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The fabrication of nanodiamond doped tellurite germanate glass with robust structure and its luminescence

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Abstract: Fluorescence of negative-charged nitrogen-vacancy centers in nanodiamond allow applications in quantum metrology, nanoscale sensor and bioimaging, of utmost relevance to domains from nanotechnologies to biosensing. However, the low color center content and collection efficiency of photons are crucial issues. Although, several studies about coupling nanodiamond into optical

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waveguides have already been proposed, the search for the most appropriate substance and simplest, most effective method are of keys. In this paper, we present a novel non-traditional way to incorporate nanodiamond with increased negative-charged nitrogen-vacancy content to 75.48% into tellurite germanate glass. The hybrid glass is stable in structure with predominant TeO_4 trigonal bipyramid. Moreover, the fluorescence intensity is enhanced in composite. Such robust nanodiamond in tellurite germanate glass optical system has the potential to be used for nanoparticle sensing and quantum metrology.

Keywords: nanodiamond, tellurite, photoluminescence, nitrogen-vacancy, composite material

1 | Introduction

Fluorescent nanodiamond (ND) has undeniable promise in fields such as quantum key distribution,¹ quantum metrology,² nanoscale electric, magnetic and temperature field sensing,³⁻⁵ and bioimaging⁶ due to its small size, great flexibility and excellent biological compatibility. Arguably, there are varieties of color centers in ND, while the negatively charged nitrogen vacancy (NV^-) color centers are the most important owing to their high-brightness, stable luminescence, relatively controllable fabrication, dull bleaching and shimmering, and room-temperature spin polarization.⁷ As a result, most of the applications mentioned above rely on the photoluminescence of NV^- color center. Whilst fluorescent nanodiamond has broad application prospects, especially in the field of quantum, two real difficulties in applying it to practical technologies are described below.

First, as the size of diamond particles reduces to the nanometer scale, only about 1% of nanodiamond contains the nitrogen vacancy (NV) center, which restricts their applications.^{8,9} Therefore, the artificial generation of NV centers in nanodiamond is an important challenge for various applications. So far, three approaches have applied to generate the NV centers in commercially available diamond. One is to efficiently generate NV centers by irradiating diamond with high-energy particles (electrons, protons, neutrons, etc.) to create vacancies, and then performing high temperature annealing in vacuum for the vacancies migrating towards nitrogen impurities.^{10,11} This most commonly used method is suitable for diamonds containing enough nitrogen impurities inside. However, this method has disadvantage of high equipment costs, time-consuming operation and some undesired results, such as electron spin resonance shift and linewidth broadening, induced

by the high energy irradiation procedure.¹² The second method generates more nitrogen substitution by implanting high-energy nitrogen ions, followed by high-temperature annealing to produce NV centers in diamonds containing deficient nitrogen impurities.¹³ The third approach is that the NV centers are formed by using the nitrogen impurity defect of ND itself to bind the moving vacancy through high temperature annealing in vacuum and then oxidation in air to remove the sp²-bonded carbon on the surface of ND. The concentration of NV color centers produced by this method is affected by N impurities in ND.¹⁴ Compared with the first two methods, this way has simple instrument, short operation time and low cost. In this work, therefore, NV centers were produced by the high temperature annealing method. Moreover, the ND is highly sensitive to external magnetic, electric, and temperature fields, of which the sensitivity to temperature fields is used for biological thermal measurement.¹⁵

Second, the collection efficiency of emitted photons which is extremely significant to varieties of applications is low. The collection efficiency of conventional detection approaches is only 2%,¹⁶ When the emission of the NV⁻ centers in bulk diamond is imaged by conventional confocal microscopy, the fluorescence collection efficiency is universally less than 10%.¹⁷ To overcome this issue, researchers have made numerous attempts, finding that coupling the NV fluorescence emission photons into optical waveguides is an attractive solution.¹⁸ Several approaches have been explored, such as the pure diamond waveguides,¹⁹ and NDs grown on the end face of fiber, or NDs manipulated on to the end face or tapered regions to form waveguide/fiber structures.²⁰⁻²³ The hybrid structures produced by these methods all require sophisticated operations to attach or grow ND onto the optical fiber surface, which is too complex and inconvenient for experimental operation. In addition, NDs are on the surface of the fiber, leading to mechanical instability which restricts the applicability and life of devices.²⁴

Thus, a method of combining NV color center quantum emitters with photonic structures to embed NDs directly into glass has attracted the attention of researchers.^{25, 26} However, to obtain ND/glass composite with excellent performance, it is necessary to select and design the glass system that matches the performance of ND. Based on the previous researches,²⁷⁻²⁹ it's proposed that the glass materials with ND should have the following characteristics: (1) low melting temperature and glass transition temperature <450°C, which minimizes the oxidation of the ND; (2) high transmittance in the NV color center excitation and emission wavelength range of 500-800nm; (3) a refractive index close to ND (2.43); (4) good chemical stability; (5) excellent anti-crystallization properties, $\Delta T > 100^\circ\text{C}$, which is beneficial for drawing into fiber; (6) low content

of hydroxyl impurities, which is easy to obtain high optical quality. In many mature glass systems, tellurite glass basically meets the above requirements.³⁰⁻³³ However, due to its unique triangular double-cone structure, tellurite glass has poor thermal stability and narrow fiber drawing temperature range. Moreover, high-valence state tellurium is apt to undergo redox reaction with NV centers, resulting in fluorescence extinction.³⁴ Thus, here, a moderate amount of germanium oxide was added to the TeO₂-ZnO-Na₂O glass system superseding a part of tellurium oxide to improve its thermal stability. Furthermore, boron oxide joined in the system to boost fluidity while mixing the NDs into the glass melt.³⁵ It is worth noting that NDs will be oxidized at high temperature.³⁶ That is the reason why NDs cannot be mixed into glass by conventional eutectic method. We used a two-step process to generate this composite: melting the raw glass material at high temperature and adding NDs at low temperature.

In this paper, we fabricated NV⁻ center with high temperature annealing method and synthesis ND/tellurite germanate glass by a two-step process. The structure and luminescence of the samples were characterized by differential thermal analysis (DTA), Raman, X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL). We determined the increase of NV⁻ color center content after high temperature annealing of NDs, and proved the successful incorporation of NDs into glass from the structure and photoluminescence point of view.

2 | Experiment

2.1 | Fabrication of NV⁻ centers in NDs

The NV⁻ centers in NDs was prepared by high temperature annealing. The ND powder used in experiment was commercially available with 60-100nm. The flow chart is displayed in the top section of Fig. 1. First, NDs were annealed in vacuum carbon tube furnace at 800°C for 2h with the heating rate of 200°C/h. In the annealing process, the vacancy existing in NDs moved to the N substitution bit and was bounded by N atom to form NV⁻ color center. The sp² hybrid graphite phases were also produced on the surface of nanocrystals at annealing process which can inhibit NV⁻ color center luminescence. Notably, the 400°C oxidation temperature of graphite is lower than 670°C oxidation temperature of ND.³⁷ Therefore, it is effective to oxidize the annealed NDs in air at 550°C for 2h to remove the sp²-bonded carbon atoms. The ND experienced the annealing and oxidation was named as treated-ND (t-ND).

2.2 | Fabrication of glass

The t-ND doped tellurite germanate glass with composition (in mol%) $65\text{TeO}_2\text{-}15\text{ZnO}\text{-}10\text{Na}_2\text{O}\text{-}5\text{GeO}_2\text{-}5\text{B}_2\text{O}_3$ was prepared by a two-step process as named tND-TZNGB. While the t-ND free tellurite germanate glass and $70\text{TeO}_2\text{-}20\text{ZnO}\text{-}10\text{Na}_2\text{O}$ tellurite glass were fabricated by the same process, named as TZNGB and TZN respectively. The process is shown in the lower part of Fig. 1. Firstly, homogeneously mixed TeO_2 , ZnO , Na_2CO_3 , GeO_2 and H_3BO_3 were melted using corundum crucible in furnace at 850°C for 15 minutes. Secondly, in order to prevent the t-NDs from being oxidized by high temperature during the incorporation process, temperature was reduced to 550°C and $0.9\pm 0.1\text{mg}$ ($90\pm 10\text{ppm}$) t-NDs were added into the 10g melt, and kept for approximately 5-10 minutes. The t-NDs doping concentration was yielded in ppm-weight by measuring the difference between the t-NDs weight before adding and the remained amount. Even though the temperature has dropped to 550°C , oxidation of t-NDs in the glass melt is still inevitably observed to a greater or lesser extent. If the t-NDs concentration was too small, almost all t-NDs doped into the melt might be destroyed by oxidation. At large concentration ($>100\text{ppm}$) in small glass melt (10g) with reduced oxygen atmosphere, as the doping concentration rising, the reduced tellurium species increase, resulting in dark color and lower transmittance in visible.²⁸ Therefore, we doped 90ppm t-NDs into melt, and remained the oxygen-rich atmosphere without lid. Finally, the t-ND doped melt was cast into a preheated brass mould, and annealed at 300°C ($\sim 10^\circ\text{C}$ lower than the glass transition temperature T_g) for 4h to eliminate internal stress.

2.3 | Performance characterization

In this experiment, the DTA of the TZNGB glass was carried out on a differential thermal analyzer (DTA404PC model, Germany) at a heating rate of 10 K/min with alumina as a reference. Raman and PL spectra were measured by Renishaw Raman laser spectrometer using the 532nm laser of an argon ion laser as the excitation source. The focused beam was illuminated onto the sample by a $L50\times$ objective of a Leica DMLP microscope. The backscattered signals from sample were collected through the same objective and detected by a CCD array detector. Chemical bonding states in glass was examined using XPS. The XPS used a monochromatic Al $K\alpha$ (1486.6 eV) as the source. For the initial survey spectra and the high-resolution spectra, pass energy of 150 eV with the step size of 1.0 eV and 30 eV with a step size of 0.05 eV were applied, respectively. Te 3d peak at 576 eV was performed as reference to energy calibration the binding energies (BE) of photoelectron spectra. The processing of the measured spectra includes a subtraction of X-ray satellites and a mixed of Gaussian-Lorentzian function for the XPS peak fitting.

3 | Results and Discussions

The DTA of TZN and TZNGB glass were tested with heating rate of 10°C/min at room temperature, illustrated as Fig. 2(a). Besides, the parameters about differential thermal of TZN and TZNGB glass were signed in graph. The glass transition temperature (T_g) lies around 314°C, which is slightly higher than that of traditional TeO₂-ZnO-Na₂O (TZN) system glass (303°C). Meanwhile the temperature of 447°C corresponds to the crystallization onset temperature (T_x) of TZNGB glass. ΔT has been frequently used as a rough measure of the glass thermal stability, which is identified as: $\Delta T = T_x - T_g$.³⁸ A large ΔT means strong inhibition of nucleation and crystallization during the fiber fabricating, reducing the scattering loss. Compare with TZN glass, the large ΔT of TZNGB glass (133°C) in this experiment suggests that the introducing B₂O₃ and GeO₂ into tellurite glass improved their thermal stability. It might be due to the replacement of part TeO₂ by B₂O₃ and GeO₂ changing the structure of glass, which will be demonstrated by the subsequent Raman test. Moreover, the transmittance at 500-800nm is excellent, shown in Fig. 2(b). The lower transmittance of tND-TZNGB glass than TZNGB glass can be explained by the illustration. It is obvious that a slight coloration exists in tND-TZNGB glass caused by t-ND incorporation, producing scattering and reducing transmittance. Even though the transmittance has decreased, it still has a high transmittance in the NV color center excitation and emission wavelength range of 500-800nm. The TeO₂-ZnO-Na₂O-GeO₂-B₂O₃ glass is suitable for nanodiamond composite.

Raman is one of the most frequently used characterization methods to analyze glass internal network structure. In order to study the performance of tellurite glass with introduction of GeO₂ and B₂O₃, normalized Raman spectra of TZN and TZNGB glass were carried out and described at Fig. 3 in detail. The spectrum is characterized by three polarized bands corresponding to a broad band near 453cm⁻¹, a shoulder band around 678cm⁻¹, and another band about 756cm⁻¹. The above bands have been contributed by three different types of stretching vibrations, i.e., the stretching modes of Te-O-Te or O-Te-O linkage, stretching modes of Te-O bond in TeO₄ trigonal bipyramid (tbp), and bending modes of Te-O bond in TeO₃₊₁ or TeO₃ trigonal pyramid (tp) units, respectively. These characteristic peaks are similar to those reported previously for tellurite glasses.³⁹⁻⁴¹ Despite the shape of the bands are not changed by bits of GeO₂ and B₂O₃ addition, slight shifts of band positions happen in TZNGB glass. The blue shift of Te-O-Te stretching vibration is due to the deformation of

Te-O-Te bond caused by the introduction of GeO₂.⁴²⁻⁴⁴ The blue shift at near 678 cm⁻¹ might be attributed to the formation of [GeO₄]⁴⁻ units after the addition of GeO₂, which can provide partial oxygen ions to achieve the network continuity and relatively stability in a tellurite glass structure.⁴⁵⁻⁴⁷

Raman and PL measurement of t-ND that have treated by annealing and oxidation and raw ND powder were performed, as shown in Fig. 4 and 5 respectively. In Fig. 4, the Raman characteristic peak of diamond appears at 1332cm⁻¹. The higher intensity sp³ diamond peak in t-ND indicates high temperature annealing process is useful. An obvious band near 1580cm⁻¹ in raw ND corresponds to the graphite Raman feature (G peak), while t-ND exhibits a small one. It represents that graphitization came up during the annealing process, following that the oxidation process eliminating the graphite.

Figure 5 (a) and (b) exhibit the fluorescence spectra of t-ND and ND measured under 532nm excitation at 80K and 300K temperature, respectively. In order to ensure the comparability, they were obtained at the same pump power of 5mW, uniform integral time of 1s and identical integral number of one time per second. PL spectra show that both raw ND powder and t-ND perform NV⁻ and NV⁰ (the neutrally charged nitrogen-vacancy color center) zero-phonon line (ZPL) luminescence peaks at 575nm and 638nm separately, regardless of at 80K or 300K, which is marked in Fig. 6 (a) and (b). As show in Fig. 6 (c), NV⁻ ZPL of t-ND at 80K can be fitted by a Lorentzian function, along with an exponential baseline:⁴⁸

$$I = y_0 + a \exp\left(-\frac{\lambda}{t}\right) + \frac{2A}{\pi} \cdot \frac{\omega}{4(\lambda - \lambda_0)^2 + \omega^2}$$

Where I is the fluorescence intensity, λ is wavelength, ω is the Lorentzian half-width, A is the Lorentzian area, λ_0 is the ZPL center, and y_0 , a , and t are fitting parameters. From this formula, the integral area A of NV⁻ ZPL was obtained, the pink region in Fig. 6 (c). The baseline was subtracted to remove the influence of phonon sideband through this fitting program. The integral area A of NV⁻ ZPL and NV⁰ ZPL of ND and t-ND at 80K were obtained by the same procedure. The NV⁻% ($NV^{-}\% = \frac{A_{NV^{-}}}{A_{NV^{-}} + A_{NV^0}} \times 100\%$) of the t-ND and ND at 80K is 75.48% and 59.82%, respectively. The enlargement of NV⁻ content confirms that the NV⁻ color center was efficiently formed by high temperature annealing. Meanwhile, the NV⁻ ZPL integral area of t-ND at 80K is five times of that at 300K, indicating the promotion of low temperature in NV⁻ center emitting. This difference demonstrates the temperature dependence of fluorescence.

As the addition of t-ND powder into the TZNGB glass, from the Raman curves in Fig. 6(a), the sp³ diamond characteristic peak at 1332cm⁻¹ and three Raman bands representing tellurite glass at 455cm⁻¹, 682cm⁻¹

¹ and 756cm⁻¹ are observed. Thus, the t-ND powders were successfully doped in TZNGB glass. The upward trend of the baseline at 1000-2000cm⁻¹ could be due to the influence of t-ND fluorescence. In addition to ND and t-ND, the PL spectra of t-ND doped glass was also measured at 80K with 532nm laser, displayed in Fig. 6(b). Markedly, NV⁰ ZPL, NV⁻ ZPL and NV⁻ phonon sideband exist, that is similar to PL spectra of t-ND. Comparing to tND-TZNGB glass, peak in PL curve of TZNGB glass is absent and there is no luminescence at 560-800nm. It is confirmed again the presence of t-ND and the coupling of NV centers in tND-TZNGB glass. The peaks at 552nm and 554nm are corresponding to TZNGB glass Raman bands at 682cm⁻¹ and 756cm⁻¹. Calculating the ratio of NV⁻ to NV⁰ integration peaks in the PL spectra, the value of NV⁻ relative to total NV in TZNGB glass is 1.4 higher than t-ND. Besides, the fluorescence intensity of NV⁻ ZPL in composite is stronger than that of t-ND. During the doping procedure, high temperature further removed the sp² carbon from the surface and promoted the formation of oxygen-containing functional groups at nanodiamond surface termination. These changes occurred at nanodiamond surface are benefit of the NV⁻ ZPL fluorescence.⁴⁹ These results indicate that the NV⁻ properties are stable in prepared tND-TZNGB glass.

XPS measurement was performed to elucidate the chemical state and local chemical environment of elements in the tND-TZNGB glass, including survey scan and high resolution scan, as shown in Fig. 7. From the XPS survey scan (Fig. 7(a)), peaks corresponding to tellurium, oxygen, boron, zinc, germanium, sodium and carbon were observed. The presence of these elements in the glass substantiates that the previously designed components have been successfully introduced into the glass. High-resolution scan spectra of Te3d, O1s and C1s of tND-TZNGB glass were undertaken to determine the elemental composition.

Figure 7(b) presents the high-resolution scan and the fitted peak for Te3d spectra. The peaks at 586.4 eV and 576.3 eV respectively corresponding to the doublets Te3d_{3/2} and Te3d_{5/2} were observed, according with the report for amorphous TeO₂.⁵⁰ The Te3d_{5/2} peak of the examined glass is deconvoluted into two peaks contributed at 575.0 and 576.3 eV. According to prior studies,^{51, 52} these binding energy (BE) are related to the presence of TeO₃ trigonal pyramid (tp) and TeO₄ trigonal bipyramid (tbp) units, respectively. The structure stick model of TeO₃ tp and TeO₄ tbp were given in illustration (1) and (2), respectively. The peak positions and fitting details for Te3d_{5/2} orbital including FWHM and area percentage are listed in Table 1. The concentration of the substance can be represented by the fitting peak area. Obviously, the 88.46% area percentage of TeO₄ tbp is higher than 11.54% of TeO₃ tp. Conclusively, both TeO₄ and TeO₃ units consist in tND-TZNGB glass but the TeO₄ amount is predominant in the amorphous structure, which is in agreement with previous XPS

studies of alkali tellurite glasses.^{44, 52, 53} The alkali metal oxide Na₂O converts TeO₄ tbp to TeO₃ ttp by disrupting the Te-O-Te bonds in the network structure, which affects the coherence and thermal stability of the network structure. The incorporation of cations with charge greater than one, such as B³⁺ and Ge⁴⁺, leads to the connection of lone pair electrons on ttp and tp, which enhances the continuity of the network structure and improves the thermal stability. The schematic was displayed in illustration (3). Besides, the addition of nanodiamond did not change the structure of TZNGB glass matrix.

In O1s high resolution spectrum (Fig. 7(c)), a slight asymmetric peak at 530.8eV can be fitted to three peaks corresponding to the peak center of 529.9eV, 530.8eV and 532.2eV. It might be indicative of contributions from different oxygen sites: NBO (nonbridging oxygen, oxygen links a glass former and a glass modifier or double bonds to a glass former), BO (bridging oxygen, an oxygen links two glass former in the glass network), and Te-O-Ge or (and) Te-O-B bonds. The O1s lines for NBO and BO are known to be about 529-530 eV and 531-532 eV respectively, which are affected by electronegativity and electron density. BO peak always has higher BE than NBO peak because glass former Te bonded by BO has larger electronegativity compared to glass modifiers Zn and Na. Electrons are apt to be attracted by high electronegative elements when elements form bonds with O. Then the reduction of electron density around BO leads to BE of core electrons increasing.⁵³ According to XPS analysis, we conclude that the NBO at 529.9eV is assigned to Te-O-Na and Te=O, while the BO at 530.7eV is distributed to Te-O-Te. In general, O1s core-level spectrum is deconvoluted to NBO and BO peaks. But, in order to better match the measurement curve, the third peak was fitted. C.L. Medrano-Pesqueira et al studied the structure of CdO-TeO₂-GeO₂ system glass, and attributed the fitting peak at 531.64eV of O1s core-level to GeO₂.⁵¹ In TeO₂-PbO-TiO₂-B₂O₃ system glass reported by Chen, B-O bond was responsible for the fitted peak at 533eV.⁵⁴ Based on these results, we suggest that the peak at 532.0eV should belong to Te-O-Ge or Te-O-B bond or both. In combination of Raman spectra, it is concluded that the structure of this glass sample is formed by predominant TeO₄ tbp with several BOs, a small amount of TeO₃ ttp with two BOs and one NBO, and little Te-O-Ge or Te-O-B bonds, as shown as the illustration in Fig. 7(c).

The C1s core level XPS spectra of the tND-TZNGB glass are shown as Fig. 7(d). The C1s peak demonstrates the presence of several components, including sp²-hybridised carbon, sp³-hybridized carbon species, and oxygen-bonded carbon components. A sharp peak centered at 285.2 eV can be attributed to sp³-hybridised carbon species, which is the feature structure of diamond. The diamond structure was pictured in illustration (2) of Fig. 7(d). The C1s line in graphite occurs at lower binding energy than that in diamond,⁵⁵ so

the peak at 284.4 eV is assigned to sp^2 carbon. The C=C bond structure model was drawn in illustration (1) of Fig. 7(d). Another peak at 285.9 eV may be contributed by C-O bond as it is similar with results of Guillevic Mazheva et al.⁵⁶ It may be caused by residual Na_2CO_3 materials after decomposition or a small amount of nanodiamond oxidation. The fitted curve of sp^3 -hybridized carbon species has the highest intensity signifying that the C element in the testing range is principally sp^3 hybrid diamond structure. It substantiates the existence of t-ND in glass network.

4 | Conclusion

Nanodiamonds experienced high temperature vacuum annealing and oxidation to synthesize more NV^- colour centers. This technology is feasible compared with conventional approaches of high-energy electron irradiation. We observed the increase of NV^- content from 59.82% to 75.48% and the enhanced fluorescence intensity.

The t-ND doped TZNGB glass was prepared by a two-step process, which directly coupled the t-ND to TZNGB glass. It overcomes the disadvantages from method of evanescent coupling diamond with photonic devices. The Raman and PL spectra confirmed the presence of nanodiamonds in TZNGB glass. The fluorescence curves show that the NV^- properties are stable in prepared tND-TZNGB glass. From Raman spectra and XPS, we obtained that the structure of tND-TZNGB is formed by predominant TeO_4 tbp, a small amount of TeO_3 tp, and little Te-O-Ge or Te-O-B bonds. The structure was hardly affected by t-ND doping. And this hybrid material combined with optical waveguide and quantum emission is a promising candidate of nano-sensing and quantum metrology.

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Table

Table 1. Details of the Curve Fitting of Te3d_{5/2} Core Level Spectra.

Binding Energy/eV (±0.20)	FWHM/eV (±0.20)	Area/% (±1.0)	Peak Species
575.0	3.26	11.54	TeO ₃ ⁵²
576.3	1.45	88.46	TeO ₄ ⁵³

Figure captions

Fig. 1. The flow chart of fabricating the NV⁻ centers in NDs and t-ND doped tellurite germanate glass.

Fig. 2. (a) DTA curves of TZN and TZNGB glass with heating rate of 10°C/min in the atmosphere. The T_g and T_x all marked in graph. (b) Transmittance curves of TZNGB and tND-TZNGB glass. The inset is optical photograph of TZNGB and tND-TZNGB glasses.

Fig. 3. Raman spectra of TZN and TZNGB glass in the 100-1000cm⁻¹ range excited by 532nm at room temperature.

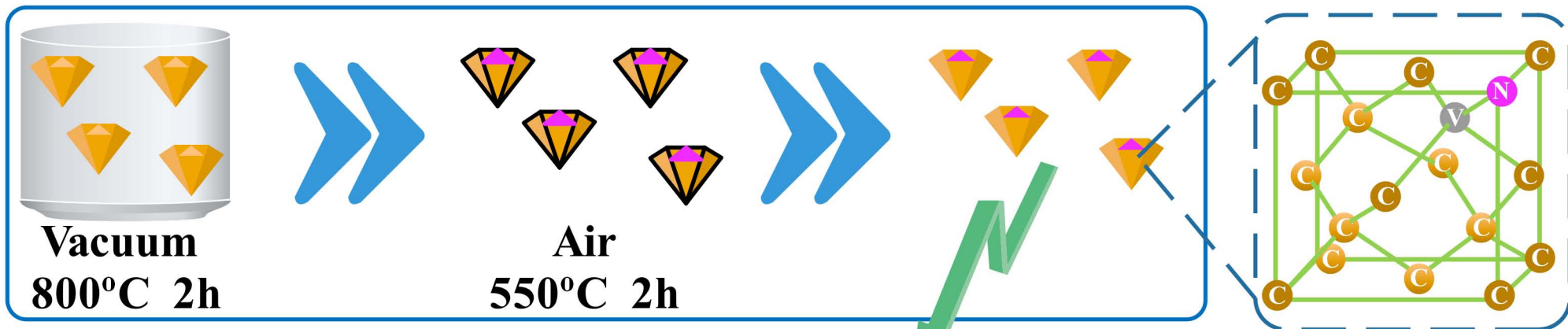
Fig. 4. Raman spectra in range of 300-2000cm⁻¹ excited by a 532nm laser at room temperature. The peaks at 1332cm⁻¹ mean the sp³ diamond characteristic peak, and that at 1580cm⁻¹ is graphite G peak.

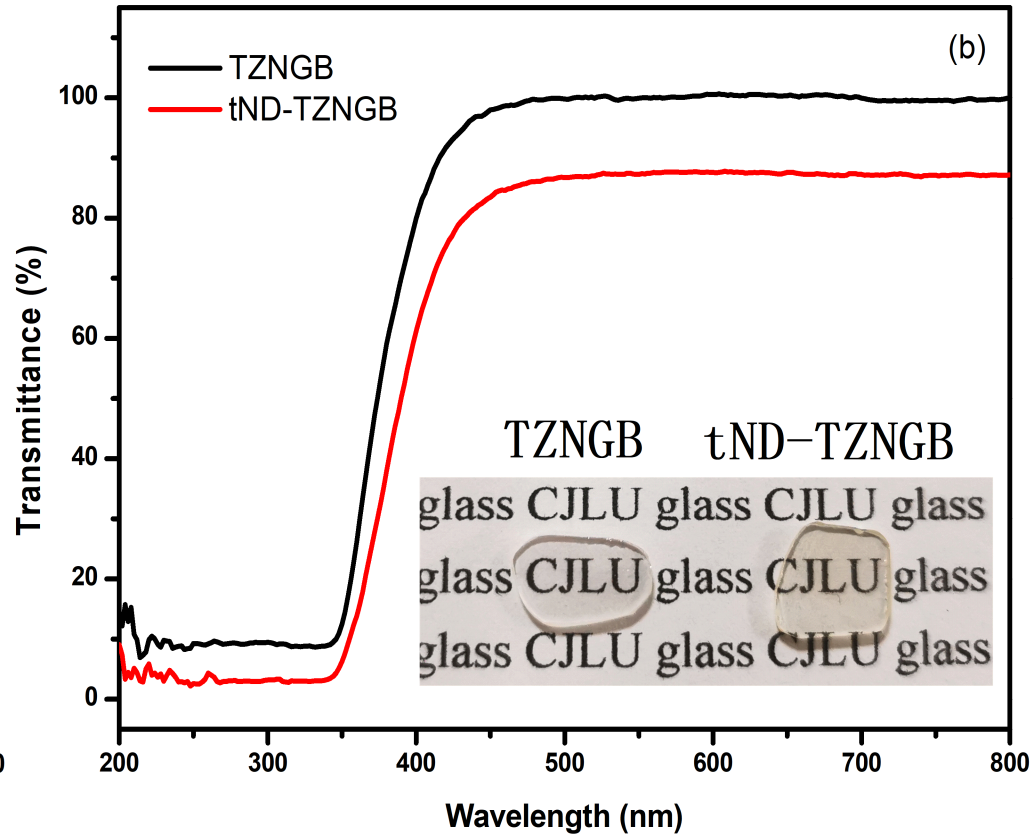
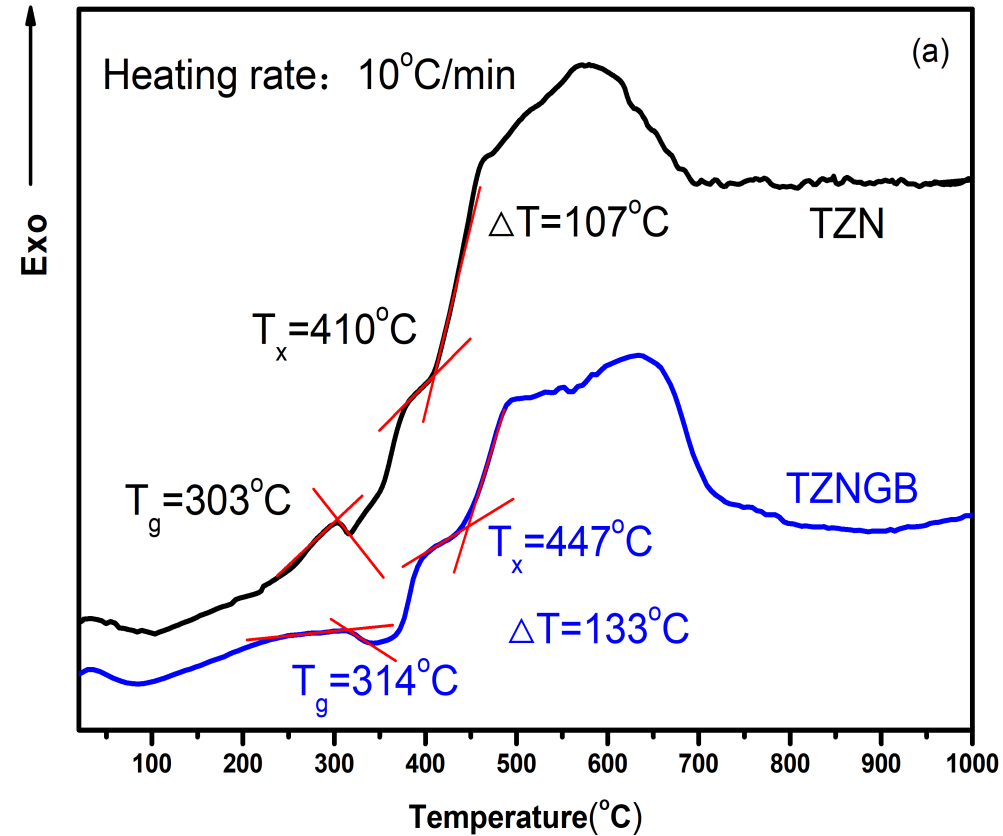
Fig. 5. PL spectra in range of 550-800nm spectra of raw ND powder (black solid line) and t-ND (red dotted line) excited by 532nm at (a) 80K and (b) 300 K. They show the NV⁰ ZPL at 575nm, NV⁻ ZPL at 638nm and NV⁻ phonon sidebands at 650-800nm. (c) Fluorescence spectrum of t-ND at 80K over 610-657nm excited by 532nm. The red solid curve is the best-fit of the data (green curve) with exponential baseline (black curve). The pink area represents the integral area of NV⁻.

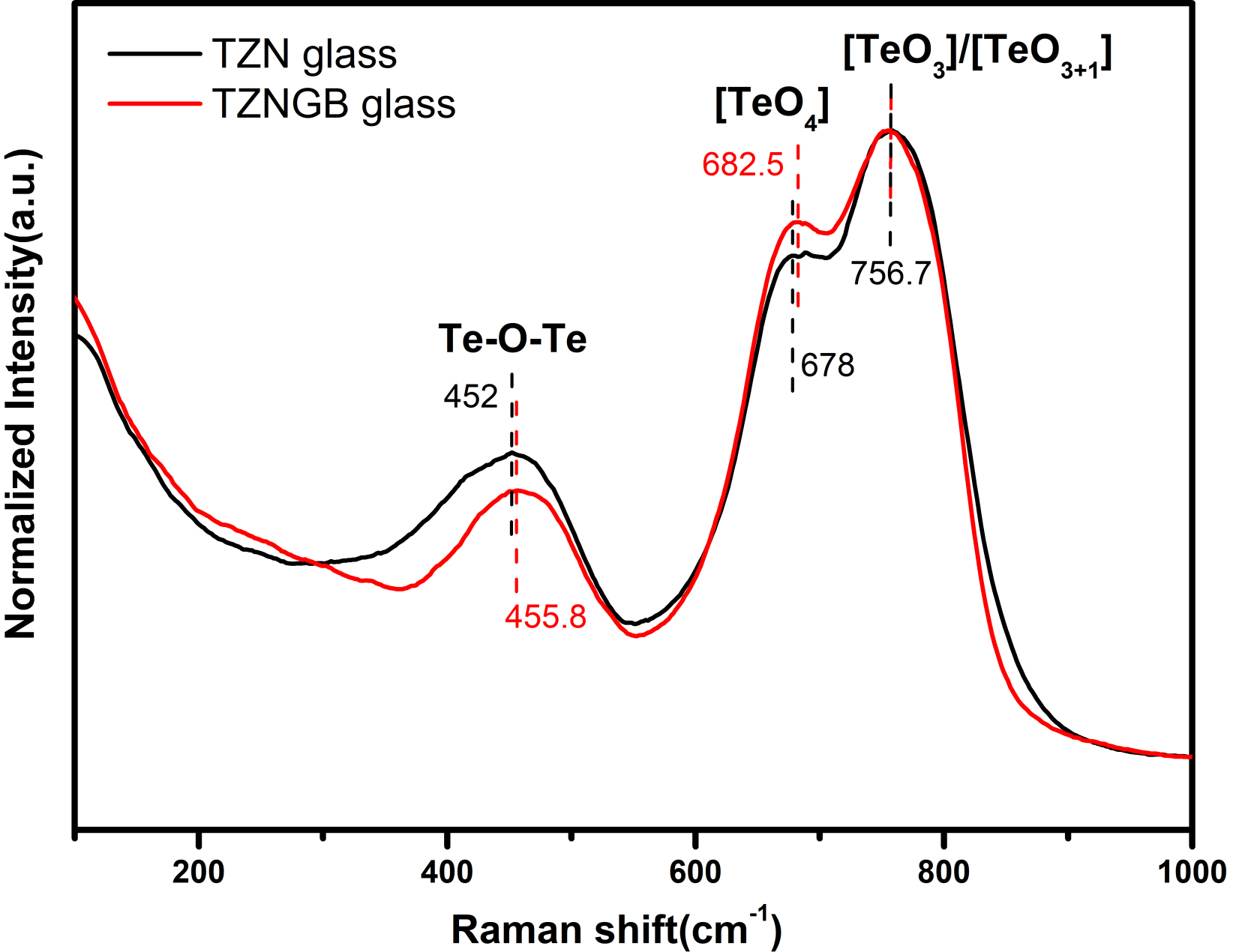
Fig. 6. (a) The Raman curves of tND-TZNGB and TZNGB glass; (b) PL spectra in 560-800nm of tND-TZNGB and TZNGB glass excited by 532nm at 80K. The tND-TZNGB glass has the sharp peaks at 573nm, 638nm and a broad peak at 650-800nm owing to the luminescence of NV color center in t-ND.

Fig. 7. (a) XPS survey scan of tND-TZNGB. (b) High resolution of Te3d core-level. Te3d_{5/2} at 576.3nm was fitted with two peaks which were assigned to TeO₃ trigonal pyramid (tp) and TeO₄ trigonal bipyramid (tbp). Illustration (1) and (2) is the structure model of TeO₃ tp and TeO₄ tbp respectively. Illustration (3) is schematic of Ge element connecting TeO₃ tp and TeO₄ tbp: A lone pair electrons site is like an oxide (O²⁻) ion. It offers equilibrium positions through interchange via delocalization when [GeO₄]⁴⁺ is incorporated into the structure for achieving the network continuity and thermal stability enhancement. (c) High resolution of O1s core-level. It was fitted with three peaks corresponding to nonbridging oxygen (NBO), bridging oxygen (BO), Te-O-Ge/Te-O-B

respectively. Illustration shows structure model of tND-TZNGB glass sample. (d) High resolution of C1s core-level. It was fitted with three peaks corresponding to C=C bond sp^2 , C-C bond sp^3 and C-O bond. The structure model of C=C bond and C-C bond in diamond are shown in illustration (1) and (2) respectively.







Intensity (a.u.)

