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Tin-based amorphous and composite materials

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Abstract In recent years increasing attention has been devoted to tin composite oxide glasses (TCO glasses), which are most promising candidates as anode materials in lithium secondary batteries and they are also desirable from environmental viewpoint low melting glasses, sensing elements, non-linear optical materials and coatings. The aim of this paper is to review the studies of SnO-based oxide glasses and to present our experience in developing such amorphous materials. The obstacles in producing such materials are oxidation or disproportionation of SnO at high temperatures. Different techniques were applied to established reproducible methods for the synthesis of Sn-containing glasses. Tin oxide glasses were obtained in the binary systems with classical glass-former oxides: $SnO–SiO_2$, $SnO–GeO_2$, $SnO–B_2O_3$, $SnO–P_2O_5$, $SnO–BPO_4$ and in oxyhalide systems $SnX_2–P_2O_5$, ($X = F$, Cl). SnO essentially improves some technological characteristics of glasses, but many unsolved problems regarding the mechanism of its influence still remain. Depending on the composition, SnO tends to change its behavior from network-modifier to network-former. But the structural role and chemistry of tin in inorganic glasses is still not clearly understood. Our studies were focused on the systems of $SnO–P_2O_5$, $SnO–P_2O_5–MO$ ($M = Zn$, Ba), $SnCl_2–P_2O_5$, $SnCl_2–P_2O_5–MeCl_2$ (Me_nO_m). The influence on the quality of glasses of different factors, such as nature of raw materials, the batch preparation and the melting conditions, has been studied. Low-melting stable glasses have been obtained at ambient atmosphere.

Introduction

Chronologically, the first studies of binary tin oxide containing glasses had for an object to determine the structural role of Sn^{2+} ion in the network of glasses because of its importance in the surface of float glass [1–3]. The results show the ability of $SnO–SiO_2$ and $SnO–B_2O_3$ systems to form stable glasses up to a very high SnO content, like $PbO–SiO_2$ and $PbO–B_2O_3$ systems. But the difficulty to make good glass samples due to disproportionation of SnO to metal Sn and SnO_2 had arisen. The specific properties of these glasses that answer the requirements of some modern techniques had resumed the researches in this field. Obtained by Tick [4–6] tin-phosphate glasses with low and ultra low melting temperature and good water durability initiate great number of studies of structure and properties of similar systems and of the factors that affect the products.

More than 40 tin oxide based systems have been researched by now, but the mechanism by which tin oxides impart beneficial effects in glass are not clearly understood. The structural studies have started by Tick, Holland and Paul and are still developing [3, 4, 7]. The aim of this paper is to review the subject, to systematize the studies of tin oxide glass systems and to summarize proposed structure models, and to resume the glass-forming abilities of Sn^{2+}-compounds (SnO, SnX_2).

The tin-oxide systems are a basis for development of many glass, glass-ceramics and nanocrystal materials that find more and more applications. Tin oxides are

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extensively used in making ruby glasses (gold and cupper ruby), as opacifiers in low melting glazes and enamels, and as glass surface coatings to increase abrasion resistance and strength [8, 9]. Important applications of tin oxide systems are crystal and amorphous thin films, which possess unique combination of transparence in visible spectra and conductivity, chemical resistance and good adhesion [10–18]. That makes them widely used in electronics, radiotechnics, aviation, sensors and other fields of techniques. Characteristics of tin-phosphate oxide and oxyhalide glasses are their low and ultra low glass transition temperature (T_g) and softening temperature (T_s). These glasses are appropriate for optical devices [4, 5, 19–22], glass-to-metal seals [23–26], enamels, semiconductors, and inorganic glass matrix as host material for various organic compounds in organic inorganic hybrids [6, 27, 28]. During the past few years the Japanese researching groups have brought into attention the TCO glasses (tin composite oxide glasses) and initiated an intensively developed of these systems [29–53]. They work as anode materials in the lithium secondary batteries for portable electronic devices. These materials exhibits four times larger volumetric and two times larger gravimetric capacity than the carbon materials used as anodes for commercial lithium-ion secondary batteries. On the other hand, the materials in Sn-containing systems are desirable from environmental viewpoint as promising candidates of Pb-free low melting glasses.

Glass systems

Tin oxide glasses have been obtained in the binary systems with classical glass-former oxides: Sn–Si–O [1, 2, 7, 20, 53–58], Sn–Ge–O [59, 60], Sn–B–O [3, 29, 34, 37–40, 43, 61–64], Sn–P–O [22–28, 30, 32, 40, 41, 53, 65–70], Sn–B–P–O [29, 36, 38, 40–52] and in oxyhalide systems: Sn–P–O–F [4–6, 71–78], Sn–P–O–Cl [27, 28, 79–85] (Table 1.). The high content of SnO in obtained glasses is common to all systems. The first obtained glasses in the system $SnO–SiO_2$ have had up to 60 mol% SnO [1, 2]. The later studies have obtained glasses in the range 17–72 mol% SnO, which is greater than the orthosilicate composition of $2SnO.SiO_2$ (Sn_2SiO_3) [7]. In the system $SnO–GeO_2$, analogically to the $SnO–SiO_2$ system, glass has been formed with $x > 2$ (Sn_xGeO_{2+x}) which is over the orthogermanate composition [59, 60]. The $SnO–B_2O_3$ and $SnO–BPO_4$ systems have wide glass-forming regions with $0 < SnO(mol\%) < 75$ in the system $SnO–B_2O_3$ [34, 61, 64] and $25 < SnO(mol\%) < 80$ in the $SnO–BPO_4$ system [61]. In the system $SnO–P_2O_5$ glasses have been obtained up to 80 mol% SnO [66], and in the tin-phosphate oxy-halide systems the total content of ($SnO + SnX_2$) in the glasses extends to 80 mol% [71–85].

The conditions of preparation and melting of the glasses are of the great importance because at the SnO oxidize and disproportionate to Sn and SnO_2 at temperatures above 300 °C [86–89]. It was found that a glass in the binary systems $SnO–SiO_2$, $SnO–GeO_2$ and $SnO–B_2O_3$ couldn't be melted without dissolving metallic tin and SnO_2 in it. However, the solubility of metallic tin in glass is low, and adjusting oxygen pressure in the furnace can control the activity of SnO_2 in the melt. With high oxygen fugacity, SnO oxidizing to SnO_2, part of which dissolving in the melt. If oxygen fugacity is lower than some critical limit, SnO reducing to metallic tin, which being insoluble in melt, settling at the bottom of the crucible. The modification of glass composition with additional components and the nature of tin compound that is used as row material for insertion of tin component in the systems essentially affect the glass-forming abilities and properties of the systems. Sn^{2+} have been inserted in the form of oxide (SnO) [19, 22–26, 32–53, 58, 61–70], halides ($SnCl_2$, $SnCl_2.2H_2O$, SnF_2) [27–28, 71–85] or others salts or metal-organic compounds (SnC_2O_4) [1–3, 7, 20, 57, 59, 60]. The melting of the systems in which tin oxide has been used, have been carried out in inert atmosphere or with reducing agent. When stannous oxalate has been used as precursor, it decomposed to SnO, CO and CO_2. The evolution of CO and CO_2 during melting has been used to maintain a nonoxidizing atmosphere over the melt by trapping the gases in the crucible inverted over that containing the melt. This does not, however, prevent disproportionation of some Sn^{2+} to Sn^0 and Sn^{4+}. Stannous oxalate has been used as a precursor in the systems $SnO–SiO_2$, $SnO–GeO_2$ and $SnO–B_2O_3$. The tin components have been inserted in phosphate systems as halide ($SnCl_2$, SnF_2) or as a combination of halide and oxide (SnX_2 + SnO). The volatilization of the halide components during melting is a significant factor in the oxyhalide systems. The systems with low $SnO:SnF_2$ ratio less tend to phase separation and crystallization. Increasing the O:F ratio at a constant Sn:P ratio in the systems Sn–P–O–F and Sn–Pb–P–O–F results in a decreased loss in weight during melting and decreasing the optical quality of the glass [72]. The main foul of these systems is the inclusion of the environmental pollutant fluorine and lead. Hu and Jiang have replaced fluorine by chlorine and have developed chlorophosphate glasses in the systems Sn–Pb–P–O–Cl and Sn–O–P–Cl [79]. Good glass formation have found to take place in the glass containing 50–65 mol% ($SnCl_2$ + SnO). Compared with Sn–O–P–F glasses, Sn–O–P–Cl glasses have found to exhibit higher glass transformation temperatures and better chemical durability. Sato et al. have studied $SnCl_2–P_2O_5$ system and have obtained glasses with very high $SnCl_2$ content—up to 80 mol% [81]. Oxygen atoms replace the chlorine atoms during melting, thus the real composition of

Table 1 Tin containing glass systems

System		SnO [mol%]	T_g [°C]	$T_{melting}$ [°C]	References	Year
Sn–Si–O	$SnO–SiO_2$	28–59			[1]	1967
Sn–Si–O	$SnO–SiO_2$	32–57		1350 –1420	[2]	1978
Sn–Si–O	$SnO–SiO_2$	17–72	651–428	950	[7]	1995
Sn–Si–O	$SnO–SiO_2–R_2{*}O$ $SnO–SiO_2–R{**}O$ ($R_2{*}O$ = Li, Na, K, Rb) (R**O = Mg, Ca)	50	600–450	1000–1200	[57]	2000
Sn–Si–O	$SnO2–SiO_2–Er_2O_3$			1050	[20]	2002
Sn–Ge–O	$SnO–GeO_2$	60		900–110	[59]	2001
Sn–B–O	$SnO–B_2O_3$	58	350	900–1100	[3]	1977
Sn–B–P–Al–O	$SnO–B_2O_3–P_2O_5–Al_2O_3$	40		1100	[29]	1997
Sn–B–O–X (X = Ca, Mg, Zn)	$SnO–B_2O_3$–XO (XO = CaO, MgO, ZnO)	8		1600	[62]	1997
Sn–B–O	$SnO–B_2O_3$	75	max 384	850–1100	[64]	2001
Sn–B–O–Li	$SnO–B_2O_3$_Li_2O	0–75	max 384	850–1100	[64]	2001
Sn–B–P–O–Li	$SnO–BPO_4–Li_2O$	25–75	490–309	850–1100	[64]	2001
Sn–B–O	$SnO–B_2O_3$	77	max 384	900–1200	[63]	2002
Sn–P–O	$SnO–P_2O_5$	50–85		500–1200	[99]	2005
Sn–P–O	$SnO–P_2O_5$	30–70			[66]	2002
Sn–P–O	$SnO–P_2O_5$	40	150–300	500–1200	[62]	1997
Sn–P–O–Zn	$SnO–ZnO–P_2O_5$	SnO:ZnO 1:1–5:1	325–375	900–1000	[23]	1992
Sn–P–O–Ba	$SnO–BaO–P_2O_5$	10–20		1100	[100]	2006
Sn–P–O–Na	$SnO–NaPO_3$	$SnO:NaPO_3$ 0:100–45:55			[70]	2001
Pb–Sn–P–O–Cl	$SnCl_2–PbCl_2–P_2O_5$	50–75	180–225	500	[79]	1994
Sn–P–O–Cl	$SnO–SnCl_2–P_2O_5$	80	75–160	450	[81]	1997
Sn–P–O–Cl	$SnO–SnCl_2–P_2O_5$	60	170–220	500	[82]	1998
Sn–P–O–Cl	$SnO–SnCl_2–P_2O_5$	70	350	500	[83]	2001
Sn–P–O–Cl	$SnO–P_2O_5$_Me_2SiO	20	–25–50	250	[28]	2002
Sn–P–O–Cl	$SnO–SnCl_2$_P_2O_5	60	120–200	500	[85]	2003
Sn–(Cu)–P–O–Cl	$SnCl_2$_$CuO–P_2O_5$	>65	150–230	500	[85]	2003
Sn–(Pb)–P–O–F	SnF_2_$SnO–P_2O_5$	60	<100	400–450	[5]	1982
Sn–P–O–F–C_xH_y	SnF_2 –$SnO–P_2O_5–C_xH_y$	60		450	[4]	1983
Sn–P–O–F	SnF_2_P_2O_5	20–75	70–260	450	[4]	1984
Pb–Sn–P–O–F	SnF_2_PbF_2_P_2O_5	40–65	150–75	450	[4]	1984
Sn–P–O–F	SnF_2_P_2O_5	70	84–200	500	[71–73]	1988
Sn–P–O–F	SnF_2_P_2O_5	50–70	95–140	500	[74]	1990
Sn–P–O–F	SnF_2_P_2O_5	60	100	500	[76]	1992
Sn–V–Te–O	$SnO–V_2O_5$_TeO_2	20		750	[93, 94]	1997

the glasses is expressed as $SnCl_2–SnO–P_2O_5$. The chlorine content depends on melting time and it has found to become to a constant value as the melting time greater than 30 min [84]. A comparison of the systems $SnO–P_2O_5$ and $SnCl_2–P_2O_5$ have indicated that substitution of chlorine to oxygen, by increasing $SnCl_2/SnO$ ratio, contributed both to a decrease of melting temperature and extension of the glass-forming region [83]. Morinaga et al. have considered that chlorine helps to form a uniform liquid without forming the high melting compound $70SnO_2 \cdot 30P_2O_5$, whereas in the $SnO–P_2O_5$ system the tin oxidized to form $70SnO2.30P_2O_5$.

Most of the tin oxide based glasses have been prepared by conventional melt quenching techniques with pressing between metal or carbon plates to fix the amorphous state. Using low-temperature solution based techniques, many of the limitations of this method, as problems of volatilization and phase separation, leading to the formation of inhomogeneous glasses, have been eliminated. Films, powders, hybrid and anode materials without classical glass-former have been obtained by sol–gel and co-precipitation methods [11, 12, 14, 17, 27, 28, 90, 91]. Synthesized by sol–gel method materials have found to be predominantly amorphous up to about 200 °C and above this temperature, the tetragonal phase SnO_2 (cassiterite) or more complicated structures crystallize. Amorphous powders of the systems $SnO–SiO_2$ and $SnO–B_2O_3–P_2O_5$ have been synthesized by mechanically milling treatment of starting materials at the room temperature [34, 35, 52]. Compared to the melt quenched glasses, amorphous powders obtained by mechanically milling can be directly used as active materials for lithium secondary batteries without pulverizing procedures.

Binary systems $SnO–SiO_2$, $SnO–GeO_2$, $SnO–B_2O_3$, $SnO–P_2O_5$ have been used as basis for development of more complicated glass compositions. Researches of incorporating typical modifying oxide have been made. The SnO have been partially replaced by alkali and alkaline earth metal oxides in the stannous silicate glasses: $SnO–SiO_2–R^*{}_2O$ (R^* = Li, Na, K, Rb) и $SnO–SiO_2–R^{**}O$ (R^{**} = Ca, Mg) [55, 57]. The replacement of SnO by alkali oxides has been found to decrease T_g and the replacement by alkaline earth oxides has been found to increase it. Incorporating of Li_2O, CaO and MgO have been found to reduce the molar volume of the glasses, whereas K_2O and Rb_2O increase it and Na_2O has little effect. Substitution of between 5–10 mol% R_2O for SnO have been found to completely eliminates the formation of the stannous metasilicate phase and the disproportionation/oxidation move to a higher temperatures. In the system $Er_2O_3–SnO_2–SiO_2$ have been obtained monolithic glasses that exhibit good transparency and absence of phase separation [20].

Referring to the application the most examined alkali modifier the tin borate glass systems have been lithium [18, 29, 33, 34, 36, 37, 41, 44, 48, 51]. The results revealed that addition of Li_2O to the systems $SnO–B_2O_3–Li_2O$, $SnO–BPO_4–Li_2O$ and $SnO–B_2O_3–P_2O_5–Al_2O_3$ lowers the thermal stability and charge-discharge capacity of glasses. Glasses and glass-ceramics in the systems $B_2O_3–SnO_2–XO$ (X = Ca, Mg, Sr, Zn) have been investigated by Braun et al. and the crystal phases have been identified [62]. The stannous-phosphorus oxy-halide glasses are low and ultra low melting and have been obtained without any presence of alkali metals, thus there are just few examples of modifying these systems with alkali [4]. $SnO–ZnO–P_2O_5$ and $SnO–MnO–P_2O_5$ glasses containing 30–70 mol% SnO, up to 30 mol% MnO and ZnO in amount such that mole ratio of Sn:Zn is in the range of 1:1 to 1:5 have been obtained [23–26]. The additives of tungsten and molybdenum oxides have been found to have inhibiting effect, i.e. reduce the crystallization ability of the tin-phosphate glasses [92]. Among the more compatible additives in the tin-phosphorus oxide and oxy-halide composition system are Pb, Zr, Ti and Fe with the most compatible additive known to be Pb [4, 30, 75, 78]. Tick has found that the glass-forming region decreases in size and sifts toward higher concentrations of tin, as Pb content increase. The addition of PbO in the system Sn–P–O–F containing 50 mol% (SnF_2 + SnO) have been found to increase the glass transition temperature (T_g) and to decrease the thermal expansion, whereas PbO additions to glass, containing 60 mol% and 70 mol% (SnF_2 + SnO) have no significant effect on either T_g or the thermal expansion [68]. In the binary system $P_2O_5–SnCl_2$, 5 mol% SnO or $PbCl_2$ substitution for $SnCl_2$, have found to increase the glass-forming tendency, but a 10 mol% SnO or $PbCl_2$ substitution for $SnCl_2$, have found to worsen it [79, 82]. CuO addition has been found to improve the chemical durability of stannous chlorophosphate glasses and to increase glass transition T_g and softening temperature (T_s) [85]. When the CuO content exceeds 5 mol% the crystallizing ability increases. The stannous-phosphorus oxy-halide glasses are reducing in nature, thus tend to reduce to metal state Bi and Cu salts which result metallic inclusions in these glasses and is undesirable for certain applications. LaF_3 and SbF_3 exhibit limited solubility and/or low solution rate in the melt, limiting the quantity of these additives, which can be incorporated into the glass. The stability of these glasses is lower than those observed in more conventional oxide systems and the tendency of the glass to phase-separate or devitrify limiting the quantity of modifiers [5, 26]. Mori et al. reported, that glasses wave been obtained in the system of $V_2O_5–SnO–TeO_2$ [93, 94].

There are some examples of glasses containing two conventional glass-formers (Table 1.) but the information about their co-existence is not enough.

According to literature sources, the tin oxide based glasses have been modified with oxides of alkali, alkaline earth metals, other Group II metals, such as Zn and Cd; Group III elements such as Al; transitional elements such as Pb, Cu, Mn, La, Mo, W, Ce, Er, Gd and Eu; and organic compounds for hybrid materials. However, there are no systematic studies of influence and behavior of modifiers and that reveals an opportunity for further researches.

Properties

This paper won't discus in details the properties of known tin oxide based glasses. The attention will be paid on the contribution of components to the parameters of glass-formation and thermal stability of the systems, as transition temperature (T_g) and softening temperature (T_s).

Different systems demonstrate different composition dependence of T_g. T_g of the stannous silicate glasses have been found to decrease sharply when SnO content increase up to 30 mol% and above this content the change in T_g is very slow [7]. In the SnO–BPO_4 glasses, the values of T_g monotonically decrease with increasing the SnO content [83]. In the SnO–B_2O_3 system, similarly to others borate systems, such as Na_2O–B_2O_3 and PbO–B_2O_3, the values of T_g initially increase, reach the maximum and then decrease with an increase in SnO content [61]. The maximum value of T_g is 384 °C at the composition with 40 mol% SnO in this glass. This value of T_g is lower, than those of others borate systems with Na_2O and PbO, which are 475 °C at 30 mol% Na_2O and 455 °C at 27 mol% PbO, respectively. In the Li_2O–SnO–BPO_4 system, the values of T_g monotonically decrease with increasing the SnO and Li_2O contents and in the system Li_2O–SnO–B_2O_3 the change in T_g is considerably complicated with SnO and Li_2O contents [61, 64] The T_g and T_s of the glasses and the viscosity of the liquids for the SnO–P_2O_5 glasses increase linearly with increasing SnO content in the range 40–60 mol% SnO [83]. The T_g and T_s of the glasses and the viscosity of the liquids of the $SnCl_2$–P_2O_5 system increase between 40 and 60 mol% $SnCl_2$, are maximum at about 60 mol% $SnCl_2$, and then decrease with further addition. The substitution of chlorine for oxygen by increasing $SnCl_2$/SnO ratio results in a decrease of T_g and T_s of the glasses and the viscosity of the liquids. The $SnCl_2$–P_2O_5 system had a decreasing viscosity, which is not observed in the SnF_2–P_2O_5 and SnO–P_2O_5 systems. In conclusion, T_g in the tin based silicate and boron-phosphate oxide systems decrease monotonically, in the phosphate systems increase and in borate and phosphate oxy-halide passes through inflect point. Investigation of composition dependence of some others glass properties, as molar volume, density and thermal extension in the SnO–SiO_2 system [7], the viscosity and the liquid fragility E_η/T_g in the SnO–B_2O_3 system [64] and the viscosity of the liquids in tin-phosphate and tin-phosphorus oxy-halide systems [83] show that these properties pass through inflect point. This is an evidence of structural changes that occur in glasses and the change in the structural role of tin component.

Summarizing the data about T_g for tin containing glass systems (Figure 1.), it reveals that at the same content of SnO (SnX_2), maximal T_g does not exceed 500 °C. The melting temperature of SnO is at about 1080 °C and of pure SnO_2—about 2000 °C [95]. Taking into account the rule of Kauzman (see Ref. [96]), $T_g = (1/2 \div 2/3).T_{melting}$ [97, 98], indirect suggestion about the oxidation state of the tin in the glass could be made.

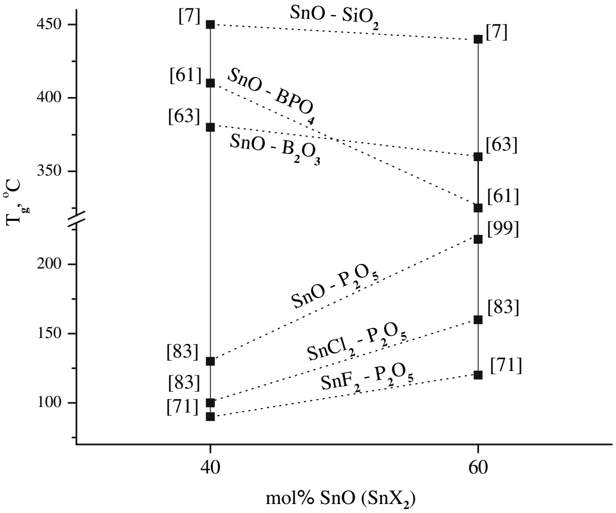

Fig. 1 T_g of glasses of different systems at equal SnO (SnX_2) content

Structure: a network modifier or a former?

More than 40 multicomponent systems have been published and several structural models for the amorphous network have been proposed, but the structure and chemistry of tin in inorganic glasses is still not clearly understood. Divalent tin, Sn^{2+}, is an s^2 ion like Pb^{2+} and it is expected to behave in a manner similar to Pb^{2+} in glass structure. Its coordination number in glasses cannot exceed three unless there is a participation of its 4d orbital in bonding. The nonbonding ('lone') pair of electrons on Sn(II) ions is sterically active and results in highly asymmetric Sn(II) environments in crystalline oxide compounds such as SnO. Researches of Holland et al. has shown that this lone pair appears to remain sterically active even when incorporated in an amorphous network and the Sn–O coordination number is reduced from four to three [7, 57, 66]. Sn(II) is found to be predominantly three-coordinated in glasses, having the form of a trigonal pyramid with a lone pair of electrons on the opposite site to the oxygens, thus giving an approximately tetrahedral steric unit [57].

The first structural investigations of the tin silicate glasses suggested the similarity of the glass structure to that of the metastable crystal phase $SnSiO_3$ [1, 2]. This assumption was based on the comparison of the data of radial distribution analysis and infrared spectroscopy for both glass and crystalline materials with common composition [2]. But the discontinuities of physical properties in the range of about 30 mol% SnO, observed by Karim et al., brought to a conclusion of a change in the structural role of SnO [7]. Bent et al. have discussed the structure of tin silicate glasses based on pulsed neutron diffraction studies and suggest the possibility of incorporation of Sn^{2+} in three

[SnO_3] and four [SnO_4] coordinated positions [56]. But in the model they have proposed, all of the tins are three-coordinated and the existence of three-coordinated oxygen, bonded to one silicon, has been discussed. Williams et al. and Johnson et al. have reported Mossbauer spectra of tin silicate oxide glasses and the data suggest that the Sn–O bonds become progressively less covalent with increasing SnO content in the $SnO–SiO_2$ glasses [54, 55].

In contrast to silicates, the neutron diffraction data has shown 3-coordinated (a peak at r~2,12 Å) and 5- and 6-coordinated (a shoulder at r~2,35 Å) Sn^{2+} positions in binary germanate glasses [59]. The Mossbauer spectroscopy of $SnO–GeO_2$ glasses has shown that the quadrupolar splitting increases with increasing the content of SnO, opposite to that in silicate glasses. Therefore the environment of Sn in a germanate matrix, initially more symmetric than in a silicate matrix, becomes more asymmetric with increasing SnO content [59].

The infrared spectra of tin borate glasses, presented by Paul et al., have shown that small additions of SnO produce tetrahedral boron and above 20 mol% SnO non-bridging oxygen groups are formed [3]. The O1s photoelectron spectra have shown that the amount of non-bridging oxygen groups increasing with increasing the SnO content up to 40 mol% and than it decreases [63] The Mossbauer spectra of these glasses have shown higher quadrupolar splitting values than in the spectra of tetragonal SnO [3]. The data presented by Hayashi et al. have shown an increase in quadrupolar splitting with increasing SnO content. That suggests lower symmetry of the tin environment in the glass, than in SnO and lowering the symmetry with increasing the tin oxide content [63]. The structural models of the glasses, proposed by Hayashi et al., are based on Raman spectra, ^{11}B MAS-NMR, XPS and Mossbauer spectra. They have presented structures for the whole range of compositions, consisting of both 6-membered boroxol rings and 6-membered boroxol rings with one or two BO_4 tetrahedral groups. The presents of BO_4 groups in glasses with high SnO content have been assigned to network-forming behavior of SnO in borate glass systems [63]. Gejke et al., using the neutron diffraction and Monte Carlo modeling, proposed a model, in which the probable average coordination number of boron in borate units is about 3.3 and tin is bridging between two neighboring borate units and therefore acting as a network former [39].

The first models of tin-containing phosphate glass systems, based on spectroscopic studies, suggested a formation of Sn–O–P bonds, which replaced P–O–P bonds and presented structures, built of [$SnPO_4$] ([$SnPO_3X$]) units, analogical to [$AlPO_4$] units [4, 71–85]. They proposed a glass network, extended by sharing of corners of tin and phosphorous polyhedra with Sn and P cations not homogeneously distributed in the structure. In these models no P–X bonds were included. Shih proposed a model built of random distributed $P(O,Cl)_4$ and $Sn(O,Cl)_3$ structural units, where the non-bridging-Cl (Sn–Cl, P–Cl), bridging-Cl (P–Cl–P, Sn–Cl–Sn), non-bridging-O (P = O, $P–O^{-}...Sn^{2+}$) and bridging-O (P–O–Sn, P–O–P) bonds are all presented in the structure [85]. He also suggested that Sn cations acts as network formers, but a fraction of Sn cations acts as network modifiers, and disrupts the structure to form non-bridging-Cl and –O. IR spectroscopic studies presented by Sato et al. shown that increasing the content of tin compound, the transition form meta- to pyrophosphate structure of the glasses had taken place [81]. Morinaga et al. suggested, that in $SnO–P_2O_5$ system with SnO < 50 mol%, SnO plays the role of modifier and above this content, its role changes [83]. Braun et al. carried out ^{119}Sn NMR measurements of $SnO–P_2O_5$ glasses and reported shifting of NMR signals of the samples to the lower chemical shift compared to crystalline SnO and therefore, lowering of the symmetry of tin polyhedra [62].

All of these models assumed, that only Sn^{2+} present in the glass structure. Bhat et al. presented structural studies of pseudo-binary system of $SnO–NaPO_3$ and established that tin is present in partially oxidized Sn^{4+} state [69, 70]. They presented ^{119}Sn Mossbauer spectra and made a conclusion, that the Sn^{4+}/Sn^{2+} ratio is nearly constant independent of meta- or pyrophosphate content. In the model, they proposed, SnO changes its role from a network modifier to a former above about 30 mol%. ^{31}P and ^{119}Sn NMR data of the glasses from the system of $SnO–P_2O_5$ was presented by Holland et al. and Bekaert et al. [65, 66]. Holland et al. found that increasing the content of SnO, the symmetry of Sn^{2+}site increases which they explained with increasing the delocalization of charge form P = O double bond into the other P–O bonds and the change in the s-p hybridization of the orbitals on Sn such that lone pair of electrons moves closer to the tin nucleus [66]. Bekaert et al. concluded that in glasses containing high amount of Sn^{2+}, the Sn^{2+} environment is a trigonal pyramid and Sn^{4+} environment is octahedral, similar to that in crystalline SnP_2O_7 and they suggested, that Sn^{4+} might segregate as SnP_2O_7 [65].

Our studies, focused on the systems of $SnO–P_2O_5$, $SnCl_2–P_2O_5$, $SnCl_2–P_2O_5–MeCl_2$ (Me_nO_m), are presented on Table 2. [99–101]. They confirm the studies, reported by now in the similar systems. The influence on the quality of glasses of different factors, such as nature of raw materials, the batch preparation and the melting conditions, has been studied. Oxyhalide glasses in the system of $SnCl_2–P_2O_5$ have been obtained at very low temperature—below 500 °C. The system has been modified with Cu^{+}, Cu^{2+}, Ba^{2+} and Zn^{2+}-compounds. They have been subjected to additional heat treatment. A change of colour has taken place in

Table 2 The ranges of compositions, SnO (SnX_2) content and melting temperatures of the systems we have examined, are presented in the table

System	SnO(SnX_2) content	$T_{melting,}$ °C	
P_2O_5–$SnCl_2$	50–80 mol%	450	Glass
P_2O_5–$SnCl_2$–SnO	$SnCl_2$ + SnO 52.5 mol%	650	Glass and crystals
P_2O_5–$SnCl_2$–$BaCl_2$	30–37.5 mol%	550	Up to 20 mol% BaCl2 – glass from 20 mol% BaCl2 – crystals
P_2O_5–$SnCl_2$–CuCl	45–49.75 mol%	450	Glass
P_2O_5–$SnCl_2$–$CuCl_2$	45–49.75 mol%	450	Glass
P_2O_5–$SnCl_2$–$BaCl_2$–CuCl	40–45 mol%	550	Grey glass
P_2O_5–$SnCl_2$–$BaCl_2$–$CuCl_2$	40–45 mol%	550	Pale yellow glass
P_2O_5–$SnCl_2$–ZnO	47.5 mol%	650	Glass and crystals
P_2O_5–SnO	50–85 mol%	500–1200	Glass
P_2O_5–SnO–CuO*	65–66.3 wt%	1100	Glass and crystals
P_2O_5–SnO–Cu_2O*	65–66.3 wt%	1100	Glass
P_2O_5–SnO–Co_2O_3*	65–66.3 wt%	1100	Glass
P_2O_5–SnO–Co_3O_4*	65–66.3 wt%	1100	Glass
P_2O_5–SnO–ZnO*	10–50 wt%	1100	With 10 wt% SnO – glass > 10 wt% SnO –crystals
P_2O_5–SnO–BaO*	10–35 wt%	1200	With 20 wt% SnO – glass > 20 wt% SnO – crystals
P_2O_5–SnO–ZnO–BaO*	10–20 wt%	1050	Crystals
SiO_2–SnO	50 mol%	1100	Glass
B_2O_3–SnO–Li_2O*	20–40 wt%	900	Glass
B_2O_3–Bi_2O_3–PbO–SnO*	10–30 wt%	1150	With 10 wt% SnO – glass with 20 and 30 wt% SnO – crystals
B_2O_3–TeO_2–GeO_2–SnO*	30 wt%	950	Glass–crystal
B_2O_3–TeO_2–WO–V_2O_5–SnO*	30 wt%	950	Crystals
TeO_2–V_2O_5–CaO–SnO*	30 wt%	950	Crystals
TeO_2–Al_2O_3–SnO*	30 wt%	950	Crystals

*Two step melting process: SnO has been introduced in previously melted glass and the SnO content is represented in wt%

Cu-containing glasses, which is an evidence of reduction of Cu^+ and Cu^{2+} to Cu^0 [101]. Low-melting stable glasses containing up to 85 mol% SnO in the system of SnO–P_2O_5 have been obtained at ambient atmosphere and without reducing agent [99]. The glass-forming ability of Sn(II)O was proved by increasing content of SnO above 50 mol% (nominal composition). Varying the composition from 60 to 85 mol% SnO, the structure changes from meta- to pyro- and orthophosphate. Increasing the time of heat treatment, the metaphosphate structure transforms and pyrophosphate groups are formed in the glass network. The ability of introduction of SnO in vitreous BaP_2O_6 has been studied by mixing of previously synthesized barium phosphate glass and SnO [100]. A dark-grey semitransparent glass with content of about 20 wt% SnO has been obtained. The introduction of tin oxide into BaP_2O_6 glass leads to a transformation from metaphosphate to pyrophosphate network.

Conclusion

Recently, the glass formation in the tin(II) containing systems is an object of intensive researches. The glass-forming ability of Sn^{2+} has been proved, but in spite of many structural diffractional and spectroscopic investigations, the contribution of tin to the network formation is still disputable. The structural models, that have been proposed, suggests that the SnO in the glass behaves like a network modifier up to certain concentration, above which it behaves as a network former. Both Sn^{4+} and Sn^{2+} have been found to present in the glasses and their ratio depend on the system and conditions of preparation. Each system requires developing a specific route of preparation in order to obtain the maximal Sn^{2+} content in the glasses. Glasses and nanocomposite materials could be obtained by modifying the composition of the tin oxide glass systems. Their extraordinary properties are of great importance and stimulate the development of this field of research.

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