Comprehensive thermal and structural characterization of antimony-phosphate glass

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A B S T R A C T

For the first time, we prepare new ternary glass systems of composition (95-\(x\))Sb\(_2\)O\(_3\)-xP\(_2\)O\(_5\)-5MgO, where \(x = 45, 40, 35\) mol%; (85-\(x\))Sb\(_2\)O\(_3\)-xP\(_2\)O\(_5\)-15MgO, where \(x = 55, 35, 25\) mol%; (75-\(x\))Sb\(_2\)O\(_3\)-xP\(_2\)O\(_5\)-25MgO, where \(x = 45, 35, 25\) mol%; and 60Sb\(_2\)O\(_3\)-(40-x)P\(_2\)O\(_5\)-xMgO, where \(x = 10, 20\) mol% via melt-quenching method. Synthesized glasses are characterized using XRD, FESEM, EDX, and TG/DTA measurements. The influence of varying modifier concentrations on their thermal properties is evaluated. The XRD patterns confirmed the amorphous nature of samples. SEM images demonstrated interesting phase formation with ribbons-like texture. Five crystalline phases are evidenced in the ternary diagram which are antimony phosphate and antimony orthophosphate as major phases as well as magnesium phosphate, magnesium cyclo-tetraphosphate and cervantite as minor phases. EDX spectra detected the right elemental traces. Detailed thermal analysis of these glasses revealed their high-molecular polymer character for Sb\(_2\)O\(_3\) content greater than 50 mol%. Three different glass transition temperatures are achieved around 276, 380–381 and 422–470 \(^\circ\)C depending on the composition. Furthermore, the solidus and liquidus temperature are found to decrease with increasing Sb\(_2\)O\(_3\) and increases for MgO contents till 15 mol% and then decrease, where the lowest recorded solidus temperature is 426 \(^\circ\)C. This observation may open up new research avenues for antimony based ternary glasses and an exploitation of the derived results for optoelectronics applications, photonic devices and non-linear optical devices.

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Introduction

Lately, there is an upsurge in binary and ternary glass research due to their extreme stability, economy, and easy fabrication benefit for advanced photonic applications. Thus, constant efforts are made to get newer glass composition with modified structural, physical, thermal, and optical properties. Glass plays many varied roles in rare-earth laser systems, because glass can be made with uniformly distributed rare-earth concentrations and has great potential as a laser host medium. In addition, rare-earth doped fibers have received growing attention recently. They could have many uses as amplifiers in optical communication systems and as optical sources. Glass waveguide lasers are another interesting subject for the development of compact laser sources and amplifier devices [1,2]. Glass as host in the practical lasers is subjected to extreme operating environment so they should own optimal thermal, optical and mechanical properties, in order to withstand it. The ideal features which make the material is eligible as a host are simple to synthesis, high chemical durability and hardness, acceptable physical properties, higher absorption cross section, and higher quantum efficiency [9]. Contemporary glass scientific research focuses on the development of specialized or unusual glasses as a novel media for photonic, plasmonic and nonlinear optical technologies by incorporating luminescent rare-earth ions, metal nanoparticles, semiconductor nanoparticles, etc and their hybrids [1,3,4]. Research in these fields are fast and lead to emerging areas require development of new glass compositions in this context, unlike the traditional silicate, borate and phosphate glasses, heavy metal oxide glasses like bismuth, tellurite, lead, and/or antimony acting as glass structure network formers is expected to play an active role as they possess some exciting properties like high refractive index, large transmission window, large non-linear optical properties, low phonon energy (resonance vibration of the matrix) and high dielectric constant. There has been considerable investigation on Bi-, Te- and Pb-glasses but Sb-based glasses remain vastly unexploited [5] due to their mild toxicity and complex phase formation attributes related to super-cooling. Consequently, the difficulty associated to achieving highly transparent and thermally stable antimony glasses posed new challenge. One of the most striking features of antimony trioxide or antimony

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orthophosphates (SbPO₄) is associated to the existence of lone electronic pairs in one of the polyhedra corners. Consequently, it offers an opportunity to acquire different phase formations with unusual electrical and optical properties [6].

In the past, antimony glass systems are combined with others components such as halides [7,8], sulfides [9,10], heavy metal oxides [11] and alkali oxides metals glasses in the form of binary (Sb₂O₃-A₂O) and ternary (Sb₂O₃-A₂O-M) with A = Li, Na, K, or Cs and M = Pb or Al [12–15] mixtures. However, literatures do not hint about the synthesis and characterizations of Sb₂O₃-P₂O₅-MgO glass systems despite their innumerable technological implications. The structures of (13.86-x)ZnO-57.89Sb₂O₃-28.21P₂O₅-xNa₂O (x = 0–12 wt.%) glasses are investigated, where SbPO₄ is existed mainly in the crystalline phase. The glass transition temperature is decreased from 398 to 328 °C as the Na₂O concentration is increased [16]. Zinc-boro-phosphate glass system of composition 50ZnO-10B₂O₃-40P₂O₅-xSb₂O₃ (x = 0–70 mol%) is prepared to determine the effects of increasing Sb₂O₃ contents on overall properties [17]. It is demonstrated that with increasing Sb₂O₃ contents the glass transition temperature is decreased from 492 to 394 °C, and density increased from 3.12 to 4.35 g cm⁻³ together with the molar volume from 33.5 to 41.7 cm³ mol⁻¹. The dissolution rate at 15 mol% of Sb₂O₃ is increased from 21.2 × 10⁶ to 34.7 × 10⁶ g cm⁻² min⁻¹ and then decreased to 12.8 × 10⁶ g cm⁻² min⁻¹ at 70 mol%. Furthermore, the depolymerisation of the phosphate chains is increased with the separation of antimonate (SbO₃) structural units [17].

Another glass system based on metal oxide glasses of the form 50V₂O₅-(50-x)P₂O₅-xSb₂O₃ (x = 15, 25, 35 and 40 mol%) are prepared to examine the influence of increasing Sb₂O₃ concentration on the structural and thermal properties. Homogenous amorphous phase is achieved, where the glass transition temperature first decreased from 365 to 325 °C and then increased to 330 °C at 40 mol% of Sb₂O₃. Both the glass density and molar volume is increased from 3.3 to 4.5 g cm⁻³ and 55.8 to 64.6 cm³ mol⁻¹, respectively. Besides, the stability is against moisture attack is remarkably improved [18]. The effect of increasing Sb₂O₃ on zinc-phosphate glasses of composition (60-x) ZnO-xSb₂O₃-40P₂O₅ (x = 0–50 mol%) is examined. The participation of Sb₂O₃ in the network is revealed by the presence of P-O-Sb linkages, where the glass transition temperature (422–377 °C), ΔT = Tg − Tc (132–78 °C) and liquidus temperature (1050–930 °C) are decreased. Moreover, the glass density (3.34–4.17 g cm⁻³), and molar volume (31.9–50.5 cm³ mol⁻¹) are increased. At different Sb₂O₃ concentrations various crystallization peaks are evidenced together with high durability against moisture attack [19].

The structural evaluation of Pbo-P₂O₅-Sb₂O₃ glass system is made [20], where the incorporation of Sb₂O₃ is found to generate two structural units as P–O–Sb linkage, one with high Sb⁺⁺⁺ cation belong to SbPO₄ phase and the other with high Sb⁺⁺⁺ cation belong to SbOPO₄ phase. The glass transition temperature exhibited broad endothermic peak in the range of 352–377 °C accompanied by a slight shift towards higher temperature. This observation is attributed to the occurrence of dissimilar structural units with diverse relaxation temperature. Increase in the crystallization temperature, thermal stability, and optical band gap is evidenced with the increase of Sb₂O₃ contents [20].

Categorically, MgO-P₂O₅ glass systems are interesting due to their peculiar structure and phase formation [21,22]. These binary oxide systems are mainly composed of four intermediate phases including magnesium ortho-phosphate (Mg₃P₂O₈), magnesium pyro-phosphate (Mg₅P₃O₁₀), magnesium tetra-meta-phosphate (Mg₆P₆O₁₇), and magnesium ultra-phosphate (Mg₈P₈O₂₃). In addition, MgO and O-P₂O₅ (stable orthorhombic polymorph of P₂O₅) are also manifested in the phase diagram, which remains insoluble in the solid state at high concentration of MgO and P₂O₅, respectively [23–34]. In terms of phase transition and melting point, these compounds (Mg₅P₃O₁₀) melts at 1357 °C and encounters a polymorphic transition at 1055 °C from β-Mg₅P₃O₁₀ to α-Mg₅P₃O₁₀ [24,28]. Meanwhile, Mg₅P₃O₁₀ melts at 1385 °C and encounters two polymorphic transitions one at 68 °C and another at 1110 °C [28]. The Mg₅P₃O₁₀ phase melts at 1165 °C [31] and Mg₅P₃O₁₀ melts at 910 °C. The eutectic reaction between Mg[PO₄]₂ and Mg₂P₂O₇ occurs at 772 °C [32]. The O-P₂O₅ phase melts at 580 °C with a eutectic reaction between Mg₅P₃O₁₀ and O-P₂O₅ at 328 °C [23,34]. Despite much effort on the synthesis and characterization of several binary and ternary glasses the magnesium-antimony-phosphate glass systems are far from being studied.

Some reports revealed the preparation of binary glass from MgO-P₂O₅ system, where the MgO, P₂O₅, Mg₂P₂O₇, and Mg₅P₃O₁₀ phases are found to dominate within the glasses formation ranges 0.4 ≤ x ≤ 0.8 mol% for P₂O₅. Much structural changes are observed under heating due to the density variation in the P-O-Mg crosslink through the glass formation or crystallization. These glass systems displayed several endothermic and exothermic reaction corresponding to the peritectic reaction (MgO + melt), liquidus phase formation, eutectic reaction or crystallization of Mg₅P₃O₁₀ [35]. Yet, no studies exist on phase formation of binary oxide system of MgO-Sb₂O₃. Literature revealed the study on tetragonal crystal structure of magnesium-antimonite (Mg₅Sb₂O₈) [36], which are prepared using solid state reaction of MgO with Sb₂O₃ at 1100 °C in the inert atmosphere. Moreover, this system showed several

Table 1

<table>
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<tr>
<th>Glass codes</th>
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</tr>
<tr>
<td>SPM11</td>
<td>60</td>
</tr>
</tbody>
</table>

Fig. 1. Glass formation region.
phases with the variation of MgO to Sb$_2$O$_3$ molecular ratio [37]. Attempts are made to determine the standard Gibbs energies of magnesium-antimonite phase formation, where pure oxides of MgO and Sb$_2$O$_3$ are used [36–40]. It is acknowledged that both MgO and MgSb$_2$O$_4$ phases together with Sb can coexist in equilibrium [38,39]. Hitherto, fundamental insight of magnesium-antimony-phosphate ternary glass systems is lacking.

In this view, we take an attempt to thrash out the bottleneck of antimony-phosphate based ternary glass research which is a complementary research of our previous study [41], and hope to unravel some basic insight in terms of structure, glass forming ability and thermal stability by synthesizing and characterizing such new glass system. Certainly, for technological applications, comprehensive determination of glass thermal properties is prerequisite. Thus, Sb$_2$O$_3$–P$_2$O$_5$–MgO ternary glass systems are prepared and inclusive thermal evaluations are made.

Materials and methods

Synthesis

Four series of ternary glasses (Table 1 and Fig. 1) are synthesized via conventional melt quenching technique. High purity analytical grade powdered oxides of Sb$_2$O$_3$, P$_2$O$_5$, and MgO are selected as raw materials. About 10 gm of constituent materials is thoroughly mixed and pre-treated at 300 °C for 1 h to reduce the presence of bubbles in the mixture and to avoid the volatility of P$_2$O$_5$ at high temperature. The mixture was then placed in an alumina crucible before being melted inside a muffle furnace (1050–1100 °C) for 1 h. Upon achieving the desired viscosity the melt is quenched onto a preheated steel plate (300 °C) to form disc-shaped samples before being annealed at 300 °C for 2 h to release the residual stress. The furnace is then switched off and the sample is naturally cooled down to room temperature. Finally, the frozen samples are cut, and polished. Some samples are milled to fine powder for further characterization.

Characterization

The thermal measurement is performed on a Perkin-Elmer Pyris Diamond TG/DTA 7 series system interfaced with built-in computer and software. The highest applied temperature is approximately 1500 °C with the heating rate of 10 °C/min. The temperature difference between the sample (5–10 mg) and the alumina batch is recorded, under controlled nitrogen gas flow (rate 200 ml/min). The DTA traces are obtained, where the glass
transition temperature \( (T_p) \) is identified from intersection of two tangents at the start of the corresponding endothermic peak (kink shape). The onset of crystallization temperature \( (T_c) \) is obtained by extrapolating the interception of the first crystallization phase (exothermic reaction) and the highest crystallization temperature \( (T_p) \) taken at the maximum of the exothermic reaction. The onset of melting point or solidus temperature \( (T_s) \) that separates the solid phase from that of liquid plus crystals is measured from. The offset temperature or liquidus temperature \( (T_l) \) which separated the liquid phase from that of liquid plus crystals depending on the derivative heat flow and derivative thermal gravimetric curves.

The glass forming ability (GFA) is calculated through Hurby parameter \( (H_r) \) and \( \Delta T_e \). The former one signifies the glass-forming tendency and the later demonstrates the glass stability. The larger value of \( H_r \) and \( \Delta T_e \) (greater 100 °C) implies the greater glass stability against devitrification [40,42]. The expression for \( H_r \) and \( \Delta T_e \) yields:

\[
T_s = (T_c - T_g)
\]

\[
H_r = \frac{(T_c - T_g)}{(T_l - T_c)}
\]

The second criteria to identifying the glass forming ability (GFA) depends on the reduced glass transition temperature \( (T_{rg}) \). For good glass-forming system the value of \( T_{rg} \) must be in the range of \( 1/2 \leq T_{rg} \leq 2/3 \) [43–45]. The value of \( T_{rg} \) is calculated via:

\[
T_{rg} = \frac{T_g}{T_l}
\]

The mass loss is computed using [45,46]:

Mass loss \( \% = \frac{M_i - M_f}{M_o} \times 100 \) (4)
where $M_i$ and $M_f$ are initial and final mass of the sample at the specific temperature range and $M_0$ is the original mass of the sample prior to the thermal analysis.

The amorphous nature and crystalline structure of the prepared samples is confirmed via X-ray diffraction (XRD) (Siemens X-ray Diffractometer D5000). It used Cu-Kα radiation and operated with 40 kV at 30 mA. The diffraction peaks are measured in the 2θ range of 10 to 80° with the step size of 0.05. The glass morphology is imaged using EIGMATm (Zeiss Supra 35 v) field emission scanning electron microscope (FESEM) with accelerating voltages of 5–30 keV. The samples are coated with Au to make them conductive prior to qualitative X-ray microanalysis.

The weight and atomic % of each elemental glass species is estimated using:

$$\text{Weight \% of atom (i)} = \frac{N_i N_a M_i}{\sum_i N_i N_a M_i} \quad (5)$$

$$\text{Atomic \% of atom (i)} = \frac{N_i N_a}{\sum_i N_i N_a} \quad (6)$$

where $N_i, N_a$, and $M_i$ represent the atom concentration, number of atom, and atomic mass, respectively for the atom $i$ and $i = 1, 2, 3$ and 4, stands for Sb, P, Mg, and O, respectively.

Results and discussion

XRD analysis

Transparent samples displayed a change in the physical appearance from almost colorless to light yellow and then to deep yellow with increasing Sb$_2$O$_3$ and MgO contents. This color variation is ascribed to the emergence of HOMO (Sb 5s and O 2p) and LUMO (Sb 5p) gap as well as the presence of the electronic excited states of contaminated cations ion in the visible region [47,48]. Furthermore, the prepared samples with greater than 50 mol% of P$_2$O$_5$ and less than 15 mol% of MgO show weak resistance against humidity. The increase in Sb$_2$O$_3$ or MgO concentration enhances the resistance against humidity. The lone pair electron of the antimony oxide interacts with water molecules and act as shield. Further addition of MgO as network modifier increase the rupture of the bridging oxygen bonds and thereby protect the network structure from moisture attack [19]. In addition, the prepared samples with high concentration of Sb$_2$O$_3$ beyond 60 mol% were opaque, due to crystallization of the samples during preparation. It is worth to mention that the number of lone pair electrons has the profound effect on increasing the glass formation ability [49], but if this number exceeds a certain limit in the structure then the glassy phase is not obtained due to high repulsive interaction among lone pair electrons which may restrain polymerization [49], and it will be confirmed in crystalline phases analysis section. So, the limited glass formation region and low chemical durability could be one of the dilemmas of this ternary glass system.

Fig. 2(a)–(d) shows the XRD pattern of prepared glass samples. The absence of any sharp peak and the presence of broad halo confirmed their amorphous nature.

FESEM analysis

Figs. 3(a), 4(a), and 5(a) show the typical SEM images of a sample from first three series such as SPM3, SPM4, and SPM9, respectively and part (b) displays the corresponding EDX spectra for samples and measured weight\% of elements which present the detected elements from experimental (EDX data). SEM micrograph clearly manifested a kind of texture/phase separation (heterogeneous glass) due to liquid-liquid immiscibility of the glass fusible upon quenching from a temperature above $T_l$ to below $T_g$ [5]. The glass separated to more than two textural phases as MgO concentration is increased, which appeared in the form of ribbons, and this is consistent with our previous results, which we explained the effect of external electric field of the ligand group (glass host) on the electronic transitions (absorption or emission) in trivalent rare earth ions and the related spectral shape of these transitions in glasses [41]. The homogeneous and heterogeneous glasses are both entirely vitrified in a macroscopic scale and the difference emerge at the microscopic scale [50], and as known the liquid-liquid immiscibility or micro-phase separation is a common phenomenon which take place in many glass systems and the separation degree depends on the melt viscosity [5]. The extensive experimental results showed that there are many reasons for the occurrence of phase separation phenomena in glass system, like cooling rates, constituents elements number of the glass system, certain additives, modifier cations field strength $Z/r^2$, tendency to formation
of induced dipoles, degree of coordination required for the modifier cation and the electrostatic interaction between cations in the melt [50–53]. According to the above, there are many factors that govern the formation of micro-phase separation in glass system, and it is difficult to definitely determine the main reason which stands behind the phase separation in antimony phosphate glass system, and the reason could be the intermediates value of MgO modifier cations field strength (0.53) [54] which can tend to form a different shape and size polyhedral from glass former polyhedral which lead to micro-phase separation, another reason could be the incorporation of Sb³⁺ cation with lone electron pair in the glass network which make structural changes in glass network and distortion of SbO₃ unit symmetry [7], [17], [55]. We assume that these structural changes are preceded by structural changes in the fusible glass and form induced dipoles in some structural phases and lead to micro-phase separation.

Thermal analysis

Figs. 6–9 display the DTA traces of all prepared samples categorized into four series. Tables 2 and 3 enlist the detailed thermal properties of these series. Thermal analyses revealed two different values of $T_g$ irrespective of the composition. The first one (weak) occurred at 276°C and the second one (prominent) around 380–381°C. However, as the MgO concentration is increased to 25 mol% another $T_g$ is appeared, which is Sb₂O₃ contents dependent. This clearly indicated the modification of amorphous network structure, which is ascribed to the rupture of bridging oxygen (BO) bonds and subsequent formation three types of glass network structure [27,35]. This supported the SEM data, where the existence of inhomogeneous composition in the amorphous state is manifested [25,26,58,59]. The $T_g$ value variation in series III (SPM7, SPM8 and SPM9) with increasing Sb₂O₃ content, could be

![Image](image-url)
attribute to the average degree of glass polymerization which has a
decisive influence on the $T_g$ values [17], the glass sample SPM8 has
the largest value of $T_g$ (470 $^\circ$C) among glass samples, and hence it
experienced the highest polymerization rate for the glassy phase.
This glass system possessing high-molecular (polymer) character
for Sb$_2$O$_3$ concentration greater than 50 mol% implies the complete
disappearance of both $T_c$ and $T_l$. Thus, these glasses are easy to
prepare and hard to crystallize. Despite their excellent thermal sta-
bility [16] the criterion for large Hruby parameters ($H_r$) and $(\Delta T_p)$
cannot be applied to this glass system [40].

A difficulty is faced to determining the onset of melting point
($T_m$), and offset temperature ($T_l$) from the DTA curves due to
absence of distinct peak. This is due to the overlap of the endother-
ic and exothermic peaks. Thus, the derivative heat flow and
derivative thermal gravimetric curves are obtained to identify the
solidus and liquidus temperature as well the phase formation in
this glass system. The disappearance of crystallization temperature
peak could be due to the presence of heterogeneous nucleation
sites inside the glass matrix need to be clarified. One major reason
for the development of sufficient nucleation centre in the glass
may be due to the samples exposure to 300 $^\circ$C (quenching temper-
ate near to $T_g$) for two hours. This prolonged duration of holding
may spontaneously induce the formation of stable crystalline
phase by reducing the energy required for the nucleation and
growth processes. This is primarily attributed to the glass re-
crystallization and subsequent disappearance of sharp peaks in
the DTA thermogram. Conversely, it may be ascribed to the too
high heating rate, where the rate of nucleation and growth are
not rapid enough to follow heating rate. Consequently, the DTA
traces (Fig. 6–9) could not detect the re-crystallization or exother-
ic peak [60,61].

Interestingly, this particular glass system displayed landmarks
of melt over a broad temperature range (incongruent melting) at
specific composition with increasing Sb$_2$O$_3$ and MgO contents. This
allowed to formation of more phases in this glass system. This glass system melts under stages depending on the phase formation and the heating process. The DTG analysis (endothermic reaction) clearly revealed the melting stages of the crystalline phase and the corresponding weight loss percent due to the vaporization of the crystalline phase at elevated temperature [60,62]. The higher mass loss percent is attributed to the presence of predominant crystalline phase in the disordered matrix and absorption of higher energy. The endothermic reaction is manifested as a sharp peak in the DTA curves, where the SPM4 glass faced the highest (40.7%) mass loss at the final stage of melting. The mass loss for others samples are fairly low at the final stage of melting.

In-depth analyses of the DTG result displayed the occurrence of a clear and distinct inflection point of the baseline, a demarcation of the phase formations that occurred in the glass successively through the heating from the onset of the mass loss. Samples with 5 mol% of MgO with the same solidus temperature (512 °C) encountered many phase changes from the onset of melting (solidus temperature) to the offset of melting (liquidus temperature). The phase formation temperature ranged between 888 and 930 °C encountered higher mass loss percent. This dominant phase among the others phases is observed for the SPM1 and SPM2 samples. Whereas, the phase formation temperature ranging between 780 and 865 °C revealed higher mass loss percent and the dominant phase is seen for SPM3 sample. Samples with 15 and 25 mol % of MgO the solidus temperature is increased with the increase of Sb2O3 concentration. Furthermore, the higher mass loss percent at specific temperature range reduced the dominate phase. Samples with 60 mol% of Sb2O3 (SPM3, SPM6, SPM10, and SPM11) showed a reduction in the solidus temperature with increasing MgO contents. The occurrence of identical solidus temperature (426 °C) for SPM6, SPM10, and SPM11 samples confirmed the
Fig. 9. Samples SPM10, and SPM11 (a) heat flow traces, (b) derivative heat flow (c) Weight Loss% (TG curves) and (d) Differential Weight Loss% (DTG curves).

Table 2
Thermal parameters for all samples.

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<td>726</td>
<td>553.5</td>
<td>500</td>
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<tr>
<td>Tl</td>
<td>881</td>
<td>875</td>
<td>873</td>
<td>950</td>
<td>945</td>
<td>937</td>
<td>973</td>
<td>965</td>
<td>925</td>
<td>874</td>
<td>836</td>
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<tr>
<td>ΔT</td>
<td>42</td>
<td>–</td>
<td>–</td>
<td>36</td>
<td>–</td>
<td>–</td>
<td>66</td>
<td>82.5</td>
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<td>–</td>
</tr>
<tr>
<td>Hg</td>
<td>0.091</td>
<td>–</td>
<td>–</td>
<td>0.067</td>
<td>–</td>
<td>–</td>
<td>0.136</td>
<td>0.21</td>
<td>–</td>
<td>–</td>
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<tr>
<td>Tg/Tl</td>
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<td>0.434</td>
<td>0.435</td>
<td>0.401</td>
<td>0.402</td>
<td>0.406</td>
<td>0.433</td>
<td>0.487</td>
<td>0.478</td>
<td>0.435</td>
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Table 3
Mass losses on heating for all samples, where Mo: Primary weight in mg, T: Temperature in °C, ML: Mass loss% and Mr: Final residual mass%.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Glass code</th>
<th>SPM1</th>
<th>SPM2</th>
<th>SPM3</th>
<th>SPM4</th>
<th>SPM5</th>
<th>SPM6</th>
<th>SPM7</th>
<th>SPM8</th>
<th>SPM9</th>
<th>SPM10</th>
<th>SPM11</th>
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<tr>
<td>Mo (mg)</td>
<td></td>
<td>8.72</td>
<td>6.28</td>
<td>7.26</td>
<td>6.97</td>
<td>9.25</td>
<td>9.48</td>
<td>8.36</td>
<td>8.75</td>
<td>8.21</td>
<td>7.05</td>
<td>9.92</td>
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<tr>
<td>Temp. (°C)</td>
<td></td>
<td>512-630</td>
<td>512-598</td>
<td>512-583</td>
<td>880-914</td>
<td>553-636</td>
<td>426-552</td>
<td>725-885</td>
<td>553-722</td>
<td>500-573</td>
<td>426-518</td>
<td>426-444</td>
</tr>
<tr>
<td>ML (%)</td>
<td></td>
<td>512-630</td>
<td>512-598</td>
<td>512-583</td>
<td>880-914</td>
<td>553-636</td>
<td>426-552</td>
<td>725-885</td>
<td>553-722</td>
<td>500-573</td>
<td>426-518</td>
<td>426-444</td>
</tr>
<tr>
<td>Mr (%)</td>
<td></td>
<td>22.70</td>
<td>27.20</td>
<td>15.20</td>
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<td>37.60</td>
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<td>59.00</td>
<td>36.00</td>
<td>30.40</td>
<td>33.60</td>
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Fig. 10. Concentration (mol%) dependent liquidus temperature (Tl) for varying (a) Sb₂O₃, and (b) MgO.

Fig. 11. XRD patterns revealing the sharp crystalline peaks for samples (a) SPM1 (b) SPM4 (c) SPM7 (d) SPM8.
encounter of eutectic reaction. This is supported by the emergence of the onset crystallization temperature (423 °C) for sample SPM1.

More interestingly, within the same sample series the solidus and liquidus temperature is found to decrease with increasing Sb2O3 contents, this result unambiguously manifest that Sb2O3 incorporation in the glass matrix made a significant structural change in the glass network and it is same results reached by Koudelka and Zhang [17,19], the incorporation of Sb2O3 at low concentration lead to depolymerisation of phosphate chains and formation of isolated pyramidal SbO3 structural units with a lone-pair on the Sb atom, with increasing Sb2O3 content lead to increases the isolated SbO3 units linking into chains and clusters with Sb–O–Sb bonds [17], the pyramidal SbO3 unit with lone electron pair has a greater angular volume compared with a bonding pair of electrons and its involvement in the glass network lead to decrease in the symmetric of Sb3+ local structure and the glass network strain energy will be increases, and hence the additional activation energy decreases which is requisite for rearrangement of the glass network [19,63]. Thus, Tg and Tc of the glasses decrease with increasing Sb2O3 concentration.

However, samples series with 15 and 25 mol% of MgO have the highest liquidus temperature than series with 5 mol% of MgO as shown in the Fig. 10(a), and the liquidus temperature revealed a decrement with increasing Sb2O3 contents, while increases with increasing MgO contents till 15 mol% and then decrease as shown in the Fig. 10(a) and (b) respectively. The occurrence of lowest liquidus temperature (836 °C) for sample SPM11 is because of the closeness of eutectic reaction of this system.

Table 4 compares the thermal properties of some well-studied ternary system with the present antimony phosphate magnesium glass system. In some cases, all the thermal parameters data are not available. It is clear that the values of Tg, Tc, Tp, Ts, and Tl of a glass system is mainly decided by the type of glass former, modifier, and their concentration in the system. The present antimony phosphate magnesium glass system thermal parameters are comparable to the tellurite and borate glass systems. Furthermore, this glass system is comparable to the tellurite and borate glass systems. Furthermore, this glass system is comparable to the tellurite and borate glass systems. Furthermore, this glass system is comparable to the tellurite and borate glass systems. Furthermore, this glass system is comparable to the tellurite and borate glass systems. Furthermore, this glass system is comparable to the tellurite and borate glass systems. Furthermore, this glass system is comparable to the tellurite and borate glass systems. Furthermore, this glass system is comparable to the tellurite and borate glass systems.
The glass system shows inhomogeneous composition in terms of phase separation (heterogeneous glass), multiple T_g values and high-molecular polymer character (excellent thermal stability), which are not the signature for other types of ternary glasses. These modulations of glass properties are highly advantageous for the advance optoelectronic applications.

Crystalline phases analysis

In order to investigate the crystalline phases in this glass system, samples SPM1, SPM4, SPM7 and SPM8 have been chosen which revealed crystallization temperature peak in the DTA traces. The crystallization process of the samples are carried out by annealing the bulk and powdered glass samples at their respective crystallization temperature, T_p for 24 h in an electrical furnace. The bulk samples are finally polished until scratch-free under light microscope to prepare them for FE-SEM image. The annealing temperature for SPM1 is (431 °C), SPM4 is (422 °C and 506 °C), SPM7 is (495 °C and 605.5 °C) and SPM8 is (558 °C). The crystalline structural phases and their morphological are identified by using powder X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM), respectively. All samples appeared opaque after annealing process except sample SPM7 – 495 °C which appeared semi-crystalline. Figs. 11(a)–(d) and 12(a), (b), 13(a), (b), 14(a), (b), 15(a), (b), 16(a), (b), and17(a), (b) show the powder X-ray diffraction patterns of the crystalline samples and the typical SEM images of the crystalline sample and corresponding EDX spectra for selected area respectively. For sample SPM1 – 431 °C the only phase was identified was antimony phosphate Sb(PO_4) which matched with ICDD (PDF-2-01-071-2275, Release 2015 RDB). For sample SPM4 – 422 °C the major phase was antimony phosphate Sb(PO_4) which matched with ICDD (PDF-2-01-071-2275, Release 2015 RDB) and the minor phase was magnesium phosphate Mg (PO_4)_2 which matching with ICDD (PDF-2-00-027-1273, Release
2015 RDB). For sample SPM4 – 506 °C the major phase was antimony orthophosphate SbPO₄ which matched with ICDD (PDF-2-01-078-1791, Release 2015 RDB) and magnesium cyclo-tetraphosphate Mg₂P₄O₁₂ as the minor phase which matched with ICDD (PDF-2-01-070-1803, Release 2015 RDB). For sample SPM7 – 495 °C the major phase was antimony phosphate Sb(PO₄) which matched with ICDD (PDF-2-01-071-2275, Release 2015 RDB). For sample SPM7 – 605.5 °C the major phase was antimony orthophosphate SbPO₄ which matched with ICDD (PDF-2-01-078-1791, Release 2015 RDB). For sample SPM8 – 558 °C the major phase was antimony orthophosphate SbPO₄ which matched with ICDD (PDF-2-01-078-1791, Release 2015 RDB), and the minor phase was cervantite, syn Sb(SbO₄) which matched with ICDD (PDF-2-01-078-2066, Release 2015 RDB). In addition, the major phase in the crystalline samples is antimony phosphate at temperature below 500 °C and antimony orthophosphate at temperature higher than 500 °C as shown in the XRD analysis, summarized in Table 5. It is also found that the MgO modifier had an impact on the phase occurrence where if its concentration is higher than 5 mol% (as 15 and 25 mol%) a new minor phases as magnesium phosphate and magnesium cyclo-tetraphosphate (at 55 mol% of P₂O₅), and Cervantite, syn (at 40 mol% of Sb₂O₃) were emerged. According to the ICDD (PDF-2-) card, there is no difference between antimony phosphate Sb(PO₄) and antimony orthophosphate SbPO₄ in terms of crystal structure, they have the same monoclinic crystal system and belong to (P2₁/m) space group, the only difference is in the edges lengths of the unit cell (a, b, c), which leads to different unit cell volume and density, for both compounds antimony phosphate and antimony orthophosphate, which are (161.80 Å³, 4.448 g/cm³) and (162.00 Å³, 4.443 g/cm³) respectively. The same case with magnesium phosphate Mg₃(PO₄)₂ and magnesium cyclo-tetraphosphate Mg₂P₄O₁₂ both have monoclinic crystal structure.
and their data are (842.91 Å³, 2.872 g/cm³) and (845.12 Å³, 2.86 g/cm³) respectively. For the cervantite Sb(SbO₄) phase which belong to orthorhombic crystal structure and Pna21 space group 307.82 Å³ and 6.635 g/cm³. The presence of three peculiar crystalline phases which are antimony phosphate Sb(PO₄), antimony orthophosphate SbPO₄ (major crystalline phases) and cervantite Sb(SbO₄) (minor crystalline phase) which known as distinct polymorph of antimony tetroxide Sb₂O₄ [77], these crystalline phases possess the lone pair property (5s²) in their structures and have large non-linear optical susceptibility coefficient (χ³) [47] and possess a large impact on the glass optical properties [6,77]. The outstanding features of the lone pair electron inside glass matrix are the flexibility character (easy to deform) of the lone pair electron, structure with lone pair produces less strain energy during amorphous polyhedra formation and strong steric effects due to interaction among lone pair electrons (electrostatic repulsion) [49]. The presence of this lone pair enhances the nonlinear optical susceptibility in the antimonite glasses described by third rank polar tensors [78]. Furthermore, the existence of different crystalline phases in this ternary glass system can modify the rare earth spectroscopic properties in terms of electronic transitions (absorption or emission) and the related spectral shape of these transitions in this glass matrix, which can be done through stark effect results from the presence of an external electric field of the ligand group (glass host) around the active ions which leads to spectral lines splitting and shifting of the active ions, and each stark level has a specific energy and a specific width [79–81]. So, trivalent rare earth elements inside glass with multi-crystalline phases might experience different local electric and magnetic fields so the transitions spectral shape is from the different type of stark level structure, and lead to manipulate the rare earth spectroscopic properties.

Fig. 16. (a) FESEM image of sample SPM7 (Tp = 605.5 °C), and (b) the corresponding EDX spectra for selected area.

Fig. 17. (a) FESEM image of sample SPM8 (Tp = 558 °C), and (b) the corresponding EDX spectra for selected area.
Conclusions

Four series of magnesium-antimony-phosphate glasses of new compositions are synthesized and thermal properties are determined as a function of varying modifiers concentrations. Glass transition temperature, crystallization temperature, thermal stability, solids temperature, and liquidus temperature are systematically measured and their origin is explained via various mechanisms. Glasses are found to be transparent, and thermally stable with inhomogeneous textural morphology. The SEM images manifested their phase formation (heterogeneous glass) and EDX spectra detected the accurate elemental traces in the presence of contamination from furnace heating elements and crucible materials. Glasses with 50 mol% of Sb$_2$O$_3$ exhibited excellent thermal stability, displaying landmarks of melt over a broad temperature range (incongruent melting). Furthermore, these glass systems encountered many phases from the onset of melting (solids temperature). The number of phase formation possibility is enhanced with increasing Sb$_2$O$_3$ and MgO modifiers content. Glass sample with composition of 60Sb$_2$O$_3$-20P$_2$O$_5$-20MgO showed lowest liquidus temperature (836 °C) and solidus temperature (426 °C) among all other samples due to eutectic reaction, also the emergence of five crystalline phases in the area studied of ternary diagram gave an evidence that this oxide system encounter many phase transition through the concentration or temperature changes. Our careful experimental evaluation on thermal properties in magnesium-antimony-phosphate glasses may contribute towards the development of phosphate glass based device fabrication and non-linear optical material.

Acknowledgements

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