Low Melting Property of Vanadate Tellurite Glass and its Characterization by IR Spectroscopy

Luo Shiyong^a, Wang Ning^b, Chen Meng^a, Xu Wencai^a and Lv Yong^a

^aLaboratory of Printing & Packaging Material and Technology-Beijing Area Major Laboratory, Beijing Institute of Graphic Communication, Beijing, 102600, P R China

^bThe Laboratory for study of Earth's interior and Geo fluids, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, 550002, P R China

(Received November 20, 2008; final form November 26, 2008)

ABSTRACT

Differential scanning calorimetry, X-ray diffraction, infrared spectra and fluidity evaluation experiments have been made for $(80-x)\text{TeO}_2 \cdot x\text{V}_2\text{O}_5 \cdot 20\text{MO}$ ($\text{M}=\text{Sn}$, Bi, Ca, Na and K) glasses as potential replacement for lead(PbO)-based glass frits with low firing temperature. Glasses with TeO_2 0-44 mol%, and V_2O_5 39-82 mol% were found unsuitable for glass frit since they were easy to crystallize. Glasses with the content of TeO_2 54-74 mol% and V_2O_5 9-29 mol% indicate appropriate fluidity and do not crystallize in the re-melting process at 723-753 K. The glass transition temperature of these glasses is at 544- 578 K. The glass structure is given by layer upon layer mainly connected by the structure units of $[\text{VO}_4]$ and $[\text{TeO}_3]$. Other modifier ions locate mainly between the layers. The isolated V=O band from the VO_5 bipyramids is not detected in the vitreous structure of the glasses presently investigated.

Keywords: Tellurite glass, Low glass transition temperature (T_g), IR characterization

1. INTRODUCTION

Vanadate tellurite glasses are of both scientific and technical interest because of their low melting temperature, high refractive index, high dielectric constant and good infrared transmission. They are

widely used in memory switching, electrical optical switching devices, solid state electrolytes /1-2/. There are various investigations focused on the structure and electrical, optical, and mechanic properties of various glass systems such as $\text{TeO}_2\text{-V}_2\text{O}_5$ /1-3/, $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ /4-5/, $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5$ /6/, $\text{ZnO-V}_2\text{O}_5$ /7/, $\text{CdO-V}_2\text{O}_5$ /7/, $\text{Sb}_2\text{O}_3\text{-V}_2\text{O}_5$ /7/, $\text{R}_2\text{O-V}_2\text{O}_5$ (where R is the alkali) /8/, $\text{PbO-V}_2\text{O}_5$ /9,10/, $\text{Fe}_2\text{O}_3\text{-BaO-V}_2\text{O}_5$ /11/, $\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$ /12/, $\text{MgO-V}_2\text{O}_5$ /13/, $\text{SrO-V}_2\text{O}_5$ /14/, $\text{FeO-SrO-V}_2\text{O}_5$ /15/, $\text{AgI-Ag}_2\text{O-V}_2\text{O}_5\text{-P}_2\text{O}_5$ /16/, $\text{CaO-V}_2\text{O}_5$ /17/, $\text{Bi}_2\text{O}_3\text{-TeO}_2\text{-V}_2\text{O}_5$ /18/, $\text{Bi}_2\text{O}_3\text{-GeO}_2\text{-V}_2\text{O}_5$ /19/, $\text{B}_2\text{O}_3\text{-PbO-V}_2\text{O}_5$ /20/, $\text{CuO-V}_2\text{O}_5\text{-TeO}_2$ /21/. However, the low melting property of vanadate tellurite glass has not been extensively reported yet. Glass frits with low firing temperature are widely used as hermetic seal materials and adhesives in electrical pastes. Lead borosilicate glass with PbO typical more than 50 mol% are widely used as seal materials or the binding agent of the electrical pastes /22-24/. Recently, lead containing low melting glasses have been restricted because of its harmful effects on health and the environment. This prompts us to force the development of lead-free low melting glass. Generally, the firing temperature of lead-free glass frits is higher than that of lead contained glasses. Thus, it is very important to develop new lead free low melting glass for electrical components.

The main purpose of this paper is to examine vanadate tellurite based glasses of $(80-x)\text{TeO}_2 \cdot x\text{V}_2\text{O}_5 \cdot 20\text{MO}$ ($\text{M}=\text{Sn}$, Bi, Ca, Na and K) as potential replacement for lead-based glass frits with

firing temperature at 723-773 K, to alternate lead contained in low melting glass for the lead free of electrical components. In this paper, vanadate tellurite based glasses were examined as potential replacements for Pb-based glass frits with low firing temperature at 723-773 K. The glass samples were evaluated by glass transition temperature, and the fluidity during re-melting process. The effects of chemical composition of the V_2O_5 - TeO_2 glass system on the low melting property and the structure of the vanadate tellurite glass were also analyzed by IR spectroscopy.

2. EXPERIMENTAL

Generally, SnO , Bi_2O_3 , BaO , Na_2O and K_2O are widely used to develop low melting lead free glass. In the present investigation, about 20mol% of the SnO , Bi_2O_3 , BaO , Na_2O and K_2O was added to decrease the firing temperature further. The chemical compositions of glass samples presently studied in mol% are listed in

Table 1. Batches prepared by mixing of the chemically pure V_2O_5 , TeO_2 , Bi_2O_3 , SnO , $BaCO_3$, Na_2CO_3 and K_2CO_3 were melted in an alumina crucible at temperature about 1223 K for 60 minutes; then the glass melts were quenched to room temperature by pouring the liquids on to a brass plate and immediately pressed by another brass plate. Samples were in the form of powders with the size from 1 to 30 microns.

The differential scanning calorimetry (DSC) measurements of the samples were performed in a differential scanning calorimeter (DSC-200PC) with a heating rate of 10 K/min in the temperature from 293 to 853 K, the flow rate of nitrogen gas was 10 mL/min. The infrared spectroscopy (IR) spectra at room temperature of the powdered glass samples in the KBr matrix were recorded with a spectrometer (FTIR-8400 SHIMADZU) in the wave number range from 4×10^4 to $4 \times 10^6 \text{ m}^{-1}$ (400 to 4000 cm^{-1}). The amorphous nature of samples was checked by X-ray diffraction (D/Max-2200 RIGAKU).

Table 1
Chemical compositions of the studied glasses in mol%

Glass No.	TeO_2	V_2O_5	Bi_2O_3	SnO_2	BaO	Na_2O	K_2O
S1	44.09	38.80	4.23	3.53	4.59	2.82	1.94
S2	33.56	49.10	4.29	3.57	4.65	2.86	1.97
S3	22.66	59.76	4.35	3.63	4.71	2.90	1.99
S4	11.48	70.69	4.41	3.68	4.78	2.94	2.02
S5	0	81.92	4.47	3.73	4.85	2.98	2.05
S6	54.40	28.70	4.18	3.48	4.53	2.79	1.92
S7	64.46	18.87	4.12	3.44	4.47	2.75	1.89
S8	74.23	9.31	4.07	3.39	4.41	2.71	1.88
S9	83.75	0	4.02	3.35	4.36	2.68	1.84

3. RESULTS AND DISCUSSION

3.1 The low melting property of vanadate tellurite glasses

The DSC curves of all samples were divided into two classes by the nature of crystallization and non-crystallization after the DSC measurements. The curve consists of an endothermic peak due to a glass transition

and an exothermic peak due to crystallization. **Figure 1** shows glass samples of S6, S7, S8 and S9, with the content of TeO_2 54-83 mol%, and V_2O_5 0-29 mol%. These glass samples were not found to be crystallized after the DSC measurements. The glass transition temperature, T_g , of these samples of S6, S7, S8 and S9 was 550, 554, 578 and 613 K, respectively. The T_g value of these glass samples increases with the

increasing of TeO_2 content. On the other hand, glass samples denoted by S1, S2, S3, S4 and S5 with the content of TeO_2 0-44 mol%, and V_2O_5 39-82 mol% were crystallized after the DSC measurements, as shown in Figure 2. The crystallization temperature was found to be in the range from 513 to 563 K, depending on the composition. For this reason, further attention focuses only on S6, S7, S8 and S9.

Fig. 1: DSC curves of the glass samples without crystallization.

Fig. 2: DSC curves of the glass samples with crystallization.

Figure 3 shows XRD pattern of as quenched glass samples of S6, S7, S8 and S9 together with that of S5, for comparison. The S5 sample clearly shows the crystalline nature and it is attributed to the contained V_2O_5 crystalline. The “other samples” in Figure 3 means XRD patterns of S6, S7, S8 and S9 samples

showing similar feature of no discrete sharp peaks. This confirms that the structure of S6, S7, S8 and S9 samples is characterized by the so-called amorphous network where the V_2O_5 component is completely contained in the glass matrix.

Fig. 3: X-ray diffraction patterns of as quenched glass samples.

3.2 The fluidity evaluation of the vanadate tellurite glasses at re-melting process

The purpose of the present work is to develop a new glass system as potential replacement for lead-based glass frits with low firing temperature at 723 -773 K. As the hermetic seal glasses or the binders for electrical pastes, the application form of the low firing glass is required as powders with size of 1-30 microns. It is an important property of the low firing glass frit that the glass powder possesses proper fluidity at the seal temperature or at the firing temperature. The fluidity was usually evaluated by an experimental result of so called “button diameter”, which was originated from Owens Corning and then modified by the China Industry Standard of SJ3232.3-1989 [25]. The main points of this “button diameter” experiment are: first, an appropriate amount of glass powder, depending on the density of the glass, is pressed by a pressure of 5Mpa in a steel mould to form a 5 mm high powder column with a diameter of 12mm. Second, the powder column is placed on a plate glass and then heated according to a specified temperature schedule, fired at a proper peak

temperature for 10 minutes in an electrical furnace. Finally, the diameter of the fired glass matrix is determined and is used to evaluate the fluidity of the low melting glass. The diameter of the glass matrix after fired at a peak temperature for 10 minutes is generally within the range from 24 to 27 mm and this peak temperature would be appropriate to be taken as the seal temperature for applying the low melting glass to seal glass or paste for the thick film of some electrical parts.

In the present investigation, for each glass sample listed in Table 1, 5.00 grams glass powder was pressed by a pressure of 5Mpa in a steel mould to form a ~5 mm high powder column with a diameter of 12mm, placed it on a plate glass, then fired in an electrical furnace. The temperature schedule is as follows. The heating rate is 10 K/min from room temperature to 673 K, 5 K/min from 673 to 723 K, and keeping at the peak temperature of 723 K for 10 minutes, then cooled to room temperature. The button diameter results are given in Table 2.

Table 2

The button diameter results of the samples after fired at 723 K for 10 minutes

Glass No.	T_g / K	Button diameter / mm	Visual phenomena of the button matrix
S1		18.5	Crystallized, no glass gloss on the surface
S2		18.0	Crystallized, no glass gloss on the surface
S3		17.3	Crystallized, no glass gloss on the surface
S4		15.5	Crystallized, no glass gloss on the surface
S5		13.2	Crystallized, no glass gloss on the surface
S6	550	27.3	Non-crystalline, has good glass gloss
S7	554	26.5	Non-crystalline, has good glass gloss
S8	578	23.1	Non-crystalline, has good glass gloss
S9	613	20.1	Non-crystalline, has good glass gloss

When the peak temperature was kept at 743 K, the button diameter of S8 was about 25 mm. The visual crystallization phenomena of the button matrix, listed in Table 2, were in agreement with those of the DSC measurements. On the basis of the fluidity and crystallization, the glass samples of S6, S7 and S8 were found to be proper for seal glass frit or the adhesive of electrical paste with the firing temperature at 723-773 K.

3.3 Characterization by IR spectroscopy of vanadium tellurite glasses

Samples of S1, S2, S3, S4 and S5, shown in Table 1, with TeO_2 0-44 mol%, V_2O_5 39-82 mol% were crystallized and good flow could not be obtained during re-melting process at 723-773 K. For these reasons, these samples are not qualified for the use of low firing seal glass frit and adhesive of electrical paste. Then, their structure was also not discussed further.

The experimental IR spectra for samples of S6, S7, S8 and S9 with TeO_2 54-84 mol%, V_2O_5 0-30 mol% are given in Figure 4. For comparison, the spectra of pure TeO_2 and V_2O_5 oxides, as well as sample S5 were also given in Figure 4. Except for S5, four glass samples show the spectra with a broad absorption band from 5.6×10^4 to $1.0 \times 10^5 \text{ m}^{-1}$ (560 to 1000 cm^{-1}).

Fig. 4: Infrared spectra of the glass samples and pure oxides

The absorption band at about 640cm^{-1} of pure TeO_2 was attributed to TeO_4 tetragonal pyramids. It was reported that this band shifted from 640cm^{-1} to 680cm^{-1} on adding other metal oxides [3]. Dimitriv *et al.* [26] report that the IR absorption band in the range from $620\text{--}680\text{cm}^{-1}$ can be attributed to TeO_3 trigonal pyramids. These bands were observed in the IR spectra of the present $\text{TeO}_2\text{--V}_2\text{O}_5$ glass samples of S6, S7, S8 and S9. Te in the glass structure is suggested mainly in the form of TeO_3 trigonal pyramids. With increasing TeO_2 content from 40 to 80 mol%, the glass structure gradually changes from the continuous vanadate network to the continuous tellurite network. The formation of TeO_3 trigonal pyramids leads to the reduction of the glass rigidity related to both the increase in ring size and decrease in melting temperature. Sidkey *et al.* [2] conclude from the structural study of $(\text{TeO}_2)_{1-x}(\text{V}_2\text{O}_5)_x$ by ultrasonic study that vanadium tellurite glasses containing more than 80 mol% TeO_2 have a continuous tellurite network which contains four-coordinated Te. One can infer that the network of the samples of S9, with 84 mol% of TeO_2 , is mainly connected by four-coordinated Te. The results of DSC analysis and fluidity evaluation for S9 sample indicate difficulty to crystallize during re-melting process. However, it is not suitable for low melting glass since its glass transition temperature is up to 613 K. For samples of S6, S7 and S8, Te in the glass structure is characterized mainly by the form of TeO_3 trigonal pyramids.

The IR band at $\sim 1020\text{cm}^{-1}$ of pure crystalline V_2O_5 is characteristic of the isolated $\text{V}=\text{O}$ vanadyl groups in VO_3 trigonal bi-pyramids. The bands at ~ 830 and $\sim 620\text{cm}^{-1}$ are due to the symmetric and antisymmetric vibration modes of the V-O-V group and the band at $\sim 480\text{cm}^{-1}$ is attributed to the angular deformation vibration of the O-V bond. The band at $\sim 1020\text{cm}^{-1}$ due to $\text{V}=\text{O}$ only appeared in the spectrum of the glass sample S5, but it was not observed in the samples of S6, S7, S8 and S9. The isolated $\text{V}=\text{O}$ bond from the VO_3 trigonal bipyramids was not found in the vitreous structure of the present glass samples. This was quite different from early reports [2,7] that the $\text{V}=\text{O}$ band occurred in the structure of amorphous vanadate tellurite glass. The difference might be due to the

different conditions of glass preparation (melting temperature, duration melting, etc). The absorption band of V-O-V at $\sim 830\text{cm}^{-1}$ is not clearly for the broad bands from 560 to 1000cm^{-1} . One can infer that the V ion is octahedrally coordinated.

V_2O_5 and TeO_2 are known to be typical conditional glass formers. The IR spectra of samples of S6, S7 and S8 show that Te in the glass structure is mainly three coordinated and the V is octahedrally coordinated. The structure of the vanadate tellurite glass, with low melting property, TeO_2 54–74 mol%, V_2O_5 9–29 mol%, may be attributed to the layer structure formed by distorted TeO_3 trigonal pyramids and VO_4 octahedra sharing edges and corners.

The addition of network modifier metal oxides such as Bi_2O_3 , SnO , BaO , Na_2O and K_2O , would make the glass network loose. In the first case, network modifier ions are mainly located between the vanadate or tellurite chains. They can interact directly with the isolated V-O and Te-O bonds and distort the TeO_3 trigonal pyramids and VO_4 octahedra further. In the second case, a few ions with strong energy may occupy positions in the chain itself, where some of the weaker V-O-V and Te-O-Te bonds break and they form new V-O -ions bridges. Thus, the glass transition temperature of glasses decreases further.

4. CONCLUSIONS

The structure and low melting property of $(80-x)\text{TeO}_2\cdot x\text{V}_2\text{O}_5\cdot 20\text{MO}$ ($\text{M}=\text{Sn}$, Bi , Ca , Na and K) glasses have been investigated. Glasses with TeO_2 0–44 mol%, and V_2O_5 39–82 mol% are not suitable for glass frit since they are easy to crystallize. The glasses with the content of TeO_2 54–74 mol%, and V_2O_5 9–29 mol% possess appropriate fluidity and do not crystallize in the re-melting process at the temperature range from 723 to 773 K. The glass transition temperature of these glasses is in the temperature range from 544 to 578 K. The structure of glasses with the content of TeO_2 54–74 mol%, and V_2O_5 9–29 mol% is layer upon layer structure mainly connected by VO_4 tetrahedra and TeO_3 trigonal pyramids. Other modifier ions such as Sn^{2+} , Bi^{3+} , Ba^{2+} , Na^+ and K^+ locate mainly between the layers

and they contribute to the decrease in glass transition temperature. The isolated V=O band from the VO₅ bipyramids is not detected in the vitreous structure of the glasses. As a result, vanadate tellurite glasses may be a potential candidate for use as a lead-free composition glass frit with low firing temperature.

ACKNOWLEDGEMENTS

The authors thankfully acknowledge the generous financial support provided by the Science and Technology Program of Beijing Municipal Commission of Education, and by the Science and Technology Research Funding Project of Beijing Institute of Graphic Communication, and by the Funding Project for Academic Human Resource Development in Institutions of Higher Learning Under The Jurisdiction of Beijing Municipal (PHR IHLB).

REFERENCES

1. D. Bersani, G. Antonioli, P. P. Lottici, Y. Dimitriev, V. Dimitrov and P. Kobourova, *J. Non-Cryst. Solids*, **232/234**, 293-299 (1998).
2. M.A. Sidkey, R. El Mallawany, R. I. Nakhla and A. Abd El-Moneim, *J. Non-Cryst. Solids*, **215**, 75-82 (1997)
3. A. Abd El-Moneim, *Mater. Chem. Phys.*, **73**, 318-322 (2002)
4. F.M. Ezz-Eldin, *Nucl. Instrum. Meth. B*, **1599**, 166-175 (1999)
5. J.E. Garbacz, P. Jozwiak, M. Wasiucione, and J.L. Nowinski, *J. Power Sources*, **173**, 743-747 (2007)
6. S. Mandal, S. Hazra, D. Das and A. Ghosh, *J. Non-Cryst. Solids*, **183**, 315-319 (1995)
7. V. Dimitrov, *J. Non-Cryst. Solids*, **192/193**, 183-186 (1995)
8. J.M. Lewis, C.P.O. Brien, M. Affatigato and S.A. Feller, *J. Non-Cryst. Solids*, **293/295**, 663-668 (2001)
9. S. Hayakawa, T. Yoko and S. Sakka, *J. Non-Cryst. Solids* **183**, 73-84 (1995)
10. K.V. Ramesh and D.L. Sastry, *Physica B*, **387**, 45-51 (2007)
11. E. Mansour, Y.M. Moustafa, G.M. El-Damrawi, S. Abd El-Maksoud and H. Doweidar, *Physica B*, **305**, 242-249 (2001)
12. S. Chakraborty, M. Sadhukhan, B. K. Chaudhuri, H. Mori and H. Sakata, *Mater. Chem. Phys.*, **50**, 219-226 (1997)
13. S. Sen and A. Ghosh, *J. Non-Cryst. Solids* **258**, 29-33 (1999)
14. G. D. Khattak and N. Tabet, *J. Electron Spectrosc. Relat. Phenom.*, **136**, 257-264 (2004)
15. M. S. Aziz, F. Abdel-Wahab, A. G. Mostafa and E. M. El-Agwany, *Mater. Chem. Phys.*, **91**, 532-537 (2005)
16. P. Machowski, M. Opallo, J. E. Garbacz and M. Wasiucione, *Solid. State Ionics*, **157**, 287-291 (2003)
17. N. Tashtoush, A.M. Qudah and M.M. El-Desoky, *J. Non-Cryst. Solids*, **68**, 1926-1932 (2007)
18. V. Rajendran, N. Palanivelu, B. K. Chaudhuri and K. Goswami, *J. Non-Cryst. Solids*, **320**, 195-209 (2003)
19. V. Dimitrov, Y. Dimitriev and A. Montenero, *J. Non-Cryst. Solids*, **180**, 51-57 (1994)
20. C. N. Reddy, V.C. Veeranna Gowda and R.P. Sreekanth Chakradhar, *J. Non-Cryst. Solids*, **354**, 32-40 (2008)
21. M. M. El-Desoky and M. S. Al-Assiri, *Mater. Sci. Eng. B*, **137**, 237-246 (2007)
22. S.A. Ketkar, G.G. Umarji, G.J. Phatak, J.D. Ambekar, I.C. Rao, U.P. Mulik and D.P. Amalnerkar, *Mater. Sci. Eng. B*, **132**, 215-221 (2006)
23. Joon-Young Song and Se-Young Choi, *Displays*, **27**, 112-116 (2006)
24. R. Morena, *J. Non-Cryst. Solids*, **263/264**, 382-387 (2000)
25. China Industry Standard of SJ3232.3-1989. Method for measurement of flowability of glass powder for soldering with low-melt point.
26. Y. Dimitriv, V. Dimitrov, M. Arnaudov and D. Topalov, *J. Non-Cryst. Solids*, **57**, 147-151 (1983)