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The Effect of Nano CuO as Sintering Aid on Phase Formation, Microstructure and Properties of Li_2O-Stabilized β″-Alumina Ceramics

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Abstract

Li_2O-stabilized β″-alumina powder was synthesized in the double zeta process with Al_2O_3, Na_2CO_3 and Li_2CO_3 as the starting materials. The effect of nano CuO additive as the sintering aid on phase formation, microstructure, mechanical and electrical properties of Li_2O-stabilized β″-alumina ceramics was investigated by means of x-ray diffraction (XRD), scanning electron microscope (SEM), biaxial flexure test (BFT) and ionic conductivity test. The results indicated that the fracture strength of the samples improved with the addition of a low concentration of nano CuO, which can be attributed to the higher density and more uniform microstructure. The optimal amount of nano CuO was determined at about 1.5 mol%, with the addition of which the ionic conductivity was approximately twice as high as that of the sintered samples without any nano CuO.

Keywords: *β″-alumina ceramics, nano CuO, microstructure, mechanical properties, ionic conductivity*

I. Introduction

Sodium beta alumina ceramics have been studied widely because of their application as solid electrolyte in sodium-sulfur and ZEBRA batteries [1,2]. Two main subgroups of sodium beta alumina are β-Al_2O_3 (hexagonal) and β”-Al_2O_3 (rhombohedral). The β”-Al_2O_3 exhibits significantly higher ionic conductivity than β-Al_2O_3 [1–3].

Conventional synthesis of sodium beta alumina is effected based on a solid state reaction of α-Al_2O_3 with sodium compounds and a small amount of MgO and/or Li_2O as the stabilizer for the β”-Al_2O_3 phase at high temperature, usually between 1200 – 1700 °C [4,5]. The loss of Na_2O, the formation of the two-phase mixture (β-and β”-Al_2O_3) and the duplex microstructure of the resulting product obtained with the solid state reaction at high temperature are deleterious to the mechanical strength and ionic conductivity of the material [1,3]. The degree of homogeneity of the starting materials is an important factor concerning the rate of transformation and β”-alumina formation. In the so-called double zeta process, the synthesized zeta-lithium aluminate (Li_2O-5Al_2O_3) and zeta-sodium aluminate (Na_2O-5Al_2O_3) were used as precursors, which could make the distribution of Li^+ and Na^+ ions more uniform in the mixture and increase the rate of conversion to β”-Al_2O_3 phase [6,7].

The addition of oxides is demonstrated as an effective way to improve the properties of conventional ceramics, such as densification characteristics, mechanical, magnetic and electrical properties [8–14]. In other works, researchers reported that some of the cations, such as Ni^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+} and Ti^{4+}, can be located in the spinel block to stabilize the β”-Al_2O_3 structure and increase the ionic conductivity of the electrolyte [15–17]. The effect of trace concentrations of metal oxides, ZnO, MgO, Nb_2O_3 and Ge_2O_3, on the resistivity of sodium beta alumina electrolyte has also been investigated [14]. Using sintering aids with nano particle size can reduce the required amount of sintering aids and improve the properties of the sintered products [18,19]. However, not only is no report available on the effect of using nano oxide particles as sintering aids on the densification characteristics and properties of β″-alumina ceramics, there have been no reports on the influence of CuO as a sintering aid on the mechanical properties and ionic conductivity of sodium beta alumina electrolyte. But, the influence of CuO as a sintering aid on the densification characteristics of different ceramics has been confirmed in many reports. The CuO additive significantly improved the densification behavior of the ceramics, which was attributed to the formation of a liquid phase during sintering [20–23]. In the present work, we study the effect of nano CuO additive as a sintering aid on the densification and mechanical and electrical properties of β″-alumina ceramic.

II. Material and Methods

(1) Synthesis method

Li_2O-stabilized β″-alumina was synthesized in the double zeta process [7]. In this method, two compounds of Na_2O-5.4Al_2O_3 and Li_2O-5Al_2O_3, designated zeta-sodium aluminate and zeta-lithium aluminate, respectively, were synthesized based on a solid state reaction. In

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this step, Na_2CO_3 and Li_2CO_3 were used as starting materials and were mixed separately with analytically pure α-Al_2O_3, in ethanol. After that, the two mixtures were calcined at 1250 °C for 2 h. According to the chemical formula of Li_2O-stabilized β″-alumina as $Na_{1.67}Al_{10.67}Li_{0.33}O_{17}$, the required mixing ratio of Na_2O-5.4Al_2O_3 and Li_2O-5Al_2O_3 was determined. The two precursors were then mixed in appropriate ratio by means of ball milling in ethanol for 15 h. After drying, the precursor powder was calcined at 1300 °C for 2 h. High-purity nano CuO powder (99.9 %, ≤ 80 nm, Advanced Materials US) was used as a sintering aid. Required amounts of nano CuO (0.5, 1.5 and 2.5 mol%) were mixed with synthesized powder by means of attrition milling using 5-mm zirconia balls in the ethanol medium for 4 h with a fixed rotation speed of 480 rpm. After the slurries had been dried, the powders were ground to < 60 mesh. To prepare the green disk samples in dimension of ∅12 mm × 2 mm, the powder was pressed under the uniaxial stress of 250 MPa. To minimize sodium loss and prevent excess grain growth, the green samples were placed in an alumina crucible and then covered with the same composition of β″-alumina powder and sintered at 1620 °C for 15 min with the heating rate of 4 K/min. During the cooling process, the samples were annealed at 1450 °C for 45 min in order to accelerate the formation of β″-alumina [1]. For investigation of the effect of annealing, some pure samples were not annealed.

(2) Characterization techniques

Phase identification of the calcined powders and the sintering samples was performed by means of X-ray diffraction (XRD) using Cu-K_α radiation (λ = 1.5418Å) over the range of 5 – 75° (2θ) with a Bruker AXS D8 ADVANCE diffractometer. The lattice constants were determined using the X-ray diffraction patterns and Full Prof program. The relative phase fractions of β-Al_2O_3 and β″-Al_2O_3 were determined according to Pekarsky's formula f(β) as follows [24]:

$$f(\beta'')\% = 100 - f(\beta)\% = 100 - 1.14I_\beta/(1.14I_{\beta+} I_{\beta''}) \quad (1)$$

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

The density of sintered samples was measured with an Archimedean method in ethanol as immersion medium. The microstructure of the sintered samples was investigated by means of scanning electron microscope (SEM, Leica Cambridge S-360, Cambridge Co., Cambridge, UK). For the SEM observations, the specimens were polished to a mirror finish and then thermally etched at 1550 °C for 15 min in air. In this study, the fracture strength of the sintered samples was determined in the biaxial flexure test (BFT). In biaxial flexure testing, the load is applied by a loading ring to a disc specimen placed on a support ring (termed "ring on ring testing", ASTM C1499, 2003). The ionic conductivity of the ceramics was obtained from the AC 2-probe impedance plots examined on a frequency response analyzer (Solartron 1260, Solartron Analytical) over a frequency range of 1 Hz to 5 MHz with the symmetric platinum electrodes and in a temperature range of 200 – 500 °C.

III. Results and Discussion

The successful formation of high-quality precursors of Li_2O-5Al_2O_3 and Na_2O-5.4Al_2O_3 powders was confirmed in XRD patterns. The x-ray diffraction patterns of the Li_2O-stabilized β″-alumina specimens after calcination, sintering and annealing are shown in Fig. 1. According to the XRD patterns (Fig. 1) and by using Eq. (1), the volume fraction of β″-Al_2O_3 phase of Li_2O-stabilized β″-alumina specimens after the calcination, sintering and annealing processes was determined to be 85, 92 and 96 %, respectively. It has been reported that the rate of densification is generally faster than the rate of phase conversion, therefore by annealing the sintered specimen at a temperature 50 to 200 °C lower than the sintering temperature, conversion can be completed without resulting in any undesirable grain growth [1].

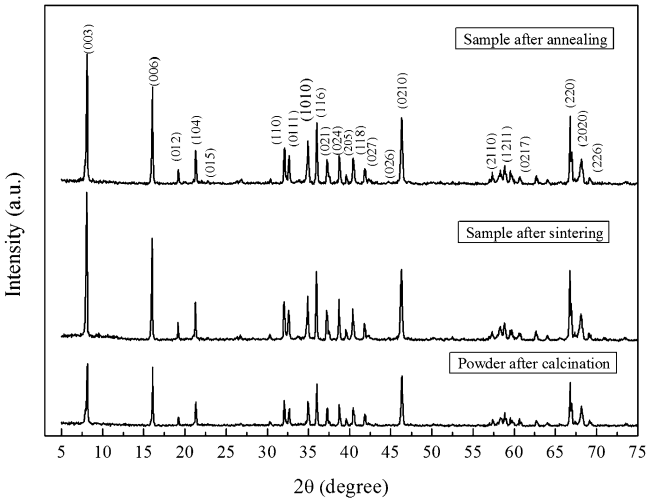

Fig. 1: XRD patterns of Li_2O-stabilized β″-alumina specimens after the calcination, sintering and annealing processes.

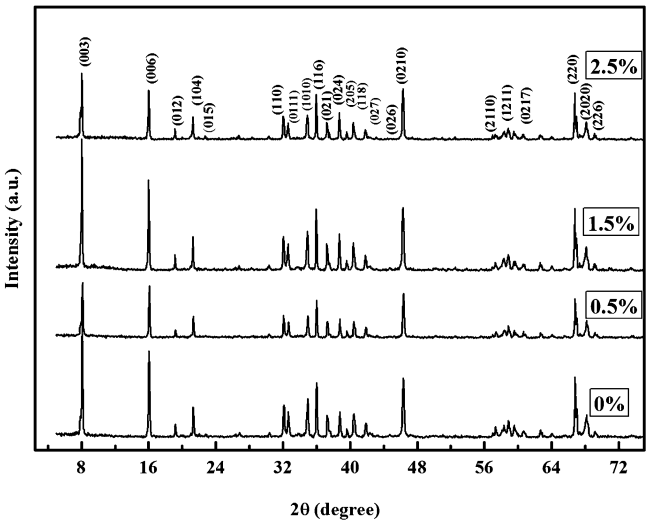

Fig. 2: X-ray diffraction patterns of the samples containing different amounts of nano CuO.

Fig. 2 shows the typical x-ray diffraction patterns of the samples with different amounts of nano CuO. The XRD patterns of all samples conformed to the pure crystalline phase of $Na_{1.67}Al_{10.67}Li_{0.33}O_{17}$. According to the XRD patterns, no impurity phases can be detected, which is

due to the low concentration of nano CuO additive. The β″-Al_2O_3 phase content with various amounts of nano CuO is summarized in Table 1. With the addition of nano CuO up to 2.5 mol%, the content of β″-Al_2O_3 phase reaches 99 %, which is about 3 % higher than that of the pure sample. According to Boilot and Thery's theory, because the ionic radius of the Cu^{2+} cation (0.087 nm) is smaller than 0.097 nm, $Cu^{2+}$is able to occupy Al^{3+} positions in the spinel block on the way to stabilizing the structure of the β″-Al_2O_3 phase [15].

As can be seen in Fig. 3, both the a and the c lattice constants of samples decreased with increasing amount of nano CuO used. Since Cu^{2+} is able to enter the spinel block, the decrease in the lattice constant can be attributed to the smaller ionic radius of Cu^{2+} in respect of Al^{3+} and the electrostatic effects [15–17].

Fig. 4 shows cross-section SEM micrographs of the sintered samples without nano CuO and for the one containing 1.5 mol% nano CuO. The dense microstructure with no pores or cracks through the ceramic was an indication of the high density of the sintered samples. The density of all samples was high (> 97 % of theoretical density) and it improved with the addition of nano CuO (Table 1). The SEM images of the thermally etched samples are shown in Fig. 5. These images reveal that the addition of nano CuO causes enormous changes in the microstructure. Fig. 5 shows that the addition of nano CuO resulted in a more uniform microstructure. With the addition of nano CuO, the grain shape changed from needle-like to spherical shape, which is probably due to the appearance of liquid phase at or below the sintering temperature, which may be formed in the grain boundary of the samples [14, 19].

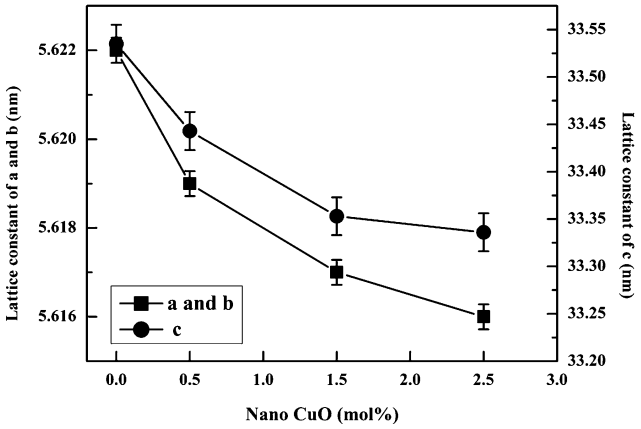

Fig. 3: Calculated lattice constant of the specimens containing different amounts of nano CuO.

Table 1: Properties of Li_2O Na-β″-alumina electrolyte containing various amounts of nano CuO.

Property	Relative density (± 0.2 %)	Content of β″-Al_2O_3 (± 0.5 %)	Average strength (MPa)	Conductivity at 350 °C (± 0.002 Ω·cm)$^{-1}$	Activation energy (± 0.005 e.V)
Pure	97.3	96	150 ± 22	0.056	0.36
0.5 mol% nano CuO	98.5	98	162 ± 26	0.073	0.35
1.5 mol% nano CuO	99.2	99	176 ± 29	0.121	0.33
2.5 mol% nano CuO	99.5	99	191 ± 25	0.112	0.34

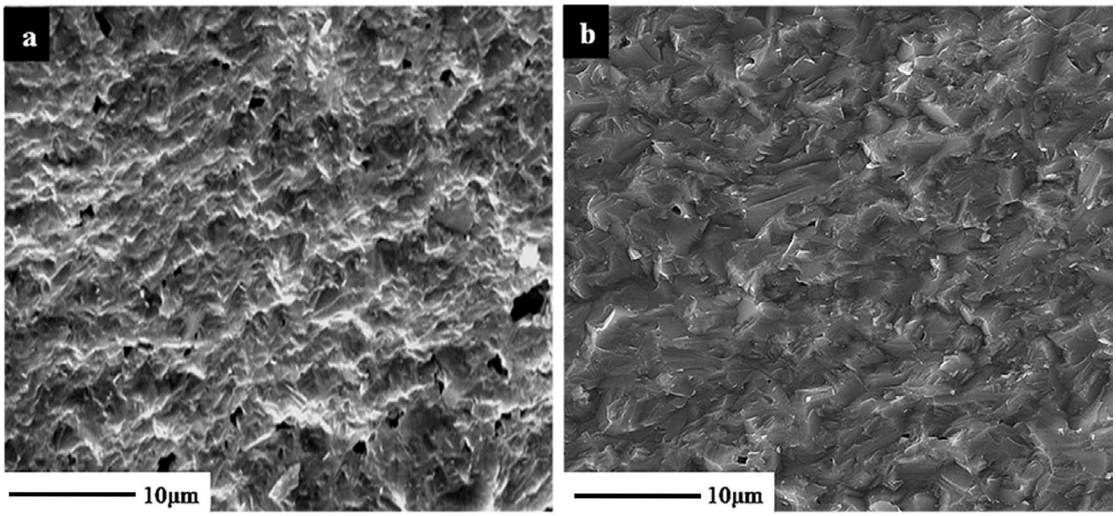

Fig. 4: Cross-section SEM micrographs of the Li_2O-stabilized β″-alumina samples (a) pure and (b) containing 1.5 mol% nano CuO additive.

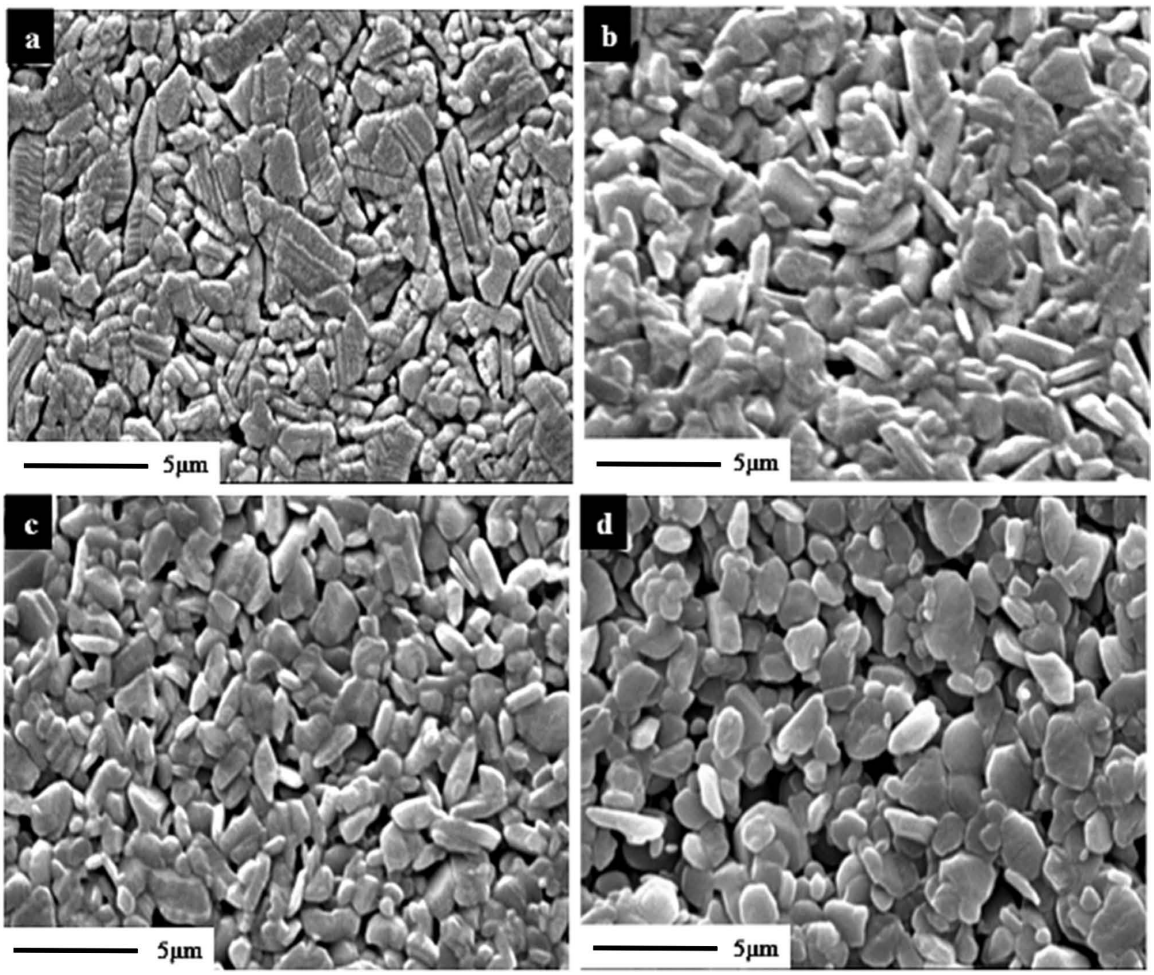

Fig. 5: SEM micrographs of thermally etched Li_2O-stabilized β″-alumina samples containing different amounts of nano CuO a) pure, b) 0.5, c) 1.5 and d) 2.5 mol%.

The biaxial flexure test was applied on 10 samples for each composition. The average fracture strength of the samples containing different amounts of nano CuO are presented in Table 1. The average fracture strength of the specimens was enhanced noticeably by increasing the amounts of nano CuO. The fracture strength of the specimens with 2.5 mol% nano CuO exceeded 190 MPa, while the fracture strength of the pure sample was 150 MPa. The results of other researchers confirm that a little increase in the density of the sintered samples significantly increases its strength [10, 25]. Consequently, the uniform microstructure and higher density can cause the higher fracture strength based on the addition of a small amount of nano CuO.

The ionic conductivity of samples containing different amounts of nano CuO at different temperatures is shown in Fig. 6. According to the results, the ionic conductivity of the electrolyte improves dramatically in the presence of nano CuO sintering aid. The Li_2O-stabilized Na- β″-alumina sample containing 1.5 mol% nano CuO exhibited more than twice the ionic conductivity of the pure sample. The relationship of the ionic conductivity and the temperature of sodium beta alumina electrolyte obeys the Arrhenius law [1]. Fig. 7 presents the Arrhenius plots of the measured ionic conductivity (σ) for the samples without nano CuO and with 1.5 mol% nano CuO in the temperature range from 200 to 500 °C. The degree of phase conversion and grain size affect the resistivity and the activation energy for Na^+ diffusion of the Li_2O-stabilized Na- β″-alumina electrolyte [14, 17].

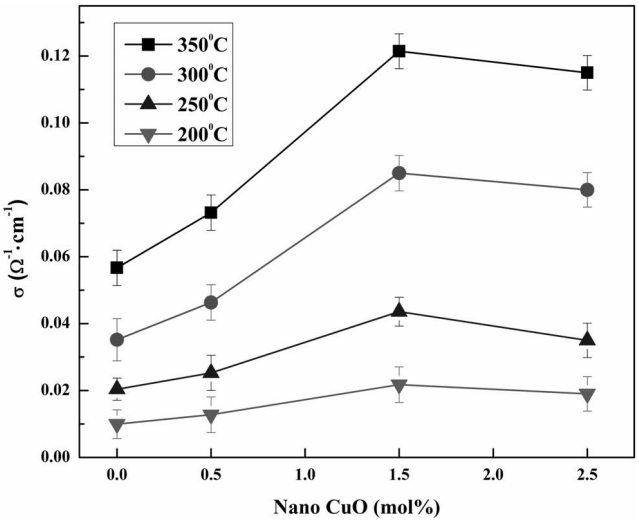

Fig. 6: Ionic conductivity of the specimens containing different amounts of nano CuO as a function of temperature.

Replacement of Al^{3+} ions by cations with a lower valence may be charge-compensated by additional Na^+ ions in the conduction plane and by the elimination of interstitial oxygen ions from the conduction plane which block

Na^+ diffusion. Therefore, the CuO additive can enhance conductivity by increasing the concentration of interstitial Na^+ ion and by removing the barriers to Na^+ ion diffusion [26,27]. 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) [28]. So this higher ionic conductivity in the presence of nano CuO sintering aid can be attributed to the higher amount of β″-Al_2O_3 phase, higher density and more uniform microstructure. In this study, the optimal amount of nano CuO sintering aid was determined at about 1.5 mol% so that the fracture strength and the ionic conductivity were approximately 176 MPa and 0.121 $(\Omega \cdot cm)^{-1}$ at 350 °C, respectively.

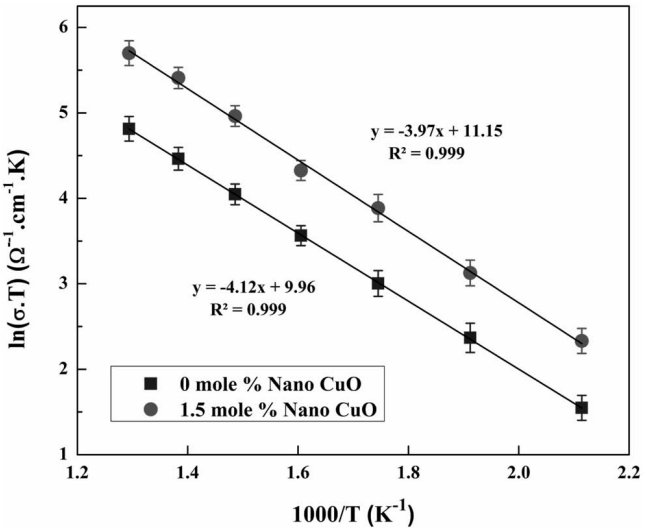

Fig. 7: Arrhenius plots of the conductivity versus temperature for the pure sample and the sample containing 1.5 mol% nano CuO.

IV. Conclusions

In this study, the effect of nano CuO additive as a sintering aid on the properties and microstructure of β″-alumina ceramics, which had been synthesized in the double zeta process, has been investigated. The obtained results indicated that with the addition of a low concentration of nano CuO, both the fracture strength and the ionic conductivity of the samples were improved effectively. The higher fracture strength can be attributed to the uniform microstructure and higher density. With addition of nano CuO, the amount of β″-Al_2O_3 phase, and the uniformity of the microstructure of the sintered samples were increased. As a result, the conductivity of the samples was improved.

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References

1 Sudworth, J.L., Tilley, A.R.: The sodium sulphur battery. Chapman & Hall, London, 1985.

2 Ormrod, S.E., Kirk, D.L.: The conduction properties of polycrystalline β″-alumina, *J. Appl. Phys.*, **10**, 1769 – 1780, (1977).

3 Lu, X., Xia, G., Lemmon, J., Yang, Z.: Advanced materials for sodium-beta alumina batteries: status, challenges and perspectives, *J. Power. Sources.*, **195**, 2431 – 2442, (2010).

4 Virkar, A.V., Miller, G.R., Gordon, R.S.: Resistivity-microstructure relations in lithia-stabilized polycrystalline β″-alumina, *J. Am. Ceram. Soc.*, **61**, 250 – 252, (1978).

5 Oshima, T., Kajita, M., Okuno, A.: Development of sodium-sulfur batteries, *Int. J. Appl. Ceram. Technol.*, **1**, 269 – 276, (2004).

6 Chen, K.G., Lin, Z.X., Fan, Z.Z., Xu, X.H., Wen, Z.Y., Yu, B.Q.: Preparation of Na-β″-Al_2O_3 by partial synthesis method, *J. Inorg. Mater.*, **12**, 725 – 728, (1997).

7 Lee, K.M., Lee, S.T., Lee, D.H., Lee, S.M., Lim, S.K.: Phase formation of Na-beta-aluminas synthesized by double zeta process, *J. Ind. Eng. Che.*, **19**, 829 – 834, (2013).

8 Nemati, A., Surani, F., Abdizadeh, H., Baharvandi, H.R.: The effects of nano mgo on physical and mechanical properties of Al_2O_3-SiC composites, *J. Ceram. Sci. Tech.*, **3**, 29 – 34, (2012).

9 Zhang, T.S., Kong, L.B., Du, Z.H., Ma, J., Li, S.: Tailoring the microstructure of mechanoactivated $Al_2O_3$and SiO_2 mixtures with TiO_2 addition., *J. Alloy. Compd.*, 506, 777 – 783, (2010).

10 Xu, D., Jiang, H., Li, M., Hai, O., Zhang, Y.: Synthesis and characterization of Y_2O_3 doped Na-β″-Al_2O_3 solid electrolyte by double zeta process, *Ceram. Int.*, **41**, 5355 – 5361, (2015).

11 Du, G.P., Hu, Z.J., Han, Q.F., Qin, X.M., Shi, W.Z.: Effects of niobium donor doping on the phase structures and magnetic properties of Fe-doped $BaTiO_3$ ceramics, *J. Alloy. Compd.*, **492**, L79 – L81, (2010).

12 Yang, L.P., Shan, S.J., Wei, X.L., Liu, X.M., Yang, H., Shen, X.D.: The mechanical and electrical properties of ZrO_2-TiO_2-Na-β/β″-alumina composite electrolyte synthesized via a citrate sol-gel method, *Ceram. Int.*, 40, 9055 – 9060, (2014).

13 Xu, Y., Fu, R., Yang, Y., Cai, J., Gu, X., Fang, J.: Raman spectra and dielectric properties of $Ca_{0.66}Ti_{0.66}La_{0.34}Al_{0.34}O_3$ microwave ceramics with Nd^{3+} additions, *J. Ceram. Sci. Tech.*, 7, 257 – 262, (2016).

14 Visco, S.J., Liu, M., Lin, F., Kimes, P., Jonghe, L.C. D.: Properties and morphology of doped polycrystalline Na-β″-alumina electrolytes, *Solid State Ionics*, **62**, 185 – 191, (1993).

15 Boilot, J.P., Thery, J.: Influence of the addition of foreign ions on the relative stability and electrical conductivity of β and β″ alumina type phases, (in French), *Mater. Res. Bull.*, **11**, 407 – 413, (1976).

16 Boilot, J.P., Kahn, A., Thery, J., Collongues, R., Antoine, J., Vivien, D., Chevrette, C., Gourier, D.: Influence of foreign ions addition on relative stability and electrical conductivity of β and β″ alumina type phases localization of impurities, *Electrochim. Acta.*, **22**, 741 – 745, (1977).

17 Wei, X.L., Cao, Y., Lu, L., Yang, H., Shen, X.D.: Synthesis and characterization of titanium doped sodium beta″-alumina, *J .Alloy. Compd.*, **509**, 6222 – 6226, (2011).

18 Hayati, R., Barzegar, A.: Microstructure and electrical properties of lead free potassium sodium niobate piezoceramics with nano ZnO additive, *Mater. Sci. Eng. B.*, **172**, 121 – 126, (2010).

19 Saeri, M.R., Barzegar, A., Ahmadi Moghadam, H.: Investigation of nano particle additives on lithium doped KNN lead free piezoelectric ceramics, *Ceram. Int.*, **37**, 3083 – 3087, (2011).

20 Sun, Y., Chang. Y., Wu, J., Wang, X., Zhang, S., Wang, R., Yang, B., Cao, W.: Domain structures and piezoelectric properties of low-temperature sintered $(Ba_{0.95}Ca_{0.05})(Ti_{0.94}Sn_{0.06})O_3$ ceramics with CuO additive, *Mater. Lett.*, 177, 128 – 131, (2016).

[21] Chen, W.S., Tseng, C.F., Lee, Y.M., Tung, H.H., Yang, H.T., Hsu, C.H.: Effect of CuO additives on sintering and dielectric behaviors of CeO_2 ceramics, *J. Mater. Process. Tech.*, **209**, 2277 – 2281, (2009).

[22] Azough, F., Wegrzyn, M., Freer, R., Sharma, S., Hall, D.: Microstructure and piezoelectric properties of CuO added (K, na, Li)NbO_3 lead-free piezoelectric ceramics, *J. Eur. Ceram. Soc.*, **31**, 569 – 576, (2011).

[23] Seoa, T., Choi, J. H,. Nahma, S., Lee, H. G.: Effect of CuO on the sintering temperature and piezoelectric properties of MnO_2-doped $0.75Pb(Zr_{0.47}Ti_{0.53})O_3$-$0.25Pb(Zn_{1/3}Nb_{2/3})O_3$ ceramics, *J. Alloy. Compd.*, **509**, 3686 – 3689, (2011).

[24] Pekarsky, A., Nicholson, P.S.: The relative stability of spray-frozen/freeze-dried β″-Al_2O_3 powders, *Mat. Res. Bull.*, **15**, 1517 – 1524, (1980).

[25] Jones, I.W.: Recent advances in the development of sodium-sulphur batteries for load levelling and motive power applications, *Electrochim. Acta.*, **22**, 681 – 688, (1977).

[26] Gordon, R.S., McEntire, B.J., Miller, M.L., Virkar, A.V.: Processing and characterization of polycrystalline β″– alumina ceramic electrolytes. In: Processing of crystalline ceramics. Palmour, H., Davis, R. F., Hare, T. M., Plenum Press, New York, 1978, pp. 405 – 420.

[27] Roth, W.L., Chung, I., Story, H. S.: Characterization of additive-modified beta alumina ceramics by nuclear magnetic resonance, *J. Am. Ceram. Soc.*, **60**, 311 – 315, (1977).

[28] Dell, R.M., Moseley, T.: Beta-alumina electrolyte for use in sodium/sulfur batteries: part 1. fundamental properties, *J. Power. Sources.*, **6**, 143 – 160, (1981).