Low-temperature sintering of sodium beta alumina ceramics using nanosized SnO$_2$ sintering aid

Hajar Ahmadi Moghadam[1,*], Mohammad Hossein Paydar[2]

[1]*Department of Material Engineering, Faculty of Engineering, Shahrekord University, Shahrekord, Iran*
[2]*Department of Materials Science and Engineering, School of Engineering, Shiraz University, Shiraz, Iran*

Abstract

Sodium beta alumina ceramics ($Na_{1.67}Al_{10.67}Li_{0.33}O_{17}$) is used in sodium sulphur batteries as solid electrolyte. In the present work, sodium beta alumina powder has been synthesized by the solid state method using Al_2O_3, Na_2CO_3 and Li_2CO_3 as the starting materials. The effect of nanosized SnO_2 additive on sintering behaviour, microstructure, mechanical and electrical properties of sodium beta alumina ceramics has been investigated. The results indicated that the addition of 1 mol% of nanosized SnO_2 particles, determined as the optimal amount, can decrease the sintering temperature of sodium beta alumina ceramics for about 100 °C, and lead to the excellent densification and proper microstructure, as well. Improvement in sintering behaviour of beta alumina ceramics in the presence of nanosized SnO_2 additive is apparently due to the formation of a liquid phase during the sintering process and lower sodium loss. The results also proved that by SnO_2 addition, ionic conductivity at 300 °C, fracture strength and Weibull modulus of the sintered samples are improved by 66%, 58%, and 45%, respectively. These improvements could be attributed to the higher amount of β''-Al_2O_3 phase, higher density and more uniform microstructure.

Keywords: sodium beta alumina, nanosized SnO_2, sintering, mechanical properties, ionic conductivity

I. Introduction

The engineering properties of ceramics are strongly dependent on the microstructural features, including size and shape of the grains, amount of remained porosity, pore size and the distribution of pores in the fired body. For most applications, microstructural control usually means achievement of the high density, small grain size and homogeneous microstructure [1]. Using sintering aids is a well known method for altering microstructure during sintering of ceramic materials which could modify densification characteristics and improve mechanical, magnetic and electrical properties of the fired sample [2–6]. In recent years, it has been shown that using sintering aids with nanoparticle size can reduce the required amount of sintering aids even down to 1 mol% and can also improve properties of the sintered products [7–13]. The unique properties of nanoparticles are primarily due to their large surface-to-volume ratio and their high activity.

Sodium beta alumina ceramics has been studied widely because of their application as solid electrolyte in sodium sulphur and ZEBRA batteries [14–16]. However, it is very difficult to obtain dense and well-sintered sodium beta alumina ceramics using an ordinary sintering process because of the high volatility of alkaline elements at high temperatures [16–18]. The sintering temperature of sodium beta alumina ceramics is generally higher than 1600 °C [19–21]. The volatilization of sodium at high sintering temperature and the poor densities at low sintering temperature are deleterious to mechanical strength and ionic conductivity of this electrolyte [16]. It would be possible to lower the sintering temperature and overcome the mentioned difficulties by using sintering aids. The effects of different sintering aids including ZnO, MgO, Nb_2O_3, Sm_2O_3 and nano-CuO on the densification behaviour and properties of sodium beta alumina electrolyte have been investigated [6, 22–24].

In the present work, the effects of the nanosized SnO_2 additive as a sintering aid on sinterability, microstructure, mechanical and electrical properties of sodium

*Corresponding author: tel: +98 383 2324438,
e-mail: hajar.ahmadi@sku.ac.ir*

beta alumina ceramics, synthesized by the solid state method, have been investigated.

II. Experimental procedure

2.1. Synthesis method

Sodium beta alumina was synthesized by the solid state method. In this method, the starting materials were: Na_2CO_3 and Li_2CO_3 (with 99.9% purity from Carlo Erba Company) and α-Al_2O_3 (with 99.9% purity from Inframat Advanced Materials Company). According to the chemical formula of Li_2O-stabilized β''-alumina as $Na_{1.67}Al_{10.67}Li_{0.33}O_{17}$, stoichiometric amounts of the starting materials were first weighed, intimately mixed and calcined at 1300 °C for 2 h. High purity nanosized SnO_2 powder (99.9%, ≤80 nm, Advanced Materials US) was used as sintering aids. Required amount of the nanosized SnO_2 (i.e. 0.5, 1 and 2 mol%) was mixed with the calcined powder by attrition milling using 5 mm zirconia balls in the ethanol medium for 4 h with the fixed rotation speed of 480 rpm. After the slurries were dried, the powder was granulated by passing through 60 mesh number screen and shaped in a die by applying 200 MPa pressure uniaxially. Disk shaped samples with a thickness of 2 mm and diameter of 12 mm were fired at different temperatures including 1520, 1570 and 1620 °C for 15 min with the heating rate of 4 °C/min. In order to minimize sodium loss, the green samples were placed in an alumina-crucible and covered with the β''-alumina powder.

2.2. Characterization techniques

The density of the sintered samples was measured by the Archimedes' method in ethanol as an immersion medium. Phase purity of the sintered samples was examined by a BRUKER X-ray diffractometer using Cu Kα radiation. The scans of the selected diffraction peaks were carried out in the step mode (step size of 0.05°, measurement time of 5 s). Relative phase fractions of β-Al_2O_3 ($f(\beta)$) and β''-Al_2O_3 ($f(\beta'')$) were calculated according to the Pekarsky's formula as follows [25]:

$$f(\beta'') = 100 - f(\beta) = 100 - \frac{1.14I_\beta}{1.14I_\beta + I_{\beta''}} \qquad (1)$$

where I_β and $I_{\beta''}$ are peak intensities of β and β'' phase at 44.50° and 45.90°, respectively.

The microstructure of the sintered samples was characterized by scanning electron microscope (SEM, Leica Cambridge S360). For the SEM observations, the specimens were polished to a mirror finish and then thermally etched at 100 °C lower than used sintering temperature for 30 min in air. In this study, biaxial flexure test (BFT) was used to evaluate the mechanical strength of the sintered samples. In this experiment, load is applied by a loading ring on the disc specimen that is placed on a supporting ring (this test is also termed "ring on ring" and is carried out under the ASTM C1499, 2003 standard). In the present work the variability in fracture strength values was analysed according to two parameters proposed in the Weibull approach [26]. The ionic conductivity of the sintered ceramics was measured by AC 2-probe impedance analysis on a frequency response analyser (Solartron 1260, Solartron Analytical) over a frequency range of 10 Hz to 5 MHz with the symmetric platinum electrodes in the temperature range from 200 to 500 °C with 50 °C interval in air.

III. Results and discussion

Figure 1 shows the relative densities of the fired samples as a function of the sintering temperature and amount of the used nanosized SnO_2 powder as sintering aid. According to these results, the density of all samples increased with sintering temperature as well as with addition of SnO_2. At sintering temperature of 1620 °C, the density of the pure samples was 3.15 g/cm³, i.e. 96.5% TD (theoretical density is 3.26 g/cm³) and it was increased to 99.4% TD by the addition of 1 mol% of SnO_2. The addition of 0.5 mol% of nanosized SnO_2 had no significant effect on the sample densities. In contrast, using 1 mol% of nanosized SnO_2 additive effectively decreased sintering temperature and improved sinterability of the parent phase. The density of the sample prepared with 1 mol% of SnO_2 and sintered at 1520 °C was 98.1% TD, which is higher than the density of the pure sample sintered at even 100 °C higher temperature (1620 °C). Thus, it can be concluded that the addition of 1 mol% nanosized SnO_2 decreases the sintering temperature of sodium beta alumina ceramics for about 100 °C. Using lower sintering temperature definitely can lead to the lower sodium loss that would cause improvement in properties of sodium beta alumina ceramics [16]. Some improvement of the sintering behaviour was observed for the samples with 2 mol% of nanosized SnO_2, but not as pronounced as when just 1 mol% of nanosized SnO_2 was added.
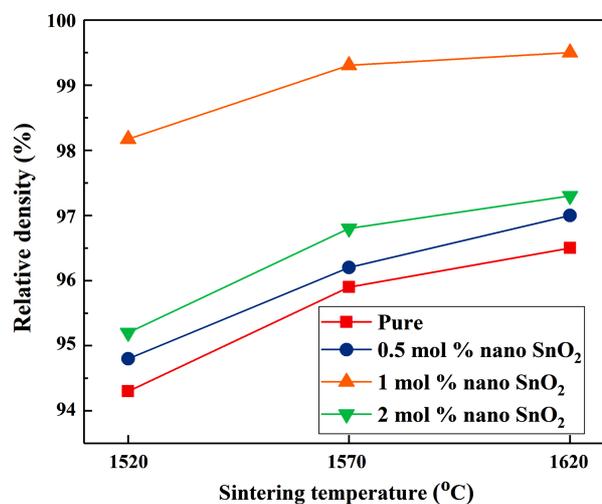
Figure 1. Relative densities as a function of sintering temperature and SnO_2 amount
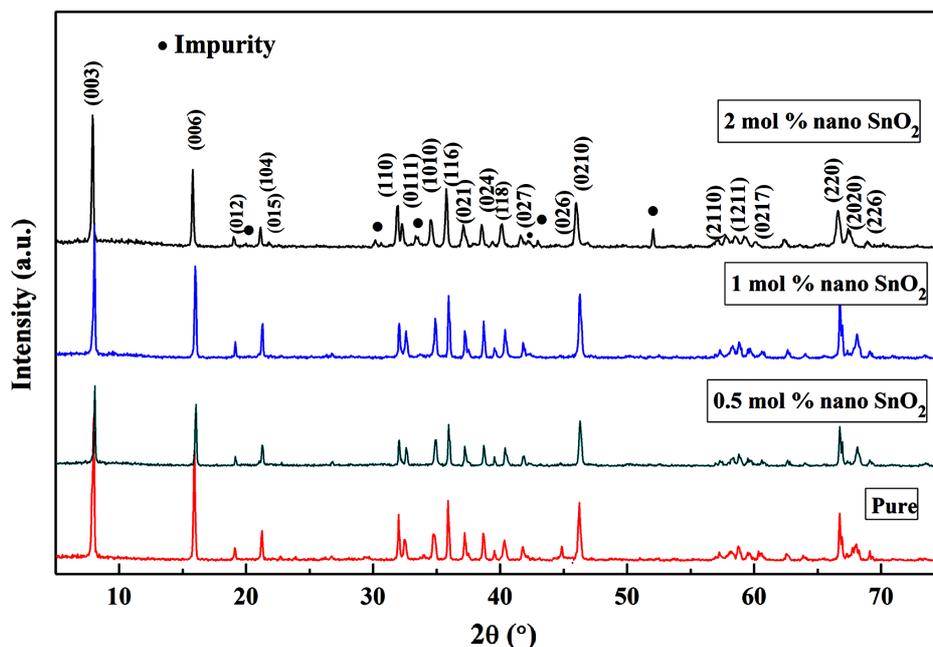
Figure 2. X-ray diffraction patterns of the samples prepared with different amounts of nanosized SnO$_2$ additive

Figure 2 shows the typical X-ray diffraction patterns of the samples sintered at 1620 °C which confirms the presence of Na$_{1.67}$Al$_{10.67}$Li$_{0.33}$O$_{17}$ crystalline phase [6,27]. According to XRD patterns, no impurity phases have been detected for the samples prepared with 0.5 and 1 mol% of nanosized SnO$_2$. However, when the amount of SnO$_2$ increased to 2 mol%, a few unknown diffraction peaks were detected. So, it is proposed that, for the samples with 0.5 and 1 mol% of nanosized SnO$_2$, Sn^{4+} can be incorporated into the sodium beta alumina crystal lattice [6]. Decrease in the density of the sample by increasing amount of SnO$_2$ from 1 to 2 mol% can also be attributed to the presence of impurity phase in this sample. β-Al$_2$O$_3$ (hexagonal) and β''-Al$_2$O$_3$ (rhombohedral) are two main subgroups of sodium beta alumina and β''-Al$_2$O$_3$ exhibits a significantly higher ionic conductivity than β-Al$_2$O$_3$ [16]. The amount of β''-Al$_2$O$_3$ was calculated using Eq. 1 and it is 99% in the sample with 1 mol% of nano SnO$_2$, which is about 4%

higher than that of the pure sample. The effect of cation additives in sodium beta alumina depends on their size and charge. The oxygen atoms in the spinel block portion of the structure are closely packed with small Al^{3+} ions in the interstices. Al^{3+} ions can be replaced by small cations without undue strain [28]. According to the Boilot and Thery's theory, as the ionic radius of Sn^{4+} cation (0.071 nm) is smaller than 0.097 nm of Al^{3+}, Sn^{4+} is able to occupy Al^{3+} positions in the spinel block in the way to stabilize the structure of β''-Al$_2$O$_3$ phase [24,29]. Regarding the densities and XRD results, it can be concluded that the optimal amount of SnO$_2$ was 1 mol%. Therefore, in further research the properties of the sample with 1 mol% of nanosized SnO$_2$, sintered at 1520 °C, are compared with the properties of the pure sample sintered at 1620 °C.

Figure 3 shows SEM micrographs of the cross-section of the sintered samples. As it can be seen, the pure sample contains few pores. The dense microstruc-
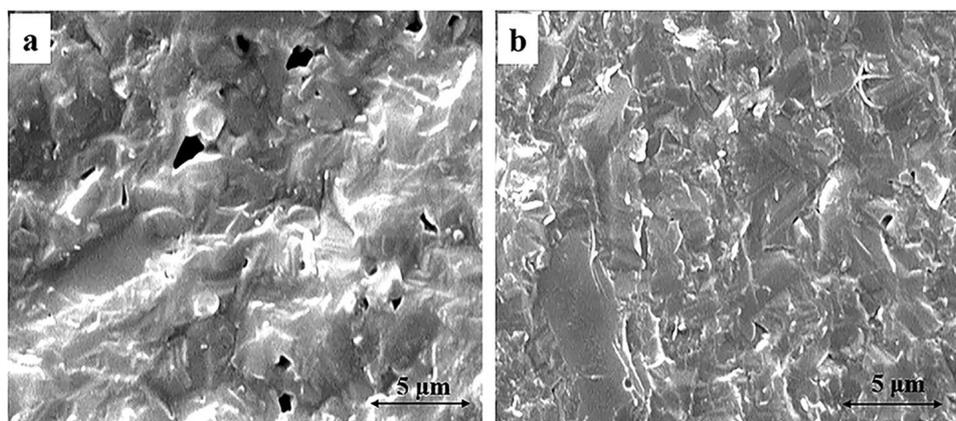
Figure 3. Cross-section SEM micrographs of the sodium beta alumina: a) pure sample sintered at 1620 °C and b) sample prepared with 1 mol% of nanosized SnO$_2$ additive sintered at 1520 °C

ture with no pores or cracks, observed for the ceramics prepared with 1 mol% of nanosized SnO_2 additive, was confirmation of higher density even at lower sintering temperature. The existence of SnO_2 could improve the densification behaviour of sodium beta alumina ceramics in virtue of lower sodium loss and formation of a liquid phase during the sintering process [11,22]. In liquid-phase sintering, the additive melts or reacts with a small part of the major component to form an eutectic liquid. The formation of the liquid phase by melting of the additive is fairly common in metallic systems, whereas, the formation of an eutectic liquid is more common in ceramics [1]. The liquid phase sintering with the addition of nanosized SnO_2 could be attributed to the formation of Li_2SnO_2 and Li_8SnO_6 phases with a lower melting point then the sintering temperature. According to the PDF files of X'Pert High Score software (PDF# 00-31-0761 and 00-024-0659), the XRD main peaks of these phases could be matched to the crystalline phase of $Na_{1.67}Al_{10.67}Li_{0.33}O_{17}$ [30,31]. The presence of these phases could improve the densification of sodium beta alumina ceramics in virtue of the formation of the liquid phase during the sintering process.

Advanced ceramics must meet very specific property requirements and therefore their microstructure must be well controlled [26]. Disadvantages of the solid state process include sodium loss and exaggerated grain growth during the high-temperature sintering [16]. SEM images of the sintered and thermally etched samples are shown in Fig. 4. These images demonstrate that the addition of nanosized SnO_2 causes changes in the microstructure. The pure sample shows typical duplex microstructure consisting of large grains in a fine-grained matrix. However, for the sample prepared with 1 mol% of nanosized SnO_2 additive more uniform microstructure has been created. As it can be recognized, the small amount of nanosized SnO_2 additive could promote sintering of sodium beta alumina ceramics and effectively restrict the grain growth at the same time. The formation of liquid phases and the inhibition of grain growth together improve densification of sodium beta alumina [32].

The strength is strongly affected by microstructure (e.g. porosity and grain size). The extensive grain growth can lead to a significant reduction in mechanical properties. The strength of sodium beta alumina
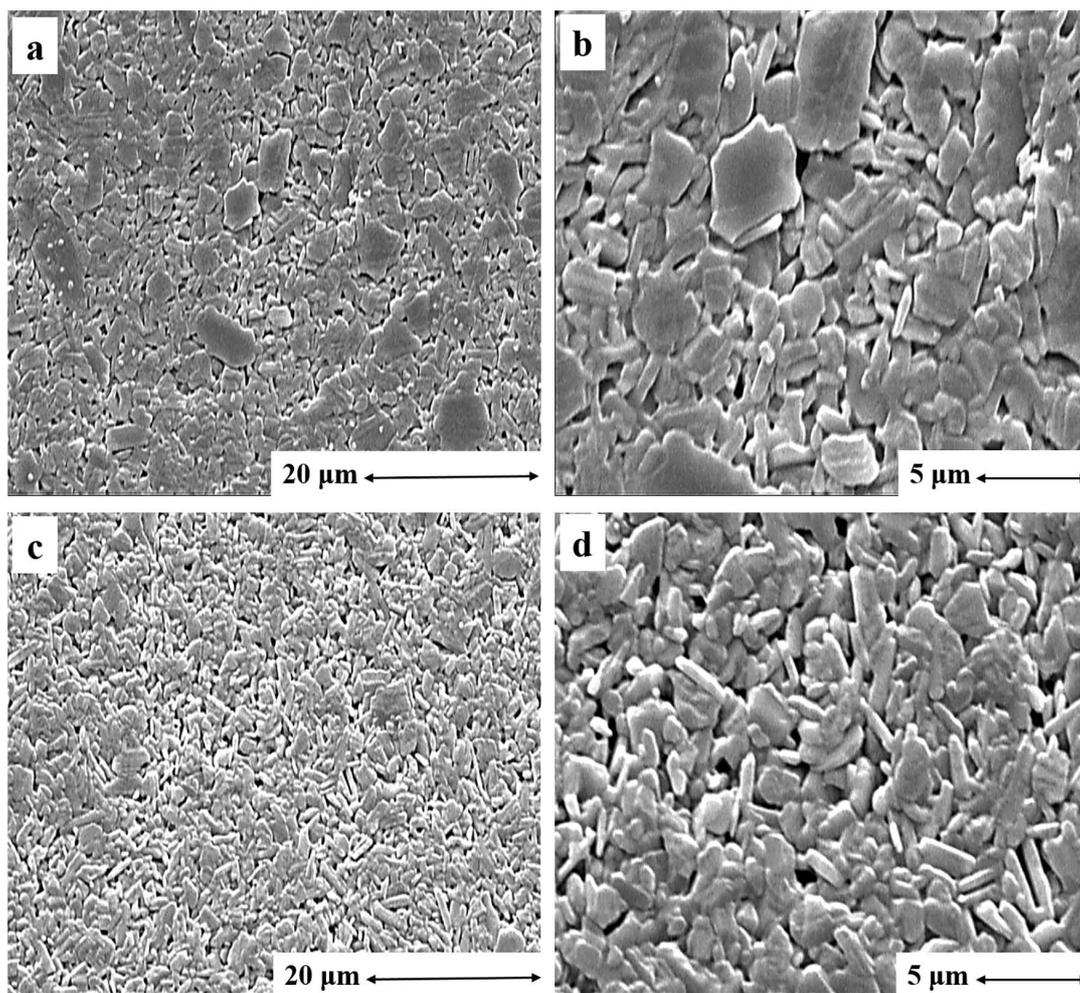
Figure 4. SEM micrographs of thermally etched pure sample sintered at 1620 °C (a, b) and sample prepared with 1 mol% of nanosized SnO_2 additive sintered at 1520 °C (c, d)
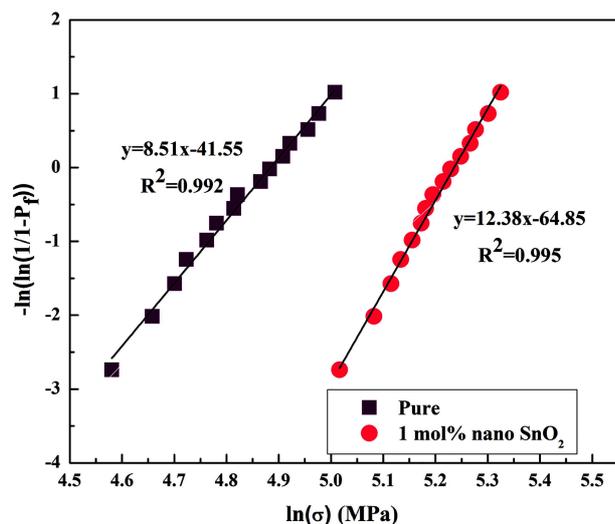
Figure 5. Two-parameter Weibull plot of the fracture strength

Figure 6. The Arrhenius plots of the conductivity versus temperature for the pure sample and the sample prepared with 1 mol% SnO₂

ceramics with a duplex structure varies from 120 to 170 MPa, depending on the size and amount of large grains in the matrix [16]. In the present work biaxial flexure test was applied to 15 samples for each composition. The average fracture strength of the sample prepared with 1 mol% of nanosized SnO_2 additive exceeded 198 ± 16 MPa, while the fracture strength of the pure sample was only 125 ± 21 MPa. The results of other researchers confirm that a small increase in the density of sintered samples significantly increases its strength [14,25]. Since Weibull modulus is a measure of the spread in fracture strength, it is very important as a gauge of mechanical reliability. Generally, when Weibull modulus is large, the variation in strength is small and the reliability of the material is excellent [33]. Weibull modulus may be affected by microstructure (porosity and interparticle necking), powder processing techniques, grain size and shape, and surface finish [33,34]. Weibull plots of the measured strength data, shown in Fig. 5, were used to calculate Weibull modulus. As it can be seen, Weibull modulus of the sample prepared with 1 mol% of nanosized SnO_2 additive is clearly higher than that of the pure sample. In this study, it was shown that Weibull modulus is in agreement with microstructural observations (Fig. 4). In other words, highly uniform microstructure, smaller grain size and higher density can cause higher fracture strength and higher Weibull modulus all as the consequence of the addition of nanosized SnO_2 [35].

Several factors influence the conductivity of sodium beta alumina ceramics including composition, the relative proportion of β and β'' phases present and microstructure (grain size, porosity, impurities, etc.) [16]. The Arrhenius plots of the measured ionic conductivity in the temperature range of 200 to 500 °C are shown in Fig. 6. According to these results, the ionic conductivity of the electrolyte was improved in the presence of nanosized SnO_2 sintering aid. Ionic conductivity of the pure sample at 300 °C was 0.031 $\Omega^{-1}\cdot cm^{-1}$ while for the
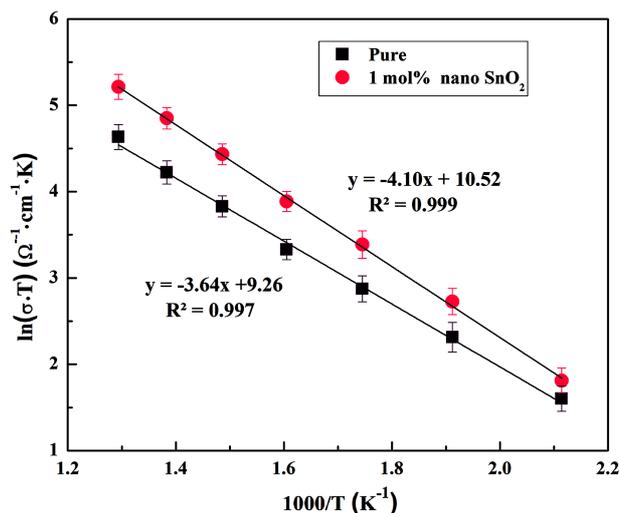
sample prepared with 1 mol% of nanosized SnO_2 additive it increased to 0.052 $\Omega^{-1}\cdot cm^{-1}$. The activation energies calculated for the measured conductivity of the pure sample and sample prepared with 1 mol% of nanosized SnO_2 additive were 0.31 and 0.35 eV, respectively. The smaller grain size and higher grain-boundary volume in the sample with 1 mol% of SnO_2 can be considered as a reason for its higher activation energy [36,37]. Since the Arrhenius plots of the conductivity data tend to converge at low temperatures (Fig. 6), it can be suggested that the effect of nanosized SnO_2 additive is manifested in the bulk resistance. The conversion to β''-Al_2O_3 phase can have the most pronounced effect in increasing the ionic conductivity (even up to factors of 4 to 5) [16,17]. Therefore, with the addition of nanosized SnO_2 sintering aid, the lower sodium loss, higher amount of β''-Al_2O_3 phase and higher density may lead to the decrease in bulk resistance and thus increase ionic conductivity.

IV. Conclusions

In this study, the effect of nanosized SnO_2 additive as sintering aid on the properties and microstructure of sodium beta alumina ceramics, synthesized by the solid state process, has been investigated. The results indicated that the addition of 1 mol% of nanosized SnO_2 decreases sintering temperature of sodium beta alumina ceramics for about 100 °C, increases the percentage of β''-Al_2O_3 phase from 95% to 99% and improves uniformity of microstructure. As a result, both the fracture strength and the ionic conductivity of the sample are also improved effectively.

References

1. M.N. Rahaman, *Ceramic Processing and Sintering*, New York, Marcel Dekker, 1995.
2. Q. Meng, Z. Zhao, Y. Sun, X. Li, H. Ji, "Low temperature pressureless sintering of dense silicon nitride using BaO-Al_2O_3-SiO_2 glass as sintering aid", *Ceram. Int.*, **43** (2017) 10123–10129.
3. N. Lamrani, A. Chaouchi, J. Bernard, B. Itaalit, D. Houivet, J.M. Haussonne, M. Aliouat, "Influence of Li_2CO_3 and V_2O_5 combined additions on the sintering and dielectric properties of $Ca_{0.5}Sr_{0.5}TiO_3$ ceramics prepared from powders synthesized by sol-gel method", *Proc. Appl. Ceram.*, **8** (2014) 101–108.
4. X. Lu, G. Li, J.Y. Kim, K.D. Meinhardt, V.L. Sprenkle, "Enhanced sintering of β''-Al_2O_3/YSZ with the sintering aids of TiO_2 and MnO_2", *J. Power Sources*, **295** (2015) 167–174.
5. X. Xu, Y. Yang, X. Wang, X. Su, J. Liu, "Low-temperature preparation of Al_2O_3-ZrO_2 nanoceramics via pressureless sintering assisted by amorphous powders", *J. Alloy. Compd.*, **783** (2019) 806–812.
6. H. Ahmadi Moghadam, M.H. Paydar, "Investigation of Sm_2O_3 additive on mechanical and electrical properties of Li_2O-stabilized β''-alumina electrolyte", *Int. J. Appl. Ceram. Technol.*, **14** (2017) 1183–1189.
7. B. Mirhadi, B. Mehdikhani, "Effect of calcium fluoride on sintering behaviour of SiO_2-CaO-Na_2O-MgO glassceramic system", *Proc. Appl. Ceram.*, **6** (2012) 159–164.
8. M.R. Saeri, A. Barzegar, H. Ahmadi Moghadam, "Investigation of nano particle additives on lithium doped KNN lead free piezoelectric ceramics", *Ceram. Int.*, **37** (2011) 3083–3087.
9. H.R. Zargar, C. Oprea, G. Oprea, T. Troczynski, "The effect of nano-Cr_2O_3 on solid-solution assisted sintering of MgO refractories", *Ceram. Int.*, **8** (2012) 6235–6241.
10. S. Huang, Q. Li, Z. Wang, X. Cheng, H. Wen, "Effect of sintering aids on the microstructure and oxidation behavior of hot-pressed zirconium silicate ceramic", *Ceram. Int.*, **43** (2017) 875–879.
11. H. Ahmadi Moghadam, A. Barzegar, "Low-temperature sintering of $K_{0.5}Na_{0.5}NbO_3$ lead free ceramics using nano CuO sintering aid", *J. Mater. Sci. Mater. Electron.*, **28** (2017)13161–13167.
12. E. Li, H. Kakemoto, S. Wada, T. Tsurumi, "Influence of CuO on the structure and piezoelectric properties of the alkaline niobate-based lead-free ceramics", *J. Am. Ceram. Soc.*, **90** (2007) 1787–1791.
13. F. Rubio-Marcos, J.J. Romero, M.G. Navarro-Rojero, J.F. Fernandez, "Effect of ZnO on the structure, microstructure and electrical properties of KNN-modified piezoceramics", *J. Eur. Ceram. Soc.*, **29** (2009) 3045–3052.
14. J.L. Sudworth, A.R. Tiley, *The Sodium Sulphur Battery*, London, Chapman and Hall, 1985.
15. H. Li, H. Fan, J. Zhang, Y. Wen, G. Chen, Y. Zhu, J. Lu, X. Jiang, B. Hu, L. Ning, "Sintering behavior and properties of lithium stabilized sodium β''-alumina ceramics with YSZ addition", *Ceram. Int.*, **45** (2019) 6744–6752.
16. X. Lu, G. Xia, J.P. Lemmon, Z. Yang, "Advanced materials for sodium-beta alumina batteries: Status, challenges and perspectives", *J. Power Sources*, **195** (2010) 2431–2442.
17. R.M. Dell, P.T. Moseley, "Beta-alumina electrolyte for use in sodium/sulphur batteries: Part I. Fundamental properties", *J. Power Sources*, **6** (1981) 143–160.
18. N.L. Canfield, J.Y. Kim, J.F. Bonnett, R.L. Pearson III, V.L. Sprenkle, K. Jung, "Effects of fabrication conditions on mechanical properties and microstructure of duplex β''-Al_2O_3 solid electrolyte", *Mater. Sci. Eng. B*, **197** (2015) 43–50.
19. R. Subasri, T. Mathews, O.M. Sreedharan, V.S. Raghunathan, "Microwave processing of sodium beta alumina", *Solid State Ionics*, **158** (2003) 199–204.
20. Y. Sheng, P.S. Nicholson, "Microstructural development of a ZrO_2 $Na\beta''$-Al_2O_3 composite", *J. Mater. Sci.*, **23** (1988) 982–986.
21. D. Xu, H. Jiang, M. Li, O. Hai, Y. Zhang, "Synthesis and characterization of Y_2O_3 doped Na-β''-Al_2O_3 solid electrolyte by double zeta process", *Ceram. Int.*, **41** (2015) 5355–5361.
22. S.J. Visco, M. Liu, F. Lin, P. Kimes, L.C. De Jonghe, "Properties and morphology of doped polycrystalline Na-β''-alumina electrolytes", *Solid State Ionics*, **62** (1993) 185–191.
23. H. Ahmadi Moghadam, M.H. Paydar, "The effect of nano CuO as sintering aid on phase formation, microstructure and properties of Li_2O-stabilized beta"-alumina ceramics", *J. Ceram. Sci. Technol.*, **7** (2016) 441–446.
24. X. Wei, Y. Cao, L. Lu, H. Yang, X. Shen, "Synthesis and characterization of titanium doped sodium beta"-alumina", *J. Alloys Compd.*, **509** (2011) 6222–6226.
25. A. Pekarsky, P.S. Nicholson, "The relative stability of spray-frozen/freeze-dried β''-Al_2O_3 powders", *Mater. Res. Bull.*, **15** (1980) 1517–1524.
26. W.A. Curtin, "Theory of mechanical properties of ceramic-matrix composites", *J. Am. Ceram. Soc.*, **74** (1991) 2837–2845.
27. K.M. Lee, S.T. Lee, D.H. Lee, S.M. Lee, S.K. Lim, "Phase formation of Na^+-beta-aluminas synthesized by double zeta process", *J. Ind. Eng. Chem.*, **19** (2013) 829–834.
28. W.L. Roth, I. Chung, H.S. Story, "Characterization of additive-modified beta alumina ceramics by nuclear magnetic resonance", *J. Am. Ceram. Soc.*, **60** (1977) 311–315.
29. J.P. Bioloy, J. Thery, "Influence de l'addition d'ions etrangers sur la stabilite relative et la conductivite electrique des phases de type alumine β et β''", *Mater. Res. Bull.*, **11** (1976) 407–413.
30. Z. Fu, P. Liu, J. Ma, B. Guo, X. Chen, H. Zhang, "Microwave dielectric properties of low-fired Li_2SnO_3 ceramics co-doped with MgO-LiF", *Mater. Res. Bull.*, **77** (2016) 78–83.
31. J.L. Hodeau, M. Marezio, A. Santoro, R.S. Roth, "Neutron profile refinement of the structures of Li_2SnO_3 and Li_2ZrO_3", *J. Solid State Chem.*, **45** (1982) 170–179.
32. S. Su, R. Zuo, X. Wang, L. Li, "Sintering, microstructure and piezoelectric properties of CuO and SnO_2 co-modified sodium potassium niobate ceramics", *Mater. Res. Bull.*, **45** (2010) 124–128.
33. X. Fan, E.D. Case, I. Gheorghita, M.J. Baumann, "Weibull modulus and fracture strength of highly porous hydroxyapatite", *J. Mech. Behav. Biomed. Mater.*, **20** (2013) 283–295.
34. O. Tokariev, L. Schnetter, T. Beck, J. Malzbender, "Grain size effect on the mechanical properties of transparent spinel ceramics", *J. Eur. Ceram. Soc.*, **33** (2013) 749–757.
35. H. Ahmadi Moghadam, M.H. Paydar, "Mechanical properties and reliability of Li_2O-stabilized β''-alumina ceramics: Effect of synthesizing method", *Int. J. Appl. Ceram. Technol.*, **13** (2016) 1053–1058.

36. G.J. May, A. Hooper, "The effect of microstructure and phase composition on the ionic conductivity of magnesium doped sodium beta alumina", *J. Mater. Sci.*, **13** (1978)1480–1489.

37. C.L. Dirksen, K. Skadell, M. Schulz, M. Stelter, "Effects of TiO_2 doping on Li^+-stabilized Na-β''-alumina for energy storage applications", *Sep. Purif. Technol.*, **213** (2019) 88–92.