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## **Tin oxide solubility in soda-lime silicate melts**

*P. Gateau<sup>1</sup>, C. Petitjean<sup>1</sup>, P.J. Panteix<sup>1</sup>, C. Rapin<sup>1</sup>, M.Vilasi<sup>1</sup>*

<sup>1</sup> *Institut Jean Lamour UMR 7198 – Département CP2S – Equipe 206*

*Faculté des Sciences et Techniques – Nancy Université*

*Boulevard des Aiguillettes*

*B.P. 70239 - 54506 VANDOEUVRE les NANCY cedex ; France*

**Key words:** Tin Oxide, Solubility, Soda-Lime Glass, Basicity

### **Abstract**

Due to its low solubility in molten glass, the lowest among non-colouring oxides, tin dioxide is commonly used as refractory material, electrodes or as opacifier in enamels. Thus, this work deals with the influence of glass composition and temperature on SnO<sub>2</sub> solubility.

The solubility of tin dioxide was first assessed as a function of time and temperature in a standard commercial soda-lime glass. This study showed that dissolution equilibrium could be reached in short time (2h). Moreover, long lasting and high temperature heat treatments led to sodium volatilisation, which lowered SnO<sub>2</sub> solubility limit. An Arrhenius dependence of solubility with temperature, describing a single dissolution mechanism, has been observed in the temperature range 1200-1400°C.

The influence of Na<sub>2</sub>O content on SnO<sub>2</sub> solubility limit suggested the consideration of glass basicity. A similar study has been performed in simple ternary glasses (Na<sub>2</sub>O-CaO-xSiO<sub>2</sub>) and in commercial glass enriched with Na<sub>2</sub>O, CaO or Al<sub>2</sub>O<sub>3</sub>. From the first results, basicity seems to be a complex parameter. The specific role of these latter oxides in the physico-chemistry of molten soda-lime glasses is discussed here, regarding the polymerisation degree of the glass network or the precipitation of new phases.

## Introduction

The glass industry requires high performance materials, with good mechanical properties and high corrosion resistance in aggressive environments such as silicate melts [1-3]. But the lifetime of ceramic refractories is directly linked to the solubility of their oxides in molten glass. Manfredo et al. [4] demonstrated that cassiterite,  $\text{SnO}_2$ , has the lowest limit of solubility among non-colouring refractory oxides at temperatures between 1300 and 1600°C. Other authors, Andrews [5] and Weyl [6], suggested that the dissolution of tin dioxide in glasses could be influenced by additions of alumina and calcia. But their considerations were mostly regarding enamels, which vitreous matrix is not exactly comparable to soda-lime glass.

Although tin dioxide behaviour has been widely studied in float glass [7,8], very few studies are reported on  $\text{SnO}_2$  solubility specifically. Therefore, this work aims to improve our knowledge of  $\text{SnO}_2$  behaviour regarding time and temperature. Its ability to remain chemically inert in molten glass is also assessed as a function of the chemical environment in a standard commercial soda-lime glass (NCSO) and 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). Regarding the works mentioned previously [5,6], particular attention is given to  $\text{Na}_2\text{O}$ ,  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$ .

The evolution of solubility limits, described by the optical basicity of silicates, is discussed.

## Experimental procedure

A commercial soda-lime glass (NCSO for  $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2 + \text{Others}$ ) has been used as a standard of glass container industry, which composition is reported in Table 1. Four other ternary glasses (NCxS) 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. [9-12]. The raw chemicals reagents  $\text{Na}_2\text{CO}_3$  (Chempur, 99.5 %),  $\text{CaCO}_3$  (Chempur, 99 %), and amorphous  $\text{SiO}_2$  (99.8 %), were mixed and grinded in a planetary ball mill during 15 minutes. The homogenized mixture has been heated in a Pt - 5%Au crucible, with a temperature slowly raised (10 hours) up to 1200°C, to enable progressive decomposition of the carbonates. It has been maintained at 1500°C during 2 hours and then kept at 1300°C for 10 hours. The glass was finally quenched in air at 20°C to avoid glass crystallisation. Glasses compositions were determined by Electron Probe MicroAnalysis (EPMA) and are reported in Table 1. Experimental x ratios are globally satisfying.

In a second time, twenty grams of each glass were ground with 20 wt% of cassiterite powder ( $\text{SnO}_2$  99.8 %, Oximet, Italia): the ratio of 20 wt% has been chosen to be higher than the solubility limit of  $\text{SnO}_2$ . Mixtures were

heated at 1200°C for 2 minutes, and then quenched. It has been done twice to ensure a better dispersion of the powder. Pieces of 100 mg of SnO<sub>2</sub>-enriched glasses were placed in graphite crucibles at 1200°C for 2 min. These crucibles have a low wettability regarding glass, and samples formed balls with an average diameter of 4 mm.

Balls, sustained by a Pt-wire in alumina crucible, were then annealed at temperatures between 1200°C and 1400°C, for times up to 100 hours in air.

SnO<sub>2</sub> over-saturation in silicate melts was controlled by Scanning Electron Microscope (Philips XL30), using Back Scattered Electrons (BSE). The total amount of dissolved oxide in the glassy matrix was measured by Electron Probe Micro-Analysis EPMA (Cameca SX100), with specific conditions to limit Na volatilisation [13]. The accelerating voltage was set at 15 kV and the beam current at 10 nA. The time count was of 10 s and the electron beam was defocalised to a 20µm diameter in the glass matrix (exempted of any crystal of SnO<sub>2</sub>). The results expressed in the latter paragraphs are estimated from 6 to 8 analyses, and error-bars correspond to standard deviations.

## Results and discussions

### Kinetic aspects

It was first necessary to verify SnO<sub>2</sub> over-saturation after heat treatments of NCSO samples. Fig. 1 shows some of the SEM micrographs, in BSE mode: tin dioxide grains (white) are not totally dissolved in the glassy matrix (black), even for long times.

After one hour (Fig. 1a), SnO<sub>2</sub> grains remain similar to the raw powder (initial granulometry was below 1 µm) and are rather finely dispersed in the glass. The dissolution process had just been initiated. For intermediate times and temperatures (Fig. 1b), few bigger grains indicate that coalescence occurs. Considering the most extreme conditions (Fig. 1c), coarsening is clearly identified and seems to be thermally activated. SnO<sub>2</sub> particles are globally all over 10 µm or forming large agglomerates. A competition may take place between the two phenomena, dissolution and coalescence. A third phenomenon could be identified on Fig. 1c: some of the grains might not be resulting from coalescence, but rather from recrystallisation, according to their angular and geometrical shapes.

Nevertheless, it is not implying that the limit of solubility has been reached. The content of tin oxide dissolved in the glass has been measured by EPMA, near the remaining oxide grains, in the glass. The plot of SnO<sub>2</sub> solubility in NCSO glass versus time is reported on Fig. 2, for temperatures of 1200 and 1300°C and times up to 100

hours. EPMA measurements of the overall composition were made near oxide grains and tin content is expressed as SnO<sub>2</sub> wt% (Sn<sup>IV</sup>), assuming that NCSO glass is sufficiently oxidized to prevent the reduction of Sn<sup>IV</sup>.

As expected, the capacity of glass to dissolve SnO<sub>2</sub> increases when temperature is raised. Both curves evolve with time in a similar way, but the usual plateau corresponding to the solubility limit is not obvious on Fig. 2. After 2 hours, the dissolved oxide content reaches a maximum (8.9 wt% at 1200°C and 10.1 wt% at 1300°C) but longer heat treatments, after 9 hours, induce a decrease of dissolved SnO<sub>2</sub>, despite no parameter was changed.

A modification of composition, more precisely sodium volatilisation, is suggested and would corroborate SnO<sub>2</sub> crystallisation observed by SEM for long heat treatments, on Fig. 1c. Compared to other glass components, especially SiO<sub>2</sub>, sodium is known to be quite volatile in melts [13]. Considering this, Figure 3 plots SnO<sub>2</sub> content (white squares) and Na<sub>2</sub>O/SiO<sub>2</sub> ratio (dotted line) as a function of time.

The loss of Na<sub>2</sub>O is clearly identified on Fig. 3 when time increases. The content of Na<sub>2</sub>O is maintained at its theoretical value (calculated from Table 1) until 4 hours at high temperatures, but drops regularly for longer times. It is not expressed here, but the loss depends also on the temperature. At 1200°C and 1250°C a decrease of Na<sub>2</sub>O/SiO<sub>2</sub> ratio was also observed, but to a lighter extend than at 1300°C, where the loss reaches 25% of the initial Na<sub>2</sub>O content after 100 hours. This is noticeable on Fig. 2, as SnO<sub>2</sub> limit of solubility is decreasing simultaneously with Na<sub>2</sub>O losses, but only slightly at 1200°C. In all cases, tin dioxide is forced to crystallise, as SnO<sub>2</sub> content in NCSO is over its limit of solubility.

These kinetic considerations enable the choice of an appropriate duration for solubility limit measurements. All further heat treatments will thus be led during 2 hours, respecting the time necessary for tin to saturate the glassy matrix near SnO<sub>2</sub> grains, and avoiding sodium losses.

The chosen protocol offers a good reproducibility, but it must be noticed that the high Na<sub>2</sub>O loss can be attributed to the high surface/volume ratio of the samples (balls with 4 mm diameter).

Limits of solubility in NCSO glass, after 2 hours at several temperatures, are summarised in Table 2.

These values, converted in atomic percents, are presented in Fig. 4. The logarithm of the amount of dissolved tin dioxide is plotted as a function of the inverse of temperature. Both parameters are correlated, according to Arrhenius law, with the following equation (1):

$$\ln(\text{at.}\% \text{SnO}_2) = -\frac{E_a}{R} \left( \frac{1}{T} \right) + \ln C \quad (1)$$

where  $E_a$  is the activation energy of SnO<sub>2</sub> dissolution,  $R$  the universal gas constant,  $T$  the absolute temperature in K and  $C$  a constant.

The linear dependence of dissolved SnO<sub>2</sub> with the inverse of temperature reveals a single mechanism for the dissolution process in the 1200-1400°C temperature range. This leads to the determination of an activation energy which is about 28 kJ.mol<sup>-1</sup>. Manfredo et al. [4] studied a commercial soda-lime glass which is close to the NCSO glass. Crucibles, containing SnO<sub>2</sub> powder at the bottom and covered by glass, had been heated for 3 days at temperatures between 1300°C and 1600°C. The resulting activation energy is about E<sub>a</sub> = 32.0 kJ.mol<sup>-1</sup>, which is in very good agreement with the one determined in this study for a similar glass composition. Furthermore, the limits of solubility measured in their work (10.2 wt% at 1340°C and 12.3 wt% at 1410°C) are in the same range as those evaluated here. The new methodology proposed here for the determination of solubility limits leads to results in accordance with the literature, with some interesting advantages: the sample small size improves the reproducibility and requires little amounts of raw materials for wide experimental sessions (only 100 mg here, whereas 10 grams minimum are necessary for the reference work mentioned above). Moreover, dissolution equilibrium may be reached in only two hours, as 36 hours were necessary beforehand. Indeed, the process promotes Na<sub>2</sub>O losses, inducing a decrease of tin dioxide solubility. Hence, kinetic aspects must be considered carefully before any further deductions on thermal behaviours of the studied oxides, in order to find the best compromise between solubilisation equilibrium and minimal soda losses.

However, the volatilisation phenomenon underlined the impact of glass composition on solubility limits. Abdelhouab et al. [14,15] succeeded in linking solubility of Cr<sub>2</sub>O<sub>3</sub> with Na<sub>2</sub>O activities and glasses optical basicity. It would also be of great interest to correlate also tin oxide solubility with glass physico-chemical properties, but working with Na<sub>2</sub>O activities would require new samples and protocol. Optical basicity is more convenient to calculate from EPMA results and to compare NCSO with ternary glasses NCxS.

#### Optical Basicity and Composition influences

Duffy and Ingram [16] developed that concept: by measuring the frequency shifts in UV spectra of s→p transition of probe ions, they obtained a numerical scale of oxides basicity. The theoretical optical basicity  $\Lambda$  of oxide glasses is calculated with equation (2):

$$\Lambda_{melt} = \sum \Lambda_{oxide\ i} \times x_i \quad (2)$$

where  $x_i$  is the molar fraction of oxide  $i$  and  $\Lambda_i$  the optical basicity measured by Duffy ( $\Lambda_{SiO_2}=0.48$ ,  $\Lambda_{Na_2O}=1.15$ ,  $\Lambda_{Al_2O_3}=0.6$ ,  $\Lambda_{MgO}=0.78$ ,  $\Lambda_{BaO}=1.15$ ,  $\Lambda_{K_2O}=1.4$ ,  $\Lambda_{ZrO_2}=0.63$ ).

Simple ternary glasses NCxS ( $x=3,4,5$  or  $6$ ) have been enriched in SnO<sub>2</sub> following the same procedure as NCSO glass and were finally heat treated 2 hours at 1200°C. The plot of dissolved SnO<sub>2</sub> wt% versus optical basicity (plain line on Fig. 5) displays an explicit dependence and solubility limit decreases with basicity. In this case,

basicity could be an effective indicator to predict the limit of solubility of tin oxide. Nevertheless, Na<sub>2</sub>O losses were operating in the opposite way as in the case of long-lasting heat treatment on NCSO glass (Fig. 3): in a glass containing more acid elements, solubility limit of SnO<sub>2</sub> was decreasing with time and Na<sub>2</sub>O losses.

The second curve appearing in Fig. 5 (dotted line) presents NCSO with variable amounts of Na<sub>2</sub>O at 1200°C. Some are due to losses after 25 and 100 hours (low basicity), others are enrichments of 5 to 10 wt% Na<sub>2</sub>O and heated during 2 hours (high basicity). The contradictory evolutions of SnO<sub>2</sub> contents are confirmed and make clear that glass basicity has an important influence on the dissolution process, even if it requires now further physico-chemical considerations. Na<sub>2</sub>O is the strongest basic oxide contained in NCSO, and only its content has been changed. In NCxS glasses, optical basicity varied with the increase of SiO<sub>2</sub>, maintaining CaO/Na<sub>2</sub>O molar ratio at a constant value equal to 1. Both contents of basic oxides have been modified simultaneously.

Considering all previous observations, NCSO has been doped with CaO (5 and 10 wt% added) and heated at 1200°C for 2 hours. SEM micrographs (Fig. 6) show a new phase precipitating (light grey) around SnO<sub>2</sub> grains (white). EPMA indicates a stoichiometric composition corresponding to CaSiSnO<sub>5</sub> (malayaite). This phase has not been observed in NCxS samples.

Attention has been paid to perform solubility EPMA analysis apart from the new phase vicinity. This avoids possible confusions between CaSiSnO<sub>5</sub> and tin oxide solubility measurements, or assessment of any glass composition changes locally induced by this new phase precipitation (e.g. lower content of CaO, SiO<sub>2</sub> and SnO<sub>2</sub>). EPMA measurements in NCSO glasses enriched with 5 or 10 wt% of CaO (Fig.7) rejects definitely the use of the sole influence of basicity to predict SnO<sub>2</sub> dissolution: introducing CaO in NCSO tends to lower tin dioxide solubility, even if CaO is also considered as a basic element. Na<sub>2</sub>O and CaO are both considered as network modifiers, and are supposed to create non-bridging oxygen (NBO) in the glass network. The presence of NBO is necessary for SnO<sub>2</sub> dissolution, forming oxygen polyhedron around the dissolved cations. SnO<sub>2</sub> dissolves as an oxo-complex of Sn<sup>IV</sup> in octahedral conformation, which stabilisation requires 2 alkali cations for charge compensation [17,18]. This behaviour is reported in the literature [19-21]. Na<sub>2</sub>O creates NBO and stabilises tin oxo-complexes, thus explaining the increase of SnO<sub>2</sub> solubility with Na<sub>2</sub>O content. In the case of CaO, NBO are created, but Ca<sup>2+</sup> cations are located between the two NBO, limiting their availability for tin dioxide dissolution. Therefore increasing basicity with addition of CaO should lower SnO<sub>2</sub> limit of solubility.

Further additions of alumina were performed in NCSO. SEM revealed no specific phenomenon except fine SnO<sub>2</sub> grains. Results displayed on Fig. 7 (crosses) are much more informative: additions of Al<sub>2</sub>O<sub>3</sub> are modifying slightly the optical basicity values, but they strongly decrease the limit of solubility of tin dioxide. This explains

the lower tin dioxide solubility measured in pure NCSO compared to NCxS glasses, in Fig. 5: NCSO contains 2 wt% of alumina (Tab. 1). Dissolved alumina might be in competition with SnO<sub>2</sub> for available NBO [22].

Lastly, another assumption should be taken into account. Tin has two oxidation degrees, which are Sn<sup>II</sup> and Sn<sup>IV</sup>. EPMA measurements only give the total content of tin dissolved in the glass (Sn<sup>II</sup>+Sn<sup>IV</sup>). Its speciation is directly linked to the medium redox, which can depend on the oxygen fugacity or glass composition [9-11]. As a consequence, studies should be performed in order to get more informations about the tin speciation in molten silicates.

## Conclusion

An innovating method has been proposed for dissolved tin oxide measurements, using EPMA, in soda-lime-silicate melts. Kinetic measurements indicated that dissolution equilibrium is reached after only two hours. Long lasting heat treatments induced sodium volatilisation, thus SnO<sub>2</sub> solubility decreased, inducing its crystallisation. It was found that 2 hours of heat treatment was a good compromise between dissolution equilibrium and minimal Na<sub>2</sub>O losses.

The limit of solubility evolved with temperature according to an Arrhenius law. Dissolution is thermally activated and is governed in NCSO by a single mechanism.

To correlate SnO<sub>2</sub> dissolution with glass composition, similar measurements were made in simple ternary glasses, NCxS, at 1200°C after 2h. Dissolution appeared to increase with glass acidity (*i.e.* SiO<sub>2</sub> content) but contradicted previous observations on Na<sub>2</sub>O influences. Optical basicity is thus not sufficient to describe SnO<sub>2</sub> solubilisation in glasses. The other components should be considered separately.

Further experiments were performed in NCSO glass with additional Na<sub>2</sub>O, CaO or Al<sub>2</sub>O<sub>3</sub>. Few quantities of Al<sub>2</sub>O<sub>3</sub> did not influence the optical basicity, but considerably lowered SnO<sub>2</sub> limit of solubility. CaO-doped glasses revealed the formation of a new phase, CaSiSnO<sub>5</sub>. Despite CaO is a glass network modifier and a basic oxide as Na<sup>+</sup>, its introduction in the melt decreased SnO<sub>2</sub> limit of solubility. As a consequence, the basicity must be considered as a complex parameter, and the influence of each basic oxide must be studied specifically.

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## References

- [1] C.A. Harper, *Handbook of Ceramic, Glasses, and Diamonds*, McGraw-Hill Professional, 2001.
- [2] G. Luo, J. Li, Q. Shen, D. Zhang, L. Zhang, Corrosion Behaviour of Tin Dioxide Based Electrode Material at High Temperature in Molten Soda-Lime-Silicate Glass, *Corrosion Science*, 2008, vol. 50, no. 2, pp. 591-595.
- [3] H. Le Doussal, *Céramiques Réfractaires, Les Techniques De l'Ingénieur*, 1986.
- [4] L.J. Manfredo, R.N. McNally, Solubility of Refractory Oxides in Soda-Lime Glass, *Journal of the American Ceramic Society*, 1984, vol. 67, no. 8, C-155-C-158.
- [5] A.I. Andrews, *Porcelain Enamels*, The Garrard Press, Illinois, 1961.
- [6] W.A. Weyl, *Coloured glasses, Society of Glass Technology*, SGT, England, 1951.
- [7] Y. Hayashi, K. Matsumoto, M. Kudo, The Diffusion Mechanism of Tin Into Glass Governed by Redox Reactions During the Float Process, *Journal of Non-Crystalline Solids*, 2001, vol. 282, no. 2-3, pp. 188-196.
- [8] R. Garkova, G. Völksch, C. Rüssel, Precipitation of SnO<sub>2</sub> Nano-Crystallites from Na<sub>2</sub>O/B<sub>2</sub>O<sub>3</sub>/SnO<sub>2</sub>/(Al<sub>2</sub>O<sub>3</sub>) Glasses, *Journal of Non-Crystalline Solids*, 2005, vol. 351, no. 27-29, pp. 2287-2293.
- [9] H. Khedim, S. Abdelouhab, R. Podor, C. Rapin, M. Vilasi, P.-J. Panteix, M. Toplis, F. Faure, Kinetic and Equilibrium Factors Affecting Saturation of Chromium Oxide in Soda-Silicate Melts, *Journal of Non-Crystalline Solids*, 2011, vol. 357, no. 1, pp. 31-42.
- [10] H. Khedim, T. Katrina, R. Podor, P.-J. Panteix, C. Rapin, M. Vilasi, Solubility of Cr<sub>2</sub>O<sub>3</sub> and Speciation of Chromium in Soda-Lime-Silicate Melts, *Journal of the American Ceramic Society*, 2010, vol. 93, no. 5, pp. 1347-1354.
- [11] H. Khedim, R. Podor, C. Rapin, M. Vilasi, Redox-Control Solubility of Chromium Oxide in Soda-Silicate Melts, *Journal of the American Ceramic Society*, 2008, vol. 91, pp. 3571-3579.
- [12] R. Mathieu, H. Khedim, G. Libourel, R. Podor, L. Tissandier, E. Deloule, C. Rapin, Control of Alkali-Metal Oxide Activity in Molten Silicates, *Journal of Non-Crystalline Solids*, 2008, vol. 354, no. 45-46, pp. 5079-5083.
- [13] J. Konta, L. Mraz, Volatility of Oxides from Silicate Melt and the Origin of Moldavites, *Mineralogical Magazine*, 1975, vol. 40, pp. 70-78.
- [14] S. Abdelouhab, C. Rapin, R. Podor, P. Berthod, M. Vilasi, Electrochemical Study of Chromium Corrosion in Na<sub>2</sub>O—xSiO<sub>2</sub> Melts, *Journal of the Electrochemical Society*, 2007, vol. 154, no. 9, C500-C507.
- [15] S. Abdelouhab, R. Podor, C. Rapin, M.J. Toplis, P. Berthod, M. Vilasi, Determination of Na<sub>2</sub>O Activities in Silicate Melts by EMF Measurements, *Journal of Non-Crystalline Solids*, 2008, vol. 354, no. 26, pp. 3001-3011.
- [16] J.A. Duffy, M.D. Ingram, An Interpretation of Glass Chemistry in Terms of the Optical Basicity Concept, *Journal of Non-Crystalline Solids*, 1976, vol. 21, no. 3, pp. 373-410.
- [17] D. Benne, C. Rüssel, Diffusivity and Incorporation of Tin in Na<sub>2</sub>O/CaO/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> Melts, *Journal of Non-Crystalline Solids*, 2005, vol. 351, no. 14-15, pp. 1283-1288.
- [18] D. Benne, C. Rüssel, O. Lehmann, M. Menzel, D. Niemeier, K. Dieter Becker, Square-wave Voltammetry and Mössbauer Spectroscopy in Tin-Doped Soda-Silicate and Soda-Lime-Silicate Glasses, *Journal of Non-Crystalline Solids*, 2003, vol. 318, no. 1-2, pp. 202-212.
- [19] T. Nishida, Advances in the Mössbauer Effect for the Structural Study of Glasses, *Journal of Non-Crystalline Solids*, 1994, vol. 177, pp. 257-268.
- [20] D. Benne, C. Rüssel, M. Menzel, D. Niemeier, K.D. Becker, Incorporation of Tin in Soda-Lime and Aluminosilicates, *Journal of Non-Crystalline Solids*, 2004, vol. 345-346, pp. 203-207.
- [21] M.H. Krohn, J.R. Hellmann, B. Mahieu, C.G. Pantano, Effect of Tin-Oxide on the Physical Properties of Soda-Lime-Silica Glass, *Journal of Non-Crystalline Solids*, 2005, vol. 351, no. 6-7, pp. 455-465.
- [22] H. Schirmer, C. Rüssel, Square-Wave Voltammetry and Impedance Spectroscopy in Tin Doped Melts with the Compositions xNa<sub>2</sub>O · 15Al<sub>2</sub>O<sub>3</sub> · (85 - x)SiO<sub>2</sub> (x = 8.5, 11 and 16), *Journal of Non-Crystalline Solids*, 2008, vol. 354, no. 10-11, pp. 889-895.

## Figures Captions

**Figure 1a** NCSO 1200°C 1h, BSE, 15 kV

**Figure 1b** NCSO 1250°C 4h, BSE, 15 kV

**Figure 1c** NCSO 1300°C 100h, BSE, 15 kV

**Figure 2** Time influence on SnO<sub>2</sub> solubility in NCSO at 1200 and 1300°C, measured by EPMA

**Figure 3** Time influence on Na<sub>2</sub>O/SiO<sub>2</sub> ratio and SnO<sub>2</sub> solubility in NCSO, at 1300°C, measured by EPMA

**Figure 4** Plot of ln[mol% SnO<sub>2</sub>] versus 1/T for NCSO, after 2 hours at 1200, 1250, 1300, 1350 and 1400°C

**Figure 5** SnO<sub>2</sub> solubility in NCxS glasses after 2 hours at 1200°C, and in NCSO with different Na<sub>2</sub>O contents, as a function of the optical basicity

**Figure 6a** NCSO, 1200°C 2h, BSE, 15 kV

**Figure 6b** NCSO with 5 wt% of additional CaO, 1200°C 2h, BSE, 15 kV

**Figure 6c** NCSO with 10 wt% of additional CaO, 1200°C 2h, BSE, 15 kV

**Figure 7** SnO<sub>2</sub> solubility in NCSO glass and NCSO doped with 5 to 10 wt% of Na<sub>2</sub>O, CaO or Al<sub>2</sub>O<sub>3</sub>, as a function of the optical basicity, after 2 hours at 1200°C

## Tables

**Table 1:** Oxidic compositions of the five glasses, measured by EPMA

**Table 2** Limits of solubility of SnO<sub>2</sub> in NCSO glass from EPMA measurements

Figure1A  
[Click here to download high resolution image](#)

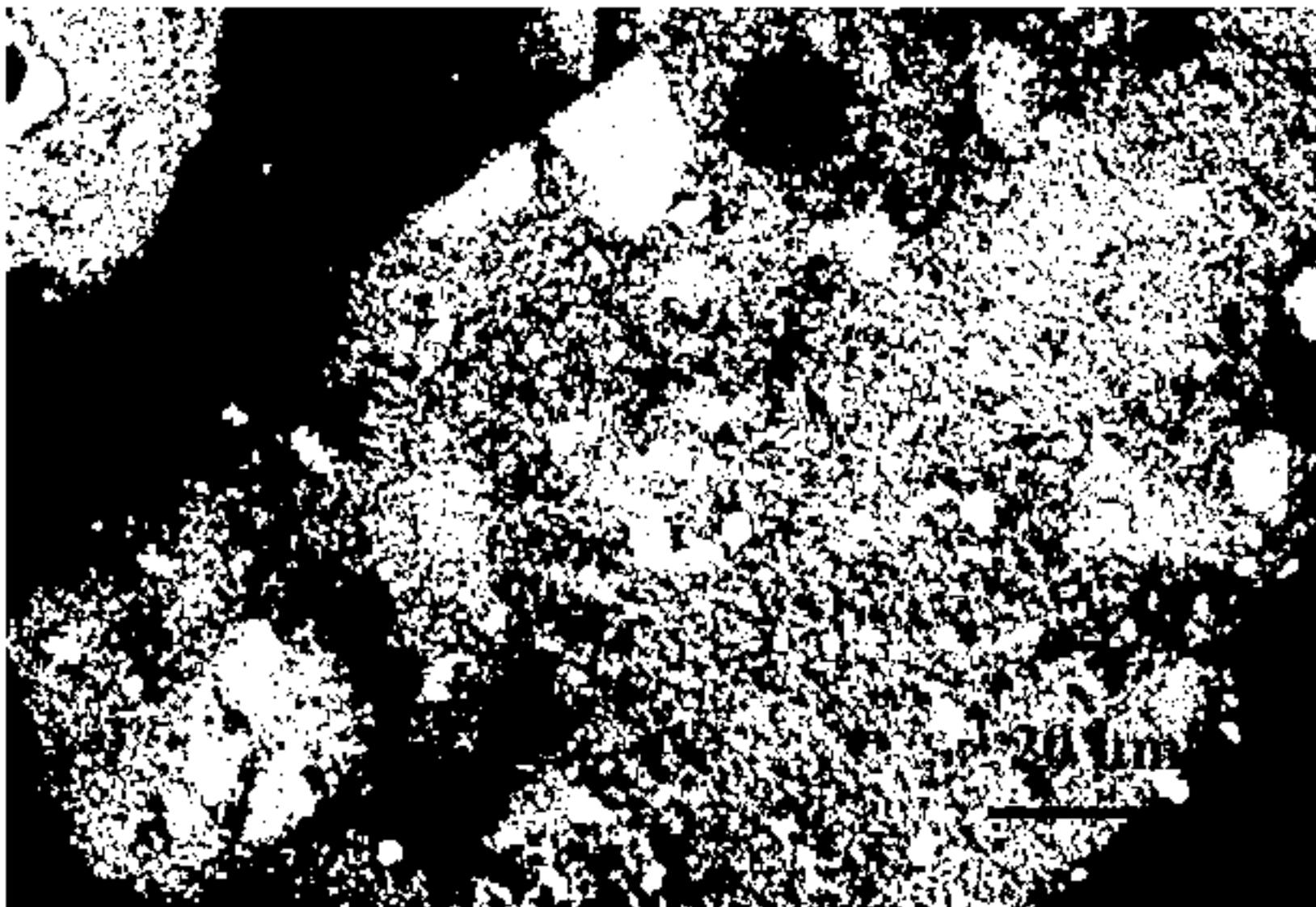


Figure1B  
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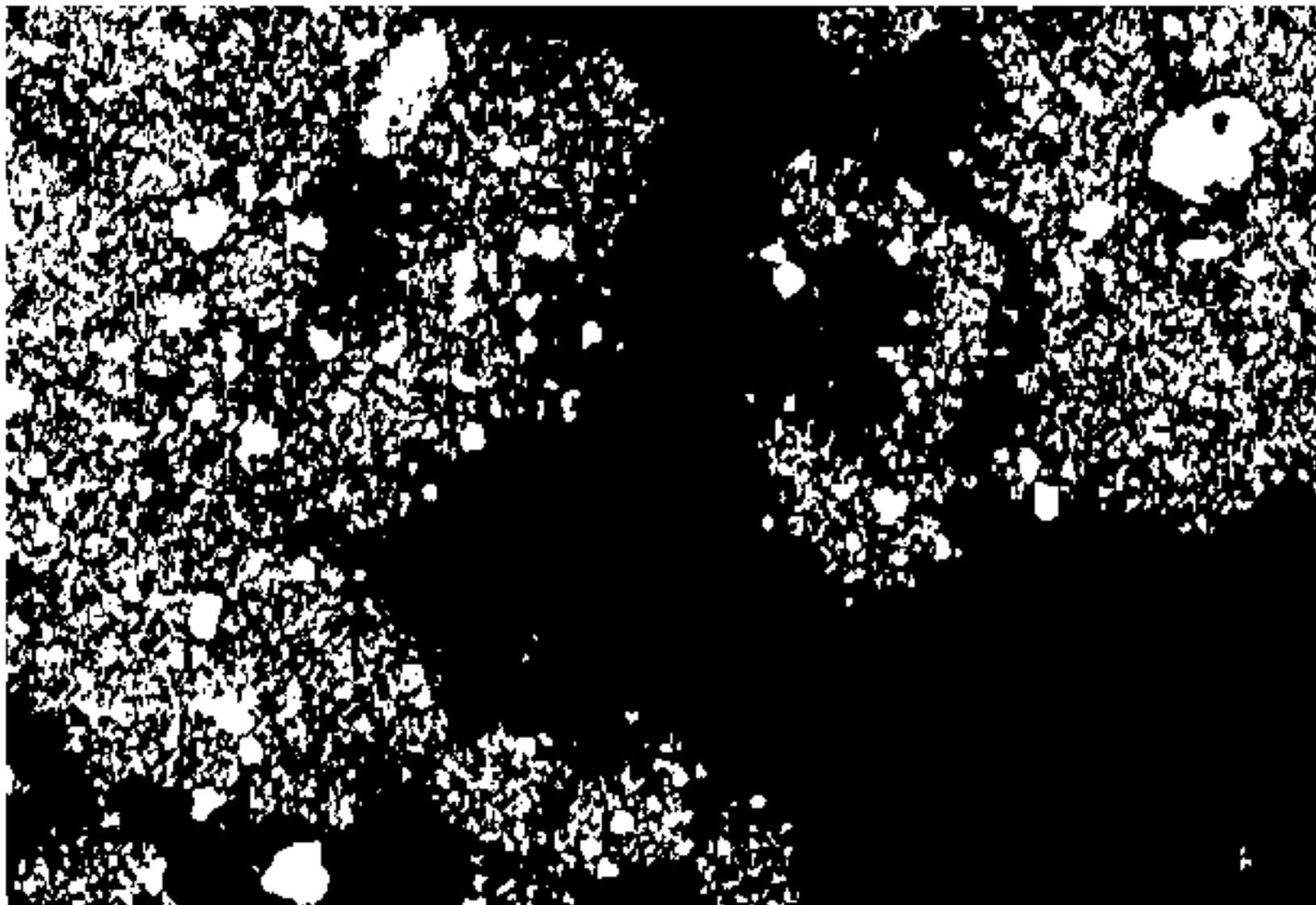


Figure1C  
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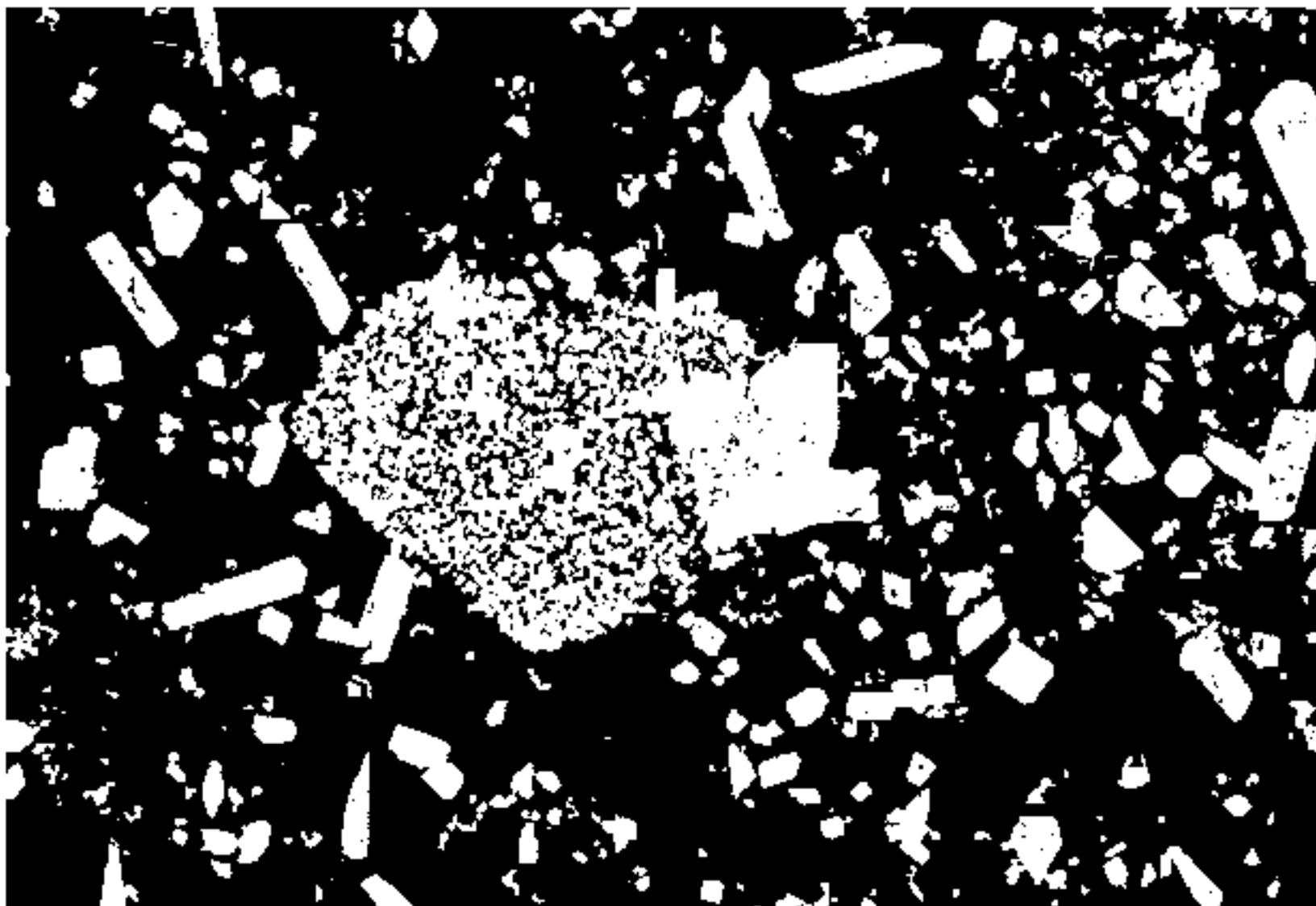


Figure2  
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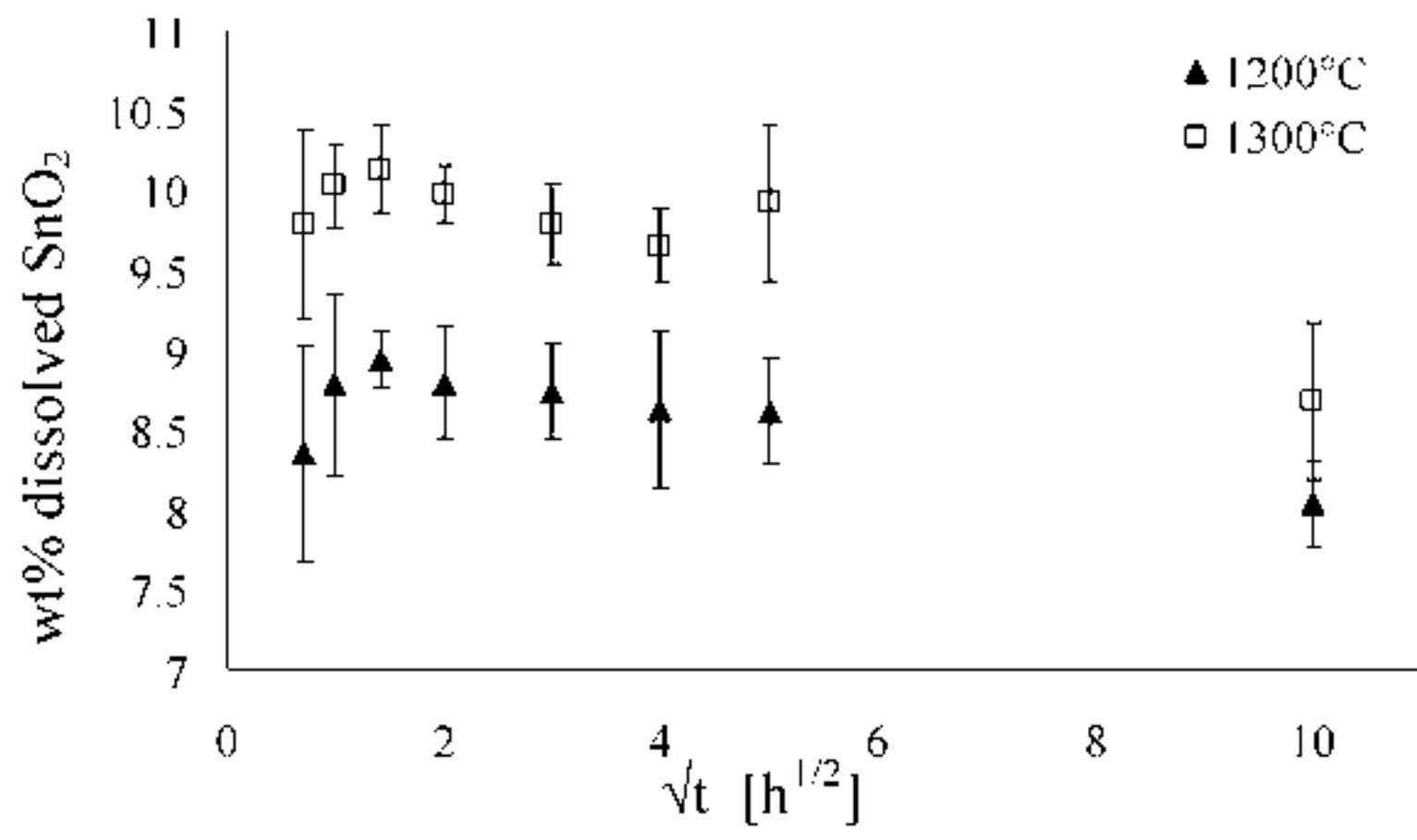


Figure3  
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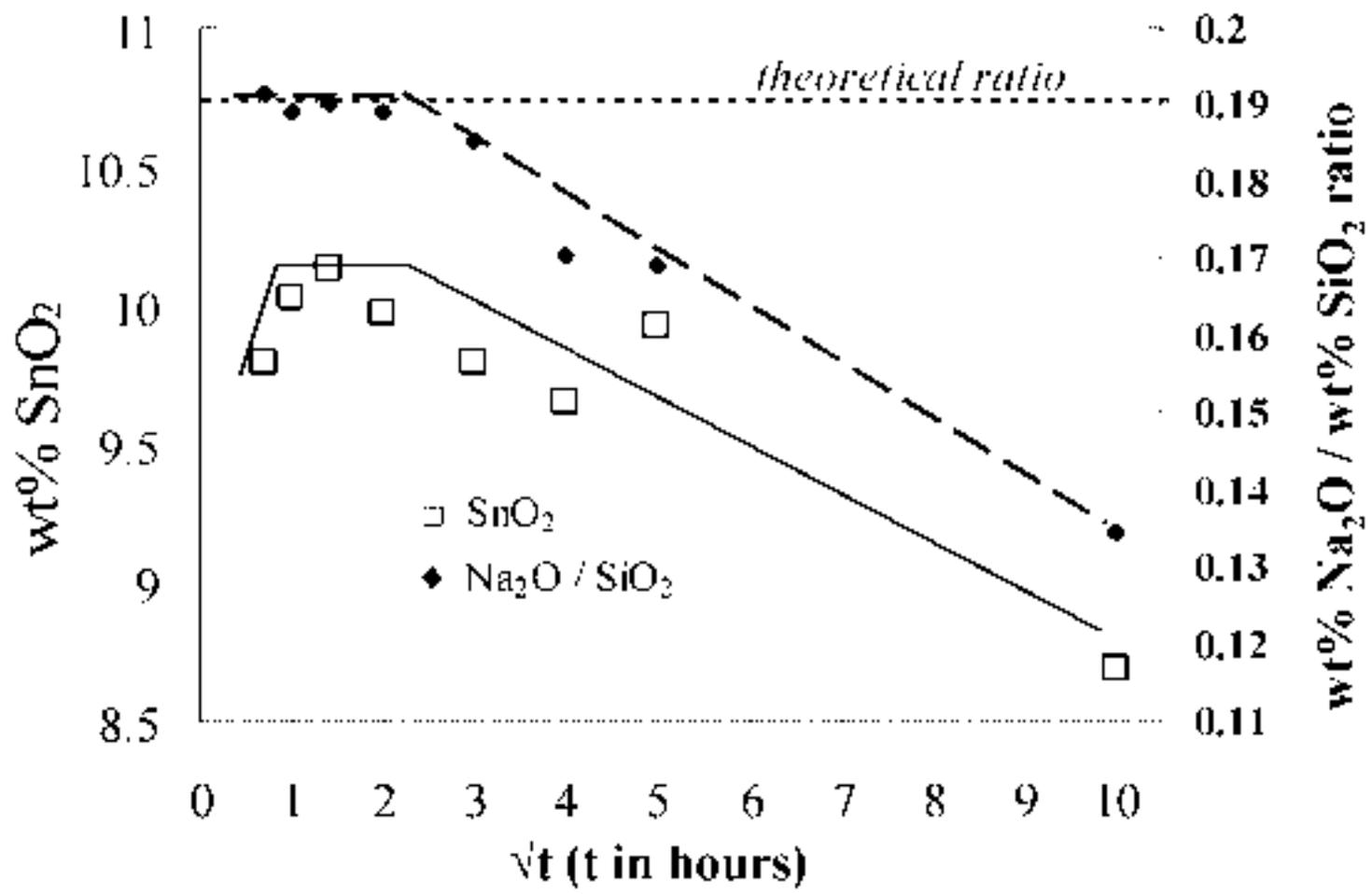


Figure4  
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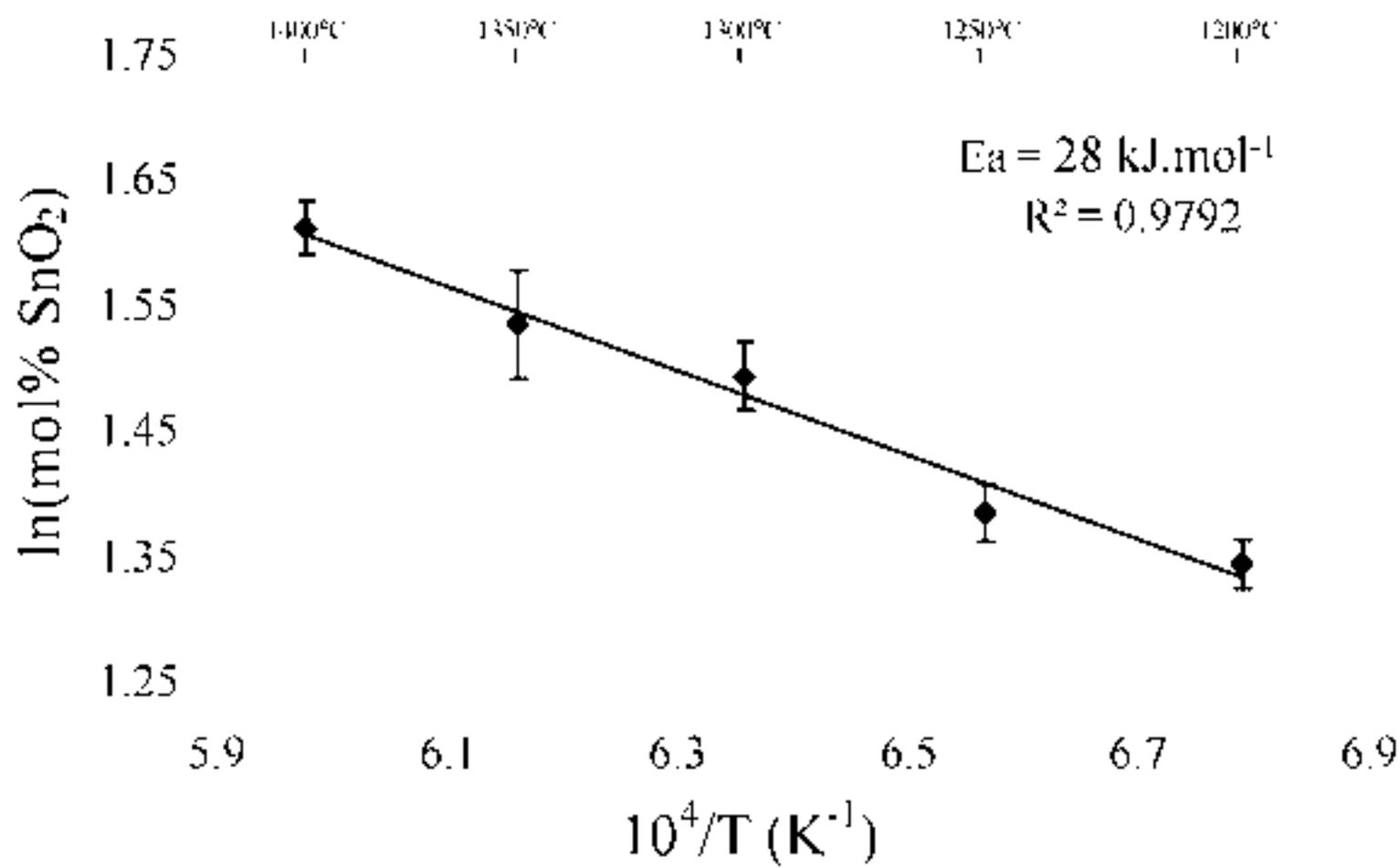


Figure5  
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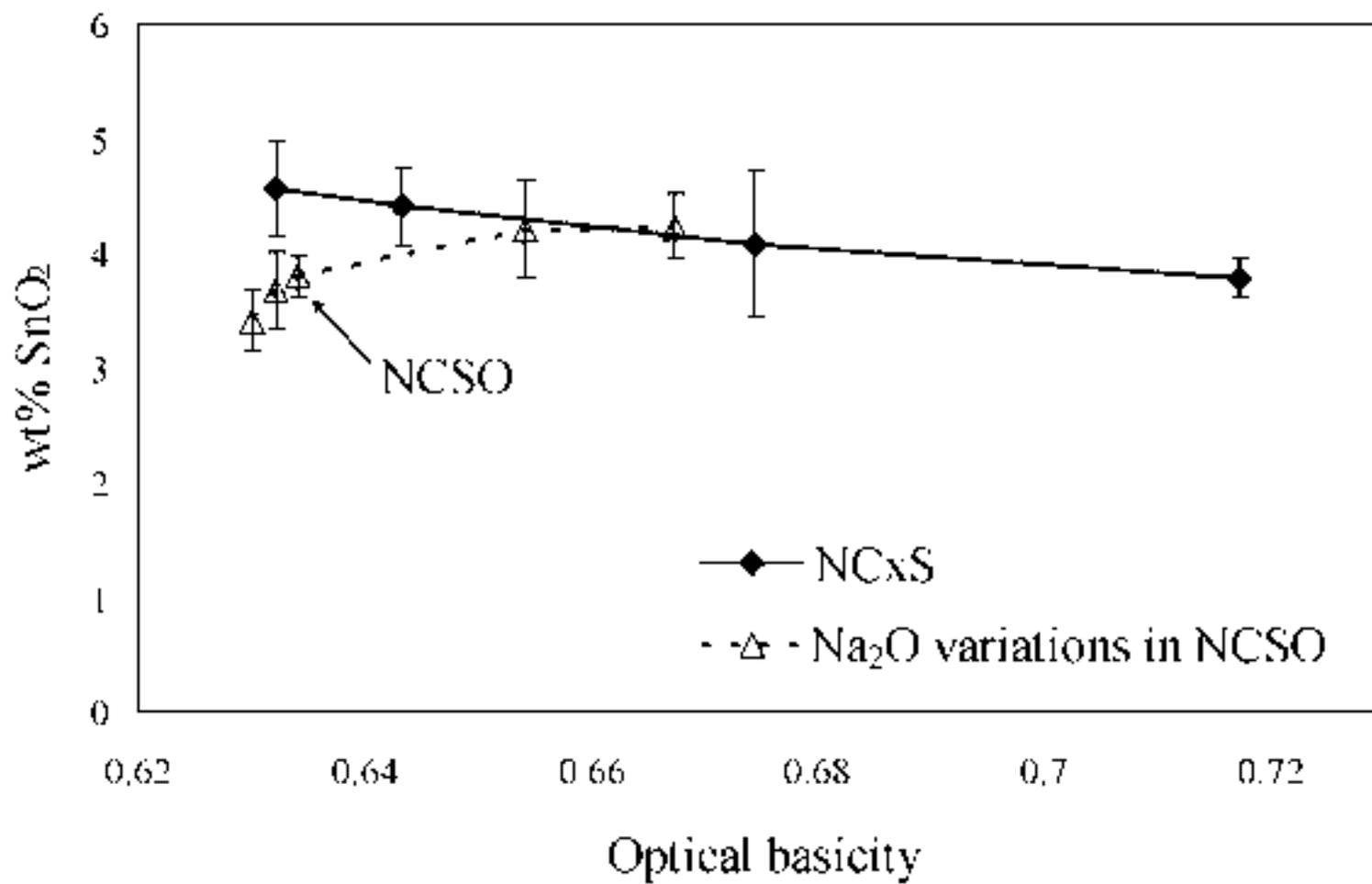


Figure6A  
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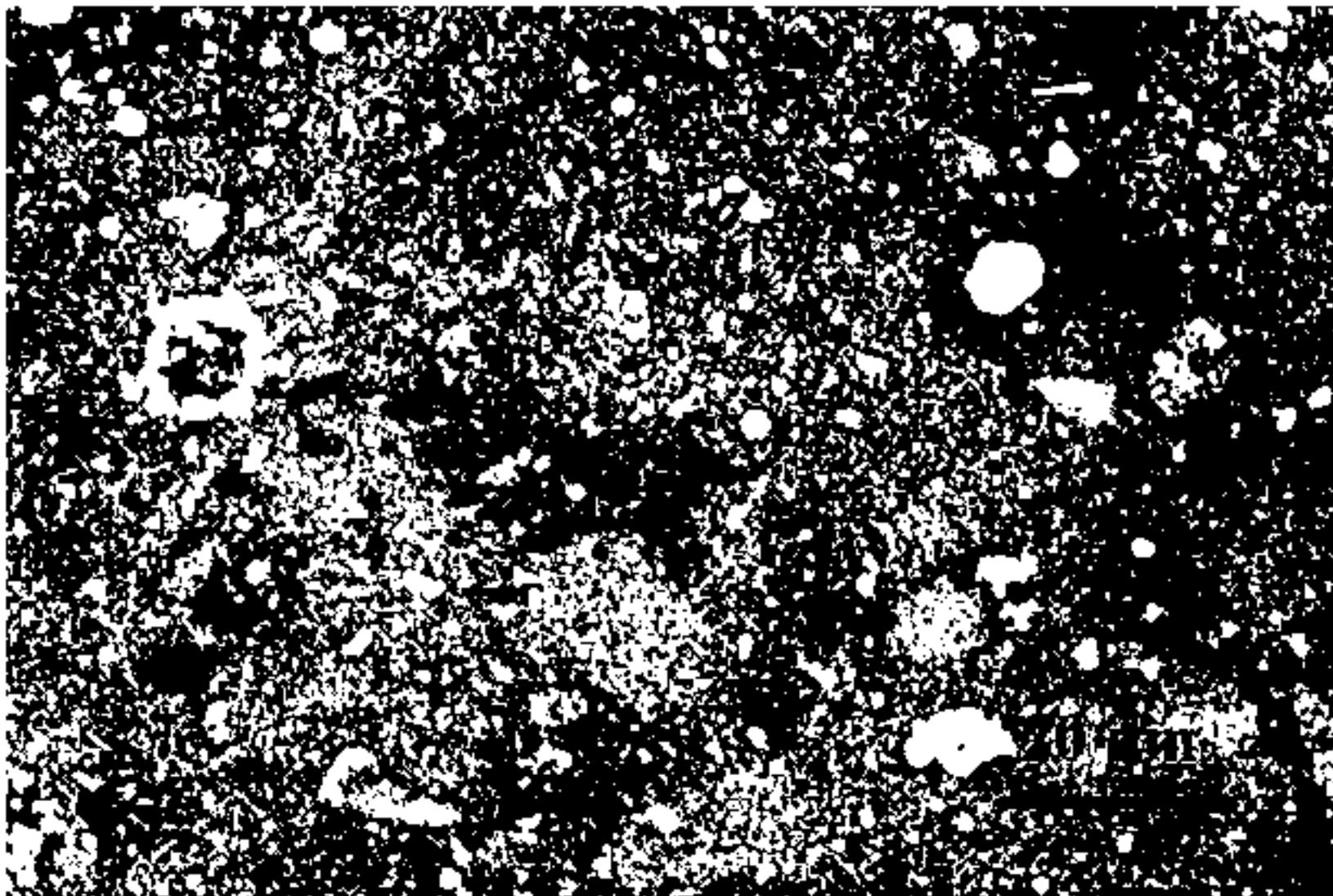


Figure6B  
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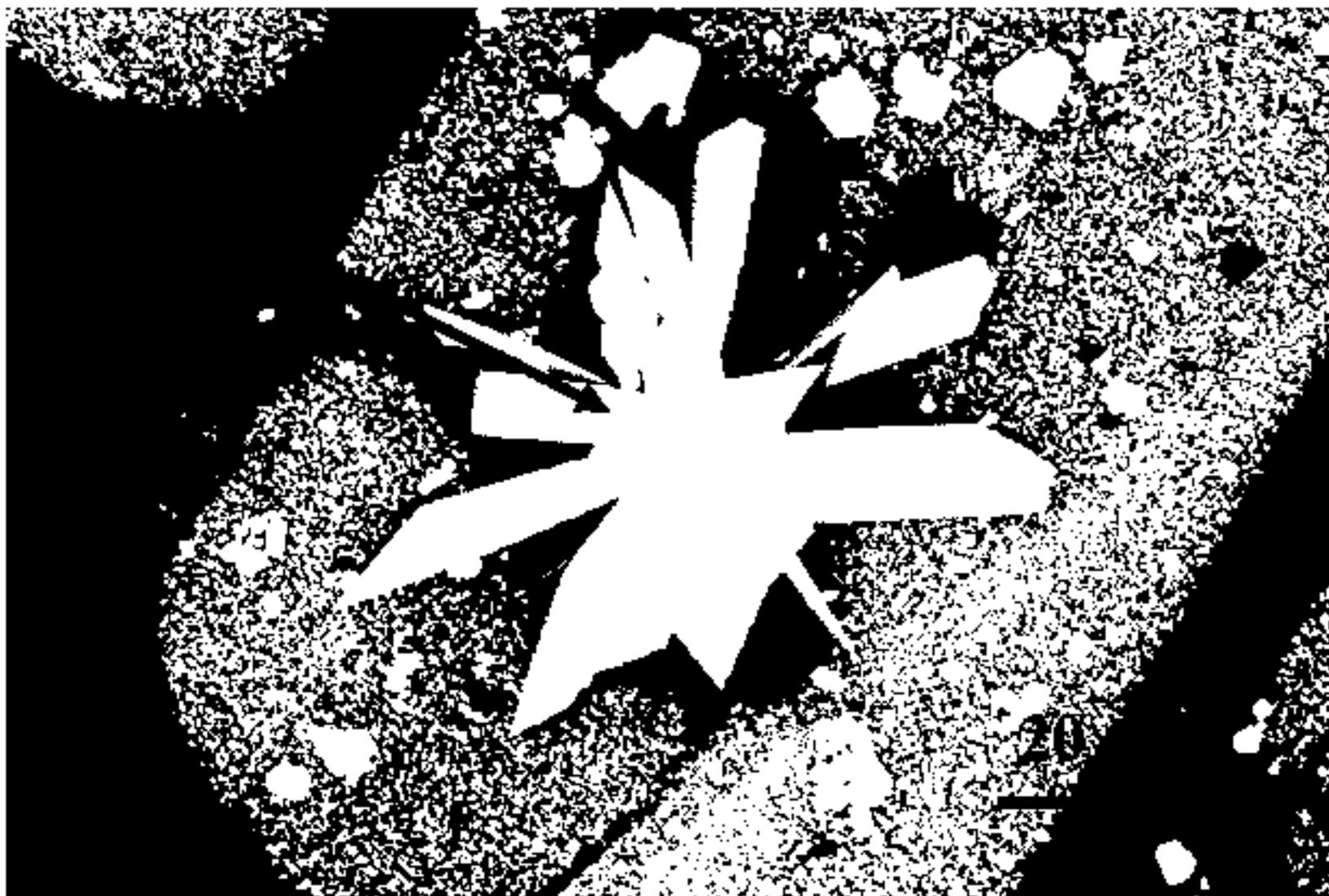


Figure6C  
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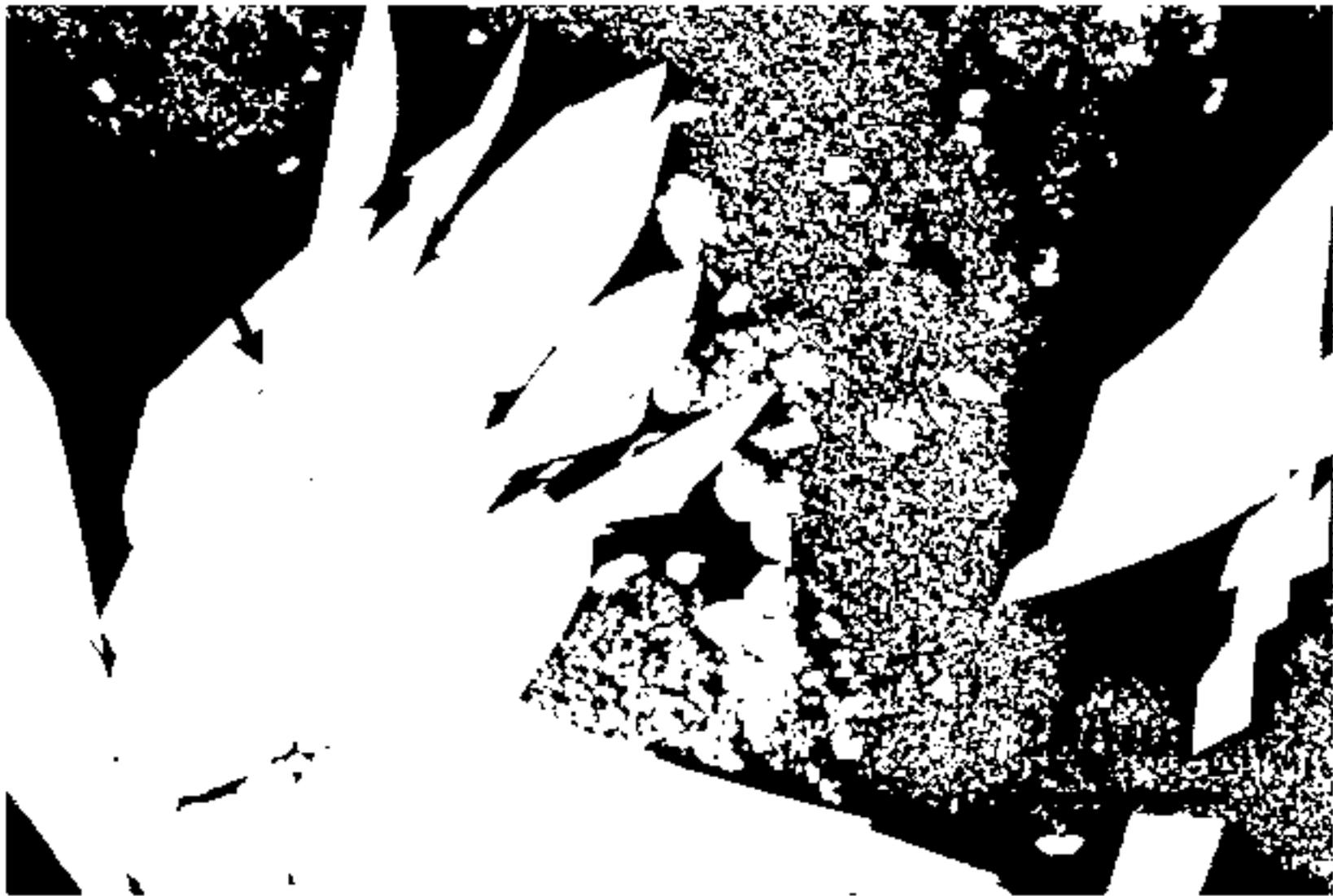


Table1

<b>wt % (EPMA)</b>	<b>Na<sub>2</sub>O</b>	<b>CaO</b>	<b>SiO<sub>2</sub></b>	<b>Al<sub>2</sub>O<sub>3</sub></b>	<b>Others</b>	<b>Na at.%</b>	<b>Ca at.%</b>	<b>Si at.%</b>	<b>x</b>
NCSO	13.5	10.0	71.3	2.0	3.2				
NC3S	20.7	18.4	60.8			14.2	7.0	21.6	3.06
NC4S	17.1	17.3	64.8			11.8	6.6	23.0	3.70
NC5S	14.8	13.4	71.3			10.1	5.1	24.9	4.91
NC6S	12.9	11.6	75.3			8.7	4.3	26.1	6.02

Table2

<i>T</i> [ $^{\circ}$ C]	<i>1200</i>	<i>1250</i>	<i>1300</i>	<i>1350</i>	<i>1400</i>
<b>wt% SnO<sub>2</sub></b>	8.9 (0.18)	9.3 (0.21)	10.1 (0.28)	10.7 (0.47)	11.5 (0.25)