Investigation and properties of novel low melting glasses in the ternary system Sb2O3-PbO-Me2O3

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INVESTIGATION AND PROPERTIES OF NOVEL LOW MELTING GLASSES IN THE TERNARY SYSTEM Sb_2O_3-PbO-Me_2O_3

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Abstract

New glasses based on Sb_2O_3–PbO association have been synthesized and characterized. The limits for glass formation have been investigated in ternary systems encompassing an oxide of IIIA group elements like Al_2O_3, Ga_2O_3 and In_2O_3 as the third component. Fast quenching is required to prevent melt crystallization, which results in thin samples. Chemical analysis of elements shows a rather good agreement between nominal and analyzed compositions. Glass transition temperature, Tg, ranges between 255°C and 280°C, depending on composition. Density and hardness have been measured for typical composition.

Keywords

Lead antimony glass. Thermal properties. Density. Hardness

1. Introduction

The use of lead oxide as a significant glass component is older than modern chemistry and physics. In 1675 George Ravenscroft defined a new glass composition containing lead oxide, leading to larger working range in the molten state, reduced hardness and higher refractive index, which increases surface brightness [1, 2].

Heavy Metal Oxide Glasses (HMOG) make a family of special glasses that has been the subject of numerous studies. They may be roughly defined as glasses free of classical vitrifiers SiO_2, B_2O_3, P_2O_5 [3]. These glasses exhibit high refractive index, close to 2, large optical non-linearity and extended optical transmission in the infrared spectrum [4, 5, 6]. Among HMOG, germanate glasses appear as an intermediate group as GeO_2 is considered as a classical network former according to Zachariasen's rules [7], and also because their refractive index is somewhat lower.

Antimonite glasses based on Sb_2O_3 have attracted growing interest, mainly because numerous glass forming systems have been identified so far, especially in polyanionic systems: oxyhalides and oxysulfides. In addition their stability against devitrification may be very large. Antimony oxide glasses have been reported in association to alkali oxides and in multicomponent systems [8, 9, 10].

According to previous reports, $PbO\text{-}Sb_2O_3$ glasses exhibit good chemical durability and low crystallization rates [11, 12]. Addition of the oxides of III A group elements like Al_2O_3, Ga_2O_3 and In_2O_3 to the $PbO\text{-}Sb_2O_3$ based glass is likely to ameliorate their physical properties. The choice of these oxides was based on the occurrence of a binary glass forming range in combination to PbO. Table 1 reports the compositional limits of these binary glasses:

Table 1

M_2O_3	Maximum reported glass forming range (mol % PbO)
Al_2O_3	50-95 mol% PbO[13]; 67 – 95 mol%PbO[14]
Ga_2O_3	69 -81mol%PbO[15]; 58 -82 mol% PbO[16]; 57 - 82 mol% PbO[17];
In_2O_3	< 5 mol% PbO[18]

The aim of the present work is to explore new glass compositions in multicomponent systems based on antimony oxide and to assess the potential of these glasses

2. Experimental

Materials used in this research are Sb_2O_3 (99,9%), PbO (99,9%), In_2O_3 (98%), Ga_2O_3 (98%), and Al_2O_3 (98%) from Aldrich, WWR and Metal Europe. Glass samples were prepared using the standard melt-quenching technique. Crystalline powders were intimately mixed in an agate mortar. Then batch was heated up to melting in glass crucible for 5 min. Finally the melts were cast and quenched between two brass plates to obtain a fast cooling rate close to a few hundred K/S. In these conditions, sample thickness ranges between 0.8 and 1mm.

Main physical characterizations include X ray diffraction, thermal analysis microhardness and density. X-ray diffraction patterns were obtained using Cu Kα radiation on Philips PW1830 difractometer. Differential scanning calorimetric measurements were performed on small samples using a DSC 2010 from TA Instrument in aluminum sealed pans under N_2 atmosphere. Current heating rate was 10 $K.min^{-1}$ and experimental error was ±2°C for glass transition and onset of crystallization. Chemical composition was checked using Oxford Link ISIS probe in a JEOL 6400 Scanning Electron Microscope dispersive –ray spectrometer working at 20 KV. Density was measured using an ACCUPYC 1330 Micrometrics Helium Picnometer with a precision of about ±0,0005g/cm^3. The samples were indented with Matsuzawa MXT set-up. The value is averaged from 10 indentations or more, made on each sample.

3. Results

3.1 Glass formation:

Our primary investigation of the binary Sb_2O_3-PbO based system confirms that the limits for glass formation are extended, when faster quenching rates are used. These limits lie between 80 and 10% mol Sb_2O_3 as shown in Fig1.

Prepared glasses are stable at room atmosphere. At visual inspection, they appear transparent and yellow colored for glass samples between 80 and 40 mol % Sb_2O_3. As PbO content increases, glass samples appear dark. This coloration arises from lead reduction: Indeed, as shown in figure 2, a metallic phase area corresponding to pure lead was observed in a dark glass sample. In practice, melt must be kept at room atmosphere for a longer time –e.g. 8 mn- to ensure oxidizing atmosphere.

In order to confirm glass composition, elemental analysis was performed for some samples with nominal composition (100-x) Sb_2O_3.xPbO (x= 50,60,70,80,90). The analytical results reported in Table 2 show a rather good agreement between nominal and analyzed Sb concentration, while lead concentration is smaller than expected. Silicon content that arises from crucible increases as PbO concentration and melting time increase.

Table 2:

Acronym	mol %		Nominal composition			Analyzed composition			
	Sb_2O_3	PbO	Sb	Pb	O	Sb	Pb	O	Si
$50Sb_2O_3$ 50PbO	50	50	28.57	17.14	57.14	29.5	13.4	55.8	1.3
$40Sb_2O_3$ 60PbO	40	60	25	18.75	56.25	21.7	17.2	54.8	0.9
$30Sb_2O_3$ 70PbO	30	70	20.68	24.13	48.27	21.5	22.3	52.6	3.5
$20Sb_2O_3$ 80PbO	20	80	15.38	30.76	53.84	15.6	27.1	54.0	3.3
$10Sb_2O_3$ 90PbO	10	90	8.69	39.13	52.17	8.2	31.8	55.6	4.4

Glass formation has been investigated in various Sb_2O_3-PbO- Me_2O_3 ternary systems, where Me = Al, In, Ga. Corresponding vitreous areas in nominal compositions are reported in fig3.

For all these systems, the experimental vitreous area is very narrow. For example, In_2O_3 content should not exceed 5 mol % while it may reach 15 mol % with Al_2O_3 and Ga_2O_3. Sample color remains yellow fro the ternary glasses containing Al_2O_3 and Ga_2O_3 but it turns to green for the largest In_2O_3 contents.

3.2 X Ray Diffraction

The XRD patterns confirm the amorphous character of the samples, as shown in figure 4 for typical glass compositions. These patterns show a broad main peak at $2\Theta = 27{,}9°$. Beyond this peak, a second one is observed at $2\Theta = 54°$.

3.3 Thermal Properties:

3.3.1 Binary system

Differential Scanning Calorimetry has been implemented between 100 and 500°C. Typical DSC scans are reported in figure 5.

The evolution of the characteristic temperatures corresponding to glass transition (Tg), onset of crystallization (Tx) and exotherm maximum (Tp) versus concentration is plotted in figure 6(a) The stability factors S [19] and ΔT=Tx-Tg [20] that give an estimate of glass forming ability appears in figure 6(b). Glass transition varies between 255 and 276°C. As one could expect, characteristic temperatures depends on Sb_2O_3 content. These results suggest that glass stability against devitrification is maximum for high Sb_2O_3 concentration (> 70 %) and for

large lead concentration (90 % PbO). Intermediate compositions appear more prone to devitrification.

3.3.2 Ternary system

For comparison, thermal measurements have been carried out on a set of three samples with the same general, formula: x Sb_2O_3- (95-x) PbO- 5Me_2O_3 (Me = Al, Ga, In, and 10< x <80)
The composition dependence of glass transition temperature (Tg) is reported in fig 7. The curves expressed the same behavior as observed in the binary system for glass transition: Tg increases for large PbO concentrations (> 40%). In a general way, Tg increases with ionic radius ($Al^{3+} < Ga^{3+} < In^{3+}$).
We have also prepared samples with different In_2O_3 contents. The basic composition - 50 Sb_2O_3-50PbO - was chosen in the range of minimum stability in order to make clear the effect of additive concentration on glass stability. As shown in figure 8, a first result concerns Tg that increases with In_2O_3 concentration.

Another set of glass samples was prepared with the general formula: 50 Sb_2O_3-(50-x) PbO-x Me_2O_3 (Me= Al, Ga, In). Glass transition Tg increases quasi-linearly with Me_2O_3 addition. Once again, larger Tg values are observed for cations with larger ionic radius.

Figure 10 reports the variation of the stability factor S as a function of Me_2O_3 concentration for the 50 Sb_2O_3-(50-x) PbO-x Me_2O_3 glasses.
These curves suggest that Me_2O_3 addition has a stabilizing effect by comparison to the binary glass. At first glance, glasses containing Ga content appear as the most stable ones. However additional experiments should be implemented to confirm these observations: first, no data were collected for Me_2O_3 concentrations between 5 and 10 mol %; and second, no stable glass was obtained for In_2O_3 concentrations larger than 5 mol % (see fig. 3). Then one would expect the sharp decrease of the stability factor beyond some threshold value that could be found experimentally.

3.4 Density

The composition dependence of the density of the binary glass samples in the Sb_2O_3-PbO system is shown in fig 11.

As one could expect, density d decreases as lead oxide is replaced by antimony sesquioxide. This change is approximately linear. Another set of density measurement has been implemented in the ternary system with the following formula: xSb_2O_3-(95-x) PbO-5Me_2O_3 (Me = Al, Ga, In). As shown in figure 12, density also decreases linearly with the substitution of PbO by Sb_2O_3.

3.5 Microhardness

Figure 13 shows the microhardness variation of the 50Sb_2O_3-(50-x) PbO-xMe_2O_3 (Me = Al, Ga, In) glasses as a function of Me_2O_3 concentration. Microhardness increases with Me_2O_3

concentration. For the same oxide content microhardness increases according to the sequence: Hv(Al)<Hv(Ga)<Hv(In)

Discussion

This study exemplifies the respective parts of the glass components. Antimony sesquioxide Sb_2O_3 is clearly a vitrifying oxide. Even though the existence of pure vitreous Sb_2O_3 has been for long a matter of discussion, the occurrence of numerous binary glasses with high Sb_2O_3 concentration confirms its glass forming ability. It complies with Zachariasen's rules[7] insofar as it forms tetrahedra in the solid state that must be written SbO_3(LP), where LP is a lone pair of s^2 electrons. In this way it offers similarities with phosphate groups PO_4 in which one oxygen is non-bridging. The vitreous network is constructed from these SbO_3(LP) tetrahedra, with up to three non-bridging oxygens.

Lead oxide PbO is known to have a dual role, depending on glass composition and also on the nature of the other vitrifyers. Solid state chemistry teaches that Pb^{2+} commonly acts as a large cation that leads to compounds isostructural with those obtained with $Sr^{2+,}$ Ba^{2+} or Eu^{2+}. Among other examples one may quote perovskite $PbZrO_3$ and fluorite-type PbF_2. In these structures, coordination number is high: 12 in perovskite and 8 in fluorite [21]. Based on this coordination and the corresponding size effect, divalent lead is considered as a modifier that fills empty space within the vitreous network. This behavior is common at low PbO content. However, at high concentrations, the structural behavior of Pb^{2+} is different and compares to that of trivalent antimony. Its coordination number drops down while a lone pair of s^2 electrons completes a smaller coordination polyhedron. This polyhedron typically consists of 4 oxygens and one lone pair. This makes the basis of the PbO structure. Then this PbO_4 group can enter the vitreous network. Indeed there are numerous examples of glass compositions with a very large content of lead oxide. In the Sb_2O_3-PbO binary system, there are two different glass domains, the first one for large Sb_2O_3 concentrations and the second one when lead is predominant. Not surprisingly characteristic temperatures reflect this situation (fig. 6): less stable glasses are found in the intermediate composition range.

The optical quality of the glass samples is very sensitive to the redox conditions. There are several redox couples that interact in glass melt: Sb^{3+}/Sb^{5+}, Pb^{2+}/Pb^{4+}, Pb^{0}/Pb^{2+}. Equilibrium constants vary with temperature. In order to limit the formation of reduced species, it is necessary to maintain an oxidizing atmosphere that can be provided by room atmosphere. However, in some cases, longer melting – and fining- time are required. When silica crucibles are used, this results in a larger contamination by silica. This drawback is avoided with other crucible materials such as alumina.

The influence of the third component on thermal properties is unexpected. In classical oxide glasses –silicates, phosphates, borates- glass transition temperature decreases as the ionic radius of the modifying element increases: Tg is smaller when sodium is replaced by potassium, rubidium or cesium. When network formers are incorporated, Tg variation is ruled by the relative bond strength of the new element. For example, the Si/Ge substitution leads to lower Tg's. In these glasses, the bond strength of aluminum *vs.* oxygen is much larger than that of gallium and indium. However, for the same nominal composition, larger Tg is observed with Ga_2O_3 and In_2O_3 (fig. 9). Then, it appears that bond strength is not the major parameter to account for this observed variation. Rather changes in glass structure should be considered. While these three cations –Al,Ga,In- are likely to enter the vitreous network, their coordination number is expected to be 6. As a result, the number of non-bridging oxygens is reduced, and consequently, glass transition temperature is lowered. This mechanism could

also explain the increase of microhardness with the incorporation of the Me_2O_3 oxides in the Sb_2O_3-PbO binary glass (fig. 13).

Conclusion

The incorporation of trivalent oxides in the Sb_2O_3-PbO binary glass has been studied. Characteristic temperatures, density and microhardness have been measured for binary glasses. The limits for glass formation have been defined by a set of systematic experiments in the Sb_2O_3-PbO-Me_2O_3 (Me=Al,Ga,In) ternary systems. Up to 10 mol % Me_2O_3 oxide could enter glass composition. Thermal measurements show that characteristic temperatures increase with oxide addition. In the mean time, glass is less prone to devitrification. Glass transition temperature increases according to the sequence: Tg(Al)< Tg(Ga)< Tg(In). Microhardness variation is similar, and maximum values are observed for indium containing glasses. It is suggested that this unexpected variation occurs from the decrease of the number of non-bridging oxygens. This decrease could result from the 6 coordination number of the trivalent cations that take place in the vitreous network.

Acknowledgment

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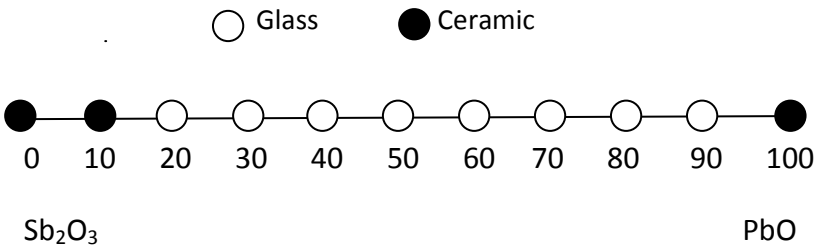
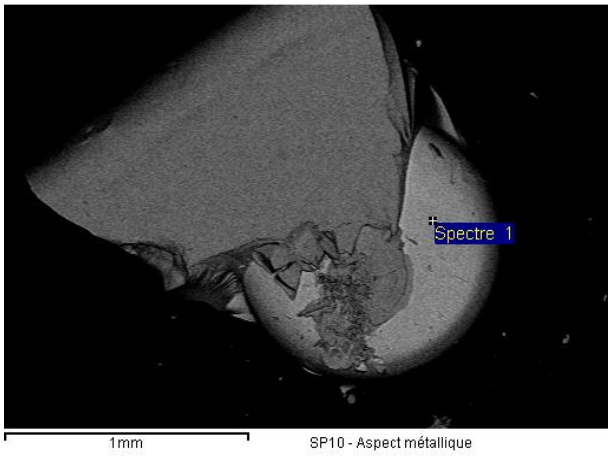
Figure

Figures of the manuscript :

INVESTIGATION AND PROPERTIES OF NOVEL LOW MELTING GLASSES IN THE TERNARY SYSTEM Sb_2O_3-PbO-Me_2O_3



(fig 1)



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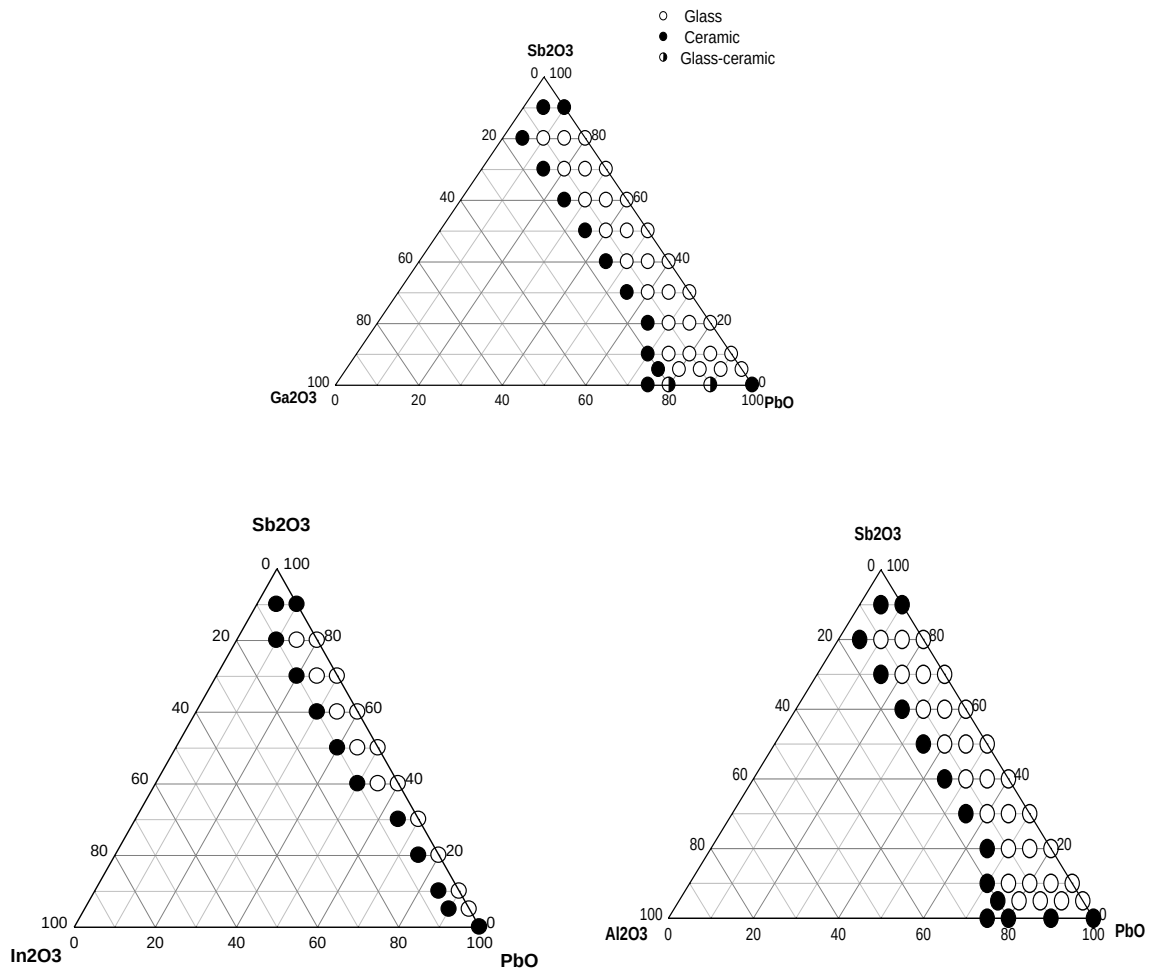
(fig 2)



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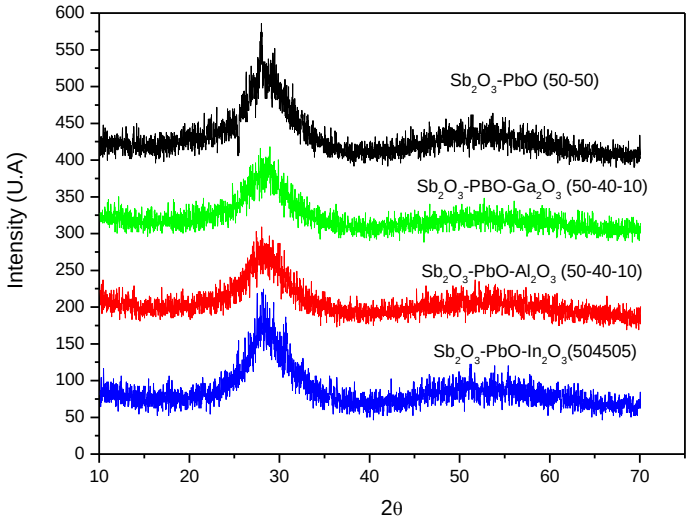
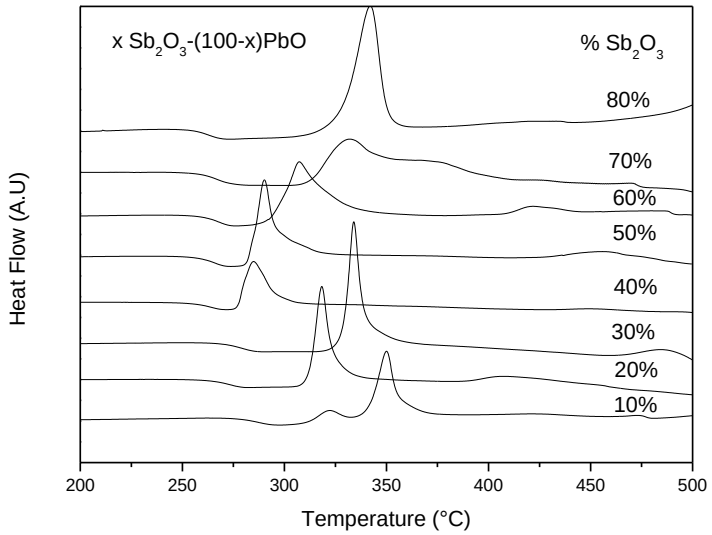
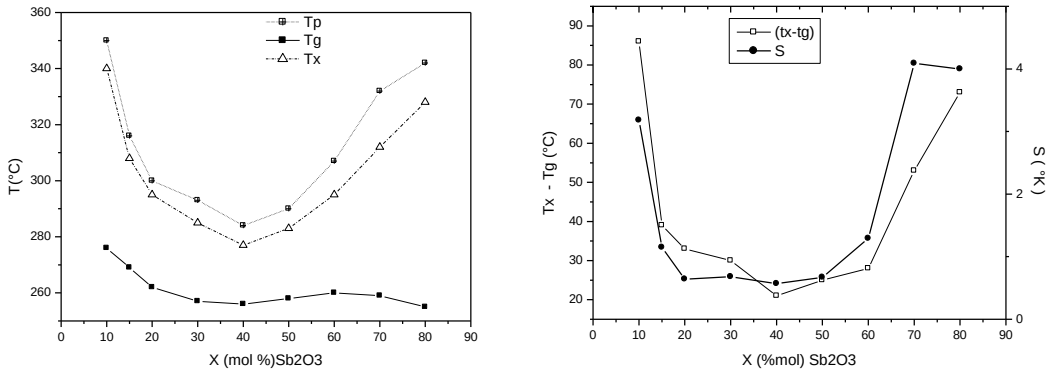

Intensity (U.A)
2θ
Sb2O3-PbO (50-50)
Sb2O3-PBO-Ga2O3 (50-40-10)
Sb2O3-PbO-Al2O3 (50-40-10)
Sb2O3-PbO-In2O3(504505)

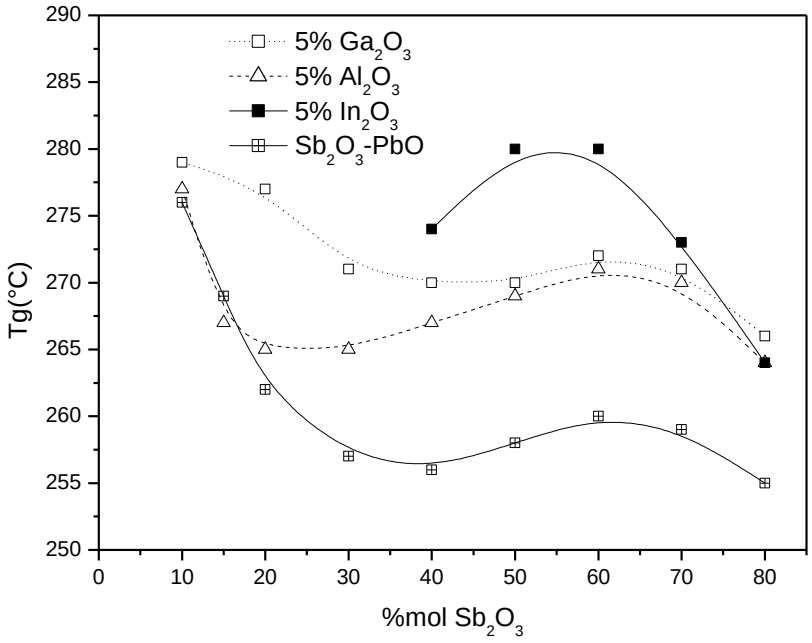
(Fig 4)


x Sb2O3-(100-x)PbO
% Sb2O3
80%
70%
60%
50%
40%
30%
20%
10%
Heat Flow (A.U)
Temperature (°C)

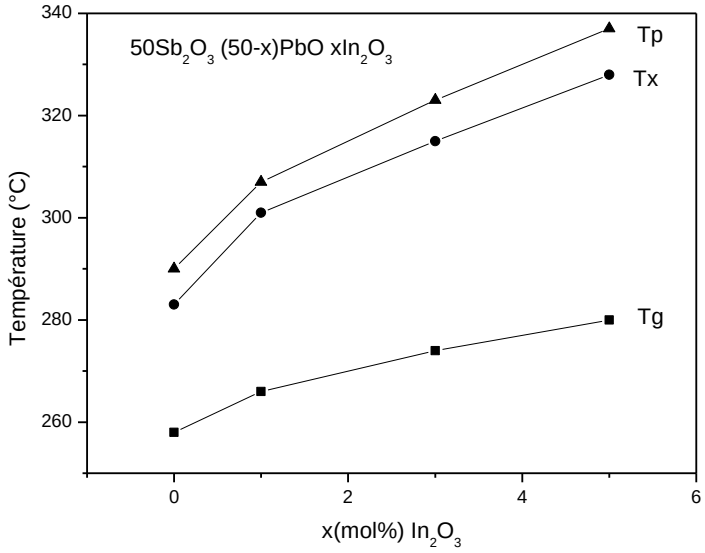
(fig 5)


Tp
Tg
Tx
T (°C)
X (mol %)Sb2O3
(tx-tg)
S
Tx - Tg (°C)
S (°K)
X (%mol) Sb2O3

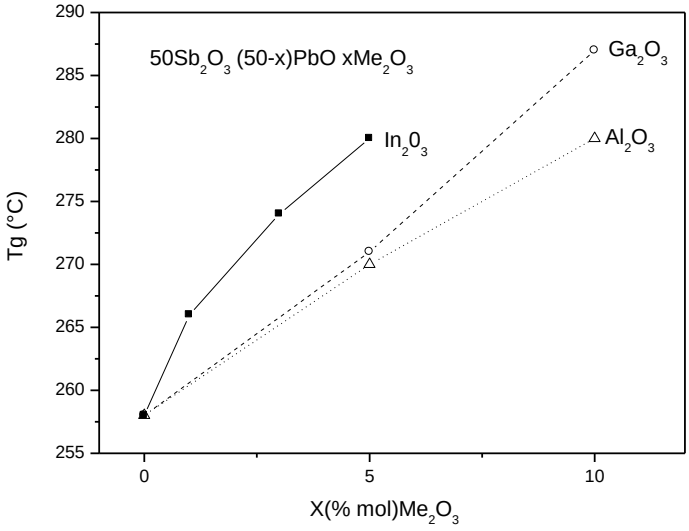
(Fig 6)


5% Ga2O3
5% Al2O3
5% In2O3
Sb2O3-PbO
Tg(°C)
%mol Sb2O3

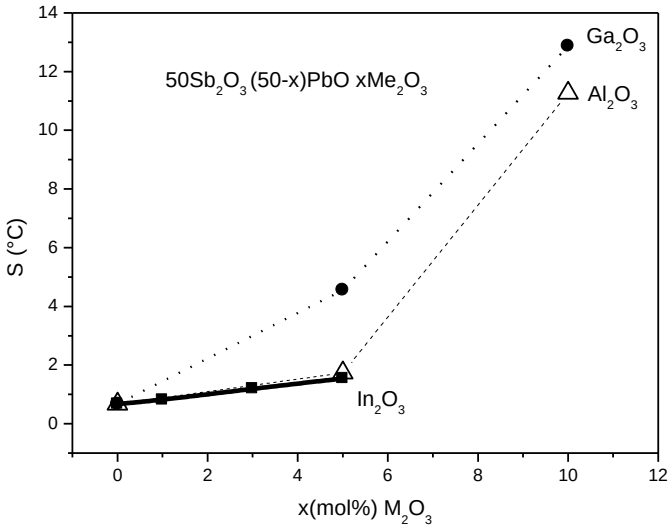
(Fig 7)


340
320
300
280
260
Température (°C)
0
2
4
6
x(mol%) In2O3
50Sb2O3 (50-x)PbO xIn2O3
Tp
Tx
Tg

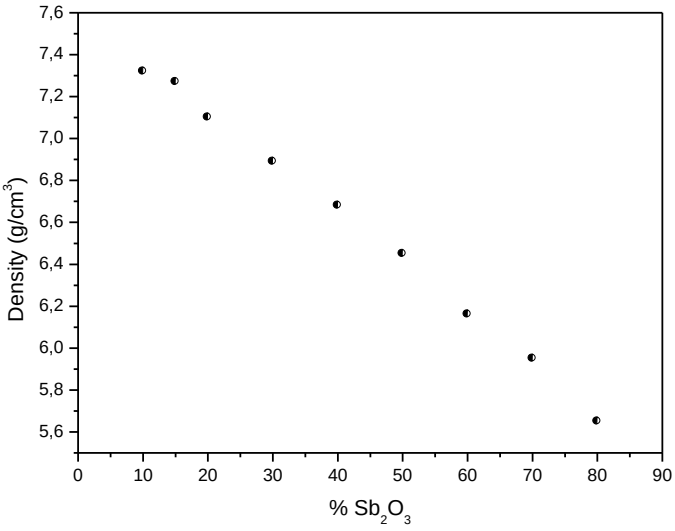
(fig 8)


290
285
280
275
270
265
260
255
Tg (°C)
0
5
10
X(% mol)Me2O3
50Sb2O3 (50-x)PbO xMe2O3
Ga2O3
In203
Al2O3

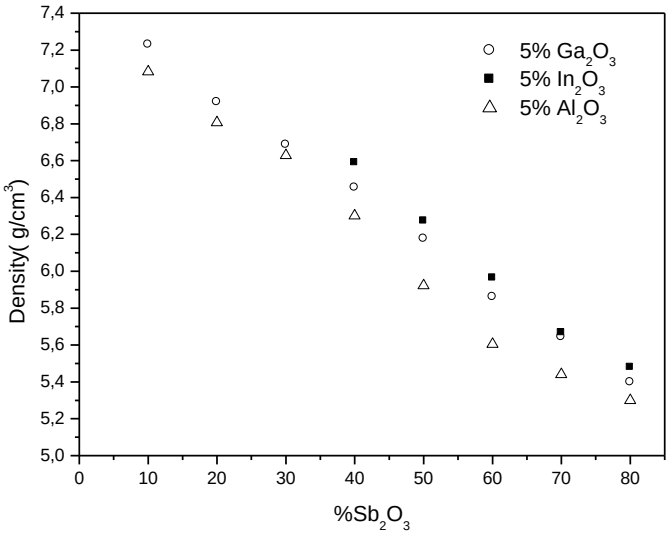
(fig 9)


50Sb2O3 (50-x)PbO xMe2O3
Ga2O3
Al2O3
In2O3
S (°C)
x(mol%) M2O3

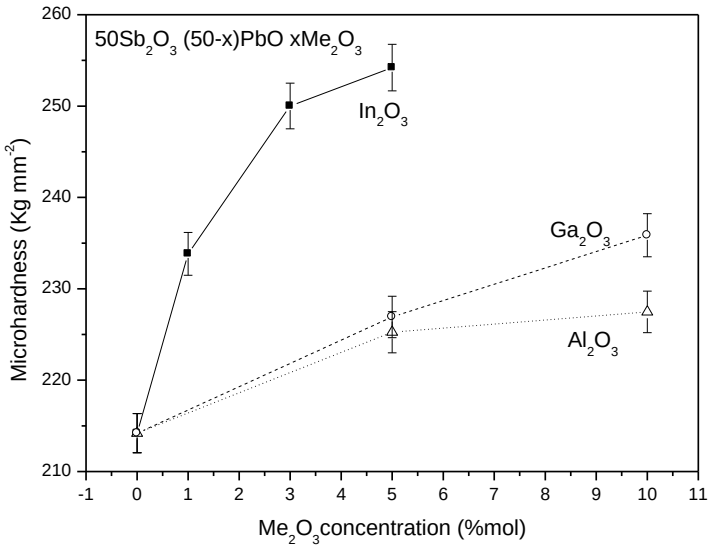
(fig 10)


Density (g/cm3)
% Sb2O3

(fig 11)


Density(g/cm3)
%Sb2O3
5% Ga2O3
5% In2O3
5% Al2O3

(fig 12)


50Sb2O3 (50-x)PbO xMe2O3
In2O3
Ga2O3
Al2O3
Microhardness (Kg mm-2)
Me2O3concentration (%mol)

(fig 13)