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Effects of melting temperature on Color-changing in Germano-tellurite Niobate Glass

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Abstract

Germano-tellurite niobate glasses have gained significant interest because of their applications in lasers and optical devices. However, germano-tellurite niobate glasses tend to turn brown or dark, which is a major disadvantage for visible optical systems. This work is devoted to exploring the mechanism of this color-changing. Glasses with a molar composition of 70TeO₂-10GeO₂-10K₂O-10Nb₂O₅ (TGKN) were synthesized by conventional melt-quenching at various melting temperatures. Different melting temperature leads the glasses to present different colors. The precise glass composition was revealed by ICP-OES, and the thermal properties, optical properties, and microstructure of the TGKN glasses were investigated. The XRD patterns and DSC curves suggest that the formation of Te metal is not the principal reason for the color-changing. A novel interpretation that the generation of T-Nb₂O₅ causes the color-changing was proposed based on the transmittance, XPS and Raman spectra. This work will provide a new perspective on clarifying the effects of melting temperature on color-changing in the germano-tellurite niobate glass.

Keywords: Germano-tellurite niobate glass; Color-changing mechanism; X-ray photoelectron spectroscopy; Raman spectra

1. Introduction

Tellurium oxide based glasses have attracted a strong interest over recent years due to their low phonon energy, good transmission at visible and infrared wavelength from ~0.4 to ~6 μm, high resistance to humidity and enhanced non-linear optical properties [1-6]. However, compared to other oxide glass systems, for

example, silicate or germanate glass systems, tellurite glasses generally present low glass transition temperature (T_g) and onset of crystallisation temperature (T_x) causing their poor thermal stability, which can be a drawback. Introducing GeO_2 into tellurite glass can improve their thermal performances, and thus germano-tellurite glasses are widely investigated [7-10]. Among various kinds of germano-tellurite glasses, germano-tellurite niobate glasses have gained significant interest because of their applications in lasers and optical devices [7, 11-15].

A number of studies have found that germano-tellurite niobate glasses have suitable visible and mid-infrared optical property [12, 13]. However, our experiments also found that the germano-tellurite niobate glasses easily become brown even dark, which is one of the main obstacles that hinder the usage of germano-tellurite niobate glasses in visible optical devices. The reasons for this color-changing are difficult to predict because of the number of variables involved, especially for multicomponent glass systems. Up to now, little attention has been paid to the color-changing mechanism in these glasses. Several studies have documented that color-changing of tellurite glass is due to the reduction of tellurium under synthesis conditions [16, 17]. Silva et al. demonstrates that in the $\text{TeO}_2\text{-Sb}_2\text{O}_3$ system glass system, the oxidation of Sb^{3+} to Sb^{5+} leads the reduction of Te^{4+} to Te^0 during the melting process, which is accompanied by a gradual devitrification and darkening process in the glass [16]. On the other hand, some studies suggest that the color-changing is because of the reduction of niobium valence states [18, 19]. Both reasons do not explain very well the phenomenon observed in our experiment, as will be detailed later.

In this work, the glasses with molar composition of $70\text{TeO}_2\text{-}10\text{GeO}_2\text{-}10\text{K}_2\text{O-}10\text{Nb}_2\text{O}_5$ presenting high thermal stability, high refractive index and relative low phonon energy were synthesized at different melting temperature by melt-quenching method [11, 20]. It was found that glasses synthesized at different melting temperatures present different colors. The accurate glass composition was investigated by inductively coupled plasma optical emission spectroscopy (ICP-OES) to exclude the effect of the evaporation process. To find the

reason for color-changing, the optical properties and thermal properties of the prepared glasses were investigated by transmission spectra and differential scanning calorimetry (DSC), respectively. The valence state of Te and Nb were verified by X-ray photoelectron spectroscopy (XPS). The microstructure and sub-microstructure of the glasses were studied by X-ray diffraction analysis (XRD), XPS and Raman spectra, respectively. Based on the results, a different interpretation was proposed to interpret the color-changing of the prepared glasses, which could be extended to explain the color-changing of other tellurite niobate glasses.

2. Experimental

2.1. Synthesis

Glasses with molar composition of $70\text{TeO}_2\text{-}10\text{GeO}_2\text{-}10\text{K}_2\text{O-}10\text{Nb}_2\text{O}_5$ were synthesized by conventional melt-quenching method, named as TGKN. All the glass samples were synthesized by using high-purity raw materials from Aladdin Co., Ltd, including TeO_2 (99.99%), GeO_2 (99.99%), K_2CO_3 (99.99%), Nb_2O_5 (99.99%), Na_2CO_3 (99.99%) and ZnO (99.99%). The stoichiometric chemicals were well-mixed and melted at 900 °C, 1050 °C and 1150 °C for 40 min in a covered alumina crucible in ambient air, respectively named as TGKN900, TGKN1050 and TGKN1150. In addition, a glass sample melted with two-step process (1150 °C for 30 min, then 900 °C for 10 min), donated as TWO-STEP, was also synthesized as shown in Figure 1. In order to study the cause of color-changing, the tellurite glasses with molar composition of $70\text{TeO}_2\text{-}20\text{ZnO-}10\text{Na}_2\text{O}$, $70\text{TeO}_2\text{-}30\text{K}_2\text{O}$, $70\text{TeO}_2\text{-}10\text{GeO}_2\text{-}20\text{K}_2\text{O}$, and $(100\text{-}x)\text{TeO}_2\text{-}x\text{Nb}_2\text{O}_5$ ($x=10$ and 20) were synthesized like the TGKN glasses. The melts were poured onto a preheated steel plate and pressed by another plate for shaping. After annealing at around glass transition temperature (355 °C), all samples were cut and polished into $10\times 10\times 1.5\text{ mm}^3$ for further measurement. The whole synthesis process is shown in Figure 1.

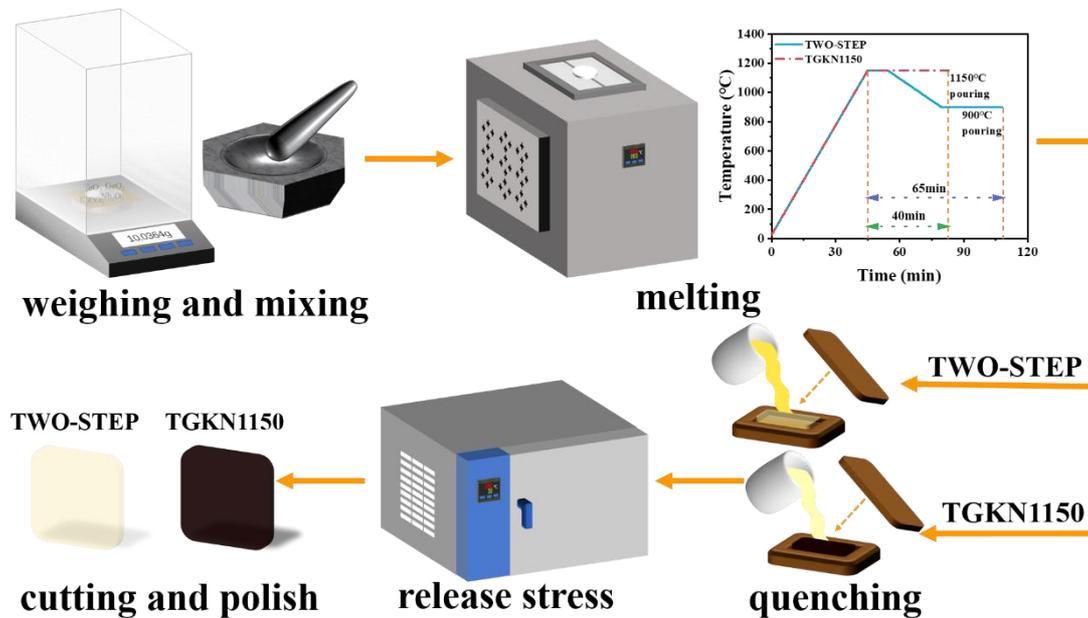


Figure 1 Schematic illustration for the synthesis of TGKN glasses

2.2. Characterizations

The elements analysis was conducted using a simultaneous axial view inductively coupled plasma optical emission spectroscopy (ICP-OES) (Agilent 720, USA). The DSC scans (NETZSCH DSC 200 PC) were carried out on samples of 10 mg in an Al pan. The overall accuracy of this measurement is expected to be within ± 1 K. The T_g was determined at a heating rate of 10 K/min. The amorphous nature of the prepared glasses was characterized by X-ray diffraction measurements (XRD) (D2 PHASE Bruker, German). All measurements were carried out at room temperature using Cu $K\alpha$ radiation ($\lambda=1.54056 \text{ \AA}$). A step size of 0.02° (2θ) was used with a scan speed of $0.1^\circ/\text{s}$. The transmittance spectrum of glass samples were measured by UV-Vis spectrophotometer (UV-3600 Shimadzu, Japanese) ranging from 300 to 800 nm. High-resolution photoelectron spectra were collected on a Thermo Scientific K-Alpha spectrometer equipped with dual aluminium-magnesium anode using Al $K\alpha$ radiation ($h\nu=1486.6 \text{ eV}$). The electron analyzer was set at a pass energy of 50 eV. For self-consistency, the C 1s line of 284.8 eV binding energy was used as a reference for all charge shift corrections as this peak arises from hydrocarbon contamination and its binding energy is generally accepted as remaining constant, irrespective of the chemical state of the sample. This hydrocarbon contamination was further enhanced as the XPS measurements had to be performed on uncleved surfaces of

the glasses as the glass rod samples shattered under vacuum cleavage. Collecting the XPS spectrum of a sample for at least 5 times of cyclic signal accumulation and the base pressure in the analysis chamber during these measurements was less than 5.0×10^{-7} mBar. Polarised Raman scattering spectra measurements were carried out on a confocal Raman spectrometer (Renishaw, UK). Raman scattering spectra were obtained in the range 200-1000 cm^{-1} by exciting the samples with the 532 nm line of a DPSS laser (RL532C50, Renishaw) with an output power of 22.5 W. The signal was detected by a thermoelectric cooled (-70 °C) standard charge-coupled array detector. Each Raman spectrum is an accumulation of ten scans with an exposure time of 10 s. Raman spectra deconvolution was done with the Origin 2021 software, using Gaussian component curves.

3. Result and Discussion

The transmittance spectra in the wavelength range of 300-800 nm of the TGKN series glasses are shown in Figure 2a. The digital photos of the glass samples are shown in the inset of Figure 2a. It displays that the glass sample melted at 900 °C (TGKN900) is slightly yellow, whereas the glass sample melted at 1050 °C (TGKN1050) and 1150 °C (TGKN1150) presents brown and black color, respectively. In addition, the TGKN900 and TGKN1050 samples are transparent, whereas the TGKN1150 sample becomes partly devitrified. Although TGKN1050 shows lower transmittance than that of TGKN900, the absorption edge of both samples is located at around 370 nm, which is consistent with other reports [21-24]. However, the absorption edge of the TGKN1150 is situated at around 600 nm.

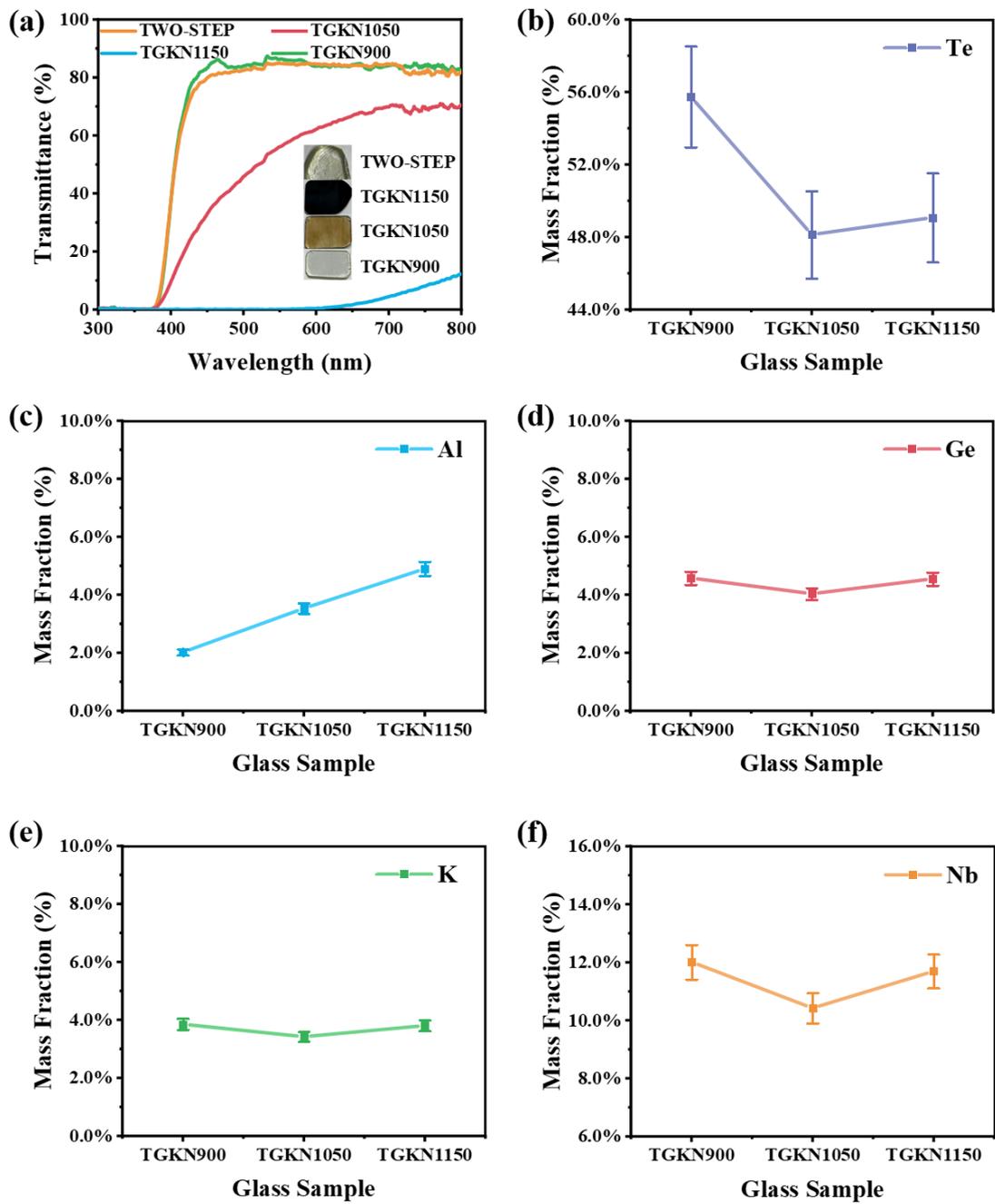


Figure 2 Transmittance spectra (a), ICP-OES data of TGKN series glasses (b-f)

Since elements evaporate during the melting process, it was necessary to check if this evaporation process had anything to do with the color-changing in glasses. The elemental profiling of the TGKN series glasses was performed by ICP-OES, as shown in Figure 1b-f. These figures show that all the elements (Te, Ge, K, and Nb) firstly decrease and then increase with the increasing melting temperature. In TGKN900, TGKN1050, and TGKN1150, the mass percent concentration of Te element is 56 %, 48 %, and 50 % respectively. Considering the experiment accuracy, the changes of Ge, K, and Nb are hardly negligible compared to the changes of the Te element. At the same time, the mass percent concentration of the Al element keeps increasing

with the increasing melting temperature because the reaction between the alumina crucible and the TGKN glass melt benefits from a higher melting temperature. However, Te evaporation is not able to explain the color change on the unique basis of the mass Te concentration change between samples TGKN1050 and TGKN1150. In order to investigate the association between color-changing and evaporation processes, some experiments have been done. Firstly, the TGKN1150 glass was re-melted at 900 °C, and the glass becomes slightly yellow. Besides, the glass synthesized by a two-step process (1150 °C for 30 min, then 900 °C for 10 min) presenting slightly yellow, as shown in Figure 1. These results suggest that 1) the evaporation process is not the direct reason for the color-changing in these glasses; 2) the color-changing in these glasses seems to be associated with kinetic processes.

It has been noted that the formation of Te metal particles may decrease the transmittance of glass and may change the color of the glass [16]. In contrast, this could not explain the phenomena well in our work. The XRD patterns of all three samples are shown in Figure 3a. Unlike the previous work [16, 17], there is no prominent Te metal crystal signal peak, and only a broad halo characteristic of amorphous samples was observed [16]. In order to further confirm if the glass sample contains Te metal particles, the DSC of the TGKN glass samples was performed, as shown in Figure 3b. It provides that the TGKN900 and TGKN1150 samples show an endothermic deep at around 450 °C, which corresponds to the melting temperature of Te, giving sense to the presence of small quantities of metallic Te in these two glass samples. As a consequence, it clearly demonstrates that the color-changing is not entirely due to the presence of metallic Te. Although it is not exactly rigorous, some other tellurite glass systems, including $\text{TeO}_2\text{-ZnO-Na}_2\text{O}$, $\text{TeO}_2\text{-K}_2\text{O}$, and $\text{TeO}_2\text{-GeO}_2\text{-K}_2\text{O}$ were synthesized at different temperatures like the TGKN series of glasses to verify the above conclusion. Compared to TGKN series of glasses, the color of all these glass samples does not change with the different melting temperature. Therefore, the principal reason for the color-changing of TGKN series glasses has to be further discussed. In addition, the T_g of TGKN1150 is the highest among the TGKN series glasses, which

suggests that TGKN1150 has the highest polymerized glass network.

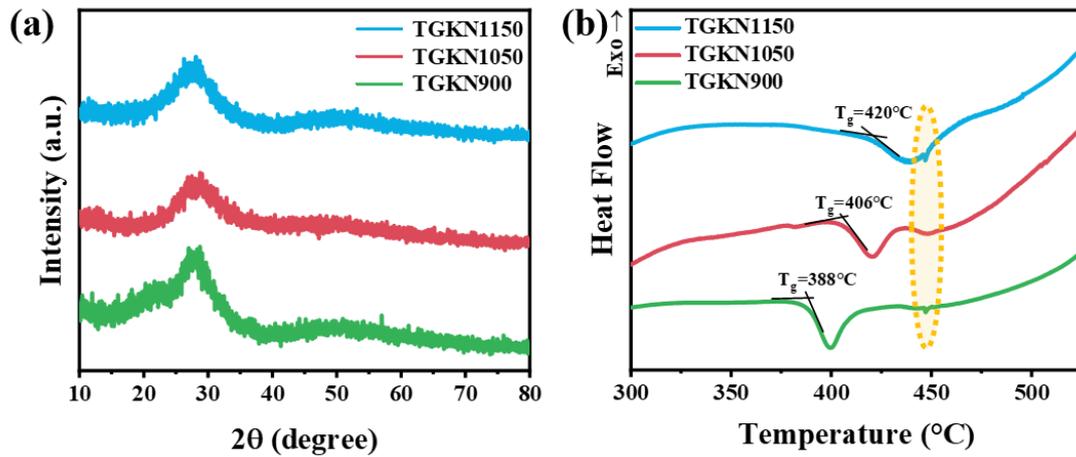


Figure 3 XRD pattern (a) and DSC curves (b) of TGKN series glasses

Niobium having various stable valence states, it can also be considered as responsible for this color-changing. Thus, the binary $\text{TeO}_2\text{-Nb}_2\text{O}_5$ glass systems were synthesized to investigate the influence of Nb on transmittance changes. It was found that the color of the binary $\text{TeO}_2\text{-Nb}_2\text{O}_5$ glass melted at different temperatures is different, which is similar to that of TGKN series glasses. Besides, the color of the glass becomes darker with increasing Nb_2O_5 content. Typically, the low valence states of niobium (Nb^{3+} or Nb^{4+}) presents deep color, whereas Nb^{5+} appears slightly yellow. However, in this work, all the glass samples were synthesized in an ambient environment at high temperatures, suggesting the glass during melting is under oxidative state, and niobium consequently tends to form Nb^{5+} . This was proved by the experiment of synthesizing TGKN glass samples utilizing NbO_2 as raw material. As shown in Figure 4a, the glass synthesized utilizing Nb_2O_5 as raw materials presents almost the same transmittance spectrum as the glass synthesized with NbO_2 .

X-ray photoelectron spectroscopy (XPS) has been found to be a helpful technique in estimating the ratio of the different valence states in a glass. In order to further investigate the valence state of Nb, the Nb 3d spin-orbit doublet spectra for the TGKN series glasses were done and are shown in Figure 3b. The position and the width of the Nb $3d_{5/2}$ and Nb $3d_{3/2}$ peaks hardly changed with the increasing melting temperature, which indicates that the valence state of niobium ions probably does not change in all TGKN series glass samples.

Besides, it was found the Nb 3d core-level spectra of TGKN series glass samples only can be fitted with two spin-orbit doublets related to Nb⁵⁺ and Nb⁴⁺ oxidation states of niobium ions [25, 26] respectively, as shown in Figure 4 c-e. It suggests that no Nb³⁺ or even lower oxidation states of niobium are present in these glass samples. Therefore, considering Nb⁵⁺ and Nb⁴⁺ presents slight yellow and blue color, respectively, it is assumed that the valence states of Nb are not responsible for the color-changing (darken) of TGKN series glasses either.

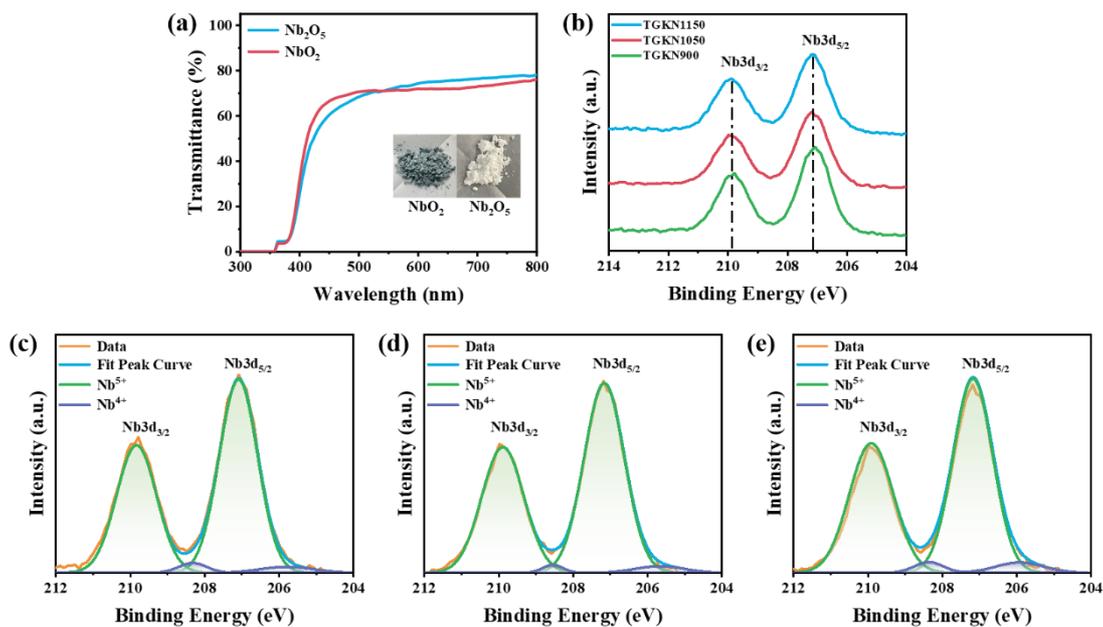


Figure 4 (a) Transmittance spectra of TGKN series glasses utilizing different niobium oxides as raw materials and digital photos of niobium oxides; (b) Nb 3d core-level spectra for the TGKN series glasses; Nb 3d core-level fitted with Nb⁵⁺ and Nb⁴⁺ peaks for TGKN900 (c), TGKN1050 (d), and TGKN1150 (e)

Thus, to find out the principal reason for the color-changing, the structure of the TGKN series glass was studied. XPS is also a useful technique in assessing the local glass structure [17]. The full spectra of the TGKN series glasses are shown in Figure 5a, and the atomic orbitals of each element are visible. No other elements except Al which comes from the Al₂O₃ crucible were observed in the spectrum of TGKN glass series, which is consistent with the ICP-OES result, as shown in the inset in Figure 5a.

The 3d spin-orbit doublet spectra for the TGKN series glasses are shown in Figure 5b. Figure 5b displays that the peak positions of Te 3d shift to higher energy with increasing melting temperature. Normally, the

conversion from $[\text{TeO}_3]$ to $[\text{TeO}_4]$ configuration may be responsible for this chemical shift. However, this is not consistent with the ICP-OES result that the content of Te in TGKN900 is highest among all the TGKN series glasses, which means TGKN900 should have the most $[\text{TeO}_4]$ configurations. Considering the change of the binding energy of Ge 3d in TGKN series glasses is neglectable, as shown in Figure 5c, these results suggest that more Te-O- configurations may convert into Te-O-X configurations (X= Al or Nb). Besides, the O1s core-level spectra can always provide information to confirm this interpretation, as shown in Figure 5d. A slight asymmetry is observed on the higher binding energy side of the prominent peak, having an average value of ~ 530.5 eV. This peak is also fitted with two contributions, as shown in Figure 5e-5f, one due to oxygen atoms in a bridging environment (BO) and the other due to oxygen atoms in a non-bridging environment (NBO) [17, 27, 28]. Obviously, TGKN1050 and TGKN1150 contain more BOs, and this is consistent with the conversion from Te-O- to Te-O-X configurations that can increase BO.

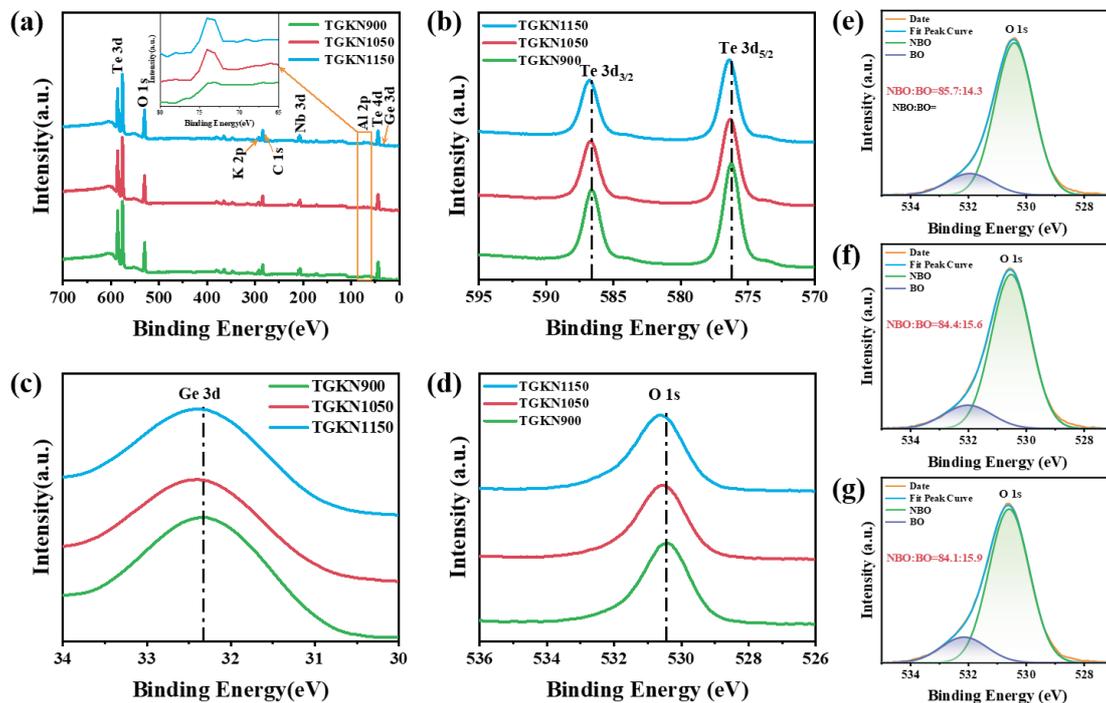


Figure 5 XPS diagrams of TGKN series glasses and different element orbitals: (a) full spectrum; (b) Te 3d core-level; (c) Ge 3d core-level; (d) O1s core-level; O1s core-level fitted with BO and NBO for TGKN900 (e), TGKN1050 (f) and TGKN1150 (g)

Raman spectroscopy is another effective method to investigate the structure of the glass. Figure 6a

displays the Raman spectra of TGKN series glasses, and Figure 6b illustrates the deconvoluted Raman spectra of the TGKN900 glass sample. The spectrum is normalized and superimposed. The broad peaks are deconvoluted into five peaks using Gaussian distribution to distinguish the exact mode of vibrations. The bands are peaked at ~ 460 , ~ 590 , ~ 680 , ~ 780 , and ~ 891 cm^{-1} . The observed first intense at ~ 460 cm^{-1} is due to the symmetric vibration of Te-O-Te, Te-O-Ge and/or Ge-O-Ge linkages.

According to the report [20], the ~ 590 cm^{-1} weak band could be assigned to the presence of GeO_6 octahedra or Nb-O-Ge linkages or NbO_6 octahedra. Notably, previous studies also point that the low-frequency side should of the ~ 590 cm^{-1} band is associated with NbO_6 octahedra [29, 30]. From Figure 6 b-d, it can be found that the band shifts from 601 cm^{-1} in TGKN900, to 596 cm^{-1} in TGKN1050, to 587 cm^{-1} in TGKN1150, respectively. Combining the XPS analysis, this indicates the vibration intensity of NbO_6 octahedra which commonly acts as glass modifiers becomes more intense in TGKN1050 and TGKN1150.

The ~ 680 and ~ 780 cm^{-1} intense band is assigned to the vibration of $[\text{TeO}_4]$ and $[\text{TeO}_3]$, respectively [31, 32]. It is worth mentioning that both ~ 680 cm^{-1} and ~ 780 cm^{-1} bands shift to higher frequency regions. The ~ 680 cm^{-1} band shifts from 668 cm^{-1} in TGKN900, to 680 cm^{-1} in TGKN1050, to 695 cm^{-1} in TGKN1150, respectively. The ~ 780 cm^{-1} band shifts from 762 cm^{-1} in TGKN900, to 781 cm^{-1} in TGKN1050, to 797 cm^{-1} in TGKN1150, respectively. Meanwhile, the FWHM of ~ 680 cm^{-1} band of TGKN900, TGKN1050, and TGKN1150 are 84 , 101 , 110 cm^{-1} , respectively, whereas the FWHM at ~ 780 cm^{-1} band of the corresponding glass are 139 , 117 , 98 cm^{-1} , respectively. This indicates that the $[\text{TeO}_3]$ configuration tends to convert to $[\text{TeO}_4]$ configuration in TGKN1050 and TGKN1150, which is consistent with the result of XPS.

Normally, the ~ 891 cm^{-1} band can be attributed to the presence of NBOs and Al-O vibrations. The FWHM at ~ 891 cm^{-1} band of TGKN900, TGKN1050 and TGKN1150 are 65 , 81 , 89 cm^{-1} . Since the XPS results indicate that NBOs decrease with increasing melting temperature, it is reasonable to assign the change of FWHM to the presence of Al-O vibrations. According to the literature, compared to Nb_2O_5 , Al_2O_3 may be

more likely to incorporate into the TeO_2 -rich glass network. Thus, combining the XPS and Raman spectrum, it can be speculated that Al may incorporate into the tellurium glass network through connecting $[\text{TeO}_3]$ configuration or replacing Nb in the glassy network, and the former increases the BO contents, while the latter induce the formation of Nb-O contents.

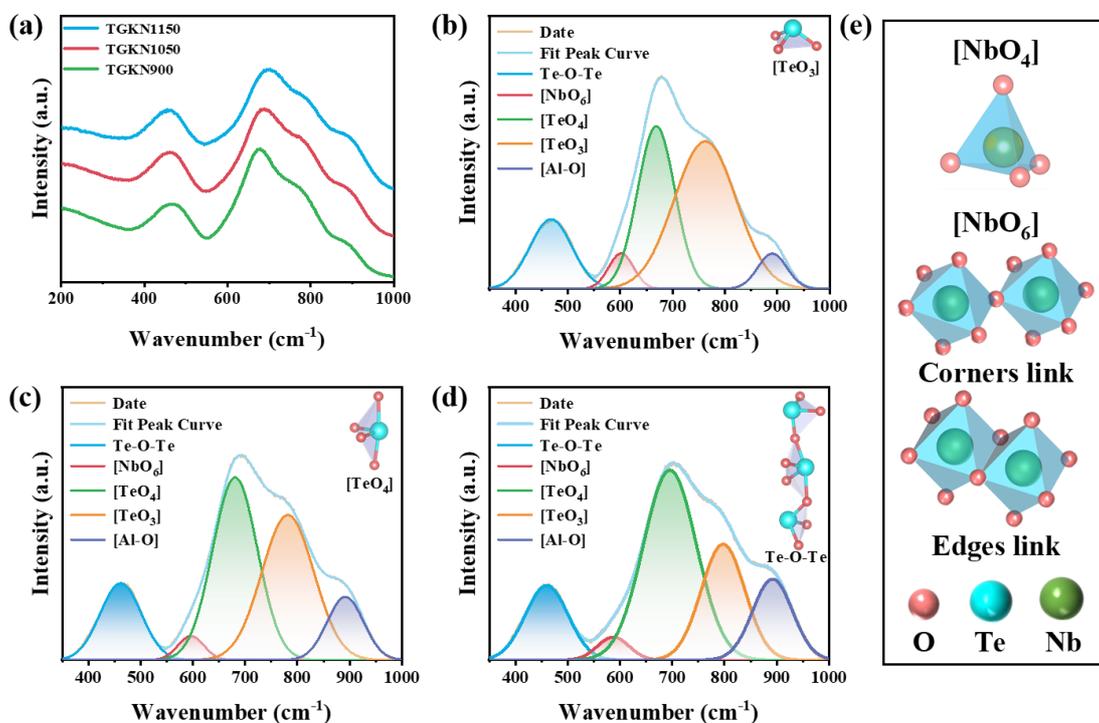


Figure 6 Raman spectra of TGKN of glass series (a); Gaussian peak deconvolution of the Raman spectra obtained for TGKN900(b), TGKN1050(c), TGKN1150(d), (e) schematic illustration for the possible connection among Nb_2O_5

Previous studies demonstrate a more ordered/crystalline Nb-rich region ($\sim 1\text{-}2$ nm) could evolve in the elastic softening period [33, 34]. Notably, the T- Nb_2O_5 (orthorhombic structure) consists of 4×4 blocks of corner-shared NbO_6 octahedra, with connected blocks sharing the octahedron edges that could induce the absorption of visible light [35]. The report [35] illustrates the bandgap of T- Nb_2O_5 is around 2.08 eV, which is close to the cut-off absorption edge of TGKN1150, as shown in Figure 2a. Nb_2O_5 is classified as an intermediate oxide and can act as a network former in the form of $[\text{NbO}_4]$ tetrahedron or a network modifier in the form of $[\text{NbO}_6]$ octahedra [36]. Therefore, Nb_2O_5 are possibly be linked through faces or edges when they act as $[\text{NbO}_6]$ octahedra, as shown in Figure 6e. Consequently, the T- Nb_2O_5 type Nb-O clusters can be

formed. Considering that the formation of T-Nb₂O₅ depends on the temperature (600-800 °C) [35], the longer the glass melt is in the corresponding time, the more T-Nb₂O₅ clusters may be formed in the glass. It just well explains the phenomenon observed in this work. TGNK1150 has the highest pouring temperature among the TGNK series glasses and consequently has the longest time during 600-800 °C. Thus, TGNK1150 may contain the most T-Nb₂O₅ clusters causing the most drastic color-changing phenomenon among TGNK series glasses. This speculation also explains why the color-changing in TGKN series glasses is associated with kinetic processes. However, more specific and direct evidence is needed to confirm the formation of T-Nb₂O₅, and further studies of these Nb-O clusters are in progress. However, more specific and direct evidence is required to confirm the formation of T-Nb₂O₅, and further studies of these Nb-O clusters are in progress.

4. Conclusion

The glasses with the molar composition of 70TeO₂-10GeO₂-10K₂O-10Nb₂O₅ were synthesized by conventional melt-quenching at different melting temperatures. It is found that these glasses present different colors, and the glasses melted at higher temperature show darker colors than those melted at low temperature. The glass composition was revealed by ICP-OES. The XRD pattern and DSC curves suggest that this color-changing is not due to the formation of Te metal particles. The Nb 3d core-level spectra indicate no Nb³⁺ or even low valence states of Nb in the TGKN series glasses. The structure of the TGKN glasses was analyzed by XPS and Raman spectra. ICP-OES and XPS full spectrum suggest that the Al was incorporated into the glass matrix. Both the Te 3d core-level XPS spectra and Raman spectra illustrate that the [TeO₃] configuration tends to convert to [TeO₄] configuration with increasing melting temperature. It can be speculated that Al incorporate into the tellurium glass network through connecting [TeO₃] configuration or replacing Nb in the glassy network, and the former increases the BO contents, while the latter induces the formation of Nb-O clusters. The transmittance spectra indicate that these Nb-O clusters can form T-Nb₂O₅ by being linked by faces or edges, inducing the color-changing. Further study for these Nb-O clusters in glasses is on-going.

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Notes

The authors declare no competing financial interest.

Author contribution statement:

Panyi Wang: Investigation, Writing - original draft.

Yingying Cui: Investigation, Validation.

Senlong Zhao: DSC analysis.

Renguang Ye: Formal analysis, Validation

Muzhi CAI: Writing - review & editing, Formal analysis, Validation.

Laurent Calvez: Formal analysis, Validation.

Jean Rocherulle: Formal analysis, Validation.

Feifei Huang: Formal analysis.

Hongli Ma: Formal analysis, Validation.

Gongxun Bai: Raman analysis, Formal analysis, Validation.

Junjie Zhang: Formal analysis, Validation.

Shiqing Xu: Formal analysis, Validation, Project administration.

Xianghua Zhang: Formal analysis, Project administration.

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