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THE EFFECTS OF CULLET LEVEL IN THE FORMATION OF P_2O_5 - CaO BASED GLASS.

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ABSTRACT

Factors in determining the right composition of the starting material for cullet-P_2O_5-CaO glass system were studied. The formation of the glass is very much compositional dependence and the best sets for the glass formation was found to be in the range between 60 wt% P_2O_5 + (40 – x) wt% cullet + x wt% CaO where $1 \leq x \leq 5$. The samples are less hygroscopic as the composition of CaO which is acting as a modifier increases. The suitable temperature for glass melting was 1450^{o}C and the time needed was 5 hours for the mixture to melt completely before it can be quenched. The microstructure of the glass samples were examined by Scanning Electron Microscopy (SEM) and X -Ray Diffraction (XRD). The actual composition of the samples were determined by The Energy Dispersive Analysis by X-ray (EDAX).

INTRODUCTION

Most glasses are soda-lime-silica type where silica is the major component and has been chosen in glass industry for commercial usage [1,2]. Other types of oxide glasses that have been useful are B_2O_3, GeO_2, P_2O_5 and As_2O_3. In this study, phosphate glass was used as the parent glass in the system. Although phosphate is hygroscopic, the criterion that allows it to be used in many applications is closely related to the glass molecule structure [5]. Beside phosphate, cullet has been chosen as one of the component in this glass system. In glass industry, the recycled glass is known as cullet. Cullet is known as the waste glass either from the rejected units or ecological waste glass [3]. Cullet has been used in glass container manufacturing industry for many years. Studies have shown that the raw cullet could give better glass properties if added with suitable amount of composition to the raw material to form glass container [2,4]. It is important to determine the right composition of the starting material and suitable condition for glass preparation. However, the lack of information and literature in describing these factors has become the motivating factor of these studies.

EXPERIMENTAL PROCEDURE

A relatively fine powder (< 50 μ) of cullet, P_2O_5 (purity 97%) and $CaCO_3$ were mixed in a proportional weight in a platinum crucible. The mixture is well mixed to ensure the

homogeneity before being sintered at 1450^{o}C for 5 hrs in normal atmosphere. The melt is then quenched in between two brass plates before being annealed at 400 ^{o}C for one hour and then allowed to cool down to room temperature. The bulk glass is then cut into regular cubic shapes of 1cm x 1cm x 1cm in dimension. The glass is then polished with 400, 600, 800 and 1200 grit SiC paper to get a scratch free surface. The glass formation were studied in terms of X-Ray and SEM analysis.

RESULTS AND DISCUSSION

There were many attempts that have been made in trying to obtain good glasses. From the experiments, the right composition of the starting material was determined. The composition was melted and sintered at selected temperature. Only by using the sets of above mentioned glass preparation techniques, good glasses can then be obtained. Other than this combination of composition and sintering condition, the glass formation are found to be unsuccessful. Table 1 shows the composition of glass samples, which were well formed under 1450^{o}C melting temperature and sintered for 5 hours.

From Table 1 the best sets for the glass formation was found to be in the range between 60 wt% P_2O_5 + (40 – x) wt% cullet + x wt% CaO where $1 \leq x \leq 5$. The samples are less hygroscopic as the composition of CaO increases. The CaO as modifier has altered the glass network because P - O - P bond in glass is easily disrupted by the excessive presence of CaO. The basic building block in phosphate glasses is the phosphorous-oxygen tetrahedron which contains a double bond to one of its surrounding oxygen atoms. The addition of alkali or alkaline earth oxides such as CaO would break up the phosphate network. According to Doremus (1973), in his study of two calcium phosphate glasses of composition 42 wt% CaO and 49 wt% CaO, it is found that one-fourth of the phosphorous-oxygen bonds are π–bonds (directed double bonds) and the glass with less calcium has more P – O – P links [5].

There were also many other attempts that have been done on various sets of composition and sintering temperature and this can be seen in Table 2. From this table, it is obvious that the formation of the glass is very much compositional dependence. It shows that, only glass with composition of 60 wt% P_2O_5, (marked by *) can form into glass. Samples with less than 60 wt% P_2O_5, will have more than 40 wt% cullet, were difficult to melt during sintering and crystallised when cooled, so glass was not formed. For samples with more than 60 wt% P_2O_5 and less than 40 wt% cullet, the mixture were difficult to melt during sintering and very hygroscopic in nature. The samples absorbed air. For composition with more than 40 wt% cullet, the mixture were hardly melted because silica which is the main component of cullet has a very high melting temperature. The addition of CaO helps to reduce the stress and lower down the melting temperature and it is found that the suitable composition of CaO added was about 5 wt%. If the composition of CaO was more than 5 wt% the mixture will become very saturated and not homogenous.

Table 1: The composition and some physical properties of well formed glass.

Sample	Nominal Composition (wt%)			Summary	XRD of glass
	P_2O_5	Cullet	CaO		
S1	60	35	5	homogenous, opaque and not hygroscopic	amorphous
S2	60	36	4	homogenous, opaque and not hygroscopic	amorphous
S3	60	37	3	homogenous, frosted and less hygroscopic	amorphous
S4	60	38	2	homogenous, less frosted and less hygroscopic	amorphous
S5	60	39	1	homogenous, very clear and less hygroscopic	amorphous

Another important factor to be considered in glass forming is the sintering temperature. There were certain samples which have more than 60 wt% P_2O_5 were found to be difficult to melt at lower temperature but easily melted at higher temperature. The suitable sintering temperature for melting glass was 1450^oC. For temperature lower than 1450^oC, the glass did not melt completely. The time needed for melting glass was noted. It takes 5 hours for the mixture to melt completely before it can be quenched. From the table, it is noticed that, although the temperature had been raised to 1450^oC, the mixture still could not melt completely if the sintering time was less than 5 hours. This is due to the fact that Si-O and P-O-P bond in the glass network were difficult to be disrupted. The addition of CaO would help in reducing the stress in the glass network and enhanced as a glass modifier [6].

Samples that were well formed were examined using the XRD analysis. This analysis is used to detect the presence of any crystallinity in the glass sample. The XRD spectra of the glasses are shown in Figure 1. It is found that there was no crystalline phase occurs as there was no significant peak in the spectra obtained. Therefore the samples were amorphous, thus confirming that the samples were glass. If there were peaks occurred in the spectra, this would indicate that the material is a crystalline solid. This is because crystals have a geometrical arrangement of atoms in long-range order in a lattice. Lattices are different types of regular arrays of points in space such as cubic, rhombic, hexagonal and others. The peaks

which occurred in the spectra would identify the lattice point. Whereas an amorphous solid does not have long-range atomic order because the sub-units are packed randomly.

Table 2 : Experimental conditions attempted for various glass composition and the result.

Set	P_2O_5	Cullet	CaO	Sintering Temp. (^oC)	Time (hrs)	Result
A	90	10	0	1000	3	not melting, very hygroscopic
	90	10	0	1000	4	not melting, very hygroscopic
	90	10	0	1200	3	not melting, very hygroscopic
	90	10	0	1200	4	not melting, very hygroscopic
	90	10	0	1300	4	not melting, need longer time
	90	10	0	1300	4	not melting, need longer time
	90	10	0	1400	4	melting, very hygroscopic
B	80	20	0	1000	3	not melting, very hygroscopic
	80	20	0	1000	4	not melting, very hygroscopic
	80	20	0	1100	3	not melting, very hygroscopic
	80	20	0	1100	4	not melting, very hygroscopic
	80	20	0	1300	3	halfly melt, crystallised
	80	20	0	1300	4	halfly melt, crystallised
	80	20	0	1400	4	melting, very hygroscopic
C	70	30	0	1000	4	not melting, turn into blue
	70	30	0	1100	4	not melting, crystallised
	70	30	0	1300	3	not melting, crystallised
	70	30	0	1300	4	not melting, crystallised
	70	30	0	1400	4	melting, crystallised easily
D	60	40	0	1000	4	not melting, white substance
	60	40	0	1300	3	not melting, crystallised easily
	60	40	0	1300	4	halfly melt, not homogenous
	*60	40	0	1400	4	melting, formed into glass but not homogenous
E	50	50	0	1000	4	not melting, hard
	50	50	0	1200	4	not melting
	50	50	0	1300	4	not melting, crystallised
	50	50	0	1400	4	halfly melt, crystallised

Table 2 : Experimental conditions attempted for various glass composition and the result (continued).

Set	Nominal comp (wt% P_2O_5	Cullet	CaO	Sintering Temp.(^oC)	Time (hrs)	Result
F	49	50	1	1400	41/2	saturated, crystallised
	48	50	2	1400	41/2	saturated, crystallised
	47	50	3	1400	41/2	saturated, crystallised
	46	50	4	1400	41/2	saturated, crystallised
	45	50	5	1400	41/2	saturated, crystallised
	45	45	10	1450	41/2	saturated, crystallised
	45	50	5	1450	41/2	saturated, crystallised
	50	45	5	1450	41/2	saturated, crystallised
G	90	5	5	1400	41/2	hardly melt
	80	15	5	1400	41/2	hardly melt
	70	25	5	1400	41/2	not melting
	*60	35	5	1400	41/2	formed into glass, hygroscopic
	50	45	5	1400	41/2	not melting
	40	55	5	1400	41/2	not melting
	30	65	5	1400	41/2	not melting
	20	75	5	1400	41/2	not melting
	10	85	5	1400	41/2	not melting
H	*60	35	5	1450	41/2	melting, opaque glass, not hygroscopic
	*60	34	6	1450	41/2	formed into glass but not homogenous
	*60	33	7	1450	41/2	formed into glass but not homogenous
	*60	32	8	1450	41/2	formed into glass but not homogenous
	*60	31	9	1450	41/2	formed into glass but crystallised easily
	*60	30	10	1450	41/2	formed into glass but crystallised easily

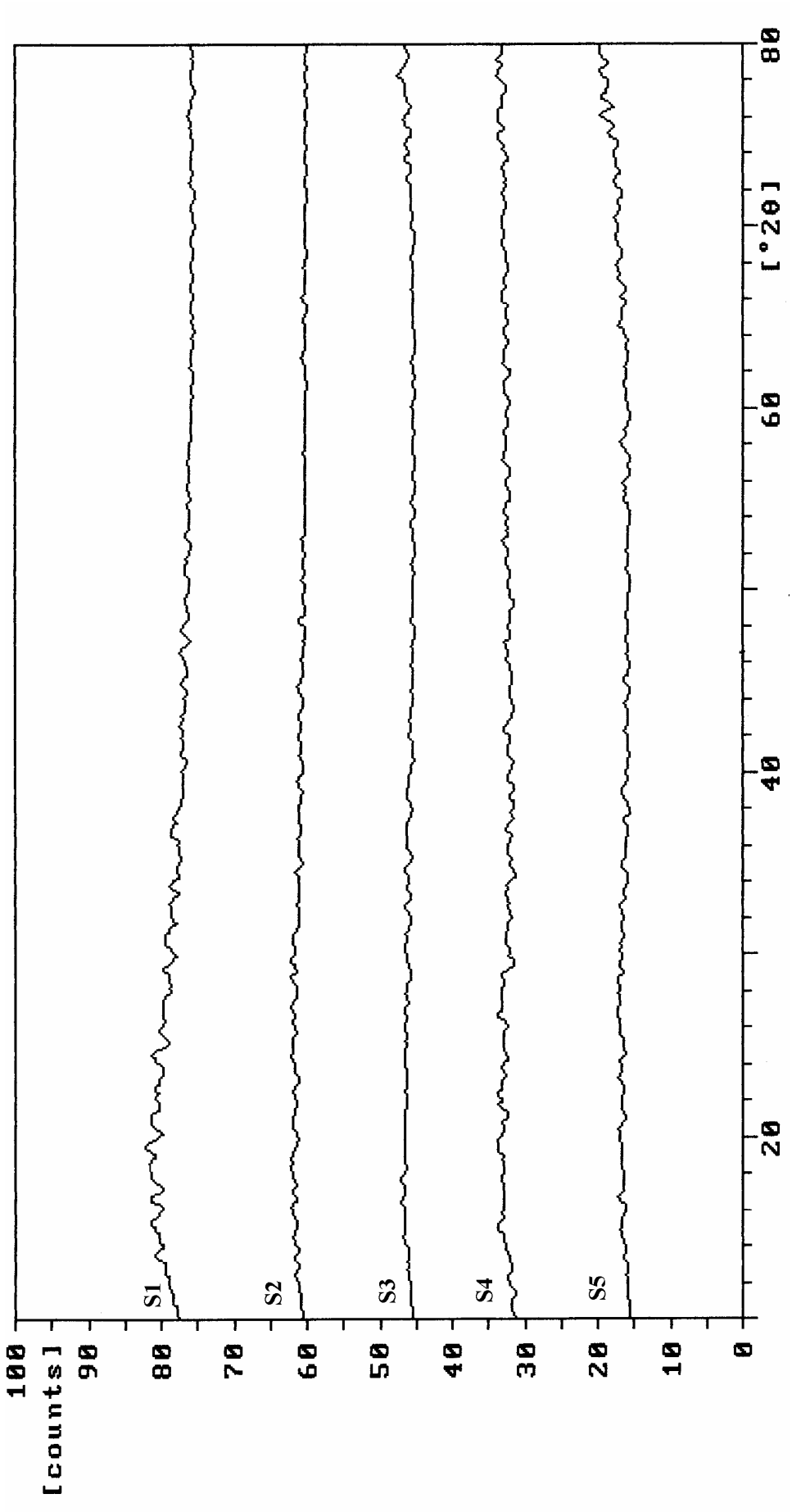

Figure 1: XRD spectra of the amorphous phases of glass samples, sintered at 1450°C for 5 hours.

Figure 2 shows the optical micrographs of the glass surface which are obtained from the Scanning Electron Microscopy (SEM). The micrographs show that, the surface structure of the samples are different from one another.

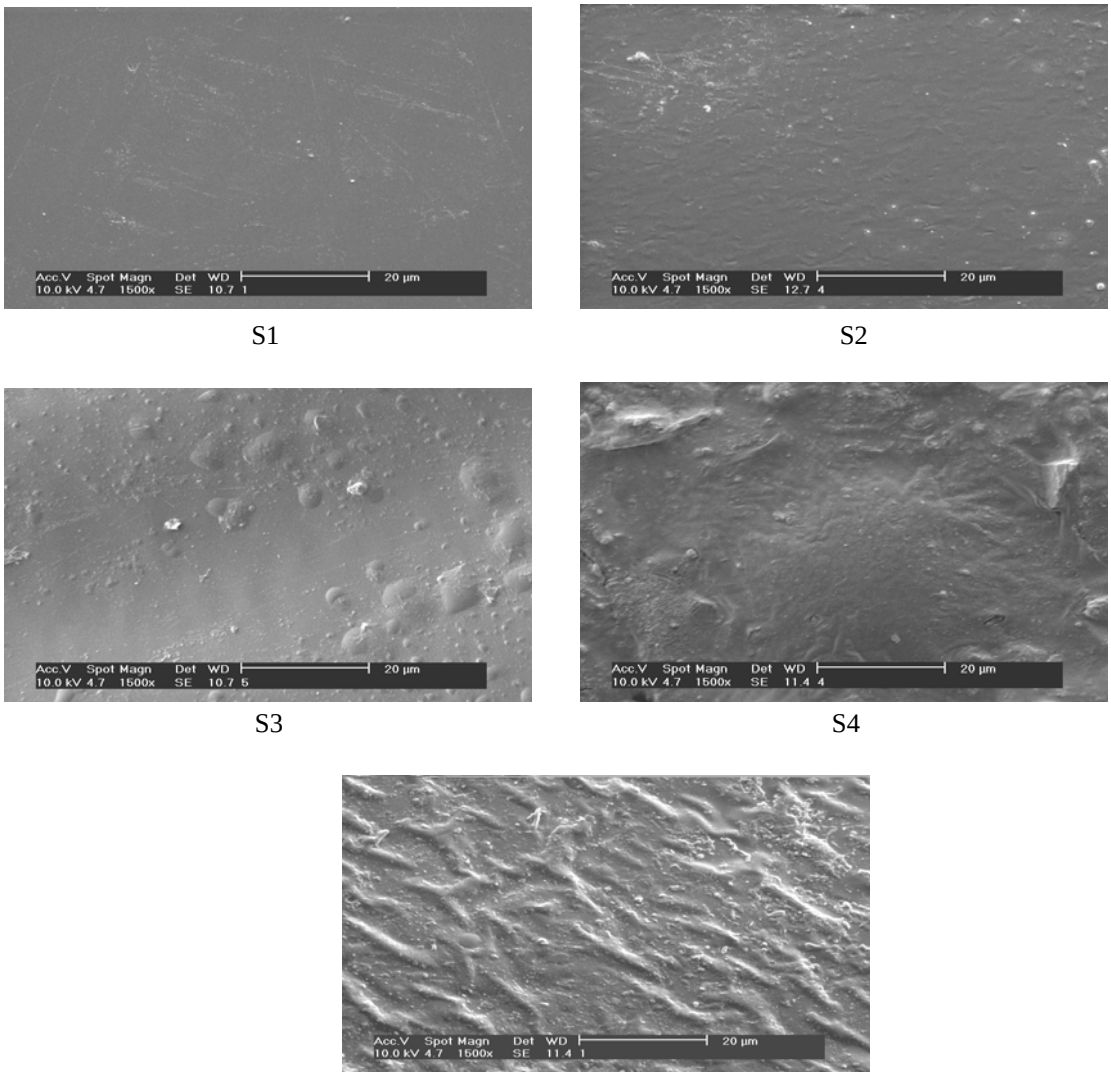

Figure 2: SEM micrographs of well-formed glasses with various cullet content.

Generally, samples with less cullet content and higher CaO are more smoother. Surface area of S1 which contained 35 wt% cullet are even and fine. As the cullet content increases, the surfaces are getting uneven and corrugated and this can be seen especially in S5. Sample S5 which contained 39 wt% cullet content has developed creases on the entire surface. This was due to the higher content of CaO that allowed the glass matrix to become uniform and help into the formation of cullet/glass network much better. According to Newton (1985), the optimum amount of CaO added is 5 wt% and the use of much more CaO will cause failure in glass formation [6].

CONCLUSION

A very good glass can be formed solely at a certain range of composition as well as the right melting temperature. From the experimental evidence, it was observed that changes in the composition would result in the changes of the glass properties. In this study, the glass formation occurs in the range of 60 wt% P_2O_5 + (40 – x) wt% cullet + x wt% CaO where $1 \leq x \leq 5$. Varying compositions and sintering conditions contribute to the changes in the properties of the glass and also its behaviour.

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