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Antimony Borate Binary Glass System

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Abstract: The present paper reports an over view of antimony borate glass system collected from the available literature which is helpful for the upcoming researchers those who wants to synthesise this binary glass system (may be doped with transition metal ions or rare-earth ions) for various applications.

1. Introduction

Glass has been used by humans since the Stone Age. Obsidian a natural glass formed from the cooling of silica-rich lava can be fractured like flint to form extremely sharp edges, a property that was exploited for use in arrowheads and simple cutting tools. The earliest known man-made glasses originated in Egypt and Eastern Mesopotamia circa 3500 B.C. in the form of glass beads (possibly an unintended by product of other industry) and by c. 1500 B.C. craftsmen were able to produce glass pots and other vessels. The Romans later spread glass making technology throughout Western Europe and around the Mediterranean, and the use of glass for practical, artistic and architectural purposes grew and developed during the middle Ages and the Renaissance. It was not until the late 19th century, however, that scientific studies to relate the properties of a glass to its composition began in earnest; the effects of certain additives such as oxides of magnesium, calcium and lead had been known of for centuries, but were discovered empirically. Modern scientific interest in glass includes its applications in the field of laser optics and in the storage of nuclear waste.

1.1 Definition and properties

Silica, in the form of sand, is commonly regarded as a prerequisite for glass-making and many SiO_2 based glasses do exist; it is not, however, an essential component of a glass. In fact, a diverse array of chemical substances can be vitrified; materials are instead characterized as a glass based on their properties, rather than their composition. A solid is generally classed as a glass if it meets two criteria: it has no long-range order in its atomic arrangement, and it experiences a 'glass transformation region' (a time-dependent behaviour over

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a temperature range). Consider a liquid at a temperature above its melting point (Fig. 1). As the temperature is lowered, the enthalpy of the substance will gradually decrease and its atomic arrangement will slowly change, being at any point characteristic of the temperature of the melt. When the liquid is cooled below its melting point Tm it will usually experience an abrupt shift to a crystalline solid (with long-range atomic order) with a correspondingly sharp decrease in enthalpy. However, if the liquid can be cooled below the melting point without crystallization ('super-cooled') it will continue to exhibit a gradual decrease in enthalpy with temperature.

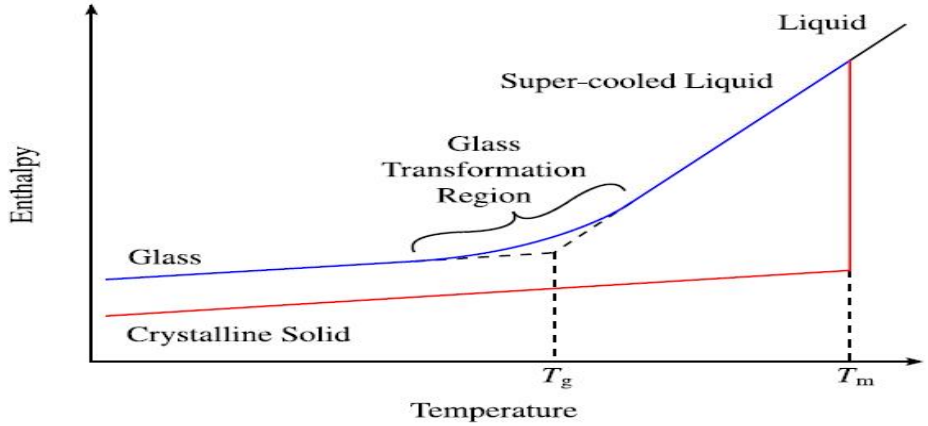

Figure 1 Thermodynamic diagram showing the changes in enthalpy of a glass-forming melt with temperature (blue line), as opposed to that of a normal liquid-solid transition (red line)

As cooling progresses, the viscosity of the liquid will increase; at some point the viscosity will be such that the atomic structure of the liquid will be unable to realign to the equilibrium arrangement for its temperature in the time available. This will cause the enthalpy of the system to lag from the equilibrium line until the point is reached where the viscosity prevents any further atomic rearrangement. In essence, the liquid has become an amorphous solid with no long-range order one of the conditions necessary for a material to be considered as a glass. In addition, the process of super-cooling has also fulfilled the second requirement: the temperature region that lies between the enthalpy being that of the equilibrium liquid and that of the frozen liquid is what is known as the glass transformation region.

1.2 An Introduction to Glass

As indicated in Figure 1, the glass transformation region exists over a range of temperatures. However, it is often useful to define a single glass transition temperature, T_g, as an indication of the onset of the glass transformation region

upon heating the glass. This is defined empirically, and the value obtained for a given glass is dependent on several factors, including the rate at which the melt was originally cooled, the experimental method used to determine T_g and the heating rate applied. Hence, T_g should not be considered a true thermodynamic property, but is a useful indicator of when the transition between glass and super cooled liquid occurs. Another temperature often quoted is the crystallization temperature, T_c, which occurs after T_g and indicates the onset of crystallization of the devitrified material. The deference in magnitude between T_g and T_c can also be used as an indicator of the stability of the glass.

Finally, it should be noted that, whilst cooling of a melt is the most common method of glass-making, it is by no means the only way of doing so: chemical vapour deposition and sol-gel processing are examples of other such techniques.

In chemical vapour deposition CVD, the wafer or substrate is exposed to one or more volatile chemical compound, which react and/or decompose on the substrate surface to produce the required layer. Usually, volatile by-products are also formed, which are removed by gas flow through the experimental chamber.

The sol–gel process is a method for producing solid materials from small molecules. The process involves conversion of monomers into a colloidal solution (*sol*) that acts as the chemical compound for gel of either discrete particles or network polymers. Usual chemical compounds are metal alkoxides.

1.3 Glass forming oxides

Silica (SiO_2) is one of a series of oxides known as glass formers (or network formers) that will readily form glasses in isolation other examples are B_2O_3, GeO_2 and P_2O_5. The cations in these oxides tend to form highly covalent bonds with oxygen, which has been shown to be a common property of glass formers. Oxides with cations whose oxygen bonding is more ionic in nature such as SeO_2, WO_3 and Al_2O_3 will not form a glass individually, but will do so when melted with a suitable quantity of a second oxide; these are termed intermediates or conditional glass formers. Finally, oxides with highly ionic bonds never form a glass, but can be used to affect the glass structure created from other glass formers these oxides are known as modifiers.

1.4 Simple structural theories of glass formation

Different chemical systems require specific cooling rates to be met or exceeded in order to form glasses. This fact has led to several attempts to produce a complete atomic theory of glass formation based on the nature of the chemical bonds and the shape of the structural units involved. Whilst it may seem strange to propose structural theories for a substance that is defined as having 'no long-range, periodic atomic

ordering', it has been found to be possible to form reproducibly the same glass from a nominal starting composition, implying that there is some short-range ordering that is sufficient to control the overall properties.

1.5 Multi-component glasses

Whilst some substances form vitreous systems with relative ease (e.g. B_2O_3, P_2O_5), other, poorer glass formers (e.g. As_2O_3) require more extreme cooling rates for this to occur. As detailed above, glass structural theories require the formation of a continuous random network of atoms, as opposed to the ordered, repeating atomic arrangement in a crystal lattice this can be made to occur more readily in poor glass formers by adding a small amount of a contaminant. In terms of enthalpy, glasses are thermodynamically less favourable than the available crystalline modifications; however, their random structures are more entropic. The tradeoff between reducing the enthalpy and decreasing the entropy during crystallization is prevented by kinetic factors: once a super cooled liquid drops below T_g the activation energy necessary to re-form the structure is no longer present, and the atoms become locked in an amorphous arrangement. The ease with which a melt forms a crystal lattice is also affected by kinetics, since crystals form by a process of nucleation and growth.

The introduction of a contaminant increases the overall entropy of the system making it somewhat less thermodynamically favourable to form a crystal structure and hinders the kinetic realignment by providing more bonds to break and atoms to rearrange, frustrating crystal formation. Thus, the presence of a contaminant in a melt can substantially improve the glass-forming ability of a system. However, such impurities can also play a significant role in the properties of the glass formed. This is an important factor since not all contamination is intentional: for example, a melt may react with a certain crucible material and thus introduce impurities to the resultant glass. Another common contaminant is water which is difficult to regulate between preparations and can form hydroxyl groups in the glass structure.

Glass melts are cooled by a variety of techniques, depending on the glass to be formed and its stability; less stable glasses require more extreme cooling techniques. Splat-quenching (pressing the melt between two cooled metal plates), roller-quenching (pouring the melt between two counter-rotating cylinders) and melt-spinning (forcing a thin stream of melt onto a roller to quench, with the aid of high-pressure gas) are some examples, and other cooling rates of the order of 10^3, 10^5 and 10^8 $^oC\ s^{-1}$, respectively.

A glass can be considered as the result of lowering the temperature of a super cooled liquid to the point at which it becomes too viscous to reach an equilibrium state for its temperature; in

other words, at the point where the energy of the system is insufficient to allow a thermodynamically favourable drop in enthalpy to occur kinetically. The resulting amorphous structure can be modelled as a continuous random network, with no long-range periodic ordering, although short range atomic alignments characteristic of the material still exist and regulate the properties of the glass. The ability of a substance to form a glass, either in isolation or when mixed with another compound, allows it to be classified as a glass-former, intermediate or modifier. The ease with which a glass-former can be used to create a vitreous system can be improved by the addition of one or more modifiers (or contaminants), although this can also affect the properties of the resultant glass. The lone-pair of electrons on certain cations can exert a strong steric influence that affects the structure of a material and, in the case of a glass, can lead to interesting properties. Antimony trioxide contains such lone-pair cations and has been reported to readily form a glass in combination with another oxide. This work will use neutron diffraction and other methods to investigate several Sb_2O_3 based glasses, with the aim of characterizing the behaviour of Sb_2O_3 in a glass network.

2. Antimony glass

Antimony oxide exists in several forms, including antimony trioxide (Sb_2O_3), antimony tetroxide (Sb_2O_4) and antimony pentoxide (Sb_2O_5). Of these, Sb_2O_3 occurs as cubic and orthorhombic polymorphs (senarmontite and valentinite, respectively), with the latter being the stable form at higher temperatures, whilst Sb_2O_4 can be monoclinic (clinocervantite) or, more commonly, orthorhombic (cervantite), and Sb_2O_5 has only been reported to have a single, monoclinic structure. Antimony tetroxide is a mixed valency compound, containing both Sb^{3+} and Sb^{5+} ions in equal proportions in its crystal lattice. It is worth noting that the 'molecular' structure of senarmontite (Fig.2) does not appear to lend itself to glass formation when compared with the 'double-chain' structure of valentinite (Fig.3) which can be expected to form the 'continuous random network outlined by Zachariasen with greater ease. Antimony trioxide (Sb_2O_3) was predicted to be a glass-former by Zachariasen and contains the lone-pair cation Sb^{3+} (antimony can also occur in the oxidation state Sb^{5+}).

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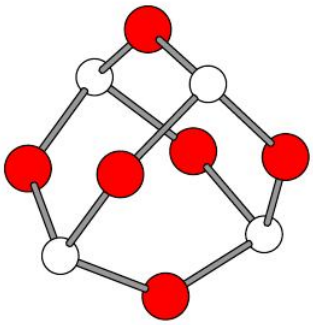

Fig.2

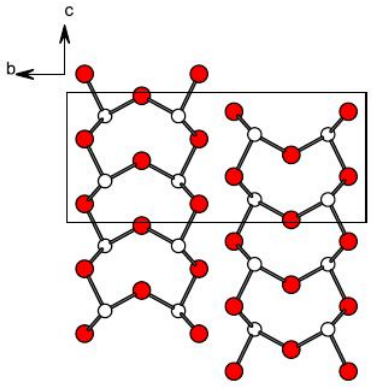

Fig.3

3. Antimony borate glasses

The antimony borate glass system has been the subject of several studies in the literature, with x Sb_2O_3 (1- x) B_2O_3 glasses reported to form across the entire compositional range. This makes the system a desirable one to exploit for non-linear optical applications. Numerous authors have reported methods of preparing antimony borate glasses: these typically involve melting at 800 °C in silica or platinum crucibles for ~20 minutes before splat-quenching between steel or copper plates; some authors report using higher temperatures, or less extreme quenching methods. Youngman et al. report SiO_2 contamination which they attribute to the silica crucibles used for the melt it seems likely that this is also the case for the other authors who reported SiO_2 content or who used such crucibles.

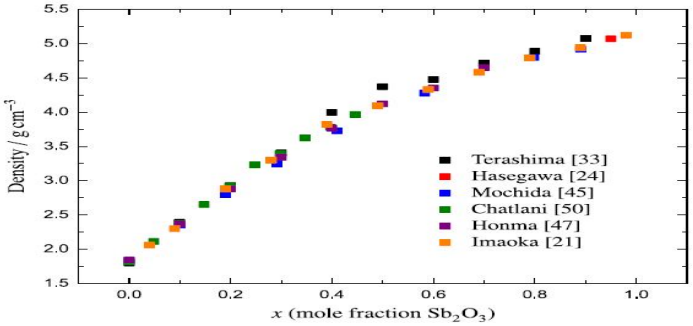

Figure 4 The densities reported for the antimony borate glass system by various authors [12, 13, 14, 15, 16, 21]

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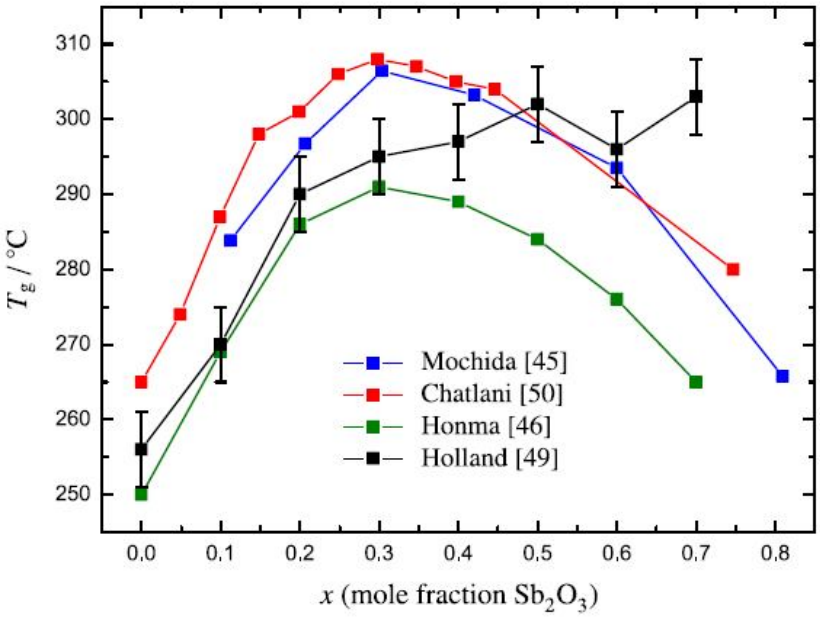

Figure 5 Values of T_g for the antimony borate glass system,

as measured by various authors [15, 17, 20, 21]

There is a general consistency in the densities that have been reported for the various antimony borate glasses (Fig. 4) the only notable exceptions are some of the values reported by Terashima et al. In that work, only the nominal batch compositions are listed for the samples, and so the discrepancies may be due to the quenched glasses having slightly different compositions.

The glass transformation temperatures exhibit much greater disagreement (Fig. 5). From the majority of the results reported, there appears to be a maximum T_g at x = 0:3, although the data of Holland et al. appears to indicate that a value at significantly higher x would be appropriate. Nevertheless, the error range reported would include a curve of similar shape to the other authors, suggesting that the data is insufficiently accurate to draw conclusions as to a maximum in T_g. The value of T_g for x = 0:7 reported by Holland et al. remains anomalous however, as do the lower values of T_g (by 15 °C to 20 °C) reported by Honma et al.

Several authors have reported 11B magic angle spinning nuclear magnetic resonance (MAS NMR) data, which they used to estimate the fraction of four coordinated boron, N4, that was present in the glass samples. These estimates (Fig. 6) show a good agreement, with the

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small discrepancies probably attributable to differences in sample preparation, as noted by Holland et al.

In a much earlier paper, Mochida and Takahashi had observed from the analysis of Raman spectra that there was evidence of an increase in boron coordination with increasing Sb_2O_3 content, but that this effect was relatively small compared with that in the bismuth borate system also studied (the Raman technique was not able to provide quantitative information): this is consistent with the observation of Holland et al. that the values of N_4 for the antimony borate system are unusually low for a binary borate glass. The consensus in the literature is that the short-range structure of the glass is based on the chains of trigonal [SbO_3] pyramids found in valentinite. Common justifications are the low viscosity of the glass melt, suggesting a layer or chain like structure, and the Sb-O bond length of ~1.97 together with a coordination of 3 or slightly higher (from X-ray diffraction or EXAFS, implying the basic structural unit to be the [SbO_3] trigonal pyramid.

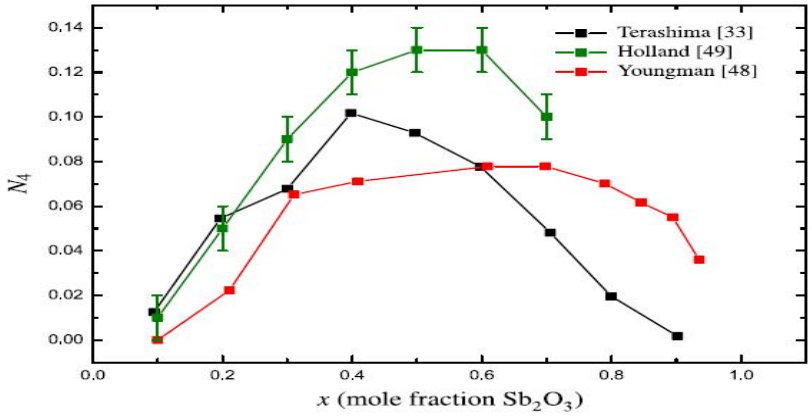

Figure 6 Values of N_4 reported in the literature for the
antimony borate system [14, 19, 20]

Authors have also published infra-red and Raman data supporting a chain-like structure, as well as reporting the glass crystallizing to valentinite, and observing quadrupole splitting in Mossbauer spectra that suggests that the [SbO_3] trigonal pyramid is the basic structural unit. Hasegawa et al. also compared the correlation function that they obtained to various models and concluded that the disorder in the structure probably arose from a small number of [SbO_3] pyramids turned over irregularly within the chains. In addition to the aforementioned EXAFS work, Youngman et al. also conducted a Raman study that showed evidence of a number of boroxol rings that decreased with increasing x, appearing to reach zero at x = 0:6, together with a small amount of four co-ordinated boron (although note that Raman spectroscopy is not

quantitative). They concluded that the structure is predominantly a corner-sharing network of [SbO_3] trigonal pyramids and [BO3] planar triangles the formation of [BO_4] species then requires the presence of three-fold coordinated oxygen, as noted by Terashima et al. However, Holland et al. associated the formation of [BO_4] with the presence of Sb^{5+}, with experimental data showing good agreement with the amount of the latter present in the samples, at least up to x = 0:5.

References

[1] V. M. Goldschmidt, Vid. Akad. Skr. Oslo 8, (1926), 137

[2] W. H. Zachariasen, J. Am. Chem. Soc. 54 (10), (1932), 3841–3851.

[3] A. Paul, Chemistry of Glasses (Chapman & Hall, New York, 1990).

[4] S. R. Friberg and P. W. Smith, IEEE J. Quantum Elect. 23 (12), (1987), 2089–2094.

[5] D. W. Hall, M. A. Newhouse, N. F. Borrelli, W. H. Dumbaugh and D. L. Weidman, Appl.

Phys. Lett. 54 (14), (1989), 1293–1295.

[6] N. V. Sidgwick and H. M. Powell, P. Roy. Soc. Lond. A Mat. 176 (965), (1940), 153–180.

[7] R. J. Gillespie and R. S. Nyholm, Q. Rev. Chem. Soc. 11, (1957), 339–380.

[8] R. J. Gillespie and I. Hargittai, The VSEPR Model of Molecular Geometry (Prentice Hall

International, London, 1991).

[9] R. J. Gillespie, Chem. Soc. Rev. 21 (1), (1992), 59–69.

[10] V.M. Jansen, Act Crystallography, B (35) 3, 1979, 539 – 542

[11] W. H. Zachariasen, J. Am. Chem. Soc. 54 (10), (1932), 3841–3851.

[12] M. Imaoka, H. Hasegawa and S. Shindo, J. Ceram. Soc. Jpn. 77 (8), (1969), 263–271

[13] H. Hasegawa, M. Sone and M. Imaoka, Phys. Chem. Glasses 19 (2), (1978), 28–33

[14] K. Terashima, T. Hashimoto, T. Uchino, S.H. Kim and T. Yoko, J. Ceram. Soc. Jpn.

104 (11), (1996), 1008–1014

[15] N. Mochida and K. Takahashi, J. Ceram. Soc. Jpn. 84 (9), (1976), 413–420.

[16] T. Honma, R. Sato, Y. Benino, T. Komatsu and V. Dimitrov, J. Non-Cryst. Solids 272 (1),

(2000), 1–13.

[17] T. Honma, Y. Benino, T. Komatsu, R. Sato and V. Dimitrov, J. Chem. Phys. 115 (15),

(2001), 7207–7214.

[18] A. J. G. Ellison and S. Sen, Phys. Rev. B 67.

[19] R. E. Youngman, S. Sen, L. K. Cornelius and A. J. G. Ellison, Phys. Chem. Glasses 44 (2),

(2003), 69–74.

[20] D. Holland, A. C. Hannon, M. E. Smith, C. E. Johnson, M. F. Thomas and A. M. Beesley,

Solid State Nucl. Mag. 26, (2004), 172–179.

[21] S. Chatlani and J. E. Shelby, Phys. Chem. Glasses-B 47 (3), (2006), 288–293.