

Preparation and properties of SnO-SnCl₂-P₂O₅ glass

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Abstract

The glass forming region in the ternary system SnO-SnCl₂-P₂O₅ has been determined. Glass transition temperature(T_g), dilatometric softening temperature(T_s) of the glass, and the viscosity of the melts in the binary SnO-P₂O₅ and SnCl₂-P₂O₅ systems were measured. Compositional dependencies of these properties have been investigated. The T_g and T_s of the glasses and the viscosity of melts for the SnO-P₂O₅ glasses increase linearly with increasing the SnO content in a range of 40-60 mol % SnO. The substitution of chlorine for oxygen by increasing the SnCl₂/SnO ratio results in a decrease the T_g and T_s of the glasses and the viscosity of the melts. The T_g and T_s of the glasses and the viscosity of the melts of the SnCl₂-P₂O₅ system increase between 40 and 60 mol%SnCl₂, show a maximum at about 60 mol%SnCl₂, and then decrease with further addition. The effects of the compositions on these properties were discussed comparing them with those of the SnF₂-P₂O₅ system.

Introduction

Glasses with low melting temperature are used for a number of electronic applications¹⁾ such as sealing materials of Hybrid IC, silicon semiconductor and PDP substrate. Until now, the glass compositions used are mainly borosilicate glasses containing large amount of PbO. However, the development of Pb free glass system will be required from the environment viewpoint. Since the finding of Tick²⁾, Sn-P-O-F glass has a low melting temperature, and thus, will be attractive in the future instead of glasses containing PbO. Many researchers³⁻⁶⁾ investigated the thermal properties and structure³⁻⁶⁾ of Sn-P-O-F glasses, in which volatilization losses during melting could result in changes in composition, with accompanying changes in properties. The volatilization of fluorine as HF was considered to be major loss. The exact compositions of the glasses could not be determined, because it was difficult to determine the content of fluorine in the glasses by chemical analysis. In the meanwhile, the Sn-P-O-Cl glass is also expected to have a lower melting temperature. Hu et.al⁷⁾ have reported the thermal properties and glass structure of this glass. However, the compositional dependencies of the properties have not been systematically studied, and the content of chlorine in the glasses by chemical analysis was not performed. Chemical analysis is possible for chlorine. Although the viscosity of the melts is becoming an important property for determining the sealing temperature, there have been no reports on it.

In this study, the glass forming region in the ternary system SnO-SnCl₂-P₂O₅ has been determined. Glass transition temperature(T_g), and dilatometric softening temperature(T_s) of the glass, and the viscosity of the melts in the binary SnO-P₂O₅ and SnCl₂-P₂O₅ systems were measured. Compositional dependencies of these properties were investigated, comparing them with those of the SnF₂-P₂O₅ system.

Experimental Procedure

Reagent grade NH₄H₂PO₄, SnO and SnCl₂ were used as raw materials for preparing of glasses. A batch of each composition shown in Table 1, consisting of 20g of raw materials, was mixed using a mortar and pestle. The glasses for measuring properties were melted in an uncovered alumina crucible at 773K for 5min in air, poured into a graphite mold heated at the glass transition temperature(T_g), and subsequently annealed at around T_g to remove the residual stress. Because the volatilization during melting could result in a change of composition, various temperatures and time for melting were examined. Using temperatures of 573, 673 and 773 K, and times for 5, 30 and 60 min, the content of chlorine and the properties of glasses were measured.

The composition of the glass samples were analyzed by the X-ray fluorescence spectroscopy (physics electrical machinery system 3270) using the fundamental parameter method, and the residual content of chlorine was determined. For the determination of glass forming region, X-ray diffraction analysis was performed. Liquidus temperature, T_L was measured by the hot thermocouple method⁸⁾. T_g was measured by differential thermal analyzer (Thermo Plus, TG8120, Rigaku, Japan) with a heating rate of 5K/min. T_s was measured using the thermomechanical analysis apparatus (Thermo Plus, TMA8310, Rigaku, Japan) with a heating rate of 5K/min using alumina as a standard sample. The viscosity of the melts were measured using the rotational crucible method⁹⁾. The infrared absorption spectrum of each glasses was measured by the KBr pellet technique.

Results and Discussions

The effect of melting temperature and time on the residual content of chlorine in SnCl₂-P₂O₅ glasses were investigated. At melting temperature of 573 K, it was independent of melting time, and was around 40-60 mol% SnCl₂. However, the glasses were readily attacked by moisture, which means that its chemical resistance was extremely low. At melting

temperature of 773 K, the residual content of chlorine varied with melting time. It was found that almost no chlorine was detected for a glass sample melted 30 min.

Figure 1 shows the glass forming region of the ternary $\text{SnO-SnCl}_2\text{-P}_2\text{O}_5$ system melted for 5 min at 573, 673 and 773K. The glass compositions shown as double open circles in Fig. 1 were chosen for measuring some properties. The batch and analyzed compositions of samples melted at 773K for 5min used are listed in **Table 1**. The residual contents of chlorine in $\text{SnCl}_2\text{-P}_2\text{O}_5$ glasses were found to be about 26-37 mol%. It was considered that the major loss of chlorine occurred by the volatilization of HCl. It was found that glasses with P_2O_5 content above 50mol% or SnO content below 30 mol% had hygroscopic nature, and thus, not suitable for practical applications. A glass with composition of 70 SnCl_2 -30 P_2O_5 had the best chemical resistance in this work. The glass samples are hereinafter expressed by their batch compositions. When comparing the $\text{SnO-P}_2\text{O}_5$ system with the $\text{SnCl}_2\text{-P}_2\text{O}_5$ systems, the substitution of chlorine for oxygen by increasing the SnCl_2/SnO ratio results in an increase of glass forming region.

Figure 2 shows the results of XRD measurement for the 70 SnO -30 P_2O_5 and 70 SnCl_2 -30 P_2O_5 glasses. Crystalline phase that existed in the 70 SnO -30 P_2O_5 composition was not identified using the JCPDS card, however, those of the 70 $\text{SnO}_2\cdot 30\text{P}_2\text{O}_5$ composition was identified based on the result of high resolution X-ray spectroscopy¹⁰⁾. It was considered that valence state of Sn ion might change from 2+ to 4+, which could be affected by compositions, temperatures and atmosphere during melting.

Figure 3 shows the result of TL of $\text{SnO-P}_2\text{O}_5$ and $\text{SnCl}_2\text{-P}_2\text{O}_5$ systems. In a range of 40 – 60 mol% SnO content, TL increased monotonically with increasing the SnO content. In the composition of 70mol% SnO, the solid state reaction was occurred at 773K to form the 70 $\text{SnO}_2\cdot 30\text{P}_2\text{O}_5$ crystal phase. In the meanwhile, TL of the $\text{SnCl}_2\text{-P}_2\text{O}_5$ are lower than those of $\text{SnO-P}_2\text{O}_5$, and the chlorine seems to contribute to the lowering of TL. A maximum in TL is observed at about 60 mol% SnCl_2 and then decreased with the further addition in SnCl_2 . Chlorine in the $\text{SnCl}_2\text{-P}_2\text{O}_5$ glasses contributed both to decrease TL and to make the melt uniform, and thus to extend the glass forming region. The variation in TL of $\text{SnCl}_2\text{-P}_2\text{O}_5$ glasses seems to be related to the Sn content, because the residual content of chlorine in the $\text{SnCl}_2\text{-P}_2\text{O}_5$ glasses was approximately constant.

Table1 summarizes the T_g and T_s of $\text{SnO-SnCl}_2\text{-P}_2\text{O}_5$ glasses examined in this study. **Figure 4** shows the effect of the Sn content on the T_s of the glass. The T_s value of $\text{SnF}_2\text{-P}_2\text{O}_5$ glasses previously reported by the author was also shown in this figure. In the $\text{SnO-P}_2\text{O}_5$ glasses, T_s increases monotonically with increasing the Sn content. The T_s of the $\text{SnCl}_2\text{-P}_2\text{O}_5$ glasses increased between 40 and 60mol% SnCl_2 , a maximum at about 60 mol% SnCl_2 , and then decreased with further addition. The variations of T_s for $\text{SnO-P}_2\text{O}_5$ and $\text{SnCl}_2\text{-P}_2\text{O}_5$ glasses were consistent with those of TL, which indicates chlorine in the $\text{SnCl}_2\text{-P}_2\text{O}_5$ glass contributes for decreasing T_s . The variation of T_s for the $\text{SnCl}_2\text{-P}_2\text{O}_5$ glass was also similar with that of $\text{SnF}_2\text{-P}_2\text{O}_5$.

Figure 5 shows the temperature dependencies of the viscosity of the $\text{SnO-P}_2\text{O}_5$ and $\text{SnCl}_2\text{-P}_2\text{O}_5$ systems. The viscosity data of the 60 SnF_2 -40 P_2O_5 glass previously reported by the author⁶⁾ are also shown in this figure. When comparing 60 SnO -40 P_2O_5 with 60 SnF_2 -40 P_2O_5 , They have nearly the same viscosity value. It was considered that the volatilization of HF during the viscosity measurement could results in a change of composition, for example, SnF_2 could change to SnOF_2 ⁶⁾. As for the $\text{SnCl}_2\text{-P}_2\text{O}_5$ system, the volatilization of HCl during the viscosity measurement in a temperature range of 500-600 K were not detected. This result indicates that the $\text{SnCl}_2\text{-P}_2\text{O}_5$ had an advantage of lowering viscosity against the $\text{SnO-P}_2\text{O}_5$ and $\text{SnF}_2\text{-P}_2\text{O}_5$ systems. Though the viscosity of 50 SnCl_2 -50 P_2O_5 was the lowest, the chemical resistance was low. Consequently, the 70 SnCl_2 -30 P_2O_5 glass, having low viscosity of 0.4 ~ 10Pa·s in a temperature range of 500-600K, would be attractive

in a practical application for sealing glasses. The activation energies for viscous flow (E_a) was calculated using linear relationships in Arrhenius plots. The E_a value of $\text{SnO-P}_2\text{O}_5$ and $\text{SnCl}_2\text{-P}_2\text{O}_5$ had ranges of 102 -138 and 97-106 kJ/mol, respectively. **Figure 6** shows the viscosity data of the $\text{SnO-P}_2\text{O}_5$, $\text{SnCl}_2\text{-P}_2\text{O}_5$, and $\text{SnF}_2\text{-P}_2\text{O}_5$ glasses as a function of Sn content measured at 673K, 573K, and 720K. The viscosity of $\text{SnO-P}_2\text{O}_5$ increases monotonically with increasing the SnO content. As the SnCl_2 content increased in $\text{SnCl}_2\text{-P}_2\text{O}_5$, the viscosity increases, exhibits a maximum at 60 mol% SnCl_2 and then decreases. The variation of viscosity with the SnCl_2 content was consistent with that of $\text{SnF}_2\text{-P}_2\text{O}_5$.

Figure 7 shows infrared absorption spectra of $\text{SnO-P}_2\text{O}_5$ and $\text{SnCl}_2\text{-P}_2\text{O}_5$ glasses. A broad peak observed around 1250cm^{-1} , which corresponds to P=O stretching vibration, decrease with increasing SnO and SnCl_2 . In the $\text{SnCl}_2\text{-P}_2\text{O}_5$ system, there was no P=O double bond over 60 mol % at the SnCl_2 , while it was observed in the $\text{SnO-P}_2\text{O}_5$ system. Although the P-Cl stretching vibration should be appear around $580 \sim 440\text{cm}^{-1}$, it was not observed in this results. Generally, the network modifier (NWM) such as CaO and Na_2O are known to break the P-O-P bond without affecting the P=O double bond. In the $\text{SnO-P}_2\text{O}_5$ system, SnO seems to work as NWM, because the P=O double bond is identified in IR spectra. In our previous study of the $\text{SnF}_2\text{-P}_2\text{O}_5$ ⁶⁾, the variation in T_g , T_s and viscosity as a function of SnF_2 content also showed the maximum at 60 SnF_2 -40 P_2O_5 composition, and $\text{Sn}^{4+}/\text{Sn}^{2+}$ in glasses had the maximum value at this composition judging from the chemical shifts of $\text{SnL}\beta_2$ in the glasses. Thus, we concluded that Sn in this system was able to bridge two PO_4 units when SnF_2 changed to $\text{SnOF}_2(\text{Sn}^{4+})$, and interacted with P=O bonds in the glasses. IR spectroscopy revealed that SnCl_2 frees the P=O double bond, because there is no P=O double bond over 60 mol % of the SnCl_2 content as shown in Fig. 7. It was also observed that the relative amount of P=O bond decreased and ν_3 vibration of PO_4 units became symmetric with increasing the SnCl_2 content. A variation of IR spectra in the $\text{SnCl}_2\text{-P}_2\text{O}_5$ system was consistent with that of $\text{SnF}_2\text{-P}_2\text{O}_5$ system. Therefore, it was suggested that Sn in the $\text{SnCl}_2\text{-P}_2\text{O}_5$ system was interacted with P=O bonds in the glasses and played a role as new network former.

SUMMARY

The glass forming region in the ternary system $\text{SnO-SnCl}_2\text{-P}_2\text{O}_5$ was determined by melting at 573, 673 and 773 K for 5min. The effect of glass composition on the glass transition temperature(T_g), and dilatometric softening temperature(T_s) of the glass, and the viscosity of the melts were investigated. The T_g and T_s of the glasses and the viscosity of melts for the $\text{SnO-P}_2\text{O}_5$ system increased linearly with increasing SnO content in the range of 40-60 mol % SnO. The T_g and T_s of the glasses and viscosity of melts for $\text{SnCl}_2\text{-P}_2\text{O}_5$ system increased between 40 to 60 mol% of SnCl_2 , showed a maximum at about 60 mol%, and then decreased with further addition. The 70 SnCl_2 -30 P_2O_5 glass having low viscosity of $0.4 \sim 10\text{Pa}\cdot\text{s}$ in a temperature range of 500-600K, would be attractive in a practical application for sealing glasses. Variation of T_s , viscosity and IR spectra in the $\text{SnCl}_2\text{-P}_2\text{O}_5$ system were consistent with those of $\text{SnF}_2\text{-P}_2\text{O}_5$ reported by our previous work. It was suggested that Sn in $\text{SnCl}_2\text{-P}_2\text{O}_5$ system interacted with P=O bonds in the glasses and played a role as new network former.

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Figure & Table Caption

Figure 1 Glass forming region of the ternary $\text{SnO-SnCl}_2\text{-P}_2\text{O}_5$ system melted for 5min at 573, 673 and 773K.

Figure 2 XRD patterns of 70 SnO -30 P_2O_5 and 70 SnCl_2 -30 P_2O_5 systems.

Figure 3 Effect of the glass composition on liquidus temperature for $\text{SnO-P}_2\text{O}_5$ and $\text{SnCl}_2\text{-P}_2\text{O}_5$ systems.

Figure 4 Effect of the glass composition on T_s of $\text{SnO-P}_2\text{O}_5$, $\text{SnCl}_2\text{-P}_2\text{O}_5$ and $\text{SnF}_2\text{-P}_2\text{O}_5$ systems.

Figure 5 Temperature dependencies of the viscosity of $\text{SnO-P}_2\text{O}_5$, $\text{SnCl}_2\text{-P}_2\text{O}_5$ and $\text{SnF}_2\text{-P}_2\text{O}_5$ systems.

Figure 6 Effect of the glass composition on viscosity of $\text{SnO-P}_2\text{O}_5$, $\text{SnCl}_2\text{-P}_2\text{O}_5$ and $\text{SnF}_2\text{-P}_2\text{O}_5$ systems.

Figure 7 Infrared spectra of glasses in the $\text{SnO-P}_2\text{O}_5$ and $\text{SnCl}_2\text{-P}_2\text{O}_5$ systems.

Table 1 Compositions and properties of $\text{SnO-P}_2\text{O}_5$ and $\text{SnCl}_2\text{-P}_2\text{O}_5$ glasses.

Table 1 Compositions and properties of $\text{SnO-P}_2\text{O}_5$ and $\text{SnCl}_2\text{-P}_2\text{O}_5$ glasses.

composition (mol%)						T _g (K)	T _s (K)
SnO	Batch SnCl ₂	P ₂ O ₅	SnO	Analyzed SnCl ₂	P ₂ O ₅		
40		60	40.5		59.5	393.0	415.4
50		50	49.8		50.2	432.3	447.5
60		40	60.7		40.3	472.6	486.8
	40	60	14.7	25.8	59.5	350.4	359.3
	50	50	15.5	35.1	49.4	386.2	397.2
	60	40	24.4	35.4	40.2	409.4	429.2
	70	30	33.1	36.8	30.1	390.7	411.2

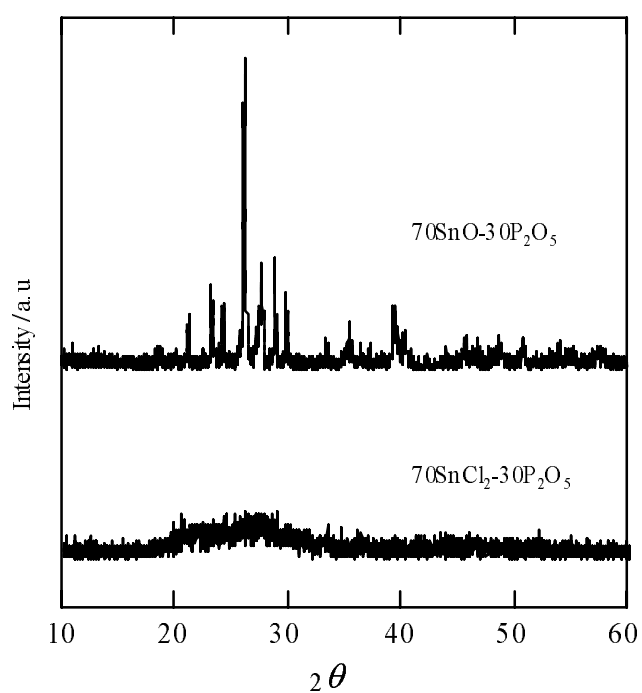


Figure 2 XRD patterns of $70\text{SnO-}30\text{P}_2\text{O}_5$ and $70\text{SnCl}_2\text{-}30\text{P}_2\text{O}_5$ systems.

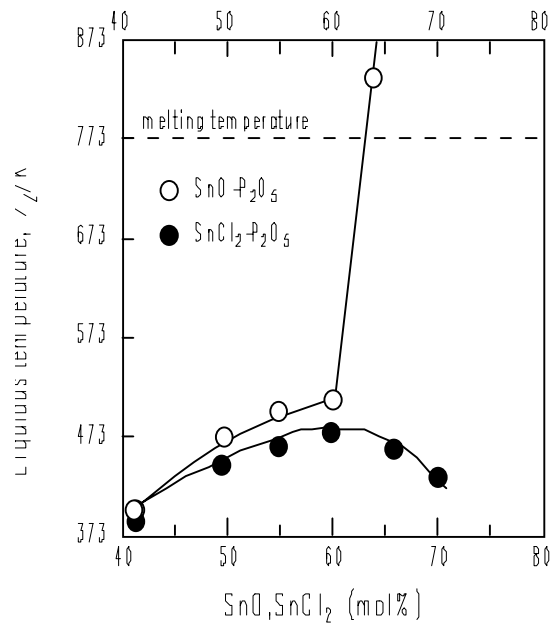


Figure 3 Effect of the glass composition on liquidus temperatures for SnO-P₂O₅ and SnCl₂-P₂O₅ systems.

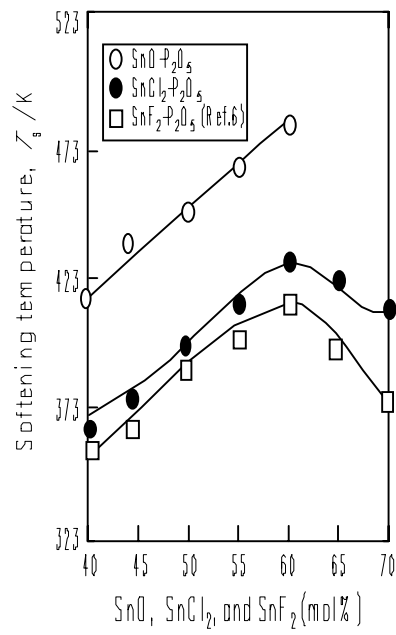


Figure 4 Effect of composition on T_s of SnO-P₂O₅, SnCl₂-P₂O₅ and SnF₂-P₂O₅ glass systems.

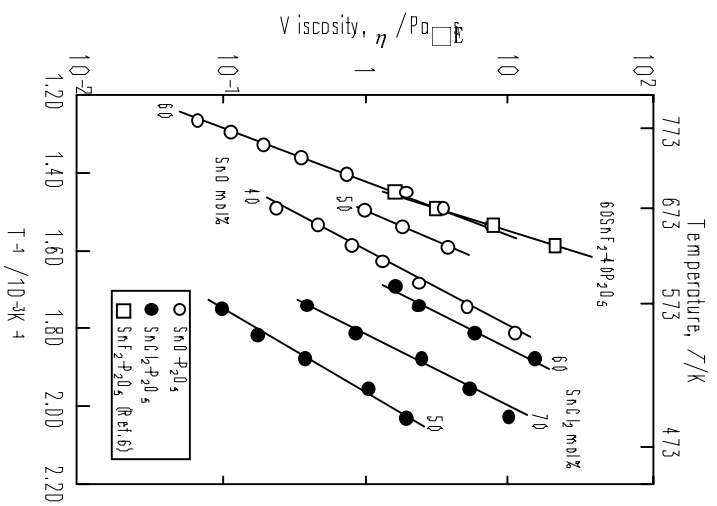


Figure 5 Temperature dependence of the viscosity of $\text{SnO}-\text{P}_{205}$, $\text{SnCl}_2-\text{P}_{205}$ and $\text{SnF}_2-\text{P}_{205}$ systems.

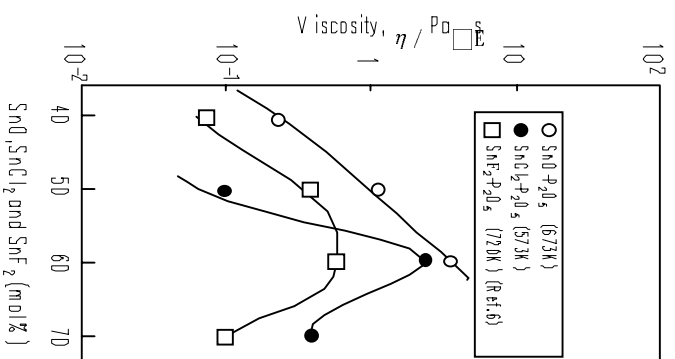


Figure 6 Effect of the glass composition on viscosity for $\text{SnO}-\text{P}_{205}$, $\text{SnCl}_2-\text{P}_{205}$ and $\text{SnF}_2-\text{P}_{205}$ systems.

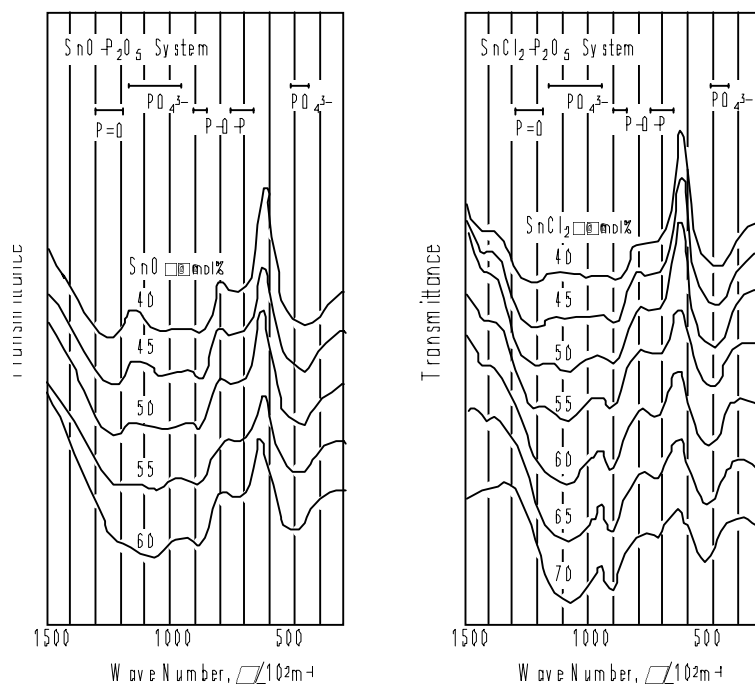


Figure 7 Infrared spectra of glasses in the $\text{SnO}-\text{P}_2\text{O}_5$ and $\text{SnCl}_2-\text{P}_2\text{O}_5$ systems.

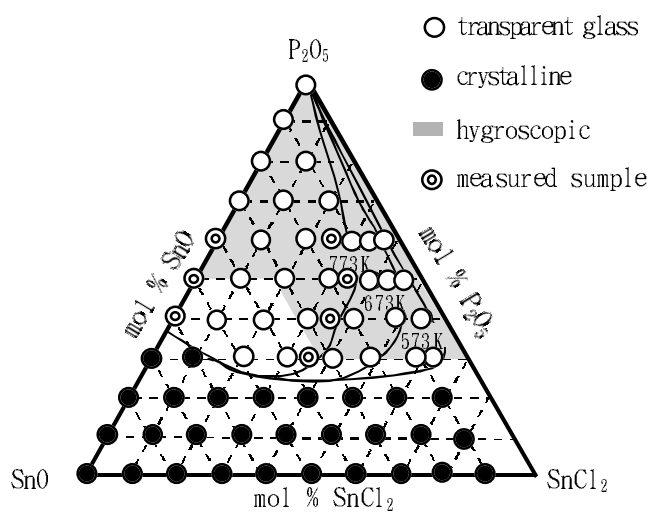


Figure 1 Glass forming region in the $\text{SnO}-\text{SnCl}_2-\text{P}_2\text{O}_5$ system at melting time for 5min.