Structural and optical properties of ZnO–Al2O3–SiO2 system glass–ceramics containing Ni2+-doped nanocrystals

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Received 22 December 2004; received in revised form 18 April 2005

Abstract

Transparent glass–ceramics were prepared from Ni2+-doped ZnO–Al2O3–SiO2 (ZAS) system glasses by annealing. The color of the glasses drastically changed from brownish yellow to green by annealing. The crystalline phase being precipitated by annealing was identified as solid solutions of spinel compounds. The crystalline sizes estimated by transmission electron microscope observation in Ni2+-doped post-annealed glasses were about 10–15 nm in diameter, while that in non-doped post-annealed glasses were 5–10 nm. This suggests that Ni2+ ions in ZAS glass were incorporated into the crystalline phases as nucleation agents of crystallization. It was confirmed from optical absorption measurements that Ni2+ ions occupied fivefold sites in the as-cast glass, while Ni2+ ions occupied octahedral sites in the post-annealed glass. The Ni2+-doped post-annealed glasses exhibited near-infrared emission. It is thought that the crystals containing Ni2+ ions act as emission centers.

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PACS: 78.55.Qr; 81.05.Pj

1. Introduction

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

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

If transition metals were active in glasses, ultra-broadband optical amplifiers could be realized. Cr4+ doped in glasses have been extensively investigated so far [5–7]. As chromium ions can easily take multi-valent states, such as Cr3+, Cr4+ and Cr6+, strict valence control is required to obtain Cr4+. 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 relaxation of the excited states of transition metals via lattice relaxations is considerably large in glasses. Non-radiative 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 fabricate 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 metal ions, since they have the advantages of both crystalline and glass materials. Glass–ceramics possess mechanical properties like glasses which can be fabricated into fibers with low attenuation. If the sizes of crystals in glass–ceramics are far less than the wavelength of interest, light scattering caused by the crystals would be negligibly low. 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 crystalline materials. 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.

We have obtained an efficient broadband near-infrared emission from a Ni$^{2+}$-doped zinc-alumino-silicate (ZAS) glasses [8]. However, the structural and optical properties of the glasses have not yet been clarified. Understanding of these properties is a clue to improve the emission efficiency of the glass. We have performed transmission electron microscopy and X-ray diffraction and thermal analysis as well as optical measurements of ZAS glasses in order to investigate the structural and optical properties of ZAS glasses in detail.

2. Experimental

58SiO$_2$–21ZnO–10Al$_2$O$_3$–5TiO$_2$–3Ga$_2$O$_3$–3K$_2$O glass was used as a host of Ni$^{2+}$. Sample glasses were prepared by a conventional casting method. The Ni content doped in the glass was 0.1 wt%. Thirty grams batches of reagent grade SiO$_2$, Al$_2$O$_3$, ZnO, TiO$_2$, Ga$_2$O$_3$, K$_2$CO$_3$ were mixed thoroughly and melted in a Pt-Rh crucible in O$_2$ atmosphere at 1600 °C for 2 h in an electric furnace. The melts were poured onto steel plate preheated to 650 °C and slowly cooled down to room temperature.

ZnAl$_2$O$_4$ polycrystalline powder was prepared by conventional solid state reaction to compare with the crystalline phase in glass–ceramics.

The glass samples were polished to optical quality before subjecting them to the optical measurements. The sample thickness was about 4 mm. The glass samples were post-annealed to make it glass–ceramics. The annealing temperature was determined from differential scanning calorimeter (DSC) analysis data. Fig. 1 shows a curve of DSC around the glass transition temperature ($T_g$) and crystallization temperature ($T_x$). $T_g$ and $T_x$ of the glass was 643 and 701 °C, respectively. The sizes of the crystallites should be as small as possible to maintain transparency of glass–ceramics and the number of the crystallites should be as large as possible to obtain efficient emission. We chose the annealing temperature as 680 °C. The crystallite sizes were confirmed by X-ray diffraction (XRD) and transmission electron microscope (TEM) observation and selected area diffraction (SAD) measurements. The crystalline phase was also identified by XRD measurements with CuK$\alpha$ radiation. Absorption spectra were recorded by using a double-beam spectrophotometer. The glass samples were excited with a 976 nm laser diode 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 detected by the photomultiplier as a detector and accumulated using an oscilloscope.

3. Results and discussion

3.1. X-ray diffraction measurements and transmission electron microscope observations

Fig. 2 shows XRD patterns of ZnAl$_2$O$_4$ polycrystalline powder, Ni$^{2+}$-doped ZAS glass post-annealed for
There are not halo patterns characteristic of amorphous phase. All diffraction peaks of the powder were attributed to that of ZnAl\textsubscript{2}O\textsubscript{4} spinel (gahnite) [9].

There is a broad halo pattern around 30° in glass samples. This shows that these samples contain glassy phase even after 10 h annealing. Diffraction peaks were seen in XRD pattern of Ni\textsuperscript{2+}-doped glasses post-annealed for more than 15 min. This indicates that the post-annealed Ni\textsuperscript{2+}-doped glass contains crystalline phase. The diffraction pattern of the Ni\textsuperscript{2+}-doped post-annealed glass was similar to that of the ZnAl\textsubscript{2}O\textsubscript{4} spinel powder. However, the lattice constant of the crystalline phase in the post-annealed Ni\textsuperscript{2+}-doped glass was about 2% larger than that of ZnAl\textsubscript{2}O\textsubscript{4} spinel. This indicates that some glass component cations such as Ga\textsuperscript{3+} and Ti\textsuperscript{4+} ions which have larger ion radii than that of Al\textsuperscript{3+} and Zn\textsuperscript{2+} should be incorporated into the spinel phase. The lattice constant of the crystalline phase in the glass did not agree with either ZnAl\textsubscript{2}O\textsubscript{4}, NiAl\textsubscript{2}O\textsubscript{4}, ZnGa\textsubscript{2}O\textsubscript{4}, NiGa\textsubscript{2}O\textsubscript{4}, Zn\textsubscript{2}TiO\textsubscript{4} or Ni\textsubscript{2}TiO\textsubscript{4}. It is naturally thought that the crystalline phases in the glass would be solid solutions of spinel type compounds consisting of Ni, Zn, Al, Ga, Ti and O.

Only weak diffraction peaks due to crystalline phase were observed in the post-annealed non-doped glass. It is found from these facts that the crystallization occurs more slowly in the non-doped glass compared with in the Ni\textsuperscript{2+}-doped glass.

The average crystallite size of the crystalline phase could be estimated from the highest XRD peak at around 36° using the well-known Scherrer equation. Fig. 3 shows the annealing time variation of the average crystallite size of spinel crystals in the ZAS glasses. The crystallite size steeply increased with annealing time no more than 30 min and then the size was saturated at about 5 nm.

A SAD pattern and TEM image of the Ni\textsuperscript{2+}-doped glass post-annealed for 10 h are shown in Fig. 4. In the SAD pattern of the Ni\textsuperscript{2+}-doped glass, ring patterns were clearly seen. It means the presence of polycrystalline phase. The lattice constant obtained by the SAD pattern of the Ni\textsuperscript{2+}-doped post-annealed glass well agreed with that obtained by XRD patterns. Open circles in the TEM image in Fig. 4 show lattice images due to crystalline phases. Lattice images could be clearly seen in the TEM image of the Ni\textsuperscript{2+}-doped post-annealed glass and the directions of the lattice images were randomly distributed. The crystallite sizes could be estimated as 10–15 nm in diameter from the TEM image. This diameter was higher than that estimated from XRD peaks.

A SAD pattern and TEM image of the non-doped glass post-annealed for 10 h in Fig. 5. In the SAD pattern of the non-doped post-annealed glass, halo patterns could be seen instead of ring patterns in the Ni\textsuperscript{2+}-doped post-annealed glass. In the TEM image of the non-doped post-annealed glass, small lattice images due to crystalline phases could be seen. The crystallite sizes could be estimated as 5–10 nm in diameter from the TEM image.

The crystallite in the Ni\textsuperscript{2+}-doped post-annealed glass was larger than that in the non-doped post-annealed glass. It is thought from this result of XRD and TEM observations that Ni\textsuperscript{2+} ions in the post-annealed glass should be incorporated into crystalline phases as nucleation agents of crystallization.

### 3.2. Optical absorption measurements

The color of Ni-doped glasses was drastically changed from brownish yellow to green without losing transparency during annealing.
Optical absorption spectra of Ni\textsuperscript{2+}-doped glass the as-cast and post-annealed glasses were shown in Fig. 6. The absorptions in the visible and near-infrared regions spectra consist of five absorption bands around 440, 650, 860, 1100 and 1760 nm. We categorize the absorption bands around 440, 860 and 1760 nm as T bands and the absorption bands around 650 and 1100 nm as O bands hereafter. In the absorption spectrum of the as-cast glass, only the T bands were observed. The T bands decreased with annealing time and vanished after 20 min annealing. This result suggests that absorption bands categorized as the T bands should derive from the same origin. In contrast, the O bands were not seen in the absorption spectra of the as-cast glass and glass annealed for 5 min. The O bands appeared after annealing for 10 min and increased in intensity with annealing time. These results suggest that the T bands changed to the O bands during annealing.

Co-ordination numbers of Ni\textsuperscript{2+} in oxide glasses have been extensively investigated but are still controversial so far. The absorption bands of the as-cast glass were similar to trigonal bipyramid fivefolded Ni\textsuperscript{2+} ions in silicate glasses [10]. The T bands at about 440, 860 and 1760 nm could be tentatively assigned to the transitions of $^3E_g^o(3F) \rightarrow ^3A_{2g}^o(3P)$, $^3E_g^o(3F) \rightarrow ^3A_{2g}^o(3F)$ and $^3E_g^o(3F) \rightarrow ^3E_g^o(3F)$ of trigonal bipyramid fivefolded
Ni\textsuperscript{2+} ions. It is thought that most of the Ni\textsuperscript{2+} in the as-cast glass occupy trigonal bipyramid fivefold sites. The absorption spectrum of the glass post-annealed for 10 h was similar to Ni\textsuperscript{2+} in octahedral sixfold sites [11]. The O bands around 650 and 1100 nm could be assigned to the spin-allowed broadband $^3A_{2g}(3F) \rightarrow ^3T_{2g}(3F)$ and $^3A_{2g}(3F) \rightarrow ^3T_{1g}(3F)$ transitions of Ni\textsuperscript{2+} ions occupying octahedral sites. It is thought from these absorption measurement results that Ni\textsuperscript{2+} ions in ZAS glass would have been changed their sites from trigonal bipyramid fivefolded in the as-cast glass to octahedral sixfolded in the post-annealed glass during annealing. Ni\textsuperscript{2+} site change in borosilicate glasses during annealing has been reported recently. Crystallization with Ni\textsuperscript{2+} co-ordination change was not observed in the borosilicate glasses [12].

The crystal field parameters $D_q$, $B$ and $C$ for Ni\textsuperscript{2+} in the post-annealed glass were calculated by using the Tanabe-Sugano diagrams [13]. The values for octahedral Ni\textsuperscript{2+} in the post-annealed glass could be fitted to $D_{qO} = 907 \text{ cm}^{-1}$, $B = 940 \text{ cm}^{-1}$ and $C_{O} = 3919 \text{ cm}^{-1}$. The observed absorption peak positions and fitted peak positions were given in Table 1. Fig. 7 shows the resultant energy diagram of octahedral Ni\textsuperscript{2+} in the post-annealed glass.

### Table 1

Comparison of the experimentally observed and fitted energy levels for Ni\textsuperscript{2+} in post-annealed ZAS glass

<table>
<thead>
<tr>
<th>Ni\textsuperscript{2+}-doped ZAS glass</th>
<th>Experimental (cm$^{-1}$)</th>
<th>Fitted (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_q$</td>
<td>907</td>
<td>-</td>
</tr>
<tr>
<td>$B$</td>
<td>940</td>
<td>-</td>
</tr>
<tr>
<td>$C$</td>
<td>3919</td>
<td>-</td>
</tr>
<tr>
<td>$^3A_{2g}(3F)$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^3T_{2g}(3F)$</td>
<td>9066</td>
<td>9066</td>
</tr>
<tr>
<td>$^1T_{2g}(1D)$</td>
<td>14124</td>
<td>14124</td>
</tr>
<tr>
<td>$^3T_{1g}(3F)$</td>
<td>14514</td>
<td>14803</td>
</tr>
<tr>
<td>$^1T_{2g}(1D)$</td>
<td>-</td>
<td>22834</td>
</tr>
<tr>
<td>$^3T_{1g}(3P)$</td>
<td>-</td>
<td>24999</td>
</tr>
</tbody>
</table>

3.3. Near-infrared emission measurements

Fig. 8 shows near-infrared emission spectra of Ni\textsuperscript{2+} ZAS glass annealed for no more than 10 h. The emission spectra were recorded at room temperature. The emission in this wavelength region could be assigned to the downward $^3T_{2g}(3F) \rightarrow ^3A_{2g}(3F)$ transition of octahedral Ni\textsuperscript{2+} ions. Emission induced by 976 nm excitation was not detected in the wavelength region from glasses annealed for less than 10 min. The emission intensity of the glasses annealed for more than 15 min increases with annealing time. The emission peak was located at about 1440 nm of glass annealed for 15 min and moved to the shorter wavelength and located at about 1350 nm for glass annealed for 10 h. This trends suggest that there are some different types of octahedral Ni\textsuperscript{2+} sites under the different crystal field strengths. In addition, octahedral Ni\textsuperscript{2+} ions in low crystal field were formed at the early stage of annealing and then octahedral Ni\textsuperscript{2+} in high crystal field were formed with proceeding of annealing, namely the crystal field of octahedral Ni\textsuperscript{2+} intensified during annealing.

Fig. 9 shows the variation of the emission peak intensity. The peak intensity steeply increased with annealing time at the first stage (0–60 min) and then gradually increased at the second stage (60–600 min). The first stage agreed with the period, in which co-ordination number
of Ni\textsuperscript{2+} changed from five to six and spinel crystallite nucleation was occurred. The second stage agreed with the period, in which crystallite sizes estimated from XRD measurements was almost constant and optical absorption spectra was unchanging. The emission intensity strongly depends on Ni\textsuperscript{2+} co-ordination number and crystallite sizes. This indicates that Ni\textsuperscript{2+} incorporated into spinel crystalline phase acted as emission centers.

4. Summary

We confirmed that transparent glass–ceramics could be prepared from Ni\textsuperscript{2+}-doped ZAS system glasses by annealing. The color of the glasses drastically changed from brownish yellow to green by annealing. The crystalline phase being precipitated by annealing could be identified as a solid solution of spinel compounds consisting of Ni, Zn, Al, Ga, Ti and O.

The crystalline sizes observed by TEM in Ni\textsuperscript{2+}-doped post-annealed glasses were about 10–15 nm in diameter, while that in non-doped post-annealed glasses were 5–10 nm. This suggests that Ni\textsuperscript{2+} ions in ZAS glass were incorporated into the crystalline phases as nucleation agents for crystallization.

It was confirmed from optical absorption measurements that Ni\textsuperscript{2+} ions occupied fivefold sites in the as-cast glass, while Ni\textsuperscript{2+} ions occupied octahedral sites in the post-annealed glass. The Ni\textsuperscript{2+}-doped post-annealed glasses exhibited near-infrared emission. The emission was only observed from the glass containing crystalline phase. It is thought that the crystals containing Ni\textsuperscript{2+} ions act as emission centers.

Acknowledgments

The authors thank Dr Yoshiki Seno of Toyota Central R&D Laboratories for TEM observations and great helpful discussions. 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 a part of studies of the Private University High-Tech Center Program.

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