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Low melting glasses in the system SnF_2-$SnCl_2$-PbO-P_2O5

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The glasses in the system SnF_2-$SnCl_2$-PbO-P_2O_5 are very interesting because their very low melting and processing temperatures combined, in some cases, with a quite satisfactory chemical stability. Experimenting procedures to avoid the PbO reduction glasses were synthesized and some properties were determined, among them Tg and Td, confirming the possibility to melt and process these glasses at temperatures under 500 °C. In a first attempt to determine the basicity of such glasses, verisimilar values were obtained placing them in the domain of the good glass forming compositions. The peaks in the recorded IR spectra were assigned and seem to confirm the glass forming ability of Sn halogenides, which forms tetrahedrons like P.

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1. Introduction

Low melting glasses are attractive from many points of view, among them, the low energy consumption for melting and processing, the longer resistance of refractory materials, the possibility of obtaining some interesting hybrid inorganic-organic materials etc. The inherent disadvantages are related to the low energy of the chemical bonds, generating weak glass structures having, especially, low chemical stability in the usual environment. With the hope to find the possibilities to avoid the main disadvantage, many research works were done throughout the world.

In principle, one may distinct two categories of low melting glasses: having melting and processing temperatures not higher than 1000 °C and other with melting and processing temperatures even under 500 °C. The second category is, for many reasons, more interesting but the mentioned disadvantages are also more pronounced. The research in this field was strongly encouraged by the results obtained by Tick [1, 2] which selected, in the system Pb-Sn-P-O-F, a region with a chemical stability comparable with that of some usual optical glasses and working temperatures of the order of 500 °C or less.

In the Laboratory of Glass Chemistry and Technology, of the faculty of Applied Chemistry and Materials Science in the University Politehnica Bucharest the study of such glasses began in 1995 resulting in some published papers [3] and reports in the frame of a program supported by Ministry of Education and Research [4]. There were obtained glasses with processing temperatures between 1000 and 500 °C, some of them of good quality and quite chemically stable in the normal medium.

Taking into account that the difficulties encountered in melting a raw materials batch containing together PbO and SnO or SnF_2 were not completely avoided the study of very low melting glasses was resumed in the last years [5] and some new results are presented in this communication.

2. Melting procedures

To obtain glasses in the system SnF_2-$SnCl_2$-PbO-P_2O_5 were used as raw materials reagent grade: SnF_2, $SnCl_2 \cdot 2H_2O$, $NH_4H_2PO_4$ and for PbO metallic Pb or, alternatively, Pb_3O_4. The compositions of the synthesized glasses are given in Table 1. The batches were melted in graphite or ceramic crucibles in electric furnaces.

Table 1. The compositions of the studied glasses, in wt. %.

Glass no.	P_2O_5	PbO	SnF_2	$SnCl_2$
1	27.87	7.45	61.51	3.17
2	40.05	10.90	44.49	4.56

The main problem was the avoiding the reduction of PbO in the medium containing a lot of Sn^{2+}. In a first tentative the way described in [2] was followed. Was prepared firstly a melt containing the $NH_4H_2PO_4$ quantity corresponding to the P_2O_5 necessary for 10 g of final glass and the quantity of powder of metallic Pb, for the needed PbO. This mixture was melted at 450 °C and after 3 hours were added the other two components and finally maintained for 1 hour more at 400 °C. The obtained glass was transparent, homogeneous with a certain luster on the surface suggesting the presence of Pb. In some cases were observed small black impurities, due, probably to the low quality of the graphite crucibles.

In the second procedure was used Pb_3O_4 as source for PbO, counting on the excess of oxygen to avoid the reduction to metallic Pb. The two components were heated at 700 °C to assure the Pb_3O_4 decomposition, which begins at 590 °C. In the resulted clear, fluid and homogeneous melt were introduced the rest of components and the new melt was maintained for 30 minutes at 450 °C. Finally the obtained in this way glasses look as of very good quality.

Using metallic molds were obtained samples for recording UV-VIS spectra and for T_g determination by

means of thermal expansion recording. After annealing, the glass samples were stored in closed boxes with silicagel to avoid the excessive contact with atmospheric humidity. In such conditions, the quality of glass can be maintained for months. For experimental basicity determination were prepared glasses containing 0.1 atomic percents of Cu^{2+} as spectroscopic probe ion, according to the method described in [6].

3. Results

On synthesized glasses were determined some of the properties used to characterize vitreous materials. Were used samples obtained by the second procedure described above. The visual estimation showed a good quality, samples being transparent, homogeneous, and stables enough in normal atmosphere. In the Table 2 are presented the properties considered more interesting in the context of this study.

The density was determined by the Archimedes method using kerosene. The obtained values are of the same order of magnitude as those published by others.

On the recorded thermal expansion curves were determined the glass transition temperatures, Tg, characterized by very low values, indicated in this way too, that the respective melts are fluid at temperatures of the order of 300 ^oC. The dilatometric softening temperatures, Td, confirm the rapid decrease of the viscosity when the temperature increases.

Table 2. Some of the determined properties of synthesized glasses.

Glass no.	Density $g \cdot cm^{-3}$	T_g ^oC	T_d ^oC	pB %
1	3.15	58.5	68.5	60
2	3.54	164	181	55.4

Because the basicity offers usually interesting information about the structure of glasses, an important effort was done to determine this property. The experimental method [6] uses the peak of the charge transfer transition of Cu^{2+} used as a probe ion. This transition is sensible to the basicity of the environment, in this case a glass. The electronic spectrum was recorded by means of a double beam spectrophotometer Shimadzu UV-160A, in comparison with a glass without copper ion. In this way only the copper transitions are recorded. In the figure 1 such a spectrum is presented as example.

The basicity, pB in percents, is obtained by means of the relationship:

$$pB = 151 - 0{,}00259 \cdot \nu \qquad (1)$$

where ν is the peak energy, expressed in cm^{-1}. The indicated, in the Fig. 1, peak position in nm corresponds to 30,211 cm^{-1} and, according to the relationship (1), to a basicity pB = 72.5 %. It is a very high value, taking into account the important concentration of the acid P_2O_5. For comparison was tried the basicity calculation in spite of some difficulties. The oxide basicity may be calculated by means of the formula [7]:

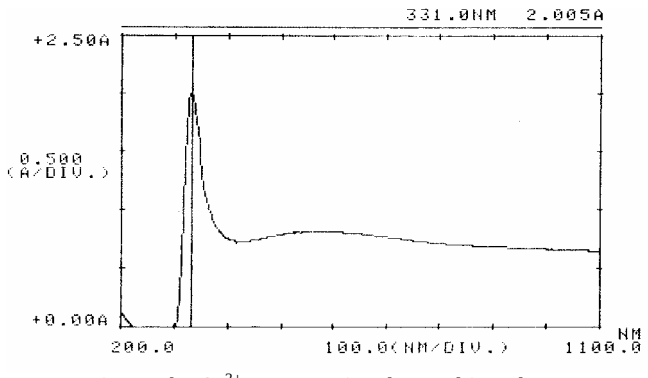

Fig. 1. The Cu^{2+} spectrum in a low melting glass.

$$\log pB = 1.9(CN)^{0.02} - 0.023\frac{P_i}{CN} \qquad (2)$$

where P_i is the ionization potential of the cation in the respective oxidation state and CN is the coordination number. For halogenides, this formula is not applicable. Taking into account that in the pB scale the amount of the ionic character, as defined by Pauling, is used as measuring unit this magnitude was calculated for halogenides using the known formula of Pauling [8]:

$$I_c = 1 - e^{-\frac{1}{4}(X_A - X_B)^2} \qquad (3)$$

using the electronegativities X_A and X_B for the bonded atoms. Resulted the basicities presented in Table 3.

Table 3. The basicity values of the glass components.

Components	P_2O_5	PbO	SnF_2	$SnCl_2$
pB values %	38	70	70.2	30.2

The basicity of glass, of the medium pB_m, is obtained with the formula:

$$pB_m = \Sigma\, pB_i \cdot c_i \qquad (4)$$

pB_i being the basicity of the component i and c_i the concentration in weight fractions. The obtained, in this way, pB values were put in the Table 2. A possible explanation of the observed differences will be discussed later.

Some IR spectra were recorded for these glasses, to compare the structural information with the published ones. One of these spectra, for the glass number 1, is presented in the Fig. 2. The absorption maxima in the region 412 – 542 cm^{-1} which are not discussed in the specialised literature, may be compared with that observed in silicates at 450 cm^{-1} and assigned to the bending of the bond between tetrahedrons. In the studied glass, the presence of tetrahedrons formed by Sn and by P is accepted in [9]. Between 750 and 900 cm^{-1} are observed bands with a strong peak at 844.8 cm^{-1}, assigned to the P –O – P linkage. The peak at 1,107.2 corresponds to the vibrations of P – O – and Sn – O – P [10]. The absence of a clear peak at 1220 cm^{-1} assigned to P = O, seems to

indicate the absence of this bond in the studied glass. The peaks at 1,633.6, 2,862.2 and 3,446.6 are assigned to the vibrations of H_2O [11], probably absorbed during the pellets preparation.

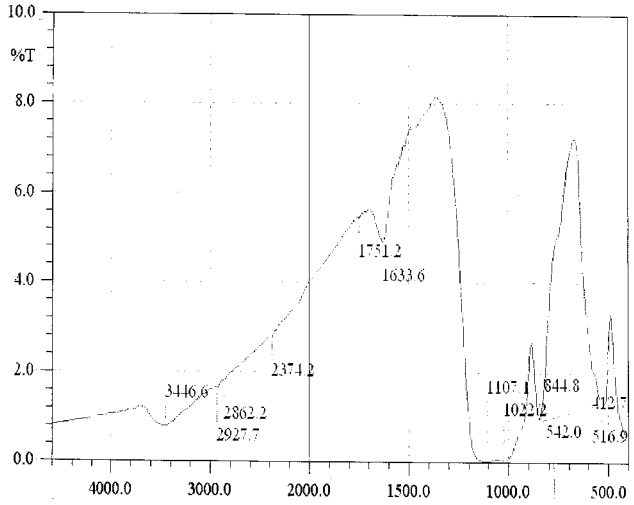

Fig. 2. The IR spectrum of a low melting glass.

4. Discussion

In that concerns the structure of these glasses, the obtained results, especially the IR data, seems to confirm the presence and the importance of bonds including both P and Sn, with oxygen and fluorine as discussed in [1] and [12]. Sn plays the role of a glass former, including the tetrahedral coordination. The increase of the concentration of bonds Sn – F – Sn and P – O – P diminish Tg values but also the chemical stability [12]. The presence of Pb increases the chemical resistance.

The basicity determination encounters difficulties both experimentally and by calculation. It seems that the probe ion Cu^{2+} is partly reduced to Cu^0 which determines the maximum centered at about 600 nm on the spectrum in Fig. 1. In this region appears the maximum of copper ruby (568 nm [13]). The sharp maximum at 331 nm, showing a very high basicity, is difficult explainable. Taking into account the modern concept concerning the nano-heterogeneous structure of glasses [14], one may suggest that the copper ion is attached preferentially to very basic structural nano-aggregates, containing PbO and/or SnF_2, (Table 3) showing on the spectrum such a local situation.

The calculation method, presented above for the halogenides, is affected by the fact that in the used Pauling's electronegativity table are not considered the oxidation state and the coordination number influence. However, the obtained results presented in the Table 2 seem to be closer to the reality.

Finally, it is worth to mention that these very low melting glasses may have interesting application based on particular properties [2] and especially in preparing inorganic-organic glasses with new characteristics [1, 15].

5. Conclusions

Were studied very low melting glasses in the system SnF_2-$SnCl_2$-PbO-P_2O_5**,** successfully experimenting procedures to avoid the PbO reduction.

Some glass properties were determined, among them Tg and Td, confirming the possibility to melt and process these glasses at temperatures under 500 ^oC.

A first attempt was made to determine the basicity of such glasses. The experimental method seems to be negative influenced by the redox reactions of the Cu^{2+} probe ion and the nano-heterogeneous structure of glasses. By calculation were obtained more verisimilar values in the domain of the good glass forming compositions.

The recorded IR peaks were assigned on the basis of published data and the general knowledge. It seems to confirm the glass forming ability of Sn halogenides, which forms tetrahedrons like P.

References

[1] P. A. Tick, Physics and Chemistry of glasses **25**(6) 149-154 (1984).
[2] P. A. Tick, N. Borelli, Optics Letters **23**(22), 1730 (1998).
[3] P. Baltă, C. Bălăşoiu, a) Materiale de Construcţii (Building materials), vol. **25**, 3 (1995), p. 279 and b) in Proced. of the Conference of Chemistry and Chemical Engineering, part II, Bucharest 1995, p. 404 (both in Romanian).
[4] P. Baltă and colaborators, Research reports in the frame of the Program suported by the Ministry of Education and Research, 1998-1999 (in Romanian).
[5] Vasilica Dima, P. Baltă, Roxana Şerban, Revue Roumaine de Chimie, Nr. 4 (2005).
[6] P. Baltă, in Proceedings of the XV-th International Congress on Glass, Vol. 1b, p. 211-215, Leningrad 1989.
[7] P. Baltă, invited conf. in Proc. of the 5th ESG Conf. Glass science and technology for the 21st century, Prague 1999, on CD, B4, Glass structure, p. 3-14.
[8] L. Pauling The nature of the chemical bond, Cornell University Press, Ithaca, New York, 1967, p. 65, 97-102.
[9] X. J. Xu, D. E. Day, Physics and Chem. of Glasses, **31**(5), 183-186 (1990).
[10] L. Hu, Z. Jiang, Physics and Chemistry of Glasses **35**(1), 38-41 (1994).
[11] A. M. Efimov, V. R. Pogareva, A. V. Shashkin, J. Non-Crystalline Solids **332**(1-3), 93-114 (2003).
[12] C. M. Shaw, J. E. Shelby, a) Physics and Chemistry of Glasses, vol. **29**, 3, (1988), p. 87-90; b) J. Am. Ceram. Soc. vol. **71**, 5, C-252-C-253, (1988).
[13] Camelia Căpăţână, P. Baltă, Romanian Journal of Materials, No. 1, 18-29 (2003).
[14] P. Baltă, J. Optoelectron. Adv. Mater. **7**(5), 2347-2352 (2005).
[15] J. M. O'Reilly, K. Papadopoulos, J. of Materials Science **36**, 1595-1600 (2001).

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