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Solubility of tin dioxide in soda-lime silicate melts

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Abstract

In the present work, the solubility of tin dioxide is assessed as a function of time, temperature and basicity in simple ternary glasses: NC3S, NC4S, NC5S and NC6S (N: Na₂O, C: CaO, S: SiO₂). An increase of silica contents in the glass composition leads indeed to a decrease of the glass basicity. First, a kinetic study of the dissolution has been performed. Consequently, the solubility limits of tin dioxide have been determined after 2 hours of heat treatment: this duration is long enough to reach the dissolution equilibrium, and short enough to limit the sodium oxide losses in the melt at high temperatures. Nevertheless the specific case of the most acid glass has been underlined, as its higher viscosity implies longer heating times. At equilibrium state, SnO₂ solubility depends on the temperature (Arrhenius law) and on the glass basicity. In the 1200°C-1400°C temperature range, in these soda-lime glasses, the solubility of tin dioxide is between 1.3 and 2.1 at.%Sn and the temperature dependence of solubility exhibits a single mechanism of dissolution. Furthermore, the basicity dependence of the solubilization process is also discussed, and the presence of another oxidation state of tin (Sn^{II}) is thus proposed.

Keywords: glass melts; tin dioxide; solubility

Introduction

Many applications in glass industry require high performance materials, with good mechanical properties and high resistance to corrosion at high temperature. Several ceramic materials, as tin dioxide, are used in the molten glass media [1]. Cassiterite, SnO_2 , is already used for specific applications such as heating electrodes, and high temperature devices [2-5]. Soda-lime glasses are 90% of the industrial glass production [6]. The lifetime of ceramic materials strongly depends on the corrosion rate of this material in high temperature conditions. In silicate melts, this corrosion rate is directly linked to the stability of the oxide, *i.e.* to its solubility in molten glass. As a consequence, a more accurate knowledge of the oxide dissolution in a simple silicate melt will provide useful information regarding the ability of this ceramic to remain (chemically) inert in glass melts.

The aim of this work is to study the influence of glass composition on the solubility of SnO_2 in simple ternary glasses $\text{Na}_2\text{O}-\text{CaO}-x\text{SiO}_2$ (with $x = 3, 4, 5$ and 6 ; noted as NCxS in this paper). These glasses exhibit low viscosity values at temperatures higher than 1200°C [7]. As a consequence, in order to get thermodynamic data about the dissolution equilibrium, the temperature range chosen in this work rises from 1200°C to 1400°C . In a first time, kinetic aspect has been considered to estimate the equilibrium time of the dissolution reaction. In a second time, the limit of solubility (once the equilibrium is reached) has been determined at different temperatures (from 1200°C to 1400°C). The solubility limits have also been discussed as a function of glasses basicity.

Experimental procedure

At first, four ternary glasses of general composition $\text{Na}_2\text{O}-\text{CaO}-x\text{SiO}_2$ ($x=3, 4, 5$, and 6) were prepared with the standard procedure settled by Khedim *et al.* and Abdelouhab *et al.* [8-12]. The raw chemicals reagents NaCO_3 (99.5 %), CaCO_3 (99 %), and amorphous SiO_2 (99.8 %), were mixed and grinded in a planetary ball mill during 15 minutes. The homogenized mixture was charged in a Pt - 10%Rh crucible and heated. The temperature has been raised slowly (10 hours) up to 1200°C in order to enable progressive decomposition of the carbonates. It has been maintained at 1500°C during 2 hours to ensure a good homogenization of the melt, and

then at 1300°C for 10 hours. The glass was finally quenched in air at 20°C to avoid glass crystallization. Glasses compositions were determined by Electron Probe MicroAnalysis (EPMA) and are reported in Table 1, as well as the theoretical compositions. The ratios x' (2at.%Ca/at.%Na) and x (average value of at.%Si/at.%Ca and 2at.%Si/at.%Na) are estimated from these measurements. The calculated optical basicities Λ_{th} of the glasses are also reported. In all the prepared glasses, the atomic ratio 2Ca/Na (x') is very close to 1, allowing the NCxS notation. Furthermore, the x ratio is close to the expected theoretical glass stoichiometry. As a consequence, these results validate the process used here for the synthesis of ternary glasses.

In a second time, the solubility of SnO₂ has been studied following the protocol previously described by Khedim *et al.* [8-10]. The process is summarized on Fig. 1. Twenty grams of each glass were crushed with cassiterite powder (SnO₂ 99.8 %, Oximet); an amount of 20 wt.% has been chosen in order to be higher than the solubility limit of SnO₂. This value has been chosen knowing that Manfredo *et al.* have measured limits of solubility of about 16 wt.% at 1500°C in a common soda-lime glass [14]. Mixtures were heated 2 minutes at 1200°C, and then quenched. It was done twice to ensure good homogeneity of the glass/oxide mix. Pieces of 100 mg of SnO₂-enriched glasses (noted here as SnO₂-NCxS) were placed in graphite crucibles at 1200°C for 2 min. Due to graphite's low wettability regarding glass, the samples formed balls with an average diameter of 4 mm. Balls, sustained by a Pt-wire in alumina crucible, were then annealed at temperatures comprised between 1200°C and 1400°C, for times up to 9 hours in air.

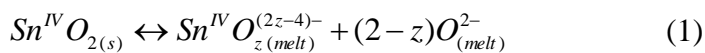
Quenched samples were embedded in epoxy resins for metallographic surface preparation ending with polishing using 1 μ m diamond suspension. SnO₂ over-saturation was controlled by Scan Electron Microscope (SEM) using a BSE detector with an acceleration voltage of 15 kV. The polished sections were then analyzed with a CAMECA SX 100 electron microprobe in order to determine the total amount of tin dissolved in the glassy matrix. Selected elements for analysis were Na, Si, Ca and Sn. The concentration of oxygen was calculated by stoichiometry assuming that the valence states of the cations are +I, +IV, +II and +IV respectively. The standards used were albite NaAlSi₃O₈ for Na and Si, andradite Ca₃Fe₂(SiO₄)₃ for Ca, and cassiterite SnO₂. Specific conditions were optimized to limit sodium migration under the electron beam [11]: the acceleration voltage was set at 15 kV, beam current at 10 nA, with time count of 10 s and electron beam defocalized to a 20 μ m diameter. Measurements have been performed in the vicinity of SnO₂ crystals to estimate the

tin content dissolved in the glass matrix. Such conditions ensure the measurement of the highest tin content in the glass to determine the solubility limit. The results are estimated from 6 to 8 analyses, and error-bars correspond to standard deviations.

Results

Tin dioxide contents measured in all samples after heat treatments at 1200°C, 1250°C, 1300°C and 1400°C for times of 1h, 2h, 4h and 9h are reported in Table 2. For each test, the samples were first observed by SEM. Fig. 2 presents micrographs of a glass enriched with SnO₂ and heated at several temperatures for different times. The results presented here only deal with NC5S, but similar observations have been performed in all the glasses studied here. The micrographs reveal the presence of remaining tin dioxide grains (white contrast: confirmed by EDX analysis shown on Fig. 2d) in the glass matrix (dark contrast). For short times and low temperatures (*e.g.* 1h at 1200°C; Fig. 2a), tin dioxide grains are similar to the ones observed in the initial glass balls: SnO₂ powder is finely dispersed in the glass and the dissolution process has just been initiated. Few bigger grains indicate a slight coalescence. This coalescence seems to be thermally activated, as more aggregates are observed at higher temperature (*e.g.* at 1300°C; Fig. 2b). The content of dissolved tin and the SEM observations show that dissolution and coalescence may be in competition. Fig. 2c displays the most extreme conditions: highest temperature and longest time (1400°C for 9 hours). SnO₂ grains of diameter between 1 and 20 µm exhibit a geometrical and angular shape. This particular morphology suggests that these grains are no more resulting from coalescence but from re-crystallization.

The study of the solubility limit of SnO₂, in several glasses at different temperatures, requires foremost determining the time necessary to reach the dissolution reaction's equilibrium. This reaction is an acid-base one and is detailed in Eq. (1).



The kinetics of dissolution of SnO₂ at 1200°C and 1400°C for the most basic glass (NC3S) and the most acid glass (NC6S) are reported on Fig. 3a and 3b respectively. At 1200°C, for both glasses, the content of dissolved tin reaches a constant value for times greater than 2 hours. Using another process, Manfredo *et al.* [14] determined the limit of solubility of tin dioxide after 3 days of heat treatment. The protocol used in the present work requires much

shorter times. It can be noticed that the glass containing the lowest amount of silica (NC3S), the most basic one, is in the equilibrium state after only 1 hour. In the same way, the glass with the highest content of silica (NC6S), the most acid one, seems to require a longer heating time to reach equilibrium.

At higher temperature (1400°C, Fig. 3b), the equilibrium state is reached for shorter times (less than 1h), independently from the glass composition. Nevertheless, in the case of NC3S, the limit of solubility tends to decrease for the longest times of heat treatment at 1400°C, whereas it tends to remain constant for the NC6S sample. Furthermore, tin dioxide presents a higher solubility in the most acid glass (NC6S) than in NC3S. Lastly, these results exhibit a great influence of the temperature on the solubility limit, which is almost twice higher at 1400°C than at 1200°C, independently from the glass composition.

Discussion

Thermo-kinetic aspect

As described previously, regarding Fig. 3a and 3b, the limit of solubility of SnO₂ in NC3S seems to decrease with time (this trend is confirmed by the tight error bars), especially for the highest temperatures (Fig. 3b). As this phenomenon is mainly observed in the glass with the highest alkali content, a modification of the glass composition of the glass by volatilization of sodium is proposed. The volatility of sodium is a quite common phenomenon in melts [13]. As the silicon content is known to be stable with temperature, evolutions of the ratio Na₂O/SiO₂ with time at 1200°C and 1400°C are reported for the glasses with the highest (NC3S) and the lowest (NC6S) sodium content on Fig. 4a and 4b respectively. Sodium losses in NC3S are clearly observed on Fig. 4a. At 1400°C the Na₂O/SiO₂ ratio decreases from 0.33 to 0.26 in 9 hours. Lower temperatures lead to lower sodium losses. During the same time the Na₂O/SiO₂ ratio in NC6S remains constant regardless of the temperature (Fig. 4b) and is in good agreement with the theoretical ratio and the one estimated from the EPMA results listed in Table 1. Furthermore, the lower solubility, linked to the sodium losses, can be correlated to the re-crystallization of tin dioxide grains observed in Fig. 2c for long times of heat treatment at the highest temperature (1400°C).

The aim of these kinetic considerations was to choose the duration of heat treatment to achieve equilibrium state. Considering these aspects, if the sodium volatilization is taken into

account for the longest times and for the highest temperatures in sodium-rich glasses, it is necessary to choose a time as short as possible. Therefore 2 hours of heat treatment seems to be a good compromise.

From this, it is possible to consider the evolution of the solubility values for Na₂O-CaO-xSiO₂ glasses after 2 hours at 1200°C, 1250°C, 1300°C and 1400°C. The logarithm of the amount of dissolved tin dioxide is plotted as a function of the inverse of absolute temperature in Fig. 5 for NC3S, NC4S and NC5S. Both parameters are correlated, according to Arrhenius law (Eq. (2)):

$$\ln(x_{Sn}) = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln C \quad (2)$$

where E_a is the activation energy of SnO₂ dissolution, R the universal gas constant, T the absolute temperature in K and C a constant.

In NC3S, NC4S and NC5S, figure 5 shows a linear evolution of ln(at.%SnO₂) vs 1/T, with a correlation coefficient higher than 0.99. As a consequence, it is assumed that there is a single dissolution mechanism. The activation energies are reported in table 2. Moreover, the activation energy increases with the glass basicity, showing a higher temperature dependence of the solubility in the most basic glasses. Manfredo *et al.* [14] studied the solubility of tin dioxide in a commercial soda-lime glass which optical basicity (0.625) is similar to the optical basicity of NC6S studied here (0.629). From their measurements performed in the 1300°C-1600°C range, an activation energy $E_a = 32 \text{ kJ.mol}^{-1}$ can be calculated. This is in very good agreement with the ones determined in this study and allows the extrapolation of the single mechanism of solubilization at temperatures up to 1600°C.

The temperature dependence of tin dioxide solubility is also presented in Arrhenius format in the case of NC6S (Fig. 6). Regarding NC6S, the quality of the linear fit ($R^2 \sim 0.95$) is much lower than for the other glasses (Fig 6a). The low linearity of the Arrhenius plot of NC6S is confirmed when including further data in the plot: the solubility measurements have also been performed for 2 hours of heat treatment at 1325°C, 1350°C and 1375°C. The temperature dependence of tin dioxide solubility in NC6S has been plotted for measurements performed after 9 hours of heat treatment (Fig. 6b). The quality of the linear fit is significantly improved, with R^2 higher than 0.99, which is comparable to the other glasses after 2 hours of heat treatment. NC6S is the most acid glass among those studied here, with the highest silica content. This implies that its network is not as opened as for the other glasses, and contains

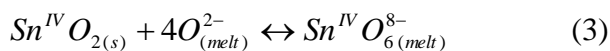
less non-bridging oxygens, leading to a viscosity significantly higher. As a consequence, the time required to reach equilibrium state of dissolution might be longer in NC6S than in the more basic glasses. The same kind of behavior has been observed in previous studies dealing with the dissolution of chromium oxide Cr_2O_3 in binary glasses [11].

The amount of dissolved tin measured after 2 hours and 9 hours of heat treatment are the same if the standard deviations are taken into account (Table 2). Further observations of Fig. 3a and 3b show for both temperatures (1200°C and 1400°C), in the case of NC6S, that the errors bars are much larger for short times and become thinner after 9 hours of heat treatment. On the other hand, for NC3S, the error bars are always quite thin, for all temperatures and heat treatments durations. As measurements are always made in the vicinity of the remaining SnO_2 crystals, this means that longer times are required to reach a homogeneous repartition of tin in this area in the case of NC6S. As a consequence, the highest quality of the results (thinner error bars, linear fit of higher quality) suggests to rather considering the measurement performed after 9h in the case of the most acid glass. The specific case of NC6S allows this, as the composition of the glass remain constant for long times of heat treatment, without any measured sodium loss, even at 1400°C (Fig. 4b). Lastly, it can be noticed that the activation energies determined after 2 hours and 9 hours of heat treatment for NC6S are quite the same (Table 2), describing a single dissolution mechanism in both cases.

Influence of basicity

Several authors have previously shown that glasses with high basicity tend to stabilize the higher degree of oxidation of the cations dissolved in the melts [15,16]. If, in the case of the most basic glass studied here (*e.g.* NC3S), we consider that tin is dissolved as a Sn^{IV} oxocomplex (Eq. (1)), the decrease of SnO_2 solubility (Fig. 3b) with time can be explained by the simultaneous sodium volatilization (Fig. 4b): decreasing basicity of NC3S does not favor the stabilization of the oxidized state of tin *i.e.* Sn^{IV} . The same trend has clearly been observed by Benne *et al.* [16] in the case of soda-lime glasses with various sodium contents.

It has also been previously reported that in silicate melts, Sn^{IV} presents an octahedral coordination and is thus surrounded by 6 oxygen atoms [16,17]. Considering Eq. (1), z should be equal to 6, imposing the presence of O^{2-} ions on the left side of the equation (Eq. (3)).



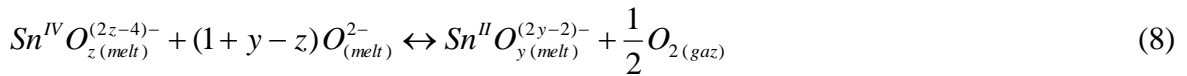
As a consequence, the dissolution of tin dioxide into Sn^{IV} oxocomplexes with octahedral environment should increase with the melt basicity.

It can be of great interest to plot the evolution of tin dioxide solubility as a function of the glasses basicity. In this work, amongst several models, the optical basicity Λ of oxide glasses is determined according to the model proposed by Duffy and Ingram Eq. (4) [18]:

$$\Lambda_{\text{melt}} = \sum \Lambda_{\text{oxide } i} \times x_i \quad (4)$$

where x_i is the molar fraction of oxide i and Λ_i the optical basicity measured by Duffy and Ingram ($\Lambda_{\text{SiO}_2}=0.48$, $\Lambda_{\text{Na}_2\text{O}}=1.15$, $\Lambda_{\text{CaO}}=1$). The optical basicities of all NCxS glasses were calculated from their compositions measured by EPMA after 2 hours of heat treatments (9 hours for NC6S) and are reported in Table 1. The plot of the amount of dissolved tin versus optical basicity is reported in Fig. 7 for several temperatures. For all the temperatures studied here, solubility is clearly decreasing when the basicity is increasing.

As the composition of the raw glasses becomes more acid, the speciation of Sn must also be taken into account. Indeed, depending on the redox conditions of the system, Sn^{IV} complexes can be reduced into Sn^{II} complexes, according to the redox reaction:



A schematic summary of all reactions occurring when SnO_2 is in molten glass is given in Fig. 8. First, the dissolution of tin dioxide into Sn^{IV} complexes has been described above in Eq. (1). It is an acid-base reaction which is independent of oxygen fugacity $f\text{O}_2$ (*i.e.* redox of the glass). Then, the reduction of Sn^{IV} into Sn^{II} given by Eq. (7) or Eq. (8) depends on both O^{2-} activity and oxygen fugacity.

In the same way, the reduction of Sn^{IV} into Sn^{II} can be considered as the basicity decreases from NC3S to NC6S glass. EPMA measurements give access to total tin dissolved in the glass, independently from the oxidation state (Eq. (9)):

$$\text{Sn}_{\text{measured}} = \text{Sn}^{\text{II}} + \text{Sn}^{\text{IV}} \quad (9)$$

As a consequence, the increase of tin solubility with glass acidity for a given temperature when equilibrium state is reached (Fig. 7), can be explained by the stabilization of an increasing amount of Sn^{II} complexes.

It could be of great interest to quantify the tin species in the silicate melts. As shown in Eq. (7) and (8), the control of the redox in a glass is possible through oxygen fugacity. An experimental protocol, as the one developed by Mathieu *et al.* [19], should be used for this, as it has already been employed to determine the solubility of oxides with multivalent cations such as chromium oxide [8-10].

Conclusions

Several important features of tin chemistry in silicate melts were drawn up in this study. Among these, some of them must be underlined:

- The development of an experimental procedure led to the determination of tin dioxide solubility limits in soda-lime silicate glasses as a function of temperature and glass composition.
- The equilibrium state has been determined (kinetic considerations). Furthermore, the volatilization of alkaline oxides has been taken into account and thus limited through optimized short heat treatments (2 hours). Nevertheless, in the case of the most acid glasses, longer times (up to 9 hours) must be considered to reach the equilibrium state, due to a higher viscosity of these glasses
- For a given glass and heat treatments long enough to reach equilibrium state, tin solubility displays an Arrhenius temperature dependence.
- This study reveals a correlation between the basicity of the glasses and the solubility of tin dioxide. Globally, the solubility of tin dioxide is enhanced in more acidic glasses (silica-rich glasses). Indeed, the presence of Sn^{II} is suspected as the acidity of the glasses increases and the total solubility of SnO_2 might be assimilated to the sum of dissolved Sn^{II} and Sn^{IV} . As a consequence, future works should deal with tin dioxide solubility in controlled atmosphere with various oxygen fugacities, in order to stabilize the different oxidation states of tin.

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Figures captions.

Fig. 1. Process used for the preparation of the samples for the study of the solubility of tin oxide in silicate melts.

Fig. 2a. Micrograph of NC5S after 1h at 1200°C (BSE, 15kV).

Fig. 2b. Micrograph of NC5S after 2h at 1300°C (BSE, 15kV).

Fig. 2c. Micrograph of NC5S after 9h at 1400°C (BSE, 15kV).

Fig. 2d. EDX analysis performed on a remaining tin dioxide grain (white contrast on micrographs).

Fig. 3a. Tin solubility at 1200°C as a function of time (1, 2, 4 and 9 hours) in NC3S and NC6S.

Fig. 3b. Tin solubility at 1400°C as a function of time (1, 2, 4 and 9 hours) in NC3S and NC6S.

Fig. 4a. Plot of the ratio of Na₂O at.% to SiO₂ at.% measured in NC3S by EPMA, as a function of time at 1200°C and 1400°C. Theoretical ratio in dotted line.

Fig. 4b. Plot of the ratio of Na₂O at.% to SiO₂ at.% measured in NC6S by EPMA, as a function of time at 1200°C and 1400°C. Theoretical ratio in dotted line.

Fig. 5. Plot of $\ln[x_{\text{Sn}}]$ (dissolved in glass) versus $1/T$ for the NC3S, NC4S and NC5S glass compositions after heating at 1200°C, 1250°C, 1300°C and 1400°C for 2 hours.

Fig. 6a. Plot of $\ln[x_{\text{Sn}}]$ (dissolved in glass) versus $1/T$ for NC6S after heating at 1200°C, 1250°C, 1300°C, 1325°C, 1350°C, 1375°C and 1400°C for 2 hours

Fig. 6b. Plot of $\ln[x_{\text{Sn}}]$ (dissolved in glass) versus $1/T$ for NC6S after heating at 1200°C, 1250°C, 1300°C and 1400°C for 9 hours

Fig. 7. at.%Sn dissolved in the 4 ternary glasses as a function of the optical basicity after heating at different temperatures for 2 hours. The straight lines are proposed here as guides for the eyes.

Fig. 8. Dissolution and speciation of tin oxide in ternary silicate melts

NCxS	mol.% theoretical			Λ_{th}	at.%Na _(EPMA)	at.%Ca _(EPMA)	at.%Si _(EPMA)	x'	x
	Na ₂ O	CaO	SiO ₂						
NC3S	20	20	60	0.718	14.23	6.96	21.57	0.98	3.06
NC4S	16,7	16,7	66,7	0.679	11.78	6.60	23.04	1.12	3.70
NC5S	14,3	14,3	71,4	0.650	10.09	5.09	24.89	1.01	4.91
NC6S	12,5	12,5	75	0.629	8.70	4.31	26.10	0.99	6.02

Table 1. Ternary glasses compositions. x' is the atomic ratio 2at.%Ca/at.%Na ; x is the average value of the atomic ratios at.%Si/at.%Ca and 2at.%Si/at.%Na. The optical basicities calculated from Eq. (4) are also reported.

Samples	Limit of solubility (at.% of Sn)				Ea (kJ.mol ⁻¹)	
	1200°C	1250°C	1300°C	1400°C		
NC3S	1h	1.38 (0.04)	1.45 (0.07)	1.62 (0.02)	1.99 (0.04)	38.5 (2h)
	2h	1.35 (0.03)	1.44 (0.03)	1.61 (0.10)	1.95 (0.03)	
	4h	1.32 (0.01)	1.44 (0.04)	1.58 (0.02)	1.92 (0.03)	
	9h	1.30 (0.03)	1.43 (0.03)	1.57 (0.10)	1.90 (0.03)	
NC4S	1h	1.37 (0.08)	1.49 (0.07)	1.67 (0.05)	2.00 (0.06)	32.3 (2h)
	2h	1.43 (0.02)	1.55 (0.03)	1.67 (0.02)	1.96 (0.03)	
	4h	1.47 (0.05)	1.58 (0.03)	1.66 (0.04)	1.96 (0.09)	
	9h	1.50 (0.05)	1.59 (0.03)	1.67 (0.02)	1.98 (0.03)	
NC5S	1h	1.42 (0.10)	1.58 (0.04)	1.72 (0.03)	2.02 (0.06)	31.8 (2h)
	2h	1.53 (0.06)	1.65 (0.05)	1.76 (0.19)	2.08 (0.08)	
	4h	1.52 (0.06)	1.60 (0.06)	1.70 (0.05)	1.99 (0.03)	
	9h	1.50 (0.03)	1.62 (0.02)	1.68 (0.19)	2.00 (0.03)	
NC6S	1h	1.06 (0.10)	1.60 (0.04)	1.68 (0.03)	2.06 (0.06)	28.2 (2h)
	2h	1.58 (0.05)	1.64 (0.10)	1.72 (0.07)	2.08 (0.06)	
	4h	1.60 (0.06)	1.68 (0.06)	1.90 (0.05)	2.06 (0.03)	27.9 (9h)
	9h	1.56 (0.03)	1.65 (0.02)	1.82 (0.03)	2.04 (0.03)	

Table 2. Limit of solubility of tin in the four ternary glasses at four different temperatures and four different times of heat treatment. The activation energies determined from the Arrhenius plots (Fig. 5 and 6) are also reported.

Fig. 1. Process used for the preparation of the samples for the study of the solubility of tin oxide in silicate melts.

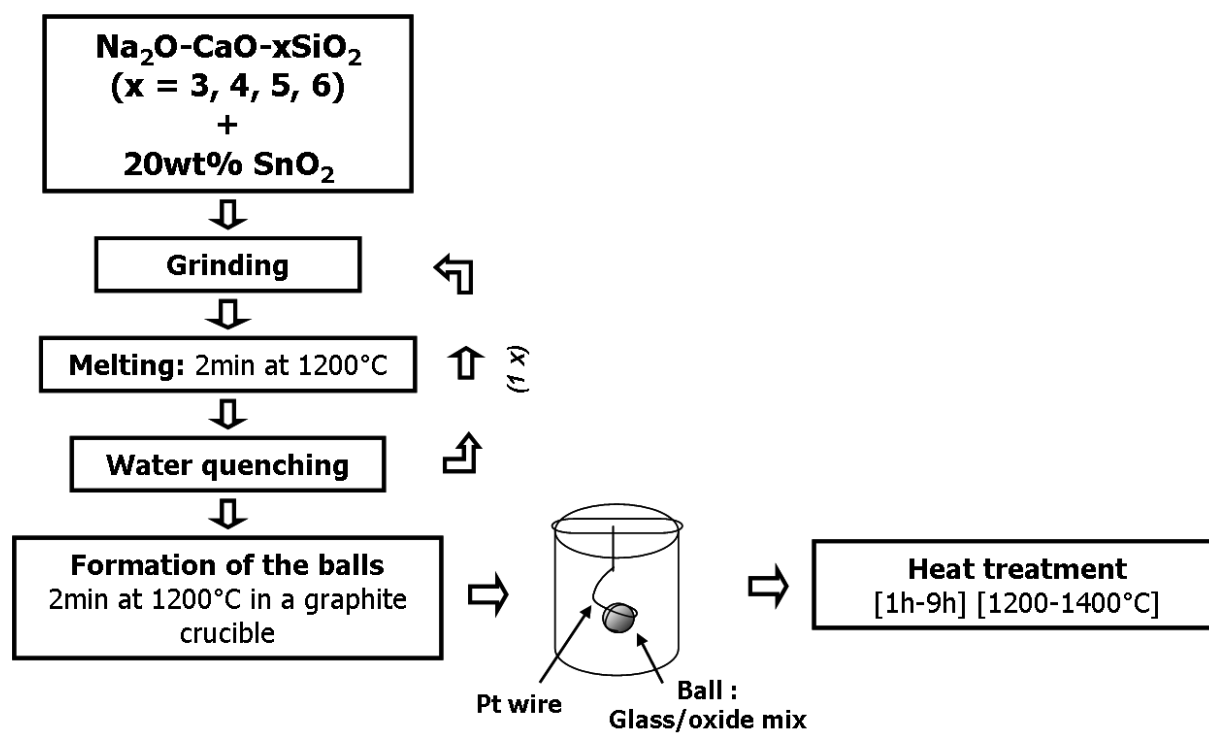


Fig. 2a. Micrograph of NC5S after 1h at 1200°C (BSE, 15kV).

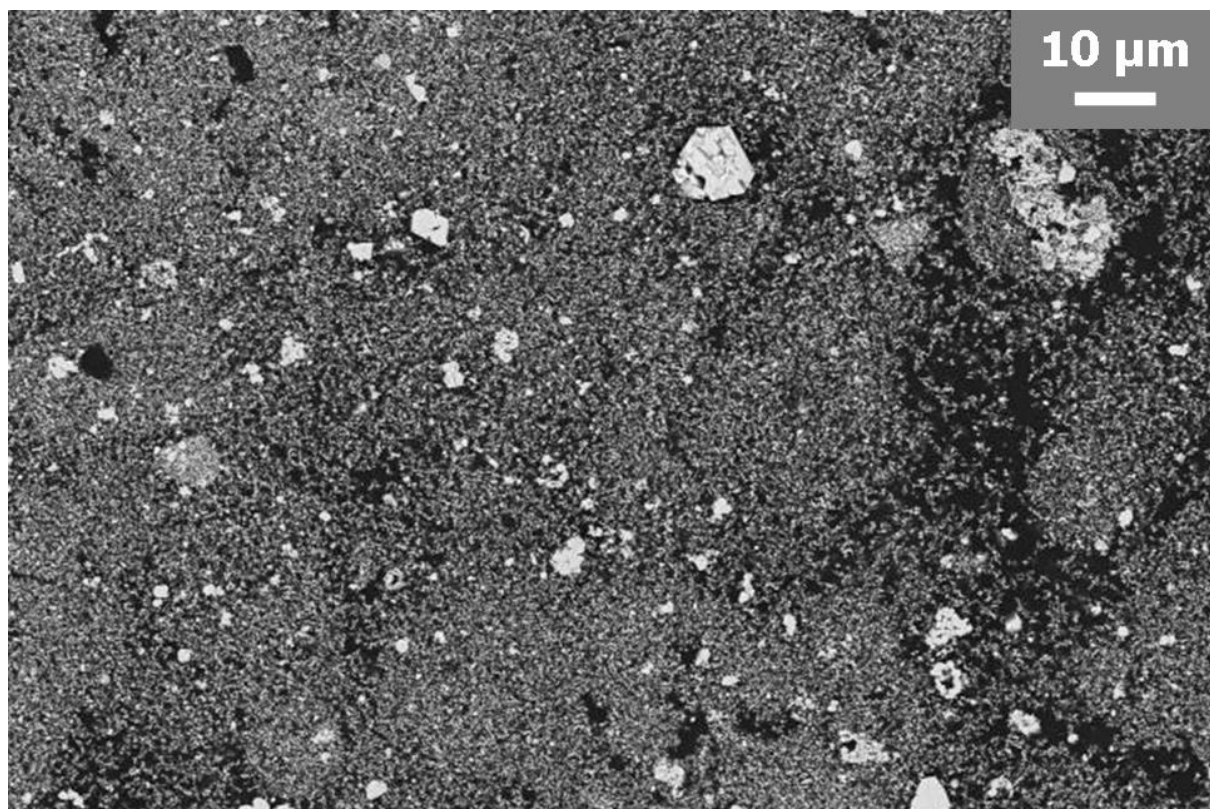


Fig. 2b. Micrograph of NC5S after 2h at 1300°C (BSE, 15kV).

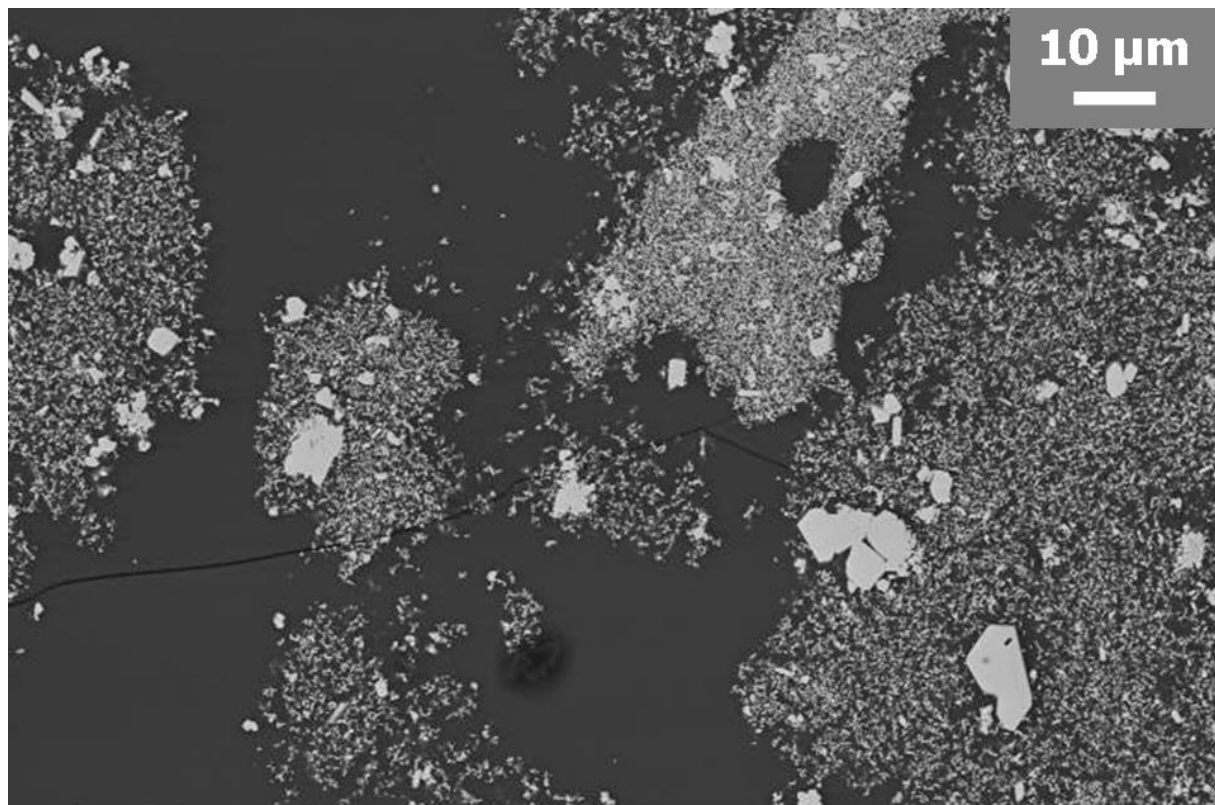


Fig. 2c. Micrograph of NC5S after 9h at 1400°C (BSE, 15kV).

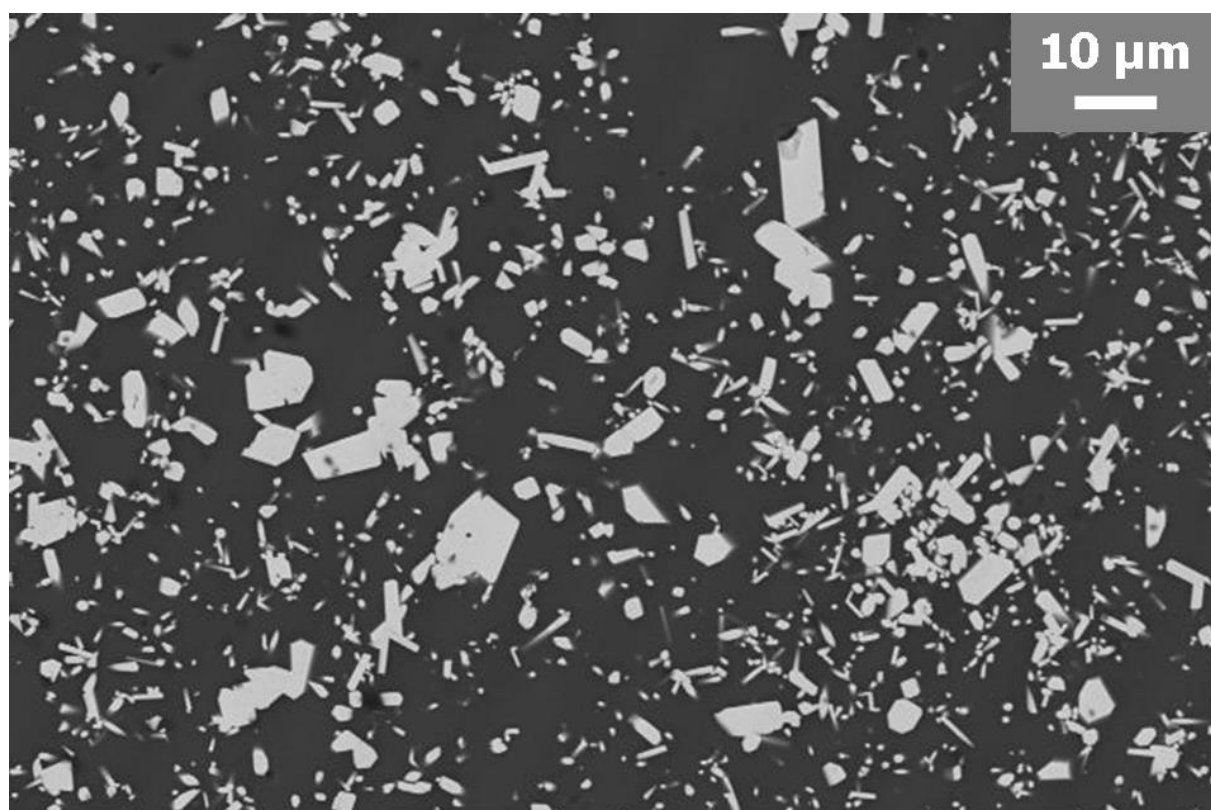


Fig. 2d. EDX analysis performed on a remaining tin dioxide grain (white contrast on micrographs).

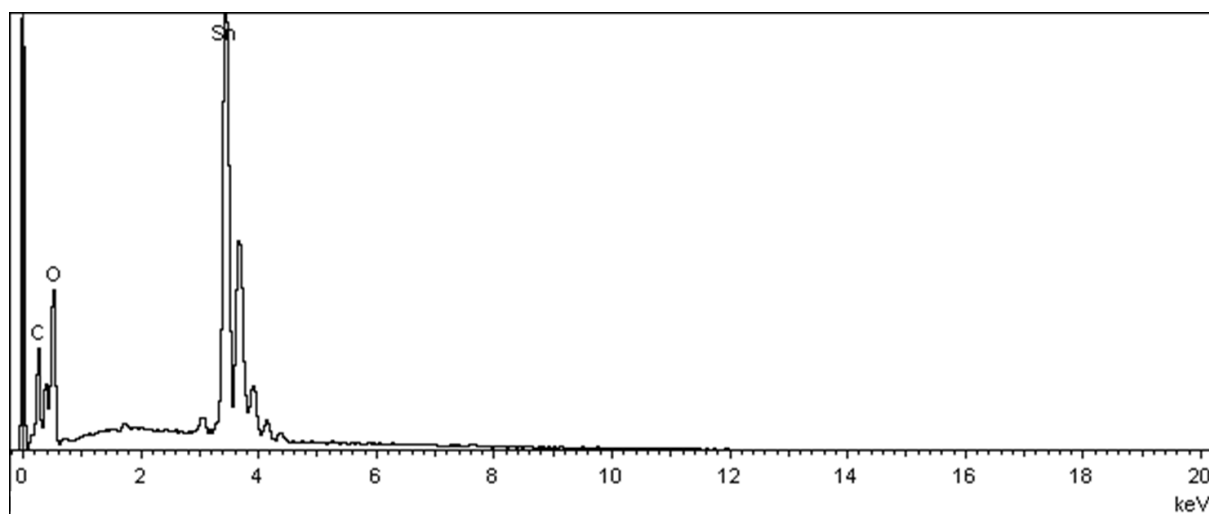


Fig. 3a. Tin solubility at 1200°C as a function of time (1, 2, 4 and 9 hours) in NC3S and NC6S.

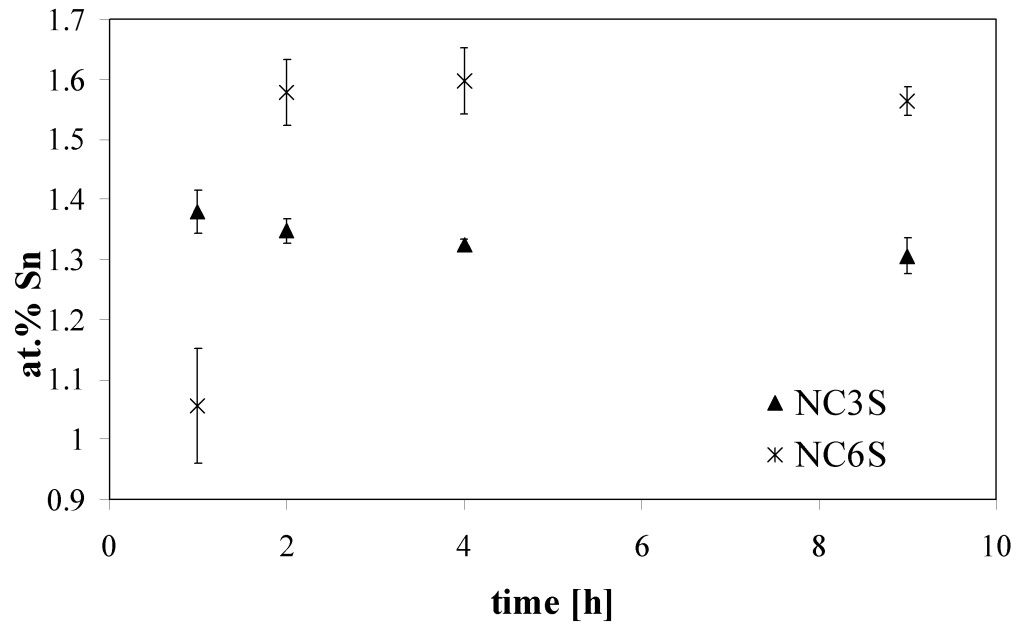


Fig. 3b. Tin solubility at 1400°C as a function of time (1, 2, 4 and 9 hours) in NC3S and NC6S.

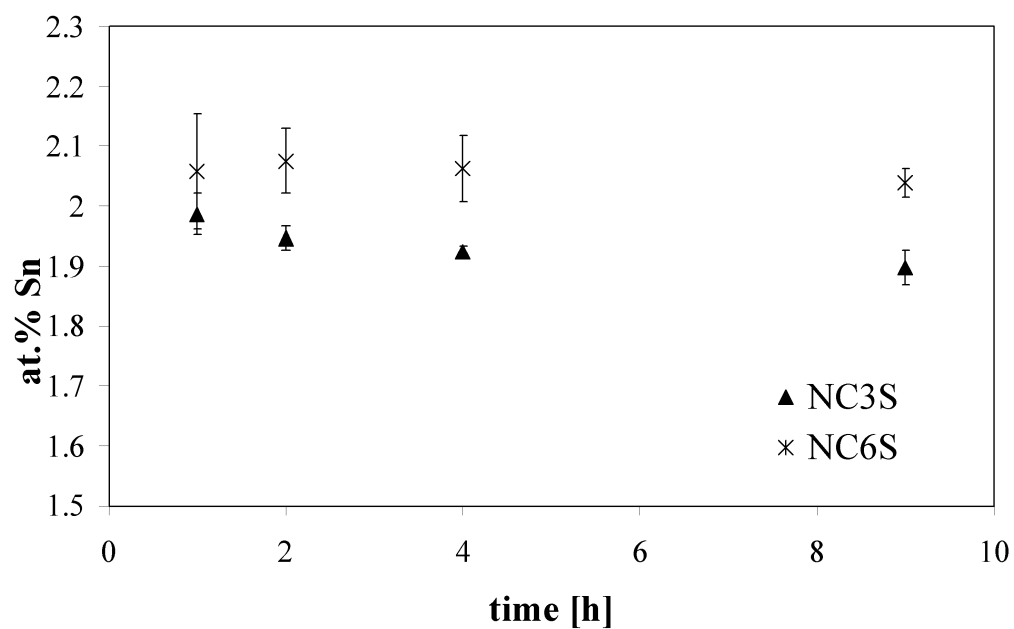


Fig. 4a. Plot of the ratio of Na₂O at.% to SiO₂ at.% measured in NC3S by EPMA, as a function of time at 1200°C and 1400°C. Theoretical ratio in dotted line.

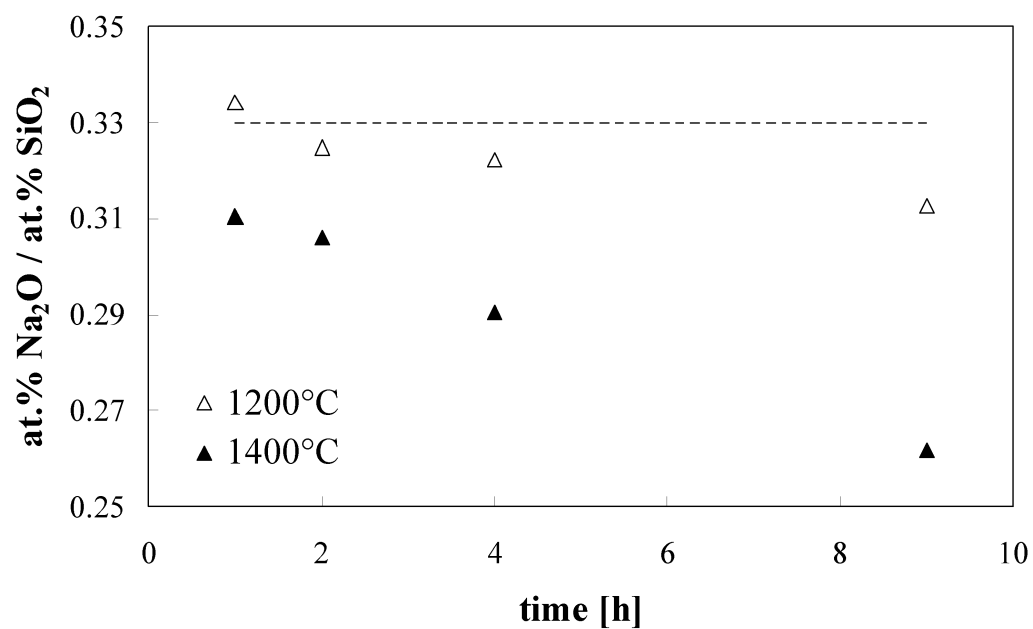


Fig. 4b. Plot of the ratio of Na₂O at.% to SiO₂ at.% measured in NC6S by EPMA, as a function of time at 1200°C and 1400°C. Theoretical ratio in dotted line.

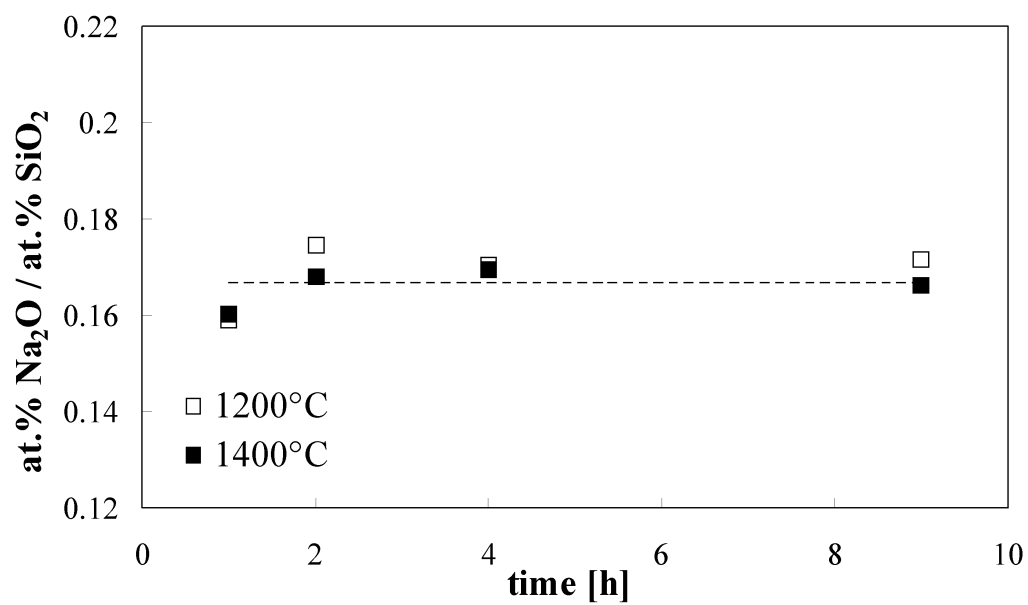


Fig. 5. Plot of $\ln[x_{\text{Sn}}]$ (dissolved in glass) versus $1/T$ for the NC3S, NC4S and NC5S glass compositions after heating at 1200°C, 1250°C, 1300°C and 1400°C for 2 hours.

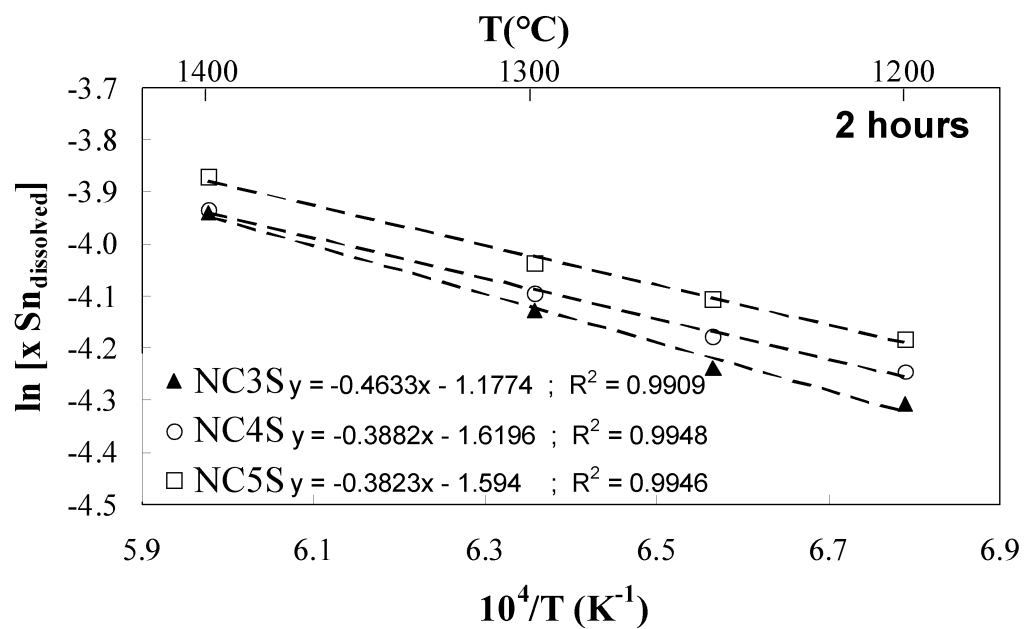


Fig. 6a. Plot of $\ln[x_{\text{Sn}}]$ (dissolved in glass) versus $1/T$ for NC6S after heating at 1200°C, 1250°C, 1300°C, 1325°C, 1350°C, 1375°C and 1400°C for 2 hours

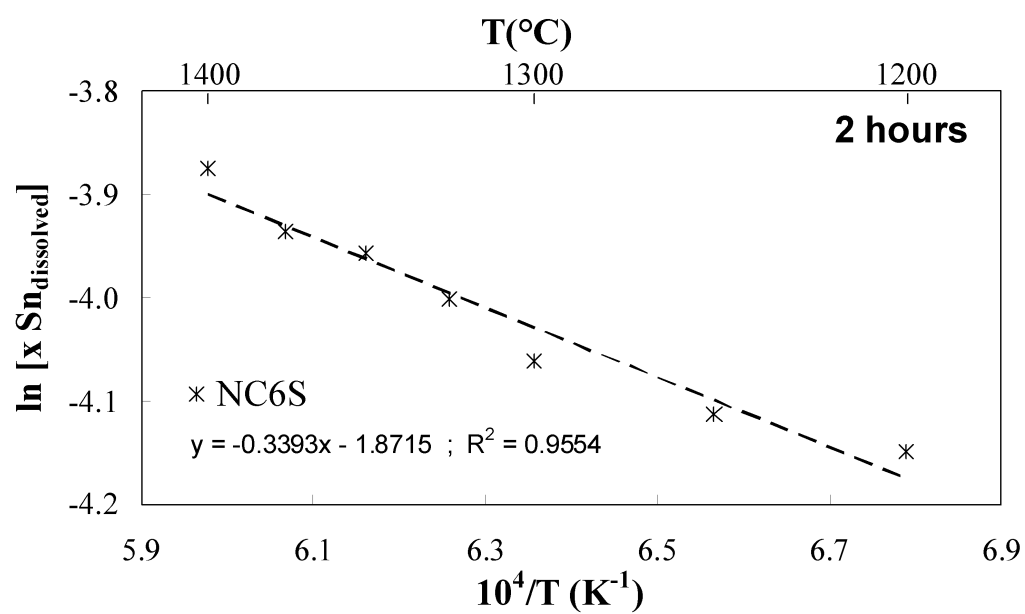


Fig. 6b. Plot of $\ln[x_{\text{Sn}}]$ (dissolved in glass) versus $1/T$ for NC6S after heating at 1200°C, 1250°C, 1300°C and 1400°C for 9 hours

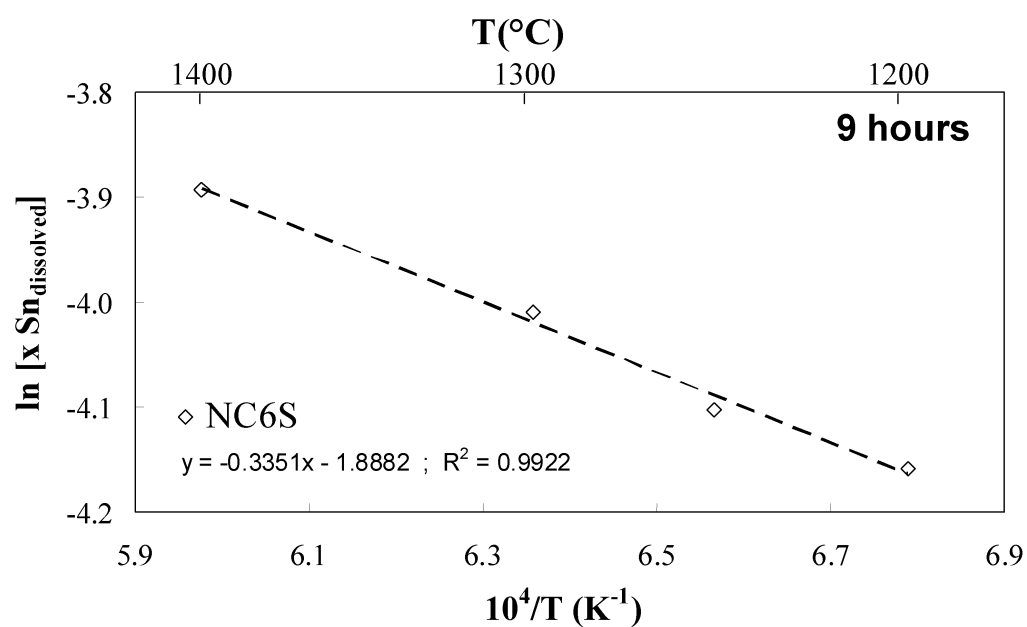


Fig. 7. at.%Sn dissolved in the 4 ternary glasses as a function of the optical basicity after heating at different temperatures for 2 hours. The straight lines are proposed here as guides for the eyes.

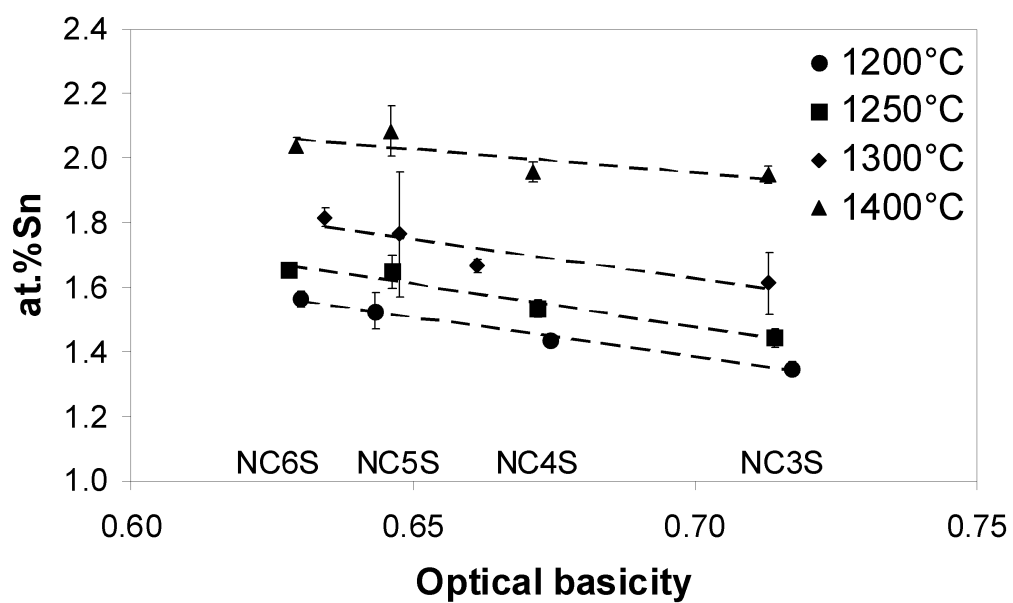


Fig. 8. Dissolution and speciation of tin oxide in ternary silicate melts

