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Original Communication

Optimum Sb_2O_3 content of V_2O_5-H_2WO_4-KPO_3-Sb_2O_3 glasses for sealants

Seigo Goto[1], Shohei Kubo[1], Yoshihiro Kouhara[2], Yoshihiro Ohzuno[1], Takayuki Takei[1] and Masahiro Yoshida[1,*]

[1]Department of Chemical Engineering, Graduate School of Science and Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan;
[2]Yamato Electronics Co. Ltd., 3816-23 Okubo Takaono-cho, Izumi-shi, Kagoshima 899-0401, Japan.

ABSTRACT

In our previous study, we prepared four types of V_2O_5-H_2WO_4-KPO_3 glasses containing Sb_2O_3 (Sb_2O_3 content: 0, 1.3, 2.6 and 5.1 mol%) and examined their physical properties as a sealant. In this paper, we evaluate the physical properties of V_2O_5-H_2WO_4-KPO_3 glass containing 3.9 mol% Sb_2O_3. The glass had both optimum high water durability and optimum high fluidity, compared with the previous glasses containing 0, 1.3, 2.6 and 5.1 mol% Sb_2O_3 and a commercial lead-based glass. Addition of $Zr_2(WO_4)(PO_4)_2$, a low thermal expansion ceramic filler, to the V_2O_5-H_2WO_4-KPO_3-3.9 mol% Sb_2O_3 glass resulted in increased bonding strength of the glass, and the strength was very close to that of the commercial lead-based glass. These results show that the V_2O_5-H_2WO_4-KPO_3-3.9 mol% Sb_2O_3 glass is promising as an alternative to lead-based glass sealant. Additionally, glass structures of V_2O_5-H_2WO_4-KPO_3-Sb_2O_3 glasses were examined to determine the possible mechanism for improved water durability by the incorporation of Sb_2O_3.

KEYWORDS: V_2O_5-H_2WO_4-KPO_3-Sb_2O_3 glasses, lead-free glass, water durability, glass structure, sealing glass, infrared absorption spectroscopy

*Corresponding author
myoshida@cen.kagoshima-u.ac.jp

INTRODUCTION

Sealing glasses with low melting point, low thermal expansion, high water durability and high fluidity are essential for successful sealing of electronic devices [1]. For the past several decades, lead-based sealing glasses have been mainly used for sealing because the glasses have low melting point, low coefficient of thermal expansion and high water durability [2-5]. However, lead eluted from the glasses causes environmental pollution and health hazard [6]. Therefore, it has been urged to develop lead-free sealing material with low melting point, low thermal expansion, high water durability and high fluidity.

Vanadate-phosphate glasses have been reported to have low melting point and low coefficient of thermal expansion [7]. However, poor water durability of the glasses limits their usefulness as sealants. It is known that the poor water durability is due to hydrolysis of P-O-P bonds [8]. It has been reported that the water durability of the sealing glasses could be improved by replacement of the hydrolysable P-O-P bonds by hydrolysis-resistant P-O-M bonds (M: metal elements that have high cationic valance such as Ti, Fe and Al) [9-12]. Based on these reports, we previously incorporated H_2WO_4 as a metal oxide with high cationic valence into vanadate-phosphate (V_2O_5-KPO_3) glasses [13]. However, the water durability hardly improved to the desired extent. Next, we attempted to improve the water durability by incorporating Sb_2O_3 into the V_2O_5-H_2WO_4-KPO_3 glasses [13]. In this attempt, we prepared four types of glasses with different Sb_2O_3 contents (0, 1.3, 2.6 and 5.1 mol%). Among Sb_2O_3 contents of 0-2.6 mol%, the water durability improved with increase in content, and the water durability of the glass containing 2.6 mol% Sb_2O_3 was close to that of lead-based glass. However, further improvement of the water durability is needed because the glass was slightly inferior to lead-based glass in the durability. Further increase in Sb_2O_3 contents (5.1 mol%) caused significant decrease in fluidity, although the water durability of the glass was further improved compared with the glass containing 2.6 mol% Sb_2O_3. Based on these results, we envisaged that there was an optimum composition between the Sb_2O_3 content of 2.6-5.1 mol% that can achieve both high water durability and fluidity.

In this study, we evaluated the physical characteristics of V_2O_5-H_2WO_4-KPO_3 glasses containing 3.9 mol% Sb_2O_3 to prove our expectation. Additionally, the glass structure was examined by infrared absorption spectroscopy (IR) analysis because we previously did not investigate the structure of V_2O_5-H_2WO_4-KPO_3-Sb_2O_3 glasses, which was essential to determine the possible mechanism for improved water durability by incorporation of Sb_2O_3. Moreover, we evaluated the effect of $Zr_2(WO_4)(PO_4)_2$ (ZWP), a low thermal expansion ceramic filler, added in the V_2O_5-H_2WO_4-KPO_3-Sb_2O_3 glasses on its thermal expansibility and bonding strength.

EXPERIMENTAL

Preparation of glasses

V_2O_5, H_2WO_4, KPO_3 and Sb_2O_3 powders (Wako Pure Chemical Industries, Ltd., Japan) were mixed and melted in a platinum crucible at 1000 °C for 1 h in an electric furnace. The melt was poured into an alumina boat and quenched at room temperature for preparing a glass bar. Compositions of the prepared glasses and their abbreviations are listed in Table 1. Polished glass cubes (weight: 1.00 ± 0.01 g) and cylinders (height: 10 mm) were prepared from the glass bar. Fine glass powders (< 100 μm in diameter) were made by pounding the glass bar. The glass powders and ZWP (KCM Corporation, Japan) were mixed in an alumina boat and heated at 450 °C for 1 h in an electric furnace. The alumina boat was quenched at room temperature for preparing a glass bar containing ZWP. Similarly, glass cubes, cylinders and fine glass powders were prepared from the glass bar.

Water durability

Glass cubes were immersed in boiling water for 1 h and dried at 50 °C. Weight loss ratio (L) was calculated from the weights of glasses before (W_b) and after (W_a) immersion in boiling water and drying ($L = 100 \times (W_b\text{-}W_a)/W_b$). The surfaces of the glasses after immersion in boiling water were observed by a scanning electron microscope (SEM, S3000-N, Hitachi, Ltd., Japan).

Thermal properties and glass structure

The coefficients of thermal expansion of the glasses were measured by thermomechanical

Table 1. Compositions and physical properties of V_2O_5-H_2WO_4-KPO_3-Sb_2O_3 glasses.

Abbreviations of glasses	Compositions [mol%]				DTA			TMA	Water durability	Fluidity
	V_2O_5	H_2WO_4	KPO_3	Sb_2O_3	T_g [°C]	T_f [°C]	T_x [°C]	α [× 10^{-6} °C^{-1}]	L [%]	S [-]
VWP-6	40.0	10.0	50.0	0	302	322	> 500	14.4	24.1	5.7
VWP-6_1.3Sb	39.5	9.9	49.3	1.3	314	339	> 500	13.4	7.2	4.8
VWP-6_2.6Sb	39.0	9.7	48.7	2.6	324	351	> 500	12.8	2.6	4.3
VWP-6_3.9Sb	38.5	9.6	48.1	3.9	347	367	> 500	11.6	0.4	4.1
VWP-6_5.1Sb	38.0	9.5	47.5	5.1	358	382	> 500	11.5	0.2	2.3

analysis (TMA, TMA-60, Shimadzu Corporation, Japan) at a heating rate of 5 °C min^{-1}. Glass transition temperature (T_g), softening temperature (T_f) and crystallization temperature (T_x) were measured by differential thermal analysis (DTA, Thermo Plus TG-8120, Rigaku Corporation, Japan) at a healing rate of 10 °C min^{-1}. The glass structure was determined by X-ray diffraction measurement (XRD, RINT2200, Rigaku Corporation, Japan) and IR analysis (Spectrum One FT-IR spectromer, ParkinElmer Co., Ltd., USA).

Sealing ability

A thinner solution containing fine glass powders was sufficiently kneaded to prepare glass paste. The glass paste was uniformly applied (10 × 10 × 0.2 mm) on flat soda lime glass (43 × 35 × 13 mm). Then, the soda lime glass was heated in an electric furnace at approximately 230 °C for removal of thinner solution from the glass paste. After that, the solid glass paste was covered with another soda lime glass and heated in an electric furnace at approximately 480 °C for sealing. Fluidity (S) was evaluated from the areas of glasses before (S_b) and after (S_a) sealing ($S = S_a/S_b$). The sealed soda lime glasses were pulled by a universal testing machine (TRC-1210A, A&D Company Ltd., Japan) at a pulling rate of 0.3 mm min^{-1} to determine the bonding strength (N).

RESULTS AND DISCUSSION

V_2O_5-H_2WO_4-KPO_3 glasses containing 3.9 mol% Sb_2O_3

Table 1 shows the compositions and physical properties of V_2O_5-H_2WO_4-KPO_3-Sb_2O_3 glasses. The data of VWP-6, VWP-6_1.3Sb, VWP-6_2.6 and VWP-6_5.1Sb are quoted from our previous report (refer to Table 1 for each abbreviation) [13]. The XRD pattern of the glass containing 3.9 mol% Sb_2O_3 (VWP-6_3.9Sb) shows that the sample had an amorphous structure (data not shown). The water durability of VWP-6_3.9Sb glass was superior to that of VWP-6_2.6Sb glass. Furthermore, VWP-6_3.9Sb exhibited higher fluidity than VWP-6_5.1Sb. These results prove our expectation (described in the introduction section) that there is an optimum composition between the Sb_2O_3 content of 2.6-5.1 mol% that can achieve both high water durability and fluidity.

Weight loss ratio (L) and fluidity (S) of lead-based glass were 2.0% [14] and 1.6% (determined in this study), respectively. These data of lead-based glass and VWP-6_3.9Sb show that VWP-6_3.9Sb has higher water durability and fluidity than lead-based glass.

Subsequently, we observed the surfaces of each glass before and after immersion in boiling water and investigated glass structures by IR analysis to determine the possible mechanism for improved water durability by incorporation of Sb_2O_3. There was significant difference in the surface morphologies of the glasses with and without Sb_2O_3 after immersion in boiling water. Many round depressions, which would have resulted from hydrolysis of P-O-P bonds and the subsequent dissolution of the glass components in hot water, were confirmed on the surface of VWP-6 glass (Figure 1). On the other hand, increased amount of incorporated Sb_2O_3 prevented generation of the depressions. Figure 2 shows IR absorption spectra of the glasses. The absorption peaks of 1150-1050 cm^{-1} and 750 cm^{-1} are attributed to the dissymmetric stretching vibration of P-O bond and the symmetric stretching vibration of P-O-P bond, respectively [15]. With increasing content of Sb_2O_3, intensities of the peaks related to P-O and P-O-P bonds decreased. These results indicate that (i) hydrolysable P-O-P bonds would be replaced by hydrolysis-resistant P-O-Sb bonds by incorporation of Sb_2O_3, and (ii) the replacement would result in the improved water durability of the glasses.

V_2O_5-H_2WO_4-KPO_3 glasses containing 3.9 mol% Sb_2O_3 and ZWP

Coefficient of thermal expansion of sealants is an important parameter for the successful sealing of electronic devices such as display panels because a mismatch between the coefficients of sealants and electronic device materials causes distortions at the bonding surface, which finally leads to failure of the sealing [16-18]. Therefore, the coefficients of sealants have to be adjusted to coincide with that of materials that are sealed. In this study, we selected soda lime glass, which is used in many electronic devices, as a sealant material.

Coefficient of thermal expansion of VWP-6_3.9Sb was higher than that of soda lime glass

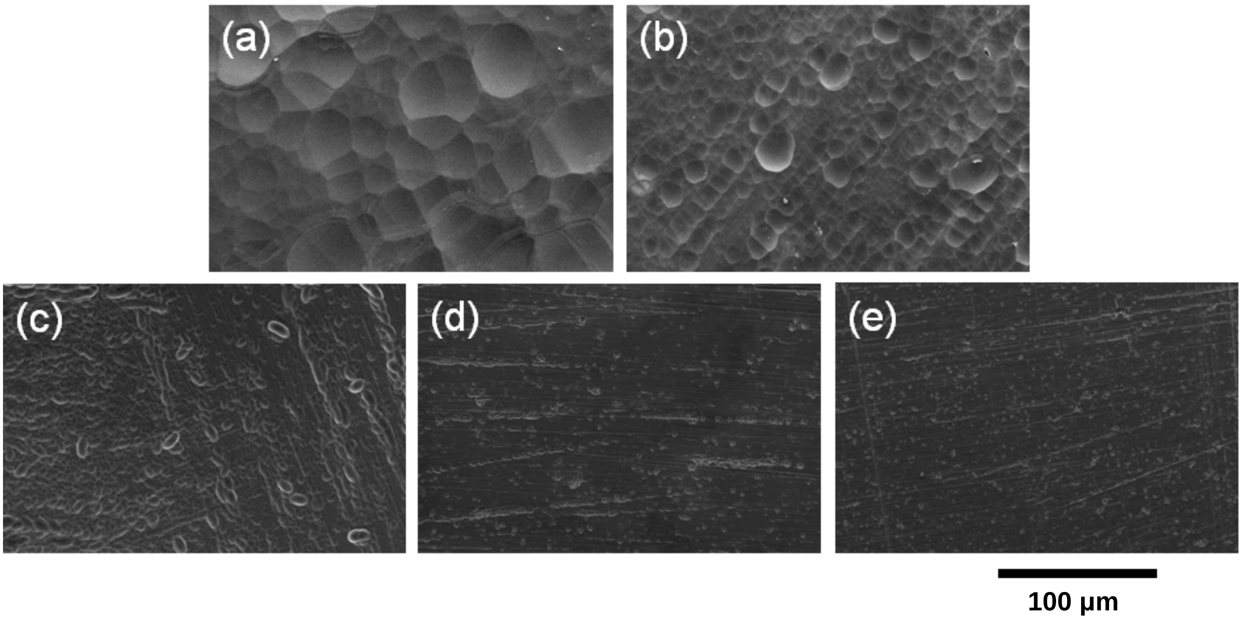

Figure 1. Surface of VWP-6 glass containing Sb_2O_3 after immersion in boiling water: (a) VWP-6, (b) VWP-6_1.3Sb, (c) VWP-6_2.6Sb, (d) VWP-6_3.9Sb and (e) VWP-6_5.1Sb.

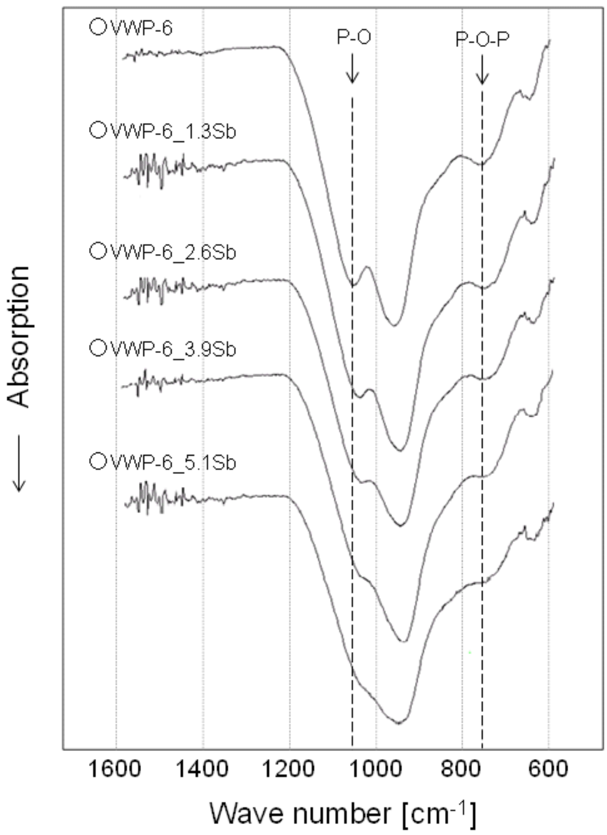

Figure 2. IR absorption spectra of V_2O_5-H_2WO_4-KPO_3-Sb_2O_3 glasses.

Table 2. Compositions and physical properties of VWP-6_3.9Sb containing ZWP.

Abbreviations of glasses	Compositions [wt%]		DTA			TMA	Fluidity	Bonding strength
	VWP-6_3.9Sb	ZWP	T_g [°C]	T_f [°C]	T_x [°C]	α [× 10^{-6} °C^{-1}]	S [-]	N [kgf cm^{-2}]
VWP-6_3.9Sb + 10 wt% ZWP	90	10	342	365	> 500	9.1	4.2	2.7
VWP-6_3.9Sb + 15 wt% ZWP	85	15	343	365	> 500	6.7	3.7	3.3
VWP-6_3.9Sb + 20 wt% ZWP	80	20	342	362	> 500	5.9	3.4	1.9

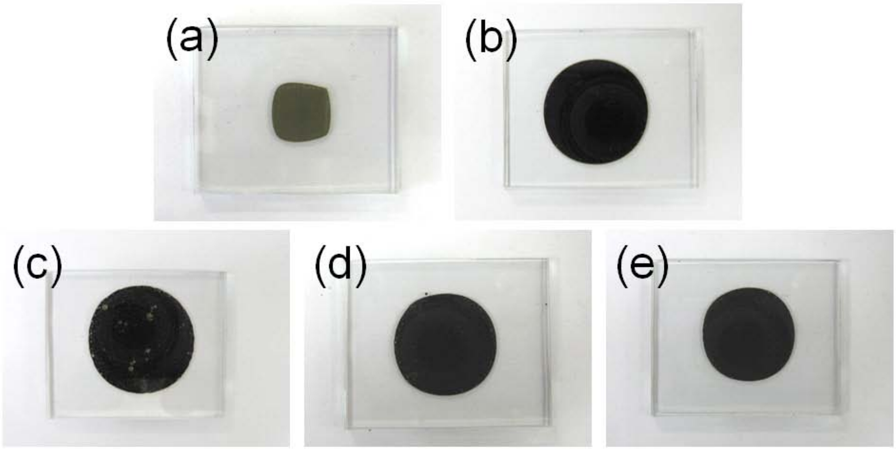

Figure 3. States of glasses after sealing: (a) lead-based glass, (b) VWP-6_3.9Sb, (c) VWP-6_3.9Sb + 10 wt% ZWP, (d) VWP-6_3.9Sb + 15 wt% ZWP, (e) VWP-6_3.9Sb + 20 wt% ZWP.

(7-8 × 10^{-6} °C^{-1}). Therefore, ZWP, a low thermal expansion ceramic filler, was mixed with VWP-6_3.9Sb at 10, 15 and 20 wt%. Table 2 shows compositions and physical properties of VWP-6_3.9Sb containing ZWP. The fluidities of all glasses containing ZWP were superior to that of a commercial lead-based glass (S = 1.6) as shown in Figure 3. The coefficient of thermal expansion of the glasses decreased with increasing of the amount of ZWP. The coefficient of VWP-6_3.9Sb containing 15 wt% ZWP was extremely close to that of soda lime glass (Table 2). This glass showed a bonding strength of 3.3 kgf cm^{-2} (Table 2). We previously reported that a commercial lead-based glass containing 10 wt% ZWP had a nearly identical thermal expansion coefficient to soda lime glass (7.0 × 10^{-6} °C^{-1}) and the lead-based glass exhibited a bonding strength of 3.4 kgf cm^{-2} [14]. These results demonstrate that VWP-6_3.9Sb containing 15 wt% ZWP showed comparable bonding strength with a commercial lead-based glass.

CONCLUSION

VWP-6_3.9Sb showed high water durability and good fluidity. The bonding strength of VWP-6_3.9Sb containing 15 wt% of ZWP was equivalent to that of a commercial lead-based glass. IR analysis suggested that improved water durability of V_2O_5-H_2WO_4-KPO_3 glasses by incorporating Sb_2O_3 was due to reduced hydrolysable P-O-P bonds.

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CONFLICT OF INTEREST STATEMENT

The authors declare that there is no conflict of interest that could be perceived as prejudicing the impartiality of the research reported.

NOMENCLATURE

L	:	Weight loss ratio, %
N	:	Bonding strength, kgf cm^{-2}
S	:	Fluidity
S_a	:	Area of glass after sealing, cm^2
S_b	:	Area of glass before sealing, cm^2
T_f	:	Glass softening temperature, °C
T_g	:	Glass transition temperature, °C
T_x	:	Crystallization temperature, °C
W_a	:	Weight of glass after immersion in boiling water and drying, g
W_b	:	Weight of glass before immersion in boiling water, g
α	:	Coefficient of thermal expansion, $°C^{-1}$

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