicate glass ceramics were synthesized. We have investigated the Ni^{2+} doping concentration dependence of the luminescence properties. The broadband emission intensity increases with the increasing Ni^{2+} doping concentration from 0 to 0.1 wt.% at first, and then decreases with the further increase of the Ni^{2+} doping concentration. Therefore, 0.1 wt.% of the Ni^{2+} doping concentration is optimal in this glass ceramics system. In this study, we only present the results of 0.1 wt.% NiO doped glass ceramic.

Thermal properties were measured by differential thermal analysis (DTA) at a heating rate of 10°C min^{-1} under N_2 atmosphere. X-ray diffraction

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measurements were carried out by using Cu $K\alpha_1$ as a radiation source to identify crystalline phases. Absorption spectra were recorded by using a double-beam spectrophotometer (JASCO FP-6500). The infrared luminescent spectrum was obtained on ZOLIX SBP300 spectrophotometer with InGaAs as the detector in the wavelength range 1000–1800 nm with excitation of a 980-nm laser diode (LD). The fluorescent lifetime was measured by exciting the sample with a modulated 980 nm LD. The signals detected by an InGaAs photodetector in TRIAX550 spectrofluorometer were recorded using a storage digital oscilloscope (Tektronix TDS3052). All the measurements were performed at room temperature.

Figure 1 shows the DTA curve of the as-made glass sample with indications of the glass transition temperature T_g and crystallization temperature T_x. Here T_g and T_x of the glass are 780°C and 897°C, respectively; ΔT $(T_x - T_g)$ is usually used as an index of the thermal stability against crystallization of glass; ΔT of the present glass is 117°C, which is larger than $\Delta T = 58$°C of ZnO-Al_2O_3-SiO_2 (ZAS) glass reported by Suzuki *et al.*[10] It is indicated that our glass is more thermostable than ZAS glass. We choose the heat treatment temperature between T_g and T_x to maintain transparency of glass ceramics.

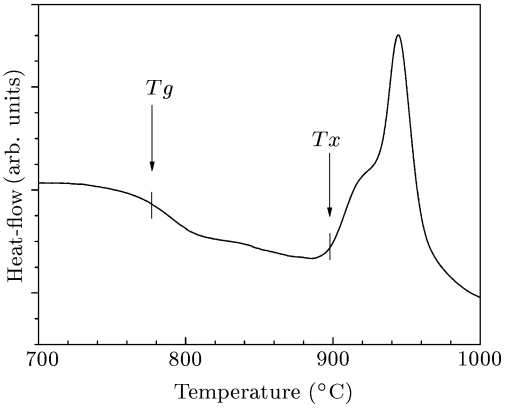

Fig. 1. Differential thermal analysis curve of the as-made glass.

XRD patterns of the samples before and after heat-treatment at 790°C+10 h→ 875°C+2 h are shown in Fig. 2. No apparent diffraction peaks are observed for the as-made glass besides a large halo, which is characteristic of diffraction of the amorphous glass matrix. After heat treatment, diffraction peaks are clearly observed. The diffraction peaks can be attributed to the crystal phase of petalite-type (ICCD Card File No. 14-0346).[12] The petalite-type phase represents a series of solid solutions on the basis of the $MgO{\cdot}SiO_2$ obtained as a result of the substitution $2Si^{4+} \rightarrow 2Al^{3+} + Mg^{2+}$ into a layered structure or the introduction of $(AlO_4)Mg_{0.5}$ between the layers.[5] The average crystallites size could be evaluated from the XRD data by using the Scherrer formula. The average crystalline size is calculated to be about 29 nm. Due to much smaller size of precipitated crystallites than the visible-near infrared wavelength, the glass ceramics still remain transparency after heat-treatment.

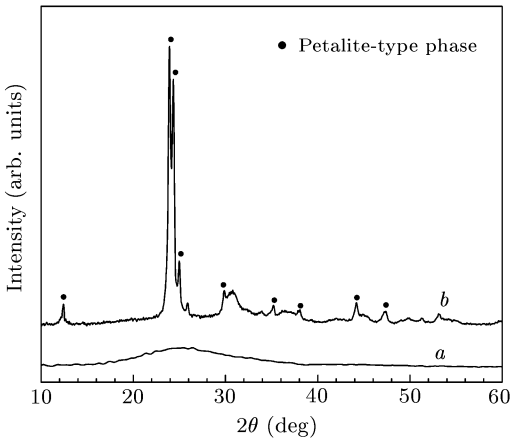

Fig. 2. X-ray diffraction patterns of (a) as-made glass and (b) transparent glass-ceramic heat-treated at 790°C+10 h → 875°C+2 h.

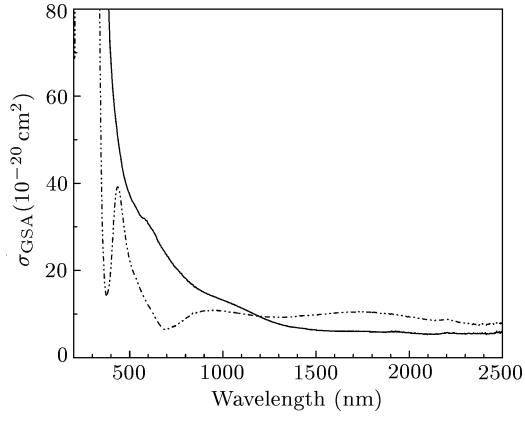

Fig. 3. Absorption spectra of as-made glass (dashed line) and transparent glass-ceramic (solid line).

The absorption spectra of the as-made glass and the transparent glass ceramic are shown in Fig. 3. The spectrum of the as-made glass consists of three main absorption bands with the maxima at about 1720 nm, 932 nm and 436 nm. These absorption bands could be attributed to the transitions of $^3E'(F) \rightarrow {}^3E''(F)$, $^3E'(F) \rightarrow {}^3A'_2(F)$ and $^3E'(F) \rightarrow {}^3A'_2(P)$ of the trigonal bipyramid fivefold Ni^{2+}, respectively.[13] Heat treatment leads to the precipitation of petalite-type crystallites in glassy phase, and the colour of glass changed from brown to light green. The petalite-type phase structure may be distorted from the structure of the nature petalite ($LiAlSi_4O_{10}$), Mg^{2+} ions replace Li^+ ions and occupy octahedral coordination.[14] Since Ni^{2+} has a valence state as the same as Mg^{2+} and their ion radii are close to each other, it would be presumed that partial Mg^{2+} ions are replaced by

Ni^{2+} ions in petalite-type phase. After heat treatment, the shape of the absorption spectrum is completely changed as compared with that of the as-made glass. Absorption bands centred at about 965 nm and 585 nm could be attributed to the $^3A_2(F) \rightarrow {}^3T_2(F)$ and $^3A_2(F) \rightarrow {}^3T_1(F)$ transitions of Ni^{2+} in octahedral sites, respectively. The highest frequency band corresponds to the $^3A_2(F) \rightarrow {}^3T_1(P)$ transition in octahedral symmetry is concealed in the edge of the UV absorption band. The crystal field parameters, Dq, and Racah parameters, B and C of Ni^{2+} ions in glass ceramics were calculated by using the Tanabe–Sugano diagrams.[15] The values of Dq, B and C are 1036 cm^{-1}, 1008 cm^{-1}, and 4748 cm^{-1}, respectively. The observed absorption peak positions and fitted peak positions are listed in Table 1.

Table 1. Comparison of the experimentally observed and fitted energy levels for Ni^{2+} in the transparent glass-ceramic.

Transitions	Absorption bands (cm^{-1})	Fit (cm^{-1})	Crystal field parameters (cm^{-1})
$^3A_2(F) \rightarrow {}^3T_2(F)$	10363	10363	$Dq = 1036$
$^3A_2(F) \rightarrow {}^1E(D)$		16924	$B = 1008$
$^3A_2(F) \rightarrow {}^3T_1(F)$	17094	17080	$C = 4748$
$^3A_2(F) \rightarrow {}^3T_1(P)$		29095	

Infrared emission spectra of Ni^{2+}-doped as-made glass and glass-ceramic in the case of 980 nm excitation are shown in Fig. 4. The as-made glass does not show any emission in the NIR region. However, after heat treatment, the broadband infrared luminescence attributed to the $^3T_2(F) \rightarrow {}^3A_2(F)$ transition of octahedral Ni^{2+} ions is observed. The FWHM of the spectrum is about 300 nm. It can be concluded that at least a part of Ni^{2+} ions which stay in the glass matrix move into octahedral sites of petalite-type crystallites in the glass ceramics and the infrared emission should be come from Ni^{2+} ions located in the petalite-type crystallites. The measured fluorescence lifetime of Ni^{2+}-doped transparent glass ceramics at room temperature is about 250 μs. By assuming a Gaussian-shaped emission band, the stimulated emission cross section is estimated by

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

where λ_0 is the band central wavelength, η is the quantum efficiency, n is the host refractive index, τ is the emission lifetime, c is the velocity of light, and $\Delta\nu_{1/2}$ is the FWHM of the emission. If quantum efficiency is assigned to 0.30 according to Ref. [16], so we obtain $\sigma = 4.7 \times 10^{-21}\,cm^2$, with $\lambda_0 = 1235$ nm, $n = 1.61$, $\tau = 250\,\mu$s, and $\Delta\nu_{1/2} = 1882\,cm^{-1}$. The product of the lifetime and the stimulated emission cross section, $\sigma\tau$, is an important parameter to characterize optical amplification and laser media, because $\sigma\tau$ is proportional to the amplification gain and inversely proportional to the laser oscillation threshold. The product $\sigma\tau$ of the present Ni^{2+}-doped transparent glass ceramics is $1.2 \times 10^{-24}\,cm^2s$, which is comparable to that of Ti^{3+}:Al_2O_3 ($\sigma\tau = 1.4 \times 10^{-24}\,cm^2s$).[17]

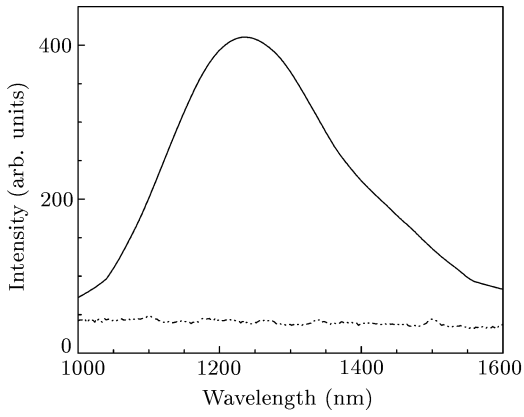

Fig. 4. Emission spectra of Ni^{2+}-doped as-made glass (dashed line) and transparent glass-ceramic (solid line) at room temperature.

In conclusion, we have synthesized transparent magnesium aluminosilicate glass ceramics embedding Ni^{2+}-doped petalite-type crystallites. X-ray diffraction analysis reveals that the precipitated crystallites sizes are about 29 nm. The near infrared broadband emission centred at about 1235 nm with the FWHM of about 300 nm is observed by exciting the glass ceramics with a 980 nm laser diode. The observed emission is assigned to the $^3T_2(F) \rightarrow {}^3A_2(F)$ transition of octahedral Ni^{2+} ions in petalite-type crystallites. The product of the fluorescence lifetime and the stimulated emission cross sections is $1.2 \times 10^{-24}\,cm^2s$. It is expected that Ni^{2+}-doped magnesium aluminosilicate glass ceramics are potential materials for broadband optical fibre amplifier and tunable laser.

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