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Crystallization of TeO_2–Nb_2O_5 glasses and their network structural evolution

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TeO_2–Nb_2O_5 glass is a kind of heavy metal oxide glass with a chain-like network structure, in which Nb^{5+} ions connect the Te–O chains and adjust the types of [TeO_x] (x = 3, 4) coordination polyhedra to stabilize the glass network. (100 – y)TeO_2–yNb_2O_5 (y = 3–20 mol %) glasses were prepared, the crystallization behaviour and their network structural evolution were studied by means of differential thermal analysis (DTA), X-ray diffraction (XRD) and Fourier transform infrared spectra (FT-IR). The results show that the stabilization of the TeO_2–Nb_2O_5 glass network is greatly influenced by the constitution of Te–O chains and their linkage. The glass structure with lower Nb^{5+} content is inhomogeneous, it is composed of edge sharing Te–O chains, partly edge sharing chains connected by Nb^{5+} ions, apical sharing chains and apical sharing chains connected by Nb^{5+} ions. Crystalline phases of β-TeO_2, $Nb_2Te_4O_{13}$, α-TeO_2 and $Te_3Nb_2O_{11}$ will be formed in turn when the treatment temperature of the glass is increased. When the concentration of Nb^{5+} ions is sufficient to well connect Te–O chains, the glass network will tend to homogenize, only one crystalline phase, $Nb_2Te_4O_{13}$, will be formed. A suitable preheat treatment will also help to homogenize the glass structure and make the glass more stable.

Key words: *glass; tellurite; niobium; crystallization; network structure*

1. Introduction

Tellurite glass is a kind of heavy metal oxide glass with such properties as high refractive index and the third order nonlinear optical property, wide optical window and low phonon energy[1–4]. However, the structure of pure TeO_2 glass is unstable because of its lack of linkage between Te–O chains. Some of the modifier ions such as niobium, zinc, lead and alkali ions, have to be introduced into tellurite glass to improve the linkage between Te–O chains and to connect Te–O chains for stabilizing the glass network [5–8].

Niobium oxide is also a kind of heavy metal oxide with high molecular refractivity and optical nonlinearity. When the Nb^{5+} ions are introduced into the tellurite glass

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network, they not only connect Te–O chains for stabilizing the glass structure, but also provide some oxygen ions for changing tellurium–oxide coordination polyhedra. As the result, the third order nonlinear optical property of the glass is improved [9]. The stabilization of niobium tellurite glasses and their optical properties are greatly influenced by the composition and network structure of the glasses [10–13]. Therefore, it is important to elucidate details of the structure of Te–O chains and their linkage, for improving the stability of the TeO_2–Nb_2O_5 glasses.

Glasses are ordered in short range and disordered in long range, the short-range structure of the glass is close to that of corresponding crystalline phase. Therefore, the crystallization behaviour of the glasses reflects each short range structure of the glass network. The objective of the present work was to study the crystallization behaviour of TeO_2–Nb_2O_5 glasses by means of DTA, XRD and FTIR, hence deducing the evolution of the glass network structure during crystallization.

2. Experimental

$(100 - x)TeO_2$–xNb_2O_5 (mol %, x = 3–20) glasses were prepared using optical grade TeO_2 and Nb_2O_5 crystalline powders. Well-mixed batches of crystalline raw materials were melted between 750 and 850 °C for 15–20 min in a gold crucible in air. The melt was then cast on cold stainless steel plate. The glass sample was milled for DTA, XRD and FTIR analyses. Some of the glass powders were pretreated between 380 and 560 °C for 10–180 min and then cooled at room temperature.

Thermal properties of the glasses were studied with a Perkin-Elmer DTA-7 device. About 45 to 50 mg of the pretreated glass powder was put in a platinum cup and heated at the rate of 10 °C/min. Crystalline phases in the glasses after heat treatment were analyzed with a D/max-B rotating anode X-ray diffractometer with a CuK_α radiation source. The network structure of the glasses before crystallization was studied with a Equinox 55 FT-IR spectrometer.

3. Results and Discussion

3.1. The network structure of the TeO_2–Nb_2O_5 glasses

The TeO_2–Nb_2O_5 glass belongs to heavy metal oxide glasses with complex structure. [TeO_4] trigonal bipyramids (tbp) and the [TeO_3] trigonal pyramids (bp) link each other to form Te–O chains [14, 15]. Nb^{5+} ions in the glass exist as [NbO_6] octahedra to link the Te–O chains [7]. The melting experiment shows that the TeO_2–Nb_2O_5 glasses were transparent and kept for long period of time when the Nb_2O_5 content was from 2 to 20 mol %.

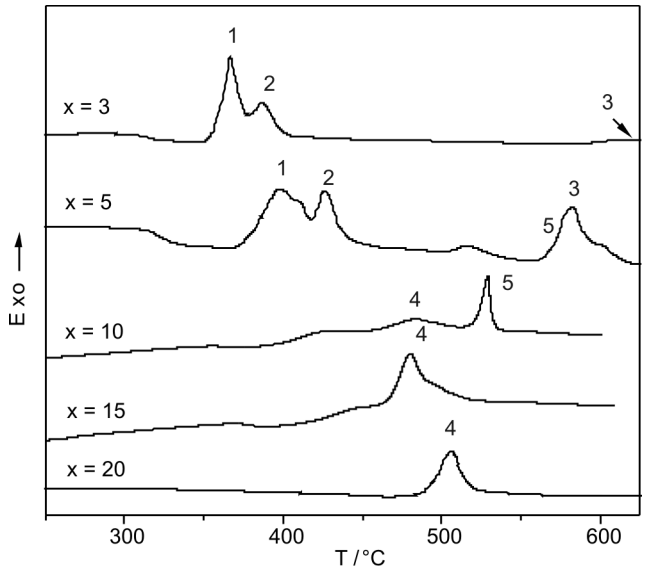

Fig. 1. DTA curves of $(100 - x)TeO_2$–xNb_2O_5 glasses and exothermic peaks corresponding to precipitated crystalline phases: 1 – β-TeO_2(I), 2 – β-TeO_2(II), 3 – α-TeO_2, 4 – $Nb_2Te_4O_{13}$, 5 – $Te_3Nb_2O_{11}$

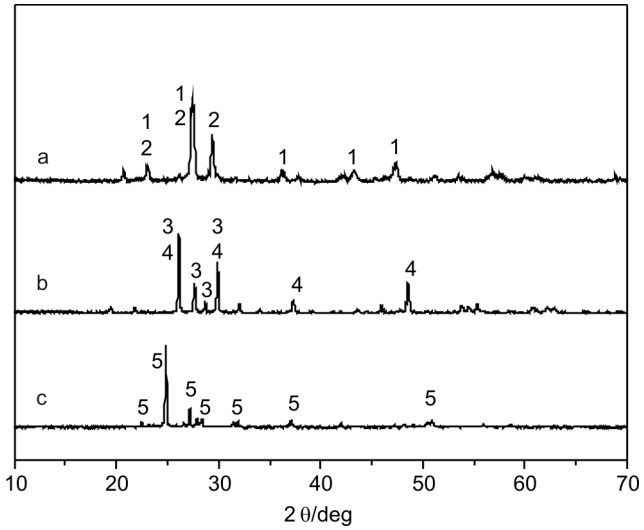

Fig. 2. XRD spectra of $(100 - x)TeO_2$–xNb_2O_5 glasses after heat treatment; curves: a – x = 3, 395 °C, 180 min, b – x = 3, 555 °C, 180 min, c – x = 15, 505 °C, 180 min; 1 – β-TeO_2 (750 882), 2 – β-TeO_2 (090 433), 3 – α-TeO_2 (410945), 4 – $Te_3Nb_2O_{11}$, 5 – $Nb_2Te_4O_{13}$

The DTA patterns of TeO_2–Nb_2O_5 glasses are shown in Fig 1. It was found that the crystallization behaviour of the glasses changed greatly when introducing Nb_2O_5 as the second component. When the Nb_2O_5 content in the glass was 3 mol %, three

kinds of exothermic peaks appeared in the DTA curve for the glass. Some of the XRD results are shown in Fig. 2, they confirm that the β-TeO_2 phase was formed at 350 °C and 380 °C, then a little of α-TeO_2 phase appeared at 620 °C. When the Nb_2O_5 content was 5 mol %, the first exothermic peak was weaker and shifted to higher temperature, and the third one was strengthened and moved to lower temperature. The XRD analysis shows that the $Te_3Nb_2O_{11}$ phase was obtained near 565 °C instead of α-TeO_2. The exothermic peaks in the DTA patterns continued to approach each other when the Nb_2O_5 content was increased, while the $Nb_2Te_4O_{13}$ phase began to be obtained instead of $Te_3Nb_2O_{11}$ and β-TeO_2. When the Nb_2O_5 content was increased to 15 mol%, the exothermic peaks appeared at 465 °C, and the precipitated crystals gradually changed to only one crystalline phase of $Nb_2Te_4O_{13}$.

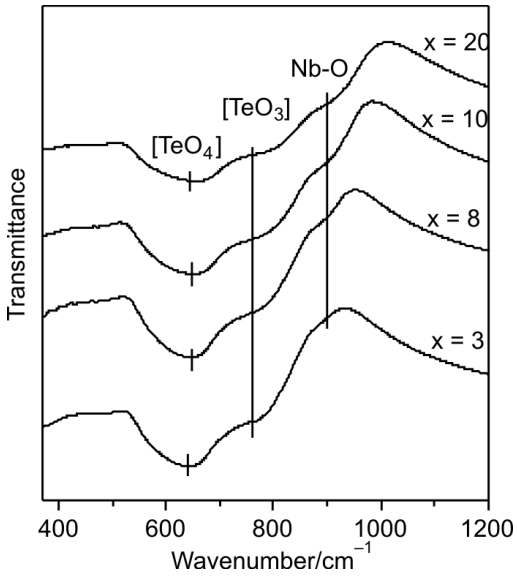

Fig. 3. FT-IR spectra of $(100 - x)TeO_2$–xNb_2O_5 glasses

The FT-IR spectra of the TeO_2–Nb_2O_5 glasses are shown in Fig 3. The band at 638–652cm^{-1} was assigned to [TeO_4] tbps. It slightly shifted to higher frequencies when the Nb_2O_5 content was increased. The shoulder at 760 cm^{-1}, which belonged to [TeO_3] bps, was improved with increasing Nb_2O_5 content. The band at 900 cm^{-1} was assigned to the vibration of Nb–O bonding, though its origin from [NbO_6] or [NbO_4] groups was in dispute [10, 16]. The absorption coefficient ratio of the [TeO_4] and the [TeO_3], and the absorption coefficient of the Nb–O band are shown in Fig. 4. The ratio of [TeO_4]/[TeO_3] decreased with increasing Nb_2O_5 content, accompanied with increasing content of Nb–O groups. It can be concluded that the introduced Nb_2O_5 changes some of [TeO_4] tbps into [TeO_3] bps, while the Nb^{5+} ions connect Te–O chains as [NbO_6] octahedra.

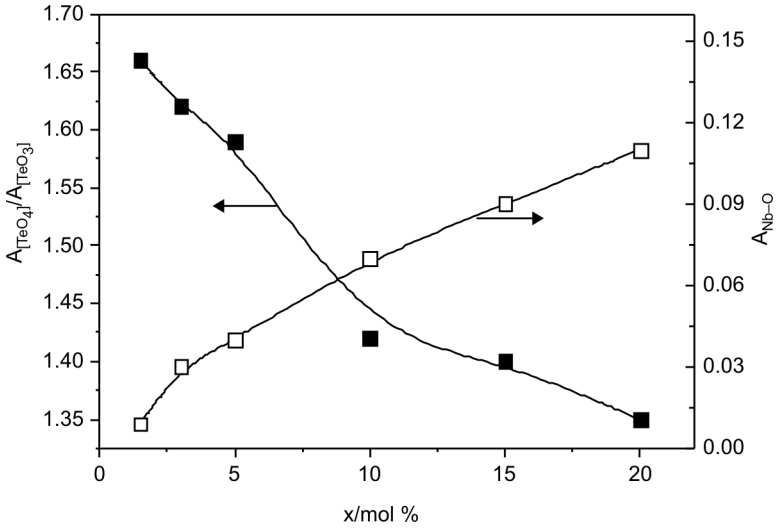

Fig. 4. The absorption coefficient of coordination polyhedra and their ratio in $(100 - x)TeO_2$–xNb_2O_5 glasses

The network structure of the TeO_2–Nb_2O_5 glasses changes with the content of Nb^{5+} ions. When the Nb_2O_5 content is lower, most of Te^{4+} ions exist as $[TeO_4]$ tbps and form Te–O chains, the $[TeO_4]$ tbps link each other both in apical sharing and in edge sharing, only a few of $[TeO_3]$ bps exist in the glass network. The Nb^{5+} ions exist as $[NbO_6]$ octahedra to link the chains as shown in Fig 5. Due to insufficient linkage of the Te–O chains because of insufficient amount of Nb^{5+} ions in the TeO_2–Nb_2O_5 glass, the glass network easier loses its stability. Therefore, the metastable edge-sharing $[TeO_4]$ tbps will first form edge-sharing β-TeO_2 phase at lower temperature. The apical-sharing $[TeO_4]$ tbps are more stable than the edge-sharing ones, they will form α-TeO_2 phase with similar structure at higher temperatures. Te–O chains connected with Nb^{5+} ions are more stable, they will form $Te_3Nb_2O_{11}$ phase with apical-sharing structure [17] at much higher temperatures.

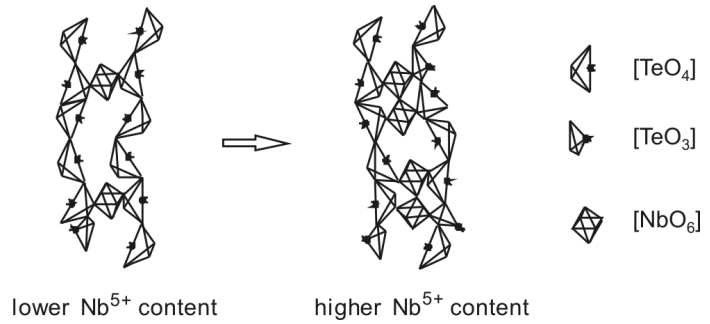

Fig. 5. Schematic diagram of the TeO_2–Nb_2O_5 glass network

When the Nb_2O_5 content in the glass is increased, more and more Nb^{5+} ions will connect Te–O chains as [NbO_6] octahedra, just like the [NbO_6] octahedral chain between [TeO_4] tbp chains in the $Nb_2Te_4O_{13}$ crystal, in which some of the polyhedra are linked by edge sharing [18]. The introduced Nb_2O_5 will also provide oxygen ions to change more [TeO_4] tbps into [TeO_3] bps. It seems that the glass network is strengthened by enhancing the linkage of Te–O chains. The tellurite network will also come to homogenization, because of uniform distribution of Nb^{5+} ions among the Te–O chains, though some of the tellurium-oxide polyhedra still link each other in edge sharing. Therefore, the precipitated crystals will contain only one crystalline phase, such as $Nb_2Te_4O_{13}$ phase.

3.2. The structural evolution of the TeO_2–Nb_2O_5 glasses under preheat treatment

The heat treatment will also affect the network structure of the TeO_2–Nb_2O_5 glasses. The DTA curves of the $90TeO_2$–$10Nb_2O_5$ glass after preheat treatment at 470 °C for various times are shown in Fig 6. Three kinds of crystallization peaks were found, which belonged to the crystalline phase of β-TeO_2, $Nb_2Te_4O_{13}$ and $Te_3Nb_2O_{11}$. This means that the glass structure consists of three kinds of Te–O chains: partly edge-sharing [TeO_4] chains, partly edge-sharing [TeO_4] chains connected by Nb^{5+} ions and apical-sharing [TeO_4] chains connected by Nb^{5+} ions. When the glass was preheat treated at 470 °C, some of the crystals were nucleated or formed from the glass before DTA analysis, it resulted in weakening crystallization peaks and in the fall of crystallization temperature in DTA patterns.

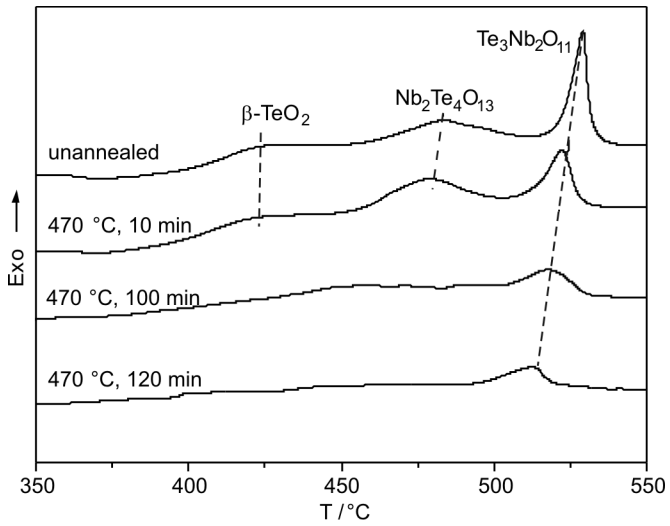

Fig. 6. DTA curves of the $90TeO_2$–$10Nb_2O_5$ glass after heat pretreatment

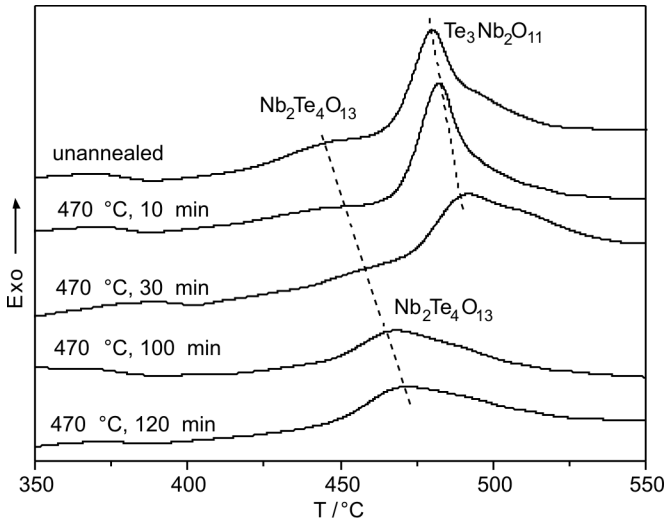

Fig. 7. DTA curves of the $85TeO_2$–$15Nb_2O_5$ glass after heat pretreatment

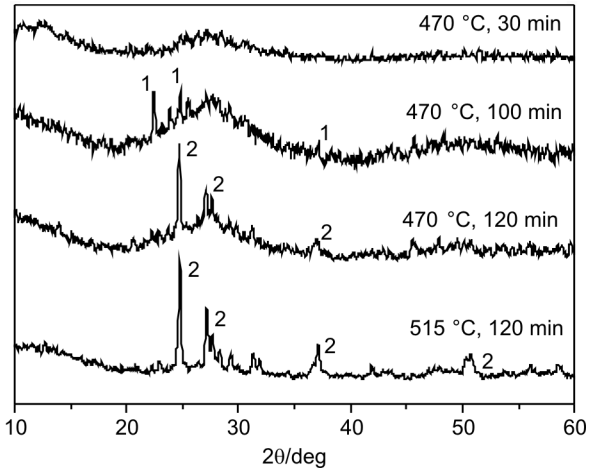

Fig. 8. XRD spectra of the $85TeO_2$–$15Nb_2O_5$ glass after heat pretreatment

The crystallization characteristic of the $85TeO_2$–$15Nb_2O_5$ glass is different from that of the $90TeO_2$–$10Nb_2O_5$ glass. The DTA curves of the $85TeO_2$–$15Nb_2O_5$ glass after pretreating at 470 °C are shown in Fig 7. The exothermic peak, attributed to β-TeO_2, disappeared. The first peak from $Nb_2Te_4O_{13}$ was strengthened and shifted towards higher temperatures at a prolonged pretreatment time, while the peak from $Te_3Nb_2O_{11}$ was weakened and shifted to higher temperatures as well. The XRD spectra of the $85TeO_2$–$15Nb_2O_5$ glass under various heat treatment conditions are shown in Fig 8. When the glass was heat treated at 470 °C for 30 min, no crystals were found. If the pretreatment time was extended to 100 min, the $Te_3Nb_2O_{11}$ phase was formed. When the pretreatment time was prolonged to 120 min, the crystalline phase was

changed into $Nb_2Te_4O_{13}$. It can be concluded that $Nb_2Te_4O_{13}$ will first be formed from partly edge-sharing [TeO_4] chains connected by Nb^{5+} ions, and then $Te_3Nb_2O_{11}$ from apical sharing [TeO_4] chains connected by Nb^{5+} ions. If the number of Nb^{5+} ions in the glass is sufficient to well connect Te–O chains, the crystalline phase of TeO_2 will not be formed from the glass without cooperation of Nb^{5+} ions. It seems that the preheat treatment at 470 °C would homogenize the network structure of $85TeO_2$ $–15Nb_2O_5$ glass and make the glass more stable.

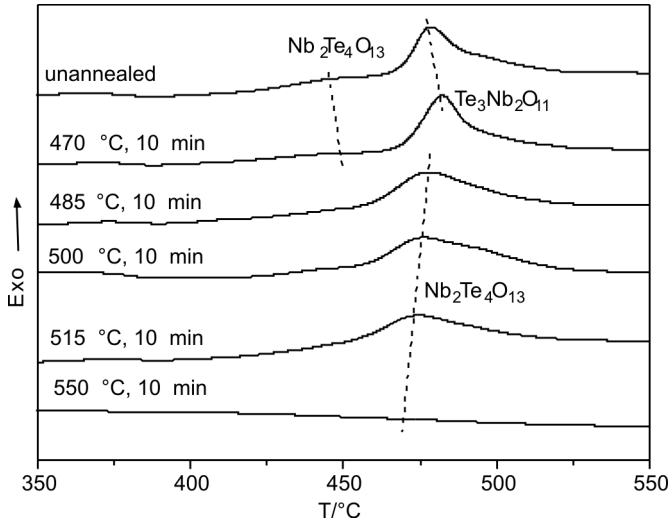

Fig. 9. DTA curves of the $85TeO_2$–$15Nb_2O_5$ glass after heat pretreatment

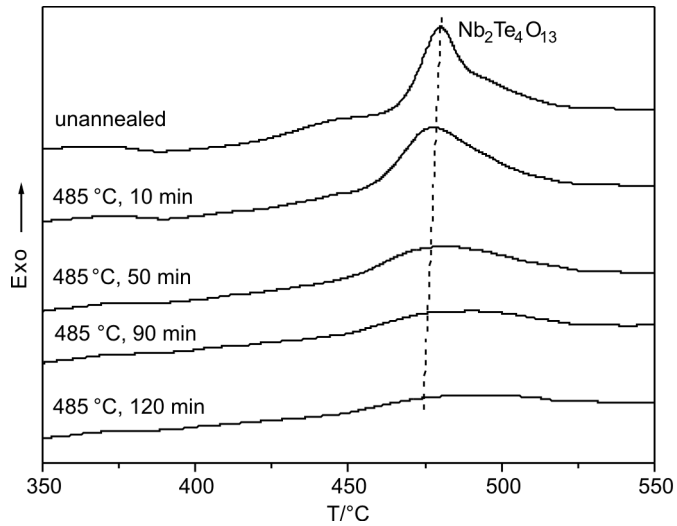

Fig. 10. DTA curves of the $85TeO_2$–$15Nb_2O_5$ glass after heat pretreatment

The effect of pretreatment temperature on the DTA curves for $85TeO_2$–$15Nb_2O_5$ glass is shown in Fig. 9. The exothermic peaks attributed to the crystalline phase of $Te_3Nb_2O_{11}$ and $Nb_2Te_4O_{13}$ shift to higher temperatures. When the pretreatment temperature is increased to 485 °C, the crystallization peaks merge into one peak attributed to the $Nb_2Te_4O_{13}$ phase, and then this peak shifts to lower temperature with increasing pretreatment temperature. The influence of the pretreatment time on the DTA patterns at 485 °C is shown in Fig 10. The crystallization peak was weakened and shifted towards lower temperatures with the increasing pretreatment time. This means that a suitable heat pretreatment will homogenize the glass network structure and make it more stable. However, the overheat treatment will result in partial nucleation and crystallization in preheat treatment and make the glass structure less stable.

4. Conclusions

The network structure of the TeO_2–Nb_2O_5 glasses consists of Te–O chains, most of $[TeO_4]$ tbps connect each other in apical sharing, whereas a few of $[TeO_4]$ tbps link in edge sharing. When Nb_2O_5 is introduced into the glass network, it provides oxygen ions to change some of $[TeO_4]$ tbps into $[TeO_3]$ bps, and the introduced Nb^{5+} ions connect the Te–O chains. The insufficient linkage between Te–O chains results in an inhomogeneous tellurite glass network. The glass will lose its stability in the edge-sharing Te–O chains during heat treatment at first, and then in the partly edge-sharing chains connect by Nb^{5+} ions, and at last in the apical-sharing Te–O chains.

When the Nb_2O_5 content in the glass is increased, more and more Nb^{5+} ions will connect Te–O chains. The introduced oxygen ions from Nb_2O_5 will also increase the content of $[TeO_3]$ bps, while the edge-sharing pyramids still exist in the glass structure. The sufficient number of Nb^{5+} ions will connect the Te–O chains, homogenize the glass network, and increase the structure stability. The structural evolution results in only one crystalline phase of $Nb_2Te_4O_{13}$ representing the partly edge-sharing Te–O chains connected by Nb^{5+} ions, being formed during heat treatment. Furthermore, a suitable preheat treatment at 470 °C will help in homogenization of the glass structure.

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