International Journal of Minerals, Metallurgy and Materials
Volume 19, Number 7, July 2012, Page 628
DOI: 10.1007/s12613-012-0605-3

Structure of V_2O_5-P_2O_5-Sb_2O_3-Bi_2O_3 glass

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(Received: 26 October 2011; revised: 17 February 2012; accepted: 22 February 2012)

Abstract: The structure of V_2O_5-P_2O_5-Sb_2O_3-Bi_2O_3 glass and its state of crystallization were studied by means of infrared spectroscopy and X-ray diffraction analysis. The results indicate that, in this glass, V and P exist mainly in the form of a single-stranded linear $(VO_3)_n$ and an isolated (PO_4) tetrahedral with no double bond. Partial V and P are connected through O, forming an amorphous structure of layered vanadium phosphate. Trivalent Sb^{3+} and Bi^{3+} open the V=O bond and appear in interlayers, so a weak three-dimensional structure is connected successfully. Along with the substitution of Sb_2O_3 for partial V_2O_5 or that of P_2O_5 for partial V_2O_5, the network structure of the glass is reinforced, and the crystallization is reduced.

Keywords: glass; structure; sealing; vanadium pentoxide; phosphorus pentoxide; antimonous oxide; bismuth trioxide

1. Introduction

The global market witnessed a surge in the demand of plasma display panel (PDP) TV sets in 2010 to reach 19 million of units, a 28% up compared to that in 2009, and the total sales amount hit \$4.9 billion. At some key markets of PDP TV, especially in North America, sales have attained a substantial growth due to its superior price (dollar per inch) in comparison with that of liquid crystal display (LCD) TV. For years, conventional lead glass has been used as a kind of sealing materials for PDP display panels because of its outstanding low-temperature softening properties and excellent chemical stability. However, nowadays, it is limited to use due to the toxic PbO issue. Therefore, it has been urged to develop a Pb-free sealing material with low transition temperature (T_g) and low soften temperature (T_s) to replace lead glass. At present, bismuthate glass [1] is the main kind of Pb-free sealing materials for PDP, while vanadate glass and phosphate glass have not obtained any application in the PDP field. Vanadate and phosphate glasses have superiorities in terms of melting at a lower temperature, low price, and Pb-free, which encourage people to study them as sealing materials. The question is that how to get them commercialized by complicated melting technology.

The structure and crystallization condition of V_2O_5-P_2O_5-Sb_2O_3-Bi_2O_3 system glass was studied in this paper to provide some experimental data for developing Pb-free sealing materials with low melting point for PDP.

2. Experimental

2.1. Composition design

The ingredients of the raw glass material for preparing V_2O_5-P_2O_5-Sb_2O_3-Bi_2O_3 system glass were V_2O_5, P_2O_5, Sb_2O_3, and Bi_2O_3, and all were in analytical purity grade. First, a regular amount of P_2O_5 and Bi_2O_3 were set in the raw material; then, a part of V_2O_5 were replaced by Sb_2O_3 according to the following rates separately: 0mol%, 5mol%, 10mol%, 15mol%, and 20mol%, and those new glasses were named as 0% Sb_2O_3 glass, 5% Sb_2O_3 glass, 10% Sb_2O_3

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glass, 15% Sb_2O_3 glass, and 20% Sb_2O_3 glass, respectively. In the second series, a regular amount of Sb_2O_3 and Bi_2O_3 were set in the raw material; then, a part of V_2O_5 were replaced by P_2O_5 according to the following rates separately: 0mol%, 10mol%, 20mol%, 25mol%, 30mol%, 35mol%, and 40mol%, and those new glasses were named as 0% P_2O_5 glass, 10% P_2O_5 glass, 20% P_2O_5 glass, 25% P_2O_5 glass, 30% P_2O_5 glass, 35% P_2O_5 glass, and 40% P_2O_5 glass. The molar ratios of the ingredients for each sample are shown in Table 1 in detail.

Table 1. Ingredients of V_2O_5-P_2O_5-Sb_2O_3-Bi_2O_3 glass

No.	Name of glass	Compositions / mol%			
		V_2O_5	P_2O_5	Sb_2O_3	Bi_2O_3
1	20% Sb_2O_3	45	30	20	5
2	15% Sb_2O_3	50	30	15	5
3	10% Sb_2O_3	55	30	10	5
4	5% Sb_2O_3	60	30	5	5
5	0% Sb_2O_3	65	30	0	5
6	40% P_2O_5	45	40	10	5
7	35% P_2O_5	50	35	10	5
8	30% P_2O_5	55	30	10	5
9	25% P_2O_5	60	25	10	5
10	20% P_2O_5	65	20	10	5
11	10% P_2O_5	75	10	10	5
12	0% P_2O_5	85	0	10	5

2.2. Preparation

Each composition of the raw glass material was weighted accurately and well mixed in a dry glove box. Then, the mixed materials were melted in a high purity alumina crucible at 1200°C for 1 h. Next, the melting liquid was poured on a preheated stainless steel mold and then annealed in a muffle furnace at 350°C for 2 h. After cooled in the furnace, resultant glass samples were obtained and stored in a dried container for further characterization.

2.3. Characterization

The infrared (IR) absorption spectra were recorded by using a 750-FTIR spectrometer.

The crystalline phases of the glass samples were checked by using a BDX3200 X-ray diffractometer (XRD) running at 40 kV and 30 mA. After the glass was sealed at 460°C for 30 min and 490°C for 30 min, their crystallization status was tested.

3. Results and discussion

3.1. IR spectra research on the influence of glass composition on its structure

Owing to the strong volatility of P_2O_5, the exact glass composition varied from the designed composition during the melting process. Therefore, the discussion, under the existed conditions, about the influence of glass composition on the glass formation and its structure may have some errors. However, under a basic identical experimental condition, checking out the difference of the glass structures obtained from little different designed compositions would be meaningful to understand the formation mechanism and the structure of glass.

(1) Results of IR spectra analysis

In order to understand more clearly the effect of glass composition on the glass structure, the IR spectra analysis was carried out, and the results are shown in Figs. 1 and 2 and Table 2.

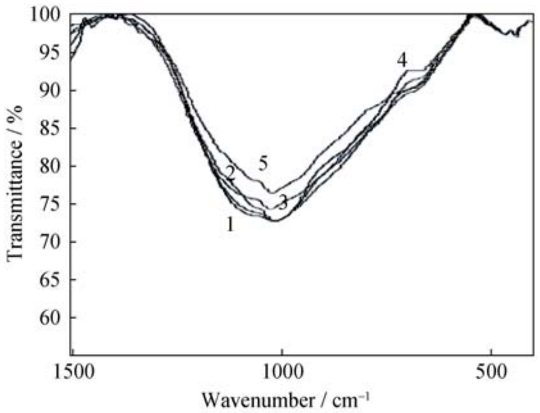

Fig. 1. IR spectra of glass samples with different amounts of Sb_2O_3 replacing V_2O_5 (1: 20% Sb_2O_3 glass; 2: 15% Sb_2O_3 glass; 3: 10% Sb_2O_3 glass; 4: 5% Sb_2O_3 glass; and 5: 0% Sb_2O_3 glass).

As shown in Figs. 1 and 2, all the glass samples exhibited obvious IR absorption bands in the range of 500-1500 cm^{-1}. Generally, vanadium in vanadium phosphate could form tetrahedron, tetragonal pyramid, trigonal bipyramid, or the octahedron coordination through the trivalent (+3), tetravalent (+4), or pentavalent (+5) oxidation states, which exhibit around 1010 cm^{-1} (V^{+5}=O) and 990 cm^{-1} (V^{+4}=O) absorption bands in the IR spectrum; however, V^{+3} could not form V=O coordination [4]. In Fig. 1, the 1004-1012 cm^{-1} absorption band denoted the existence of V^{+5}=O in glass samples. It meant partial vanadium was of pentavalent. This peak was coincidental with the dissymmetric stretching

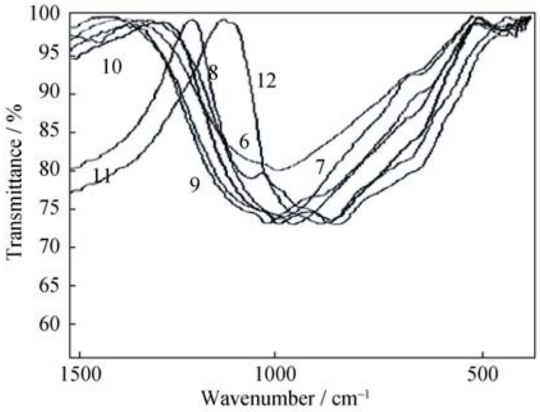

Fig. 2. IR spectra of glass samples with different amounts of P_2O_5 replacing V_2O_5 (6: 40% P_2O_5 glass; 7: 35% P_2O_5 glass; 8: 30% P_2O_5 glass; 9: 25% P_2O_5 glass; 10: 20% P_2O_5 glass; 11: 10% P_2O_5 glass; and 12: 0% P_2O_5 glass).

vibration F_2 (σ_3) of the [PO_4] tetrahedral. Along with P_2O_5 being replaced by V_2O_5, the peak got very weak, indicating that the content of V^{+5}=O in glass was scare. The presence of the weak absorption bands at 955 and 961 cm^{-1} denoted the existence of a small amount V^{+4}=O in glass samples, which meant that partial vanadium was of tetravalent state. The absorption band at 852-880 cm^{-1} could be assigned to the symmetric stretching vibration of VO_2 and VO_4, the deformation vibration of VO_2 in VO_4^{3-}, and the stretching vibration of VO_2 and VO_3. The 643 cm^{-1} absorption band could be ascribed to the synthetic vibration of a single chain in $(VO_3)_n$, 613 cm^{-1} to the stretching vibration of V–O–V, and the 420-421 cm^{-1} band to the bending vibration of VO_2 and VO_3 in glass. In this glass system, vanadium was the main host and provided the basic network. V_2O_5 in this glass was mainly in the form of the single chain of $(VO_3)_n$, the zigzag chain of $(V_2O_8)_n$, the branch of VO_4, the group of $V_2O_7^{4-}$, *etc.*, wherein both the single chain of $(VO_3)_n$ and the zigzag chain of $(V_2O_8)_n$ were dominant, and they determined the properties of the glass. After Sb_2O_3 and Bi_2O_3 were introduced into the system, the structure of the equilibrium intermediate state was broken, and the zigzag chain structure of $(V_2O_8)_n$ transformed into the single chain structure of $(VO_3)_n$.

Table 2. Corresponding vibrated models of different IR absorption peaks for glass samples

Vibrated model	Wavenumber / cm^{-1}	
	References	Measured data
Stretching vibration of P=O bond	1240-1270, 1320 [2]	—
Dissymmetric stretching vibration of [PO_4] tetrahedron	940, 1001, 1065 [3]	961, 1004-1012, 1063-1071
V^{+5}=O absorption band in trigonal bipyramid or octahedral coordination	1010 [4]	1004-1012
V^{+4}=O absorption band of tetragonal pyramid	990 [4]	955-961
Stretching vibration of P–O–P	766-775, 889-906 [5-9]	—
Symmetric stretching vibration of VO_2, VO_4, deformation vibration of VO_2 in VO_4^{3-}	831, 844, 887 [10]	852-880
Stretching vibration of VO_2, VO_3	820-956 [11]	852-880
Synthetic vibration of $(VO_3)_n$ single bond	646-698 [11]	643
Vibrational absorption of Bi–O$^-$	610 [3]	613
Antisymmetric stretching vibrations of bridge bond Sb–O–Sb of V'_3	605 [12]	
Stretching vibrations of V–O–V	574, 578, 620 [11]	613
Bending vibrations of P–O–P	506 [13]	
Bending vibrations of VO_2, VO_3	423-545 [11]	420-421
Bending vibrations of P–O bond in [PO_4] tetrahedron	514, 540 [3]	446-464, 551
Dissymmetric stretching vibration of Sb–O bond of V_3	465 [12]	446-464
Symmetric stretching vibration of Sb–O bond of V_1	400 [12]	397-400

(2) Analysis of the structure of glass

The fracture of P=O double bonds in the [PO_4] tetrahedron often leads to the deformation of [PO_4], which means that different tetrahedral units like Q^i may exist in the glass. Moguš-Milanković *et al.* [14] described the structure of phosphate glass by Q^n (n=1, 2, and 3), where n represents the amount of bridge oxygen in a tetrahedral unit. As shown in Fig. 3, the Q^3 structure group represented that there were three bridge oxygen atoms and one non-bridge oxygen atom in the [PO_4] tetrahedral configuration, Q^2 represented two bridge oxygen atoms in the structure of the metaphosphate, Q^1 represented one bridge oxygen atom in the structure of the pyrophosphate, and Q^0 represented four non-bridge oxygen atoms in the structure of the orthophosphate.

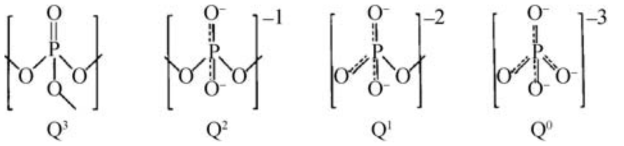

Fig. 3. Possible tetrahedral structure units in a phosphate glass system.

As shown in Figs. 1 and 2, the stretching vibration band of P=O bonds (usually at 1240-1270 and 1320 cm^{-1}) were not observed, which implies that the P=O double bond did not exist in the glass samples. Meanwhile, due to the broadening and overlapping of the absorption bands at 766-775 and 889-906 cm^{-1}, there also was no obvious evidence to confirm the characteristic stretching vibrations of the P–O–P framework network. The characteristic bending vibration of P–O–P (usually at 506 cm^{-1}) was also absent. These declared that there was no P–O–P bond in these glass samples. Therefore, it could be concluded that P_2O_5 in the glass existed in the form of an isolated [PO_4] tetrahedron without P=O bonds.

There were four basic vibration modes [15]: the symmetric stretching vibration Al (σ_1=950 cm^{-1}), the bending vibration E (σ_2=360 cm^{-1}), the dissymmetric stretching vibration F_2 (σ_3=1080 cm^{-1}), and the bending vibration F_2 (σ_4=500 cm^{-1}). If the [PO_4] tetrahedron had Td symmetry, according to the selection rule of IR spectra, only two vibration modes, the F_2 (σ_3, σ_4), were IR active among the four basic vibration modes. Judging from the experimental IR data, the [PO_4] tetrahedron in glass samples did not possess the Td symmetry of free PO_4^{3-}, and the degeneracy of dissymmetric stretching vibration F_2 (σ_3) was removed and its vibration spliced into many peaks (961, 1004-1012, and 1063-1071 cm^{-1}). These peaks could be assigned to the polarization of V^{5+}, V^{4+}, Sb^{3+}, and Bi^{3+} cations. Besides, the removal of degeneracy of $P–O^-$ bond bending vibration F_2 (σ_4) also showed a split of many peaks (446-464 and 551 cm^{-1}), which were also the results from the polarization of V^{5+}, V^{4+}, Sb^{3+}, and Bi^{3+} cations. The peak around 610 cm^{-1} could be assigned to the vibration absorption of $Bi–O^-$.

Zan *et al.* [12] reported the stretching vibration frequency of glassy Sb_2O_3 (Table 3, Fig. 4). However, for the present glass samples, the absorption band at 600 cm^{-1} did not appear in the IR spectra, which implied that there was no corresponding Sb–O–Sb bridge bond. Additionally, the absorption band at 446-464 cm^{-1} could be assigned to the antisymmetric movement V_3 of Sb–O bond and the 397-400 cm^{-1} band could be assigned to symmetrical stretching vibration V_1 of Sb–O bond.

Table 3. Stretching vibration mode of Sb_2O_3 glass

Way of vibration*	Experimental data / cm^{-1}	Calculated data / cm^{-1}
V_1	400^{**} (IR)	398
V_3	465 (IR)	466
V_3'	605 (IR)	605

Note: *V_1 and V_3 were the symmetric and antisymmetric movement of the non-bridge Sb–O bond, and V_3' was the antisymmetric stretching vibration of the bridge Sb–O–Sb bond. **Shoulder peak.

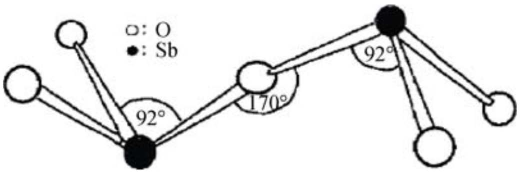

Fig. 4. Structure model of Sb_2O_3 glass.

Bi_2O_3 in the network structure would appear in three kinds of form: octahedral [BiO_6], triangular [BiO_3], and independent [BiO_3] triangle. The evidence for the existence of the [BiO_3] triangle was that an absorption band would occur at 830 cm^{-1} in the IR spectrum [16]. However, the band was not observed in the IR spectra of the present glass samples, as was evidence of the absence of the [BiO_3] triangle in this glass system.

After P_2O_5 entering into the V_2O_5 network, it had a similar structure feature with V_2O_5. The P=O and V=O double bonds could not form a high-dimensional structure and, as usual, the conjugated degree of network $Y<3$, which meant that the layered or bond structure was still kept. The trivalent metal cations of Sb^{3+} and Bi^{3+} were able to open the P=O double bond, so that the existence of phosphorus that scattered in a network of vanadium took the main way of isolated [PO_4] tetrahedrons without P=O double bonds, which mainly connected with vanadium atoms. For vanadium phosphate, it formed a layered structure through an alternative connection with the triangle-bipyramidal [VO_5] and the tetrahedron [PO_4], which meant that partial V and P had connected each other through O atoms and formed a kind of layered amorphous glass structure, while trivalent cations existing in the interlayer. In the dissymmetric structure unit of vanadium phosphate, as shown in Fig. 5, there were 10 atoms, in which 7 of them were skeletal atoms and the others were object atoms. There existed independent V and P atoms in the skeleton structure, five oxygen atoms, and one trivalent cation. The vanadium ion and the phosphorus ion were five-coordinated and four-coordinated, respectively. In the five oxygen atoms connecting with the vanadium atom, the V(l)–O(l), V(l)–O(3), V(l)–O(4), and

V(1)–O(5) were typical V–O bonds, while the V(l)–O(2) bond was the V=O bond [17]. The P atom connected with its four neighbor oxygen atoms by a four-coordinated way and formed a kind of two-dimensional layered vanadium phosphate. The polyhedron VO_5 and the tetrahedron PO_4 connected alternatively, and a big negative ion layer appeared along the *bc* plane. The trivalent cation between the layers opened the V=O bond and finally connected the two layers into a three-dimensional stereoscope structure. Therefore, the trivalent cation not only balanced the negative charge of vanadium phosphate but also stabilized the whole skeleton.

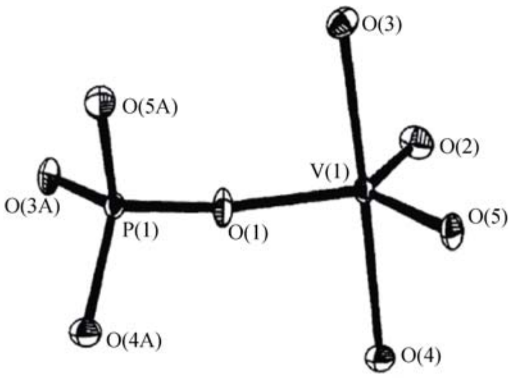

Fig. 5. Structure model of vanadium phosphate.

Compared with the traditional net forming ion and the intermediate net ion, heavy metal ions such as Sb^{3+} and Bi^{3+} had a lower electronic field intensity. The field intensity was directly proportionate to the cation charge and was inversely ratio to the square of the ionic distance. This indicated the intensity of mutual attraction between the cations and the oxygen anion. Sb^{3+} and Bi^{3+} ions had a lower electronic field intensity (Table 4), so the combination between Sb–O and Bi–O was weaker.

Table 4. Characteristics of cations in oxide glass

Cation	Charge, *Z*	Coordination number	Distance of cations, *a* / nm	Field intensity, Z/a^2	Relative atomic mass
P	+5	4	0.152	216	31
Sb	+3	6	0.211	67	122
Bi	+3	6	0.237	53	209
Bi	+3	8	0.246	50	209

In phosphate glass, trivalent metal ions could present a P=O double bond. They joined the network structure of glass according to the tetradentate model, leading to the phosphate glass structure from the layered and chain structure to skeleton structure. This could help improve the properties of phosphate glass. Once the metal oxide Sb_2O_3 was added into phosphate glass, the physical properties and the chemical properties would be changed, as a non-bridging oxygen bond was formed for keeping the balance of electronic valence and finally leading to the network structure of a [PO_4] tetrahedron to be de-polymerized. Along with the increasing amount of the added oxide *K* ($K=n_{Sb2O3}/n_{P2O5}$), the structure would change from Q^3 to Q^2, Q^1, and Q^0. The [PO_4] tetrahedron, which did not have a double bond, was unable to connect with each other directly, the surplus positive charge of the P^{5+} cation could only get saturation by oxygen anions surrounding it, and those oxygen anions would form a crystallite of phosphate (such as $SbPO_4$ and $BiPO_4$) with V^{5+}, V^{4+}, Sb^{3+}, or Bi^{3+} cations under the mutual attraction of static electricity. This kind of [PO_4] tetrahedral could be connected partially by V^{5+}, V^{4+}, Sb^{3+}, or Bi^{3+} cations and showed some properties of amorphous glass (V^{5+}, V^{4+}, Sb^{3+}, or Bi^{3+} cations could form a weak connection with several oxygen atoms from [PO_4]. The P–O–Bi, P–O–Sb, V–O–Bi, and V–O–Sb connected by bridge oxygen changed the layered structure of glass to the weak three-dimensional network structure).

(3) Influence of the structure of the glass with components change

Along with the amount of Sb_2O_3 decreasing to zero (meanwhile increasing the amount of V_2O_5), the degeneracy of dissymmetric stretching vibration F_2 (σ_3) of the [PO_4] tetrahedron was moved from 1004.73 to 1010.39 cm^{-1}. The absorption peaks around 852-880 cm^{-1} corresponding to the symmetrical stretching vibration of VO_2 and VO_4 and the deformation vibration of VO_2 in VO_4^{3-} increased slightly. The absorption peak corresponding to the synthetic vibration of the single linear bond $(VO_3)_n$ around 643 cm^{-1} increased clearly. The absorption peak corresponding to the stretching vibration of V–O–V around 613 cm^{-1} increased slightly. The absorption peak corresponding to the dissymmetric stretching vibration V_3 of the Sb–O bond around 465 cm^{-1} decreased gradually until disappearance. The absorption peak around 420-421 cm^{-1} increased, which was corresponding to the flexural vibration of VO_2 and VO_3. The absorption peak around 400 cm^{-1} corresponding to the symmetrical stretching vibration V_1 of the Sb–O bond decreased gradually until disappearance.

Along with the amount of P_2O_5 decreasing to zero (meanwhile increasing the amount of V_2O_5), the degeneracy of the dissymmetric stretching vibration $F_2(\sigma_3)$ from the [PO_4] tetrahedron around 961, 1010, and 1064 cm^{-1} decreased clearly until disappearance. The degeneracy of the flexural vibration $F_2(\sigma_4)$ of the P–O$^-$ bond from the [PO_4] tetrahedron around 1064 cm^{-1} also decreased gradually until disappearance. The degeneracy of the flexural vibration $F_2(\sigma_4)$ of the P–O$^-$ bond from the [PO_4] tetrahedron around 446-464 cm^{-1} decreased clearly until disappearance. Three kinds of absorption peaks around 852-880 cm^{-1} increased clearly, which were corresponding to the symmetrically stretching vibration of VO_2 and VO_4, the deformation vibration of VO_2 in VO_4^{3-}, and the stretching vibration of VO_2 and VO_3; the absorption peak of the synthetic vibration of the $(VO_3)_n$ single bond around 643 cm^{-1} increases clearly and the absorption peak of the stretching vibration of the V–O–V bond around 613 cm^{-1} increased clearly. Besides, the absorption peaks at 1004-1012 and 955-961 cm^{-1} are very weak, which were corresponding to V^{+5}=O in a trigonal dipyramid or octahedron ligancy and to V^{+4}=O a tetragonal, respectively. This denoted that the existence of V_2O_5 in the system is preferred to the formation of a P–O–V bond with [PO_4] or forming a P–O–V bond alone.

3.2. XRD analysis of the influence of glass composition on glass structure

XRD measurement was carried out for the selected 1-10 samples. The XRD patterns of the samples treated at 460°C for 30 min showed that there were no peaks of crystallization, just some amorphous diffusive scattering peaks. This denoted that crystallization did not occur at that temperature for those sealed glasses, and the stability was good. After being treated at 490°C for 30 min, partial samples showed peaks of crystallization, as shown in Figs. 6 and 7.

(1) XRD patterns of the glass with different Sb_2O_3 contents

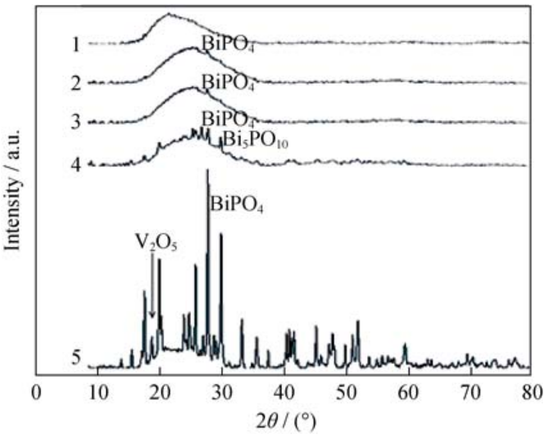

Fig. 6. X-ray diffraction patterns of the glass with different Sb_2O_3 contents after heat treatment at 490°C for 30 min (1: 20% Sb_2O_3 glass; 2: 15% Sb_2O_3 glass; 3: 10% Sb_2O_3 glass; 4: 5% Sb_2O_3 glass; and 5: 0% Sb_2O_3 glass).

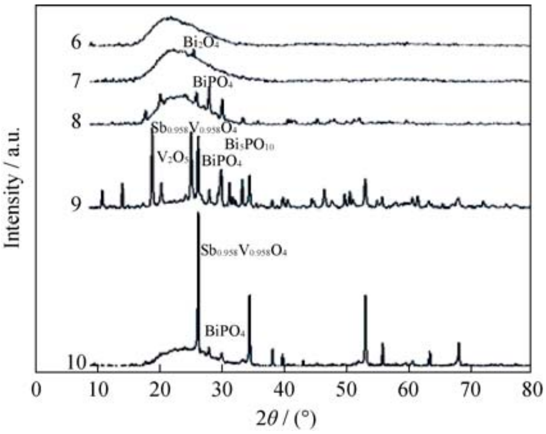

Fig. 7. X-ray diffraction patterns of the glass with different P_2O_5 contents after heat treatment at 490°C for 30 min (6: 40% P_2O_5 glass; 7: 35% P_2O_5 glass; 8: 30% P_2O_5 glass; 9: 25% P_2O_5 glass; and 10: 20% P_2O_5 glass).

It could be seen that the XRD and scattering characteristics of sample 5 (corresponding to 0% Sb_2O_3) was similar to crystallite glass, denoting that some microcrystal state was included in this sample. From diffraction data, it could be assumed that the crystallite contained a large number of $BiPO_4$ and a little of V_2O_5.

Both vanadium and phosphorus oxides were the net frame former. In the glasses formed by vanadium and phosphorus oxides, the molar ratio of the cations and oxygen anion would be 1:2.5, if all the cations were pentavalent. Therefore, there exists an oxygen anion with a double bond inside in order to form a tetrahedral network. In that condition, the linkage of the network skeleton would be more porous and easy to deform and relax. Owing to the high-valent cations V^{5+} in glass, it could form many kinds of varied coordinating polyhedrons for the needs of the charge balance and some influences from surrounded microenvironment. Generally speaking, the vanadium-oxygen tetrahedron had the highest share and formed distorted [VO_4], in which one bond presented partial characters of a double bond; [VO_4] was thus active and easy to crystallize. Non-bridge oxygen in the V=O double bond was easy to coordinate with other low field intensity cations. The length of this bond was longer and the bond energy was lower. Once Sb_2O_3 and Bi_2O_3 were added in, it would be possible to coordinate with non-bridge oxygen in the V=O double bond. It could help form a bigger ionic group, increasing the viscosity of glass, decreasing the migration ability of V^{5+}, and finally turning down the crystallization ability of glass. Besides, the field intensity of V^{5+} cations was high. Owing to the repulsion effect of V^{5+} to each other, the glass tended to form interval distribution. If a certain amount of Sb^{3+} and Bi^{3+} cations were introduced in, $[VO_4]$ would be separated to decrease the repulsion effect of V^{5+} and damp its migration ability, so that the glass crystallization was slowed down. On the other hand, when Sb_2O_3, Bi_2O_3, V_2O_5, and P_2O_5 were combined, Sb_2O_3 and Bi_2O_3 would be the network former. It could be imagined that Sb^{3+}, Bi^{3+} and V^{5+}, P^{5+} would alternatively exist in the tetrahedral of the glass and form a continuous three-dimensional structure. Of course, the alternative level and the continuous range of this structure would be dependent on the relative content. Furthermore, Sb^{3+} and Bi^{3+} cations carried positive charge, while the vanadium-oxygen polyhedra and the phosphorus-oxygen tetrahedral carried negative charge. When they were combined together, an electric neutral could be gained, and a three-dimensional network structure would form to increase the amount of bridge oxygen in glass, so the network structure would be reinforced. With a fixed amount of P_2O_5 and Bi_2O_3, the replacement of V_2O_5 by Sb_2O_3 made the glass uneasy to crystallize.

Fig. 6 shows that sample 4 (corresponding to 5% Sb_2O_3) had a more crystal peak of $BiPO_4$ and Bi_5PO_{10}, sample 3# (corresponding to 10% Sb_2O_3) just had a little crystal peak of $BiPO_4$, and sample 2 (corresponding to 15% Sb_2O_3) only had a trace crystal peak of $BiPO_4$. Sample 1 (corresponding to 20% Sb_2O_3) showed the diffusive scattering and the diffraction peaks of an amorphous state and did not crystallize. Along with the increasing amount of Sb_2O_3, crystallization was suppressed clearly.

(2) XRD patterns of the glass with different P_2O_5 contents

When a regular amount of Sb_2O_3 and Bi_2O_3 were set in the raw material, and a part of V_2O_5 were replaced by P_2O_5 gradually, the change of the peaks were as follows: sample 10 (corresponding to 20% P_2O_5) showed the character of X-ray scattering and diffraction of a microcrystalline glass and contained a very large amount of $(Sb_{0.958}V_{0.958})O_4$ crystals and a little amount of $BiPO_4$ crystals; sample 9 (corresponding to 25% P_2O_5) also showed the character of X-ray scattering and diffraction peaks of a microcrystalline glass and contained a large amount of $(Sb_{0.958}V_{0.958})O_4$, V_2O_5 crystals and a little of $BiPO_4$, Bi_5PO_{10} crystals.

As usual, if the melt had undercooling degree, the rise and fall of density would cause the formation of a new phase nucleus embryo. The viscosity of vanadium oxide was very low. While melting, the activation energy of the particle diffusion needed for V^{5+} and O^{2-} was also weak, so the nucleus embryo was easy to grow into a crystal nucleus and then enlarge to a crystal. Meanwhile, those factors that were not beneficial for the formation and growing of the nucleus would be beneficial for the formation of an amorphous glass. Once a fixed amount of an isolated $[PO_4]$ structure group existed in the melt, those groups would break up V^{5+} and O^{2-} ions into a small accumulative area during the cooling process or, in other words, the accumulation of V^{5+} and O^{2-} ions could only occur among the encirclement formed by $[PO_4]$ oxygen polyhedra. The accumulative area would get smaller if more cations entered the network. When the introduced amount reached an extent, it was very likely that the accumulation area of V^{5+} and O^{2-} could not attain its critical radius, or those nucleus embryos would be difficult to grow up to form the crystal nucleus. On one hand, the occurrence of $[PO_4]$ oxygen polyhedra must occupy a fixed space and hinder the migration of V^{5+} and O^{2-}. On the other hand, the electric valence of corner sharing oxygen for those oxygen polyhedra was unsaturated, so they must connect with V^{5+} to keep an electric neutral. In this condition, it would make a diversionary effect on the migration of V^{5+}. Given connection between the four P–O bonds and V^{5+} in the $[PO_4]$ tetrahedral was not even, it would cause both the $[PO_4]$ tetrahedral and vanadium-oxygen polyhedra to distort and form a kind of amorphous glass structure. When partial V_2O_5 was replaced by P_2O_5, the electronic field intensity of the cations would be relative higher, causing the respective focusing effect to be smaller, so the system was easy to get mixed melt. With a wider range, the formed glass was hard to crystallize.

In addition, with V_2O_5 was gradually replaced by P_2O_5 in the glass, the single linear bond structure of $(VO_3)_n$ was likely to change to the layered structure. The system contained both the layered structure of vanadium phosphate and the chained structure of vanadate. With the decrease of chained structures and the increase of layered structures, the overall system was strengthened. Moreover, as the electric field intensity of P^{5+} was higher than that of V^{5+}, when P_2O_5 partially replaced V_2O_5, the network of glass changed gradually from low electric field intensity to a higher one, causing the structure tend to get closer together.

Therefore, it could be concluded that, along with the increase of the amount of P_2O_5 and the decrease of the amount of V_2O_5, the state of crystallization was inhibited obviously. Only a weak $Bi(PO_4)$ crystal peak appeared in sample 8 (corresponding to 30% P_2O_5 sample in Table 1); a better result had been obtained in sample 7 (corresponding to 35% P_2O_5 sample in Table 1), which showed a weak Bi_2O_4 crystal; and sample 6 (corresponding to 40% P_2O_5 sample in Table 1) only presented some amorphous diffusive scattering and diffraction peaks and did not crystallize again. The XRD result of samples 1-10 had verified the conclusion obtained from IR spectra analysis above.

It was quite clear that the diffusive scattering and diffraction peaks of amorphous silicate glass were superior to those of sample 1 (corresponding to 20% Sb_2O_3 sample in Table 1) and sample 6 (corresponding to 40% P_2O_5 sample in Table 1). This may result from that the network structure of the former was better and denser than that of the vanadium-phosphorus sealed glass system, featuring double-bond, three-dimensional skeleton structure, mixed layered structure, chain structure, *etc*.

4. Conclusions

(1) By analyzing the IR spectra of V_2O_5-P_2O_5-Sb_2O_3-Bi_2O_3 glass, it can be found that vanadium and phosphorus are incorporated in the glass network mainly as $(VO_3)_n$ single chains and isolated $[PO_4]$ tetrahedra that do not have double bond. Partial V and P ions connect with each other through O, forming a layered vanadium phosphate amorphous structure. Trivalent Sb^{3+} and Bi^{3+} cations open the V=O bond and exist in interlayers, connecting and forming a weak three-dimensional stereoscope structure. When V_2O_5 is partially replaced by Sb_2O_3 and P_2O_5, all the glass network structures are reinforced.

(2) By analyzing the XRD results, V_2O_5, Bi_2O_4, $(Sb_{0.958}V_{0.958})O_4$, $BiPO_4$, and Bi_5PO_{10} crystalline phase have been found to exist in different compositional glass regions. When V_2O_5 is partially replaced by Sb_2O_3 or P_2O_5 and they are incorporated in vanadate glass, the crystallization is reduced, the overall performance of this structure is strengthened, and the crystal glass has gradually turned into amorphous glass.

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