Selective doping of Ni$^{2+}$ in highly transparent glass-ceramics containing nano-spinels ZnGa$_2$O$_4$ and Zn$_{1+x}$Ga$_{2-2x}$Ge$_x$O$_4$ for broadband near-infrared fiber amplifiers

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Selective doping of Ni$^{2+}$ in octahedral sites provided by nanocrystals embedded in glass-ceramics (GCs) is crucial to the enhancement of broadband near-infrared (NIR) emission. In this work, a NIR emission with a full-width-at-half-maximum (FWHM) of 288 nm is first reported from ZnGa$_2$O$_4$: Ni$^{2+}$ nano-spinels embedded GCs with excellent transparency. A comparison is made of the NIR luminescence properties of Ni$^{2+}$ doped GCs containing ZnGa$_2$O$_4$, germanium-substituted ZnGa$_2$O$_4$ nano-spinels (Zn$_{1-x}$Ga$_{2-2x}$Ge$_x$O$_4$), and Zn$_2$GeO$_4$/Li$_2$GeO$_3$ composite nanocrystals that are free of Ga$^{3+}$. The results show that ZnGa$_2$O$_4$: Ni$^{2+}$ GCs exhibit a significantly enhanced NIR emission. The incorporation of the nucleating agent TiO$_2$ is favored in terms of the increased luminescence intensity and prolonged lifetime. The possible causes for the enhancement effect are identified from the crystal structure/defects viewpoint. The newly developed GCs incorporate good reproducibility to allow for a tolerance of thermal treatment temperature and hence hold great potential of fiberization via the recently proposed “melt-in-tube” method. They can be considered as promising candidates for broadband fiber amplifiers.

Broadband tunable near-infrared (NIR) light sources are extremely useful for a wide range of applications in optical communications, photochemistry, spectroscopy and pump-probe experiments etc. The ability of transition metal (TM) ions (e.g., Ti$^{3+}$, V$^{3+}$, Cr$^{3+}$, Cr$^{4+}$, Ni$^{2+}$ etc.) doped bulk crystals and glass-ceramics (GCs) to lase in the broadly tunable NIR (1000~1700 nm) wavelength region have attracted intense attention over the last two decades. Because nickel is very stable in its divalent oxidation state (Ni$^{2+}$), Ni$^{2+}$ doped phosphors can be readily synthesized in ordinary lab conditions without strict valence control. However, Ni$^{2+}$ cannot lase in glasses because Ni$^{2+}$ is generally five-fold (trigonal bipyramidally, 5Ni$^{2+}$) and/or four-fold (tetrahedrally, 4Ni$^{2+}$) coordinated in glassy networks, whereas only six-fold octahedrally coordinated 6Ni$^{2+}$ exhibits luminescence in the NIR wavelength range. Even when Ni$^{2+}$ adopts an octahedral coordination in fluoride glasses, the strong electron-phonon coupling of 6Ni$^{2+}$ in amorphous materials severely limits the radiative quantum efficiency. These problems can be resolved provided GCs containing nanocrystals that provide octahedral sites for Ni$^{2+}$ can be produced, which is very possible through ingenious composition design and well controlled crystallization.

Selective doping of 6Ni$^{2+}$ in ZnAl$_2$O$_4$, LiGa$_5$O$_8$, Ga$_2$O$_3$, and most recently ZnF$_2$ and KZnF$_3$ embedded...
transparent GCs and even glass-ceramic (GC) optical fibers have been produced. Promising results such as the ligand-field driven wavelength tunable and broadband NIR emission of Ni2+ have also been observed.

The pursuit of Ni2+ doped GCs is being driven continuously by newly invented crystals with excellent luminescence properties, for example, the germanium-substituted ZnGa2O4 spinel of the general formula Zn1−xGa2−xGe2O4 (0 ≤ x ≤ 1) and this has attracted significant attention due to the unprecedented persistent luminescence observed in Zn1−xGa2−xGe2O4:Cr3+. Such nanocrystals can simultaneously provide tetrahedral (occupied by 4Zn2+ and 4Ge4+) and octahedral (occupied by 0Ga3+) sites for Mn2+, Co2+, Ni2+, Cr3+ and Mn4+ etc., and thus can be used as a multi-functional platform for diverse applications in lighting, display, telecommunication and bio-imaging etc. Additionally, transparent GCs containing Zn1−xGa2−xGe2O4 nanocrystals have been recently fabricated. Selective doping of Ni2+ in Zn1−xGa2−xGe2O4 nanocrystals embedded in GCs has been reported; however, the NIR luminescence properties were not clearly identified in this case. To date the authors of this article are not aware of any study relating to the luminescence properties of ZnGa2O4: Ni2+ GCs, although GCs containing ZnGa2O4: Cr3+ nanocrystals, showing persistent luminescence and temperature sensing properties, have recently been extensively studied.

In the work reported in this article a detailed study has been undertaken and comparison made of the NIR luminescence properties of Ni2+ doped GCs containing ZnGa2O4 and germanium-substituted ZnGa2O4 (Zn1−xGa2−xGe2O4) nano-spinels. To underline the important role of “Ga5+”, other Ni2+ doped GCs containing Zn1−xGa2−xGe2O4 composite nanocrystals that are free of Ga3+ were also prepared for comparison. The synthesized ZnGa2O4: Ni2+ GCs are highly reproducible which allows for a tolerance of thermal treatment temperature, and thus are perfectly matched for the recently proposed “melt-in-tube” method. For functional GC fibers cannot be obtained using the conventional “rod-in-tube” method, the ‘melt-in-tube’ method has recently facilitated fabrication of GC fibers doped with Ni2+ and Bi3+, Cr3+, or quantum dots which have exhibited excellent optical quality. The study described in this article is expected not only provide a candidate fiber amplifier material, but also advance understanding of the correlation between the structure of the nanocrystals and NIR luminescence of Ni2+, and thus will provide useful guidance for designing novel Ni2+ doped GCs with enhanced luminescence properties such as ultra-broadband tunable NIR emission. Moreover, the present work may also advance the understanding of the mechanism underlying the persistence luminescence of Cr3+ doped spinels which is currently still open to question.

**Experiments**

Three different types of the nominal composition (in mol %) of Ni2+-doped glasses and GCs were prepared using high purity (4N) raw materials of SiO2, GeO2, Ga2O3, ZnO, Na2CO3, K2CO3, Li2O, ZrO2, TiO2 and NiO.

1. 51SiO2-18Ga2O3-18ZnO-6Na2O-4ZrO2-3TiO2-xNiO (x = 0, 0.15, 0.3, 0.5) was chosen to generate the ZnGa2O4 nanocrystal, hereafter this group of glasses and glass-ceramics are denoted as ZGO-xPG and ZGO-xGC respectively. Glasses were melted in a platinum crucible at 1600°C for 2h, quenched onto a cold brass plate and then annealed at 300°C for 3h. GCs were fabricated by heating the annealed glasses at 680°C for 12h followed by a further heating at 780–800°C for 12 h, refer to Tanaka et al.25; 2. 62GeO2-20ZnO-10Ga2O3-5K2CO3-3TiO2-xNiO (x = 0, 0.15, 0.3 and 0.5) was chosen to generate Zn1-xGa2-xGe2O4 nanocrystal, hereafter this group of glasses and glass-ceramics are denoted as ZG-xPG and ZG-xGC, respectively. Glasses were preheated at 850°C for 30 min and then melted in an alumina crucible at 1400°C for 30 min. The glasses were then annealed at 500°C for 3h. GC was made via a heat-treatment at 650°C for 2h, as described in ref. 21; 3. 70GeO2-15ZnO-15Li2O-0.15NiO was chosen to generate Zn2GeO4 and Li2Ge4O9 nanocrystal, hereafter, this group of glasses and glass-ceramics are denoted as ZLGO-0.15PG and ZLGO-0.15GC, respectively. The glasses were melted in a platinum crucible at 1300°C for 30 min and annealed at 450°C for 2h. GCs were fabricated by heating the annealed glasses at 545°C for 2h, similar to the process reported in ref. 29.

Transmission spectra were measured using a Perkin-Elmer Lambda 950 UV-VIS spectrophotometer in the spectral range of 200–1800 nm. Refractive indices were measured using an Abbe refractometer AR2008 (KRÜSS, Germany). Photoluminescence (PL) spectra were recorded using a Fluorolog-3-P UV-vis-NIR fluorescence spectrophotometer (JobinYvon, Longjumeau, French). The decay curves were measured using a FL920 Fluorescence spectrometer (Edinburgh Instruments) from room temperature (300K) down to liquid helium temperature (10 K). The samples used for the PL measurement were plane-parallel well polished plates with the identical dimension of ~10 x 10 mm2 and thickness of 1 mm. The fluorescence was collected in the direction perpendicular to the direction of the pump beam, and the pump light was focused (to a spot of diameter ~4 mm) using a lens and incident at a 45° angle to the normal of the front surface of the sample. In the experiment, both the power of the pump light and the configuration of the light path were kept the same. Because only very thin samples were used for the measurement, reabsorption is not significant and any effects due to this can be omitted in the present study, in accordance with the work of Loiko.

X-ray diffraction (XRD) patterns of all the samples were recorded under the same measurement conditions using an X-ray diffractometer (D/MAX 2550VB/PC, Rigaku Corproation, Japan) with Cu-Kα irradiation. The microstructure of the crystallized glasses was studied using a JEM-2100 high-resolution transmission electron microscope (HRTEM). Raman spectra were measured by RenishawInvia Raman microscope (Renishaw, Gloucestershire, UK) with an excitation wavelength of 515 nm.

**Results and Discussion**

From the XRD patterns of the crystallized glasses, the precipitation of ZnGa2O4 (Fig. 1(a)), and Zn1+xGa2−xGe2O4 nano-spinels (Fig. S1(a), supporting information), as well as Zn2GeO4/Li2Ge4O9 composite phases (Fig. S2 in the
supporting information) can be discerned in accordance to the literature. The formation of the target nanocrystals were also confirmed from the Raman spectra where the crystallized glasses show sharp scattering peaks well match those of the standard polycrystals (Fig. 1(b)). According to the work of Zhuang et al., it is very difficult to determine unambiguously the exact $\text{Zn}^{1+}_{x}\text{Ga}^{2-}_{2x}\text{Ge}^{x}$ phase in GCs, owing to the undistinguishable XRD patterns between the two end-members, $\text{ZnGa}_2\text{O}_4$ ($x=0$) and $\text{Zn}_2\text{GeO}_4$ ($x=1$). By comparing the Raman spectra of the crystallized glasses with the standard $\text{Zn}^{1+}_{x}\text{Ga}^{2-}_{2x}\text{Ge}^{x}$ polycrystals synthesized in our lab by solid-state reaction (for more detail, refer to our previous work), we provide the first direct evidence for the formation of $\text{Zn}^{1+}_{x}\text{Ga}^{2-}_{2x}\text{Ge}^{x}$ with $x \geq 0.4$ in GCs (Fig. S1(b), supporting information).

The crystallinity (volume fraction of the crystalline phase) of the GCs can be estimated by the ratio of the area under the indexed diffraction peaks to that under the whole XRD patterns. For $\text{ZnGa}_2\text{O}_4$ and $\text{Zn}^{1+}_{x}\text{Ga}^{2-}_{2x}\text{Ge}^{x}$ GCs, the crystallinities are approximately 37% and 32%, respectively, which are close in value to each other. The total molar concentration of $\text{ZnO}$ and $\text{Ga}_2\text{O}_3$ is only 36 mol. % for the $\text{ZnGa}_2\text{O}_4$ GCs, which is less than the calculated crystallinity. The reason for the discrepancy is not clear and the validity of this result has yet to be confirmed. Here, it should be noted that the presence of nucleating agent such as $\text{TiO}_2$ in gallium-containing GCs favors the substitution of $\text{Ni}^{2+}$ (ionic radius: 0.69 Å) for $\text{Ga}^{3+}$ (ionic radius: 0.62 Å) via the following substitutional mechanism: $\text{Ti}^{4+} + 2\text{Ga}^{3+} \rightarrow 2\text{Ga}^{2+}$, where $\text{Ti}^{4+}$ acts as charge compensator. The incorporation of $\text{Ti}^{4+}$ in the precipitated nanospinels was confirmed by the TEM-EDS analysis on the selected crystallization area in the $\text{ZGO-0.15GC}$ sample (Fig. S3, supporting information). It is possible that a certain degree of inversion may occur in realistic spinels during crystallization, i.e., a fraction of the $\text{Ni}^{2+}$ can occupy non-luminescent tetrahedral sites as found in $\text{NiAl}_2\text{O}_4$ crystals, and hence the selective doping of $\text{Ni}^{2+}$ in octahedral sites is highly desirable for enhanced NIR luminescence.

The morphology, distribution and particle sizes of nanocrystals were determined from the HRTEM measurements. The precipitated nanoparticles, approximately 15 nm in diameter, are distributed uniformly in all the GCs (Fig. 1(c) and (d)). The ultra-fine particle size allows these materials to be polished as they are in the glass state and then crystallized without any significant degradation of the surface quality (shown photographically in Fig. 2(a) and Figs S4 and S5, supporting information). The crystallization process was highly reproducible as
verified by the fact that GCs show similar performance can be obtained repeatedly under the same experimental condition.

The coordination states of Ni$^{2+}$ can be approximately inferred from the color of the glasses and GCs, for example, blue, brown and yellow-green in the case of 4Ni$^{2+}$, 5Ni$^{2+}$, and 6Ni$^{2+}$ coordination, respectively. The as-made ZGO (Fig. 2(a)) and ZGGO glasses (Fig. S4, supporting information) are light brown in appearance, suggesting 5Ni$^{2+}$ and 4Ni$^{2+}$ coordination states, whereas the color of the crystallized glasses becomes light green and blue, indicative of 6Ni$^{2+}$. Since 6Ni$^{2+}$ possesses a larger crystal field stabilization energy (CFSE) value than that of 5Ni$^{2+}$, the unstable 5Ni$^{2+}$ in glasses tends to transform into 6Ni$^{2+}$ during crystallization of the spinel phases. The absorption related to 6Ni$^{2+}$ (e.g., around 1160 nm due to the $^3A_2(3F) \rightarrow ^3T_2(3F)$ transition) in GCs increases with the concentration of NiO, indicative of an efficient partition of Ni$^{2+}$ in ZnGa$_2$O$_4$ nanocrystals, e.g. more than 90% of Ni$^{2+}$ can be successfully embedded in gallium-containing GCs, whereas it is well known that substitutional doping a large fraction of TM ions into semiconductor nanocrystals is extremely difficult because of the intrinsic self-purification mechanism. The absorption bands can be well fitted to the Tanabe-Sugano (TS) diagram for $d^8$ ions (Fig. 2(d)), with the values of Racah parameter ($B$) and crystal field strength ($D_q$) equal to 767 cm$^{-1}$ and 917 cm$^{-1}$, respectively.

An inspection of the transmission spectra of the Zn$_2$GeO$_4$/Li$_2$Ge$_4$O$_9$ GCs (Fig. S5, supporting information) also indicates the presence of 6Ni$^{2+}$, which is possible via the substitution of 6Ni$^{2+}$ for 6Ge$^{4+}$ in Li$_2$Ge$_4$O$_9$ nanocrystals. Meanwhile, since both the valence and ionic radius of Zn$^{2+}$ (0.60 Å) matches those of Ni$^{2+}$ (ionic radius: 0.55 Å), the substitution of Ni$^{2+}$ for Zn$^{2+}$ in ZnGa$_2$O$_4$ and Zn$_2$GeO$_4$ nanocrystals may also occur, similar to the embedding of Ni$^{2+}$ in Zn$_2$SiO$_4$ crystals. For a detailed analysis and discussion of the absorption spectra, refer to Supporting Information (Fig. S6). The fabricated GCs with transmission larger than 80% demonstrate great potential to be drawn into fibers for use as fiber lasers and amplifiers.

The use of the nucleant TiO$_2$ is very important; it drastically increases both the emission intensity (Fig. S7, supporting information) and lifetime (Fig. S8, supporting information) of the GCs as compared to those free of TiO$_2$; but otherwise the GCs containing TiO$_2$ were thermally treated under identical conditions. The enhancement effect can be understood based on the substitution mechanism by which Ni$^{2+}$ substitutes for Ga$^{3+}$ favorably as mentioned above. An intense broadband NIR emission (from 1100 to 1700 nm) was recorded from ZnGa$_2$O$_4$: Ni$^{2+}$ and Zn$_{1-x}$Ga$_{2-x}$Ge$_x$O$_{4-x}$:Ni$^{2+}$ GCs but was very weak from Zn$_2$GeO$_4$/Li$_2$Ge$_4$O$_9$: Ni$^{2+}$ GCs. Both the emission intensity (Fig. 3(a)) and lifetime (Fig. 3(b)) (defined as the time taken for the emission intensity to decay to 1/e of its initial value) increase with NiO for the Zn$_{1-x}$Ga$_{2-x}$Ge$_x$O$_{4-x}$:Ni$^{2+}$ GCs, in contrast to ZnGa$_2$O$_4$: Ni$^{2+}$ GCs.
where concentration quenching has already set in at the lowest doping level (~0.15 mol.%). However, in the cases with a fixed NiO, the ZnGa\(_x\)Ge\(_{2-x}\)O\(_4\) crystals were assumed to be a solid solution between the normal ZnGa\(_2\)O\(_4\) and inverted Zn\(_2\)GeO\(_4\) spinel structures\(^{36,37}\). Pure Zn\(_{1+x}\)Ga\(_{2-x}\)Ge\(_x\)O\(_4\) spinels can be synthesized for \(x\) ranging from 0 to 0.5\(^{38}\). Our recent study of Mn doped Zn\(_{1+x}\)Ga\(_{2-x}\)Ge\(_x\)O\(_4\) phosphors shows that the substitution of Ga\(^{3+}\) for octahedrally coordinated Ga\(^{4+}\) helps to separate Mn\(^{4+}\) which also substitutes for Ga\(^{4+}\), thus resulting in an enhanced emission of Mn\(^{4+}\)\(^{39}\). It is assumed that a similar separating effect exists for Ni\(^{2+}\) as well, i.e., Ni\(^{2+}\) ions are well separated in the ZGO GCs, and thus the concentration quenching is postponed. As more Ni\(^{2+}\) ions diffuse from the surface to the inside of the nanocrystals and/or are shielded by the nanocrystals from the outside high-phonon energy environment, the non-radiative relaxation rate is reduced, and the lifetime increases accordingly. However, in the case of ZnGa\(_2\)O\(_4\) GCs, Ni\(^{2+}\) substitution for Ga\(^{3+}\) is not well separated because there is no “separating agent” akin to Ni\(^{2+}\) (doped Ga\(_2\)O\(_3\)) GCs where concentration quenching already starts at 0.10 mol.% low content of Ni\(^{2+}\), and this accounts for the observed decreasing lifetime in the ZGO GCs.

Previous studies have shown that the Cr\(^{3+}\)-doped and germanium-substituted compounds (Zn\(_{1-x}\)Ga\(_x\)Ge\(_{2-x}\)O\(_4\), \(x \leq 0.5\)) exhibit much brighter and longer persistence luminescence than pure Cr\(^{3+}\)-doped ZnGa\(_2\)O\(_4\) spinels\(^{37}\). The 2Ga\(^{3+}\) → Ge\(^{4+}\) + Zn\(^{2+}\) substitution induces an inversion increase in the spinel structure, that is, an increased amount of Ga\(^{3+}\) now occupies the tetrahedral \(\text{Zn}^{2+}\) sites, forming the so-called anti-site defects (Ga\(^{4+}\)\text{Zn}\(^{2+}\)). According to ref. 37, the enhancement of Cr\(^{3+}\) emission relies on the formation of anti-site defects, however, the presence of such defects definitely has an adverse effect on the luminescence of Ni\(^{2+}\) because of the reduced proportion of \(6\text{Ga}^{3+}\) sites. On the other hand, it is possible that the substitution of Ge\(^{4+}\) for \(\text{Ga}^{3+}\) may generate octahedrally coordinated Ge\(^{4+}\), which may in turn be substituted by Ni\(^{2+}\). However, considering the fact that only weak Ni emission was observed from the Zn\(_2\)GeO\(_4\)/Li\(_2\)Ge\(_4\)O\(_9\): Ni\(^{2+}\) GCs, and the large mismatch in valence and ionic radii between \(6\text{Ni}^{2+}\) and \(6\text{Ge}^{4+}\) (ionic radius: 0.53 Å), the substitution of \(6\text{Ni}^{2+}\) for \(6\text{Ge}^{4+}\) is severely limited, akin to the partition of Ni\(^{2+}\) in K\(_2\)SiF\(_6\) nanocrystals embedded GCs\(^{37}\). Moreover, no NIR emission related to the tetrahedrally coordinated \(6\text{Ni}^{2+}\), e.g., Ni\(^{2+}\) doped Zn\(_2\)SiO\(_4\), Zn\(_2\)GeO\(_4\) crystals, has been recorded even at cryogenic temperatures\(^{40}\). All these effects account for the observed weaker emission intensity of the ZGO GCs than that of the ZGO GCs.

The ZnGa\(_2\)O\(_4\): Ni\(^{2+}\) GCs, were selected for further study of internal fluorescence quantum efficiency (\(\eta\)) due to the stronger NiR emission and longer lifetime of Ni\(^{2+}\). Figure 4 shows the NiR emission lifetime of Ni\(^{2+}\) as a function of temperature from room temperature (300 K) down to liquid helium temperature (10 K). The sudden drop in lifetime at around 100 K indicates the occurrence of phonon-assisted non-radiative relaxation\(^{39}\). As shown in the inset, the decay curve has a strong non-exponential characteristic, implying multiple site effects of Ni\(^{2+}\) and non-radiative multipolar interactions among Ni\(^{2+}\). The value of \(\eta\) can be calculated as \(\eta = \tau_{300K}/\tau_{0K}\), where \(\tau_{300K}\) (~0.17 ms) and \(\tau_{0K}\) (~0.62 ms, obtained by linear extrapolation to 0 K) are the lifetimes at the room and absolute zero temperatures, respectively. It is about 25% for the ZnGa\(_2\)O\(_4\): Ni\(^{2+}\) GCs, which is less than that of ZnAl\(_2\)O\(_4\): Ni\(^{2+}\) (~55%)\(^{40}\), LiGa\(_2\)O\(_4\): Ni\(^{2+}\) (~60%)\(^{12}\) and BaAl\(_2\)Ti\(_6\)O\(_{16}\): Ni\(^{2+}\) (~65%)\(^{39}\) GCs. However, it is comparable to that of Ga\(_2\)S\(_2\): Cr\(^{4+}\) chalcogenide GCs (~25%)\(^{4}\) and even larger than that of pure Ni\(^{2+}\) doped ZnGa\(_2\)O\(_4\) crystals (~18%)\(^{41}\).
The stimulated emission cross section ($\sigma_e$) was calculated using the McCumber formula $^4$ and was found to be $0.52 \times 10^{-20}$ cm$^2$. The product of $\sigma_e$ and $\tau_{300K}$ (proportional to the amplification gain and inversely proportional to the laser oscillation threshold) taken as a figure of merit (FOM) for the ZGO-0.15GC sample is $1.23 \times 10^{-24}$ cm$^2$·s if the 1/e lifetime is used for the calculation, and is about $3.79 \times 10^{-24}$ cm$^2$·s if the average lifetime $\tau_m = \int I(t)dt / \int I(t)dt$ is used for the calculation, which is comparable to that of ZnAl$_2$O$_4$ Ni$^{2+}$ ($3.1 \times 10^{-24}$ cm$^2$·s) $^{80}$, LiGa$_5$O$_8$: Ni$^{2+}$ ($3.7 \times 10^{-24}$ cm$^2$·s) $^{33}$, and BaAl$_2$Ti$_6$O$_{16}$: Ni$^{2+}$ ($3.3 \times 10^{-24}$ cm$^2$·s) $^{39}$ GCs, and much larger than Ga$_3$S$_2$: Cr$^{4+}$ chalcogenide (ChG) GGS ($0.62 \times 10^{-24}$ cm$^2$·s) which are known for the difficulty of preparation $^4$. Light amplification at similar O-band wavelengths can be also achieved for Pe$^{3+}$ or Dy$^{3+}$ doped fluoride and ChG glasses of very low phonon energy. In comparison, the FOM of the ZGO-0.15GC is less than that of Pr$^{3+}$ doped Ge-Ga-S ChG glass ($1.4 \times 10^{-24}$ cm$^2$·s) $^{40}$, but it is much larger than in the case of Pr$^{3+}$ doped ZBLAN ($0.38 \times 10^{-24}$ cm$^2$·s) and Dy$^{3+}$ doped Ge-Ga-S ChG glasses ($1.4 \times 10^{-24}$ cm$^2$·s) $^{30, 44}$. Moreover, the present GCs are superior to rare-earth doped glasses in terms of the availability of a broad tuning range of wavelength. A comparison of the luminescent properties ($\lambda_{peak}$: peak emission wavelength, $\tau_{300K}$: decay lifetime at the room temperature, and FOM) and crystal field parameters ($Dq$ and $B$) of Ni$^{2+}$ in GCs containing different spinels is shown in Table 1. The magnitude of crystal field strength $Dq$ is a measure of the interaction of the 3$d$-electrons with the rest of the lattice, and the main contribution arises from the nearest neighbors. Although Ni$^{2+}$ substitutes for Ga$^{3+}$ in both ZGO and ZGGO GCs, the $Dq$ value of the latter is slightly less than that of the former GCs, which, according to the ligand field theory, is due to the distortion of ligands inducing a weakening effect on the crystal field strength of the central ion $^{85}$.

It is important to stress that the synthesized ZnGa$_2$O$_4$: Ni$^{2+}$ GCs are highly reproducible to allow for a fluctuation in the thermal treatment temperature, for example, transparent GCs with the broadband near NIR emission can be obtained at a crystallization temperature ranging from 750 to 800 °C (Fig. S9 in the supporting information). This is a very important advantage for the “melt-in-tube” method, for which the core fiber is covered with the SiO$_2$ cladding, and the heat transfer process during the heat treatment can be different from that of the glass sample. Because of different thermal treatment temperature, higher for the “melt-in-tube” method, GCs with required luminescent properties and transparency should be obtained in a temperature range as broad as possible.

Table 1. Comparison of luminescent properties and crystal field parameters of GCs containing different nanospinels. Rare earth (Pr$^{3+}$ or Dy$^{3+}$) doped glasses emitting at similar O-band wavelengths are also listed for comparison. $^1$/e lifetime and $^2$average lifetime.

| Spinel/Host | $\lambda_{peak}$ (nm) | $\tau_{300K}$ (μs) | FOM $\times 10^{-24}$ cm$^2$·s | Ref. |
|-------------|----------------|----------------|----------------|------|
| ZnGa$_2$O$_4$ | 1320, 1350 | 1300, 1300 | / | this work |
| Zn$_{1-x}$Ga$_{x}$Ge$_2$O$_4$ | 1300, 1300 | 1200, 1200 | / | this work |
| (Ga$_2$O$_3$)$_2$(GeO$_2$)$_3$ | 1290, 1350 | 1300, 1300 | / | / |
| LiGa$_5$O$_8$ | 254, 254 | 240, 240 | 3.1 | / |
| BaAl$_2$Ti$_6$O$_{16}$ | 583, 583 | 360, 360 | 4.79 | / |
| $\sigma_e$ | $1.23^{3}$/3.8$^{11}$/3.7$^{33}$/3.1$^{12}$ and BaAl$_2$Ti$_6$O$_{16}$: Ni$^{2+}$ ($3.3 \times 10^{-24}$ cm$^2$·s) $^{39}$ GGS, and much larger than Ga$_3$S$_2$: Cr$^{4+}$ chalcogenide (ChG) GGS ($0.62 \times 10^{-24}$ cm$^2$·s) which are known for the difficulty of preparation $^4$. Light amplification at similar O-band wavelengths can be also achieved for Pe$^{3+}$ or Dy$^{3+}$ doped fluoride and ChG glasses of very low phonon energy. In comparison, the FOM of the ZGO-0.15GC is less than that of Pr$^{3+}$ doped Ge-Ga-S ChG glass ($4.79 \times 10^{-24}$ cm$^2$·s) $^{32}$, however, it is much larger than in the case of Pr$^{3+}$ doped ZBLAN ($0.38 \times 10^{-24}$ cm$^2$·s) and Dy$^{3+}$ doped Ge-Ga-S ChG glasses ($1.4 \times 10^{-24}$ cm$^2$·s) $^{30, 44}$. Moreover, the present GCs are superior to rare-earth doped glasses in terms of the availability of a broad tuning range of wavelength. A comparison of the luminescent properties ($\lambda_{peak}$: peak emission wavelength, $\tau_{300K}$: decay lifetime at the room temperature, and FOM) and crystal field parameters ($Dq$ and $B$) of Ni$^{2+}$ in GCs containing different spinels is shown in Table 1. The magnitude of crystal field strength $Dq$ is a measure of the interaction of the 3$d$-electrons with the rest of the lattice, and the main contribution arises from the nearest neighbors. Although Ni$^{2+}$ substitutes for Ga$^{3+}$ in both ZGO and ZGGO GCs, the $Dq$ value of the latter is slightly less than that of the former GCs, which, according to the ligand field theory, is due to the distortion of ligands inducing a weakening effect on the crystal field strength of the central ion $^{85}$. It is important to stress that the synthesized ZnGa$_2$O$_4$: Ni$^{2+}$ GCs are highly reproducible to allow for a fluctuation in the thermal treatment temperature, for example, transparent GCs with the broadband near NIR emission can be obtained at a crystallization temperature ranging from 750 to 800 °C (Fig. S9 in the supporting information). This is a very important advantage for the “melt-in-tube” method, for which the core fiber is covered with the SiO$_2$ cladding, and the heat transfer process during the heat treatment can be different from that of the glass sample. Because of different thermal treatment temperature, higher for the “melt-in-tube” method, GCs with required luminescent properties and transparency should be obtained in a temperature range as broad as possible.
In this respect, the studied ZGO GCs are perfectly matched to the "melt-in-tube" method, which will be the subject of our next study to succeed in making them into fibers.

Conclusion
The selective doping of Ni\(^{2+}\) in ZnGa\(_2\)O\(_4\) and Zn\(_{1-x}\)Ga\(_2\)Ge\(_x\)O\(_4\) nano-spinsels via the controlled crystallization results in a broadband NIR emission. The use of nucleating agents, such as TiO\(_2\) promotes occupation of the octahedral Ga\(^3+\) sites by Ni\(^{2+}\) and leads to enhanced luminescence and prolonged lifetime, whereas the partition of Ge\(^{4+}\) in ZnGa\(_2\)O\(_4\) spinsels leads to a reduced NIR emission, which is assumed to be related to the formation of anti-site defects. The large mismatch of valence and ionic radii between Ni\(^{2+}\) and Ge\(^{4+}\) considerably limits the substitution of Ni\(^{2+}\) for Ge\(^{4+}\), which also partly accounts for the comparatively weaker NIR emission from the Zn\(_{1-x}\)Ga\(_2\)Ge\(_x\)O\(_4\) Ni\(^{2+}\) GCs. The stronger NIR emission, excellent optical quality and reproducibility, as well as a tolerance for thermal treatment temperature make ZnGa\(_2\)O\(_4\) Ni\(^{2+}\) nano-spinsels embedded GCs highly promising candidates for broadband fiber amplifiers. Future work will focus on fabricating GC fibers by the "melt-in-tube" method.

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Acknowledgements
This study was supported by the National Natural Science Foundation of China (61227013, 51302082, 61307104, 61422505, 61405044 and 61575050), National Key Scientific Instrument and Equipment Development Project (No. 2013YQ040815), Open Project Program of the Jiangsu Key Laboratory of Advanced Laser Materials and Devices (KLALMD-2015-07), the Fundamental Research Funds for the Central Universities and the 111 project (B13015) to the Harbin Engineering University.

Author Contributions
Z. Gao and J. Ren designed the experiments and wrote the draft. Y. Liu, X. Lu and Z. Fang did the measurements. E. Lewis, G. Farrell, J. Yang and P. Wang discussed the results and commented on the manuscript. All authors reviewed the manuscript.

Additional Information
Supplementary information accompanies this paper at doi:10.1038/s41598-017-01676-6

Competing Interests: The authors declare that they have no competing interests.

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