Synthesis and characterization of NiO doped beta-Al₂O₃ solid electrolyte

Chengfei Zhu*, Yongfei Hong, Pan Huang

College of Materials Science and Engineering, Nanjing Tech University,

5 Xinmofan Road, Nanjing, Jiangsu 210009, PR China

Abstract

The beta-Al₂O₃ solid electrolyte with NiO doped and Li₂O stabilized is synthesized via the solid state reaction method, which is starting with α -Al₂O₃, Li₂CO₃, Na₂C₂O₄ and Ni(NO₃)₂·6H₂O as the raw materials. Effects of the NiO content on the mechanical and electrical performances are studied by means of thermogravimetry/differential scanning calorimetry (TG/DSC), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Meanwhile, the relative density, the bending strength and the electrical properties of the prepared samples are also measured in this paper. The beta-Al₂O₃ solid electrolyte with the appropriate amount of NiO has a higher β'' -Al₂O₃ phase content and uniform microstructure with dense and plump grains. However, the excess NiO doping can lead the grain to molten state and make the pores become larger. It deteriorates the ionic conductivity. When the NiO content of the beta-Al₂O₃ solid electrolyte is 0.25wt%, the β'' -Al₂O₃ phase

* Corresponding author. [Tel:+86 25 83172117](tel:+862583172117) Fax:+86 25 83172118
E-mail address: zhucf@njtech.edu.cn(C.-F. Zhu)

content is 98.91%, the microstructure is uniform and compact, the relative density is 98.73% of theoretical density, the bending strength is up to 296 MPa and the ionic conductivity can reach 0.066 S cm^{-1} at 350°C .

Keywords: Sodium-sulfur battery; $\beta\text{-Al}_2\text{O}_3$ solid electrolyte; NiO doping; bending strength

1. Introduction

As a new energy storage battery, sodium sulfur batteries have many advantages, such as high specific energy, high charge and discharge power, long cycle life, low cost, no pollution and so on [1-5]. It takes $\beta\text{-Al}_2\text{O}_3$ as an electrolyte and separator, sodium polysulfide and sodium metal as the positive electrode and the negative electrode in the sodium sulfur batteries, respectively. The operating temperature of sodium sulfur battery is $300\text{-}350^\circ\text{C}$, so the requirements on the $\beta\text{-Al}_2\text{O}_3$ solid electrolyte are very strict. More and more people pay attention to studying the preparation and performance of the $\beta\text{-Al}_2\text{O}_3$ solid electrolyte in the sodium-sulfur batteries.

In order to improve the ionic conductivity and mechanical property of the Na- $\beta\text{-Al}_2\text{O}_3$ solid electrolyte, some elements were doped in the matrix material. For example, it could improve the conductivity by adding an appropriate amount of Li_2O or MgO to the $\beta\text{-Al}_2\text{O}_3$ solid electrolyte [6-10]. But it decreased the mechanical properties at the same time. Shan et al. [11] pointed out that the bending strength of the $\beta\text{-Al}_2\text{O}_3$ solid electrolyte was up to 180 MPa by using TiO_2 doping. Sheng et al.

[12,13] found the flexural strength increased with the increasing of the content of ZrO_2 . Yang et al. [14] studied the $\beta\text{-Al}_2\text{O}_3$ solid electrolyte by adding ZrO_2 to increase the mechanical properties and adding TiO_2 to enhance the conductivity. Xu et al. [15] found that a small amount of Y_2O_3 could improve the mechanical strength and electrical conductivity by using the double zeta process to prepare the $\beta\text{-Al}_2\text{O}_3$ solid electrolyte.

However, the Ni doping could increase the density, the superconducting properties and the toughness of Bi-2212 superconducting ceramics [16]. Ma [17] found that NiO doping could improve sintering properties and electrical conductivity of 4YSZ. Xiao et al. [18], who doped with different concentrations of Ni in $\text{Bi}_4\text{NdTi}_3\text{FeO}_{15}$ ceramics, found that a small amount of Ni doping didn't change the structure of ceramic but improved the properties. Das et al. [19] pointed out that the magnetic of BTO ceramics was also enhanced with the increasing of the NiO concentration. So the NiO doping in ceramics could not only improve the ceramic sintering activity, but also enhance the conductivity and mechanical properties. But there are no reports about the effect of NiO doping on the performance of the $\beta\text{-Al}_2\text{O}_3$ solid electrolyte currently.

The $\beta\text{-Al}_2\text{O}_3$ solid electrolyte is often synthesized by solid state reaction method [20-23] or novel soft-chemical methods such as sol-gel processing [10,11], alkoxide hydrolysis [24,25], solution combustion technique [26], co-precipitation [27] and electrophoretic deposition [28]. The solid state reaction method is both economic and easy to carry out, so it is used in this article.

In this paper, we investigate the effects of NiO doping on the mechanical and electrical properties of the beta-Al₂O₃ solid electrolyte by thermogravimetry/differential scanning calorimetry (TG/DSC), X-ray diffraction (XRD), scanning electron microscopy (SEM). The relative density, mechanical strength and ionic conductivity are also measured and discussed in detail.

2. Experimental

2.1. Synthesis

The beta-Al₂O₃ solid electrolytes with different contents of NiO were synthesized via the solid state reaction method using high-purity α -Al₂O₃(model VK-L30), Na₂C₂O₄(AR), and Li₂CO₃(AR). The stabilizer was Li₂O. Then the mixed powders were divided into 9 groups and added NiO with 0wt%, 0.01wt%, 0.05wt%, 0.1wt%, 0.15wt%, 0.25wt%, 0.50wt%, 1wt%, 1.5wt% ratios, respectively. The 9 groups were ball-milled in an absolute alcohol medium for 10 h with the fixed rotation speed of 400 rpm, dried at 80 °C, and then calcined at 1250 °C for 2h. These products were the precursor powders of beta-Al₂O₃. The precursor powders were ball-milled with ethanol for another 10h, then dried, and mixed with an appropriate amount of 5wt% polyvinyl alcohols. In order to prepare the ceramic samples, the powder was pressed into two sizes: 3 mm (D) × 4 mm (W) × 40 mm (L) and Φ16 mm×2 mm (D). The green ceramics were covered with the precursor powders and fired at 1600 °C for 10 min. In order to accelerate the formation of β''-Al₂O₃, 2 h holding time at 1450 °C in the cooling process was added.

2.2. Characterization

The thermal stabilities of the powders were analyzed by using a thermogravimetric analyzer (TG, STA449C, Netzsch, Germany) and a differential scanning calorimeter (DSC, 204/1/F, Netzsch, Germany) from room temperature (20°C) to 1400 °C in air atmosphere, with a heating rate of 10 °C min⁻¹.

To determine the phase composition of the precursor powders and sinters, X-ray diffractometer (XRD, Rigaku, Japan) analysis was carried out for all the samples with Cu K α radiation ($\lambda=1.5406\text{\AA}$). The scanning speed was 10° min⁻¹ in the 2 θ ranges from 5° to 80°. The relative ratio of Na- β -Al₂O₃ and Na- β'' -Al₂O₃ were quantitative calculated by the following equation [29].

$$f(\beta'')\% = 100 - f(\beta)\% - \frac{I_{\beta}}{I_{\beta} + 0.85I_{\beta''}} \times 100\% \quad (1)$$

Where I_{β} and $I_{\beta''}$ were the peak intensities at 44.50° and 45.90°, respectively. $f(\beta'')\%$ and $f(\beta)\%$ were the relative ratio of Na- β'' -Al₂O₃ and Na- β -Al₂O₃, respectively.

The microstructure of the sinters was observed by a scanning electron microscope (SEM, JEOL, JSM5900). The discs were cut into small pieces, polished, and etched by the boiling phosphoric acid for 45s. The cross sections were examined.

The bending strength measurements were performed in three point bending (span 30mm) on rectangular sintered specimens with cross-section of 3mm×4mm. They were determined on the Electronic Universal Testing Machine (CMT 6203) at room temperature (20 °C) with 0.5 mm min⁻¹ indenter loading.

The density of the sintered samples was measured using Archimedean principle

under the room temperature (20 °C). The measured density D_b (g cm^{-3}) calculated by Eq (2).

$$D_b = \frac{m_1 \cdot D_1}{m_3 - m_2} \times 100\% \quad (2)$$

Where m_1 (g) was the weigh of the dry samples, m_2 (g) was the weigh of the saturated sample suspended in the anhydrous ethanol, m_3 (g) was the weigh of the saturated sample in the air, D_1 was the density of the anhydrous ethanol at 20°C (0.7903 g cm^{-3}).

The ionic conductivity of the sintered samples was examined at 50-400°C in the air using a frequency response analyzer (Solartron 1260) and an electrochemical interface (SI 1287). The frequency range applied was from 0.1Hz to 10^7 Hz with signal amplitude of 20mV. The sintered specimens for ionic conductivity measurements were disc-shaped with the diameter of 16mm diameter and thickness of 1mm. Both faces of the pellets were carefully polished, covered with silver paste and fired afterwards to obtain silver electrode as the current collector. Then Platinum lead was well attached to the silver electrode surfaces, and impedance measurements were carried out in these two-electrode symmetric cells. The impedance spectra were analyzed by the equivalent circuit of the program Zview.

3. Results and discussion

3.1. Thermogravimetric Analysis

Fig.1 shows the TG and DSC curves of the raw material containing 0.15wt% NiO. The mass loss is 5.86wt% during 300 °C and 500 °C, and an exothermic peak is

existed near 430 °C. It should be present in the decomposition reaction of $\text{Na}_2\text{C}_2\text{O}_4$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The mass loss is 5.90wt% between 500 °C and 800°C, while an endothermic peak is existed near 768 °C in the DSC curve. It should be the melting and decomposition of Na_2CO_3 and Li_2CO_3 . During 900 °C and 1050 °C, some waves are existed in the DSC curve, but the mass is almost unchanged. It should be the phase transition process from β phase to β'' phase [30]. The DSC curve trends to the balance at about 1250 °C, it can illustrate that the phase transition to the balance. Then it combines with the literatures [6,8]. So the sintering temperature of the precursor powder is at 1250 °C in this paper.

3.2. XRD analysis of precursor powder

Fig.2 shows the XRD patterns of the precursor powders doped with different amounts of NiO. The phase of $\alpha\text{-Al}_2\text{O}_3$ exists in the samples with the NiO content of 0wt % and 0.01wt %. When the NiO content is above 0.05wt%, the XRD patterns is presented that all of the samples almost comprise both β - and β'' - Al_2O_3 phases. It can improve the sintering activity of ceramics by adding NiO [17]. According to the Eq. (1), the ratios of the β'' - Al_2O_3 phase are calculated and listed in Table 1. The β'' - Al_2O_3 phase content reaches a maximum (82.54%) when the content of NiO is 0.25wt%. It is indicated that an appropriate amount of NiO doping can promote β - Al_2O_3 transformation at lower temperature and produce more β'' - Al_2O_3 .

3.3. Analysis of the sinters

3.3.1. Phase analysis

The XRD patterns of the beta-alumina sinters with different NiO contents are shown in Fig.3. All the samples are composed of the β - and β'' -Al₂O₃ phases. The β'' -Al₂O₃ phase contents in sinters are calculated according to Eq. (1) and summarized in Table 2.

According to Table 2, the β'' -Al₂O₃ phase contents remain above 95% with the NiO amount from 0.05wt% to 1.5wt%. The β'' -Al₂O₃ phase content is the maximum (98.91%) when the content of NiO is 0.25wt% in all the samples. It can be observed that the NiO doping improves the stability of β'' -Al₂O₃ effectively at a high temperature. The radius of element Ni is 0.069 nm. According to Boilot and They's theory [31], when the radius of divalent metal ions is under 0.097 nm, the divalent metal ions are able to enter the spinel block to stabilize the β'' -Al₂O₃ structure. With the increasing of NiO content, the β'' -Al₂O₃ phase content is enhanced. When the morphology of the samples appears molten state, the β'' -Al₂O₃ phase content is decreased. It can be inferred that the molten state prevents the β'' -Al₂O₃ phases from producing.

3.3.2. Microstructure analysis

Fig.4 is the cross section micrograph of the sinters with various amounts of NiO. The undoped sample possesses loose structure, nonuniform particles and many pores in Fig.4a. After being doped by NiO, the particles of the samples become more homogeneous and denser. It can refine grains and strengthen the grain boundaries by NiO doping [32]. Although the samples containing 0.01-0.25wt% NiO are denser,

there are still some areas nonuniform and some large particles. When the amount of NiO is 0.01wt%, the microstructure is mainly the cone-like and short rod-like grains. When the amount of NiO is 0.15wt%, the grains of the sinters are obviously refined, and the size of them is more uniform, but it also exists some small pores. When the amount of NiO is 0.25wt%, the microstructure begins to appear the molten state, but it isn't very obvious. The size of the grains is relatively uniform. While the amount of NiO is more than 0.25wt%, the microstructure of the samples appears the obvious molten state, so the size of their grains becomes irregular and the pores become larger and larger. At the same time, their grain boundaries become less and less clear. According to the analysis of the XRD patterns and the literature [17], it can improve the sintering activity and increase the β'' -Al₂O₃ phase content of the beta-Al₂O₃ solid electrolytes by adding NiO. It indicates that the excess NiO content reduce the sintering temperature of the sinters, and make the microstructure more easy to appear the molten state. But the grains are too massive. It would significantly deteriorate the bending strength and ionic conductivity of the material [11].

3.3.3. Volume density analysis

Fig.5 displays the measured density and the relative density of all the sinters, which calculated according to the Eq. (2). With the increasing of NiO content, the densities become enlargement first and then decreased. The relative density of the sinter can reach 98.73% (3.1987 g cm⁻³) when the amount of NiO is 0.25wt%. The changing process of the density is consistent with the microstructure analysis. The denser the particles are, the larger the densities are.

3.3.4. Bending strength analysis

The bending strengths of the β - Al_2O_3 solid electrolytes are also shown in Table 2. The bending strength of the non-doping sample is only about 194 MPa. It enhances with the increasing of NiO contents (0.01-0.25wt%). The maximum bending strength is 296 MPa when the NiO content is 0.25wt%. Because a small amount of the molten state can make the microstructure have no obvious pores, and increase the binding force between the particles (Fig.4f). When the NiO amount exceeds 0.25wt%, the bending strength decreased. This can be attributed to the large size pores and the irregular size of the grains according to Fig.4g-i. Because adding NiO can improve the sintering activity, it leads the grain to the molten state and makes the pores become larger, then destroys the binding force between the particles and reduces the bending strength of the sinters.

3.3.5. Ionic conductivity analysis

Fig.6 is the AC impedance spectra of the samples with different content of NiO at 350°C. There are a small semicircle and a tail in these impedance spectra. Fig.7 shows the equivalent circuit used to represent the β - Al_2O_3 solid electrolytes in contact with silver electrode. The ionic conductivities of the sintered samples with various amounts of NiO at 350 °C are shown in Table 2. Due to its loose structure, the ionic conductivity of the undoped sample is only 0.015 S cm^{-1} . With the increase of NiO doping amounts, the ionic conductivity enhances. The ionic conductivity reaches to the maximum (0.066 S cm^{-1}) when the NiO content is 0.25wt%. While the content of NiO exceeds 0.25wt%, the ionic conductivity decreases quickly. Because the

excess of NiO improves the sintering activity of the sinters, it makes the grains appear the molten state and the grain boundaries become blurred. At the same time the particles are not uniform and dense. They lead the pores between the particles to become large and it enhances the grain boundary resistance of sinters. So the ionic conductivity reduces when the increase of NiO content.

It is found that the plots of $\ln(\sigma T)$ verses $(1000/T)$ are linear over the temperature range. Fig.8 shows the Arrhenius plot of resistivity data for the sintered samples with various amounts of NiO. The relationship conforms to Arrhenius equation.

$$\sigma T = A \exp(-E_a/RT) \quad (3)$$

Where R is the gas constant, T is the absolute temperature.

The corresponding values for E_a (activation energy) of all the samples are listed in Table 2. The low E_a indicates that the Na ions migrate easily. The lowest E_a of all the samples is 0.166 eV when the NiO content is 0.25wt%.

4. Conclusions

In the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{Li}_2\text{O}-\text{NiO}$ system, the $\beta''-\text{Al}_2\text{O}_3$ phase is formed at the low temperature of 1250 °C. All the $\beta''-\text{Al}_2\text{O}_3$ phase contents of 0.05-1.5wt% NiO doping samples are above 94%. The samples with 0.05-0.25wt% doping possess uniform microstructure with dense and plump grains. And it shows a high density and bending strength. However, the excess NiO doping would lead the grain to molten state and make the pores become larger. It deteriorates the ionic conductivity. When the content

of NiO of beta-Al₂O₃ solid electrolyte is 0.25wt%, the β'' -Al₂O₃ phase content is 98.91%, the microstructure is uniform and compact, the relative density is 98.73% of theoretical density, the bending strength is up to 296 MPa and the ionic conductivity can reach 0.066 S cm⁻¹ at 350°C.

Acknowledgements

The authors appreciate the financial supports from the National Natural Science Foundation of China (Grant No.21203095), the National Science Foundation for Post-doctoral Scientists of China (Grant No. 2012M511261), the Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM) and the Priority Academic Program Development of Jiangsu Higher Education Institutions.

References:

- [1] E.C. Kluiters, D. Schmal, W.R. Veen, KJCM Posthumus, Testing of a sodium/nickel chloride (ZEBRA) battery for electric propulsion of ships and vehicles, J. Power Sources 80 (1999) 261-264.
- [2] C.W. Park, H.S. Ryu, K.W. Kim, J.H. Ahn, J.Y. Lee, H.J. Ahn, Discharge properties of all-solid sodium-sulfur battery using poly (ethylene oxide) electrolyte, J. Power Sources 165 (2007) 450-454.
- [3] J.L. Wang, J. Yang, Y. Nuli, R. Holze, Room temperature Na/S batteries with sulfur composite cathode materials, Electrochem. Commun. 9 (2007) 31-34.
- [4] C.W. Sun, Developing trends of Sodium/Sulfur and Sodium/Metal Chloride

batteries(I), Battery Bimon. 23 (1993) 75-78.

[5] C.W. Sun, Developing trends of Sodium/Sulfur and Sodium/Metal Chloride batteries(II), Battery Bimon. 23 (1993) 138-140.

[6] C.F. Zhu, J.H. Xue, Structure and properties relationships of beta-Al₂O₃ electrolyte materials, J. Alloys Compd. 517 (2012) 182-185.

[7] J.H. Park, K.H. Kim, S.K. Lim, Influence of stabilizers on Na-beta"-Al₂O₃ phase formation in Li₂O(MgO)-Na₂O-Al₂O₃ ternary systems, J. Mater. Sci. 23 (1998) 5671-5675.

[8] C.F. Zhu, G.H. Ji, J.H. Xue, Influence of stabilizers on the performance of Beta-Al₂O₃ solid electrolyte, Rare Metal Mat. Eng. 43 (2014) 2535-2540.

[9] T.C. Girija, A.V. Virkar, Low temperature electrochemical cells with sodium beta"-alumina solid electrolyte(BASE), J. Power Sources 180 (2008) 653–656.

[10] G.X. Zhang, Z.Y. Wen, X.W. Wu, J.C. Zhang, G.Q. Ma, J. Jin, Sol-gel synthesis of Mg²⁺ stabilized Na-beta"/beta-Al₂O₃ solid electrolyte for sodium anode battery, J. Alloys Compd. 613 (2014) 80-86.

[11] S.J. Shan, L.P. Yang, X.M. Liu, X.L. Wei, H. Yang, X.D. Shen, Preparation and characterization of TiO₂ doped and MgO stabilized Na-beta"-Al₂O₃ electrolyte via a citrate sol-gel method, J. Alloys Compd. 563 (2013) 176-179.

[12] Y. Sheng, P.S. Nicholson, Microstructural development of a ZrO₂-Na-beta"-Al₂O₃ composite, J. Mater. Sci. 23 (1988) 982-986.

[13] Y. Sheng, P. Sarkar, P.S. Nicholoso, The mechanical and electrical-properties of ZrO₂-Na-beta"-Al₂O₃ composite, J. Mater. Sci. 23 (1988) 958-967.

- [14] L.P. Yang, S.J. Shan, X.L. Wei, X.M. Liu, H. Yang, X.D. Shen, The mechanical and electrical properties of $\text{ZrO}_2\text{-TiO}_2\text{-Na-}\beta/\beta''\text{-alumina}$ composite electrolyte synthesized via a citrate sol-gel method, *Ceram. Int.* 40 (2014) 9055-9060.
- [15] D. Xu, H.Y. Jiang, M. Li, O. Hai, Y. Zhang, Synthesis and characterization of Y_2O_3 doped $\text{Na-}\beta''\text{-Al}_2\text{O}_3$ solid electrolyte by double zeta process, *Ceram. Int.* 41 (2015) 5355-5361.
- [16] N. Wang, L.X. Fu, J. Zhang, Effect of Ni-doping on the framework structure of mesoporous silica, *Fine Chem.* 23 (2006) 452-455,468.
- [17] X.L. Ma, Effect of NiO doping on 4YSZ conductivity properties, *China's Ceram.* 47 (2011) 19-21.
- [18] J. Xiao, H.F. Zhang, Y. Xue, Z.W. Lu, X.Q. Chen, P. Su, F.J. Yang, X.B. Zeng, The influence of Ni-doping concentration on multiferroic behaviors in $\text{Bi}_4\text{NdTi}_3\text{FeO}_{15}$ ceramics, *Ceram. Int.* 41 (2015) 1087-1092.
- [19] S.K. Das, R.N. Mishra, B.K. Roul, Magnetic and ferroelectric properties of Ni doped BaTiO_3 , *Solid State Commun.* 191 (2014) 19-24.
- [20] J.D. Hodge, Powder processing and crystallization of beta-aluminas and beta''-aluminas, *Am. Ceram. Soc. Bull.* 62 (1983) 244-248.
- [21] K.M. Lee, S.T. Lee, D.H. Lee, S.M. Lee, S.L. Lim, Phase formation of Na^+ -beta-aluminas synthesized by double zeta process, *J. Ind. and Eng. Chem.* 19 (2013) 829-834.
- [22] X.C. Lu, G.S. Li, J.Y. Kim, K.D. Meinhardt, V.L. Sprenkle, Advanced materials for sodium-beta alumina batteries: status, challenges and perspectives, *J. Power*

Sources 295 (2015) 167-174.

[23] X.L. Wei, Y. Cao, L. Lu, H. Yang, X.D. Shen, Synthesis and characterization of titanium doped sodium β "-alumina, *J. Alloys Comp.* 509 (2011) 6222–6226.

[24] W. Zhou, Z.P. Shao, W.Q. Jin, Synthesis of nanocrystalline conducting composite oxides based on a non-ion selective combined complexing process for functional applications, *J. Alloys Comp.* 426 (2006) 368–374.

[25] V. Jayaraman, T. Gnanasekaran, G. Periaswami, Low-temperature synthesis of β -aluminas by a sol-gel technique, *Mater. Lett.* 30 (1997) 157–162

[26] T. Mathews, Solution combustion synthesis of magnesium compensated sodium-beta-aluminas, *Mater. Sci. Eng. B* 78 (2000) 39–43.

[27] H.C. Park, Y.B. Lee, S.G. Lee, C.H. Lee, J.K. Kim, S.S. Hong, S.S. Park, Synthesis of beta-alumina powders by microwave heating from solution-derived precipitates, *Ceram. Int.* 31 (2005) 293-296.

[28] X.L. Wei, Y. Xia, X.M. Liu, H. Yang, X.D. Shen, Preparation of sodium β "-alumina electrolyte thin film by electrophoretic deposition using Taguchi experimental design approach, *Electrochim. Acta* 136 (2014) 250-256.

[29] A. Pekarsky, P.S. Nicholson, The relative stability of spray-frozen/freeze-dried β "-Al₂O₃ powders, *Mat. Res. Bull.* 15 (1980) 1517-1524.

[30] Z.Y. Wen, Y.Y. Hu, X.W. Wu, J.D. Hang, Z.H. Gu, Main challenges for high performance NAS battery: materials and interfaces, *Adv. Funct. Mater.* 23 (2013) 1005-1018.

[31] J.P. Boilot, J. Thery, Influence De L'addition D'ions Etrangers Sur La Stabilité

Relative Et La Conductivite Electrique Des Phases De Type Alumine β et β'' , Mater. Res. Bull. 11 (1976) 407-413.

[32] M.X. Jing, X.Q. Shen, D.H. Li, W.X. Li, Effects of coexistence of Ni and ZrO_2 inclusions on microstructure and properties of Al_2O_3 ceramics, J. Chin. Ceram. Soc. 35 (2007) 35-40.

Captions list:

Table 1 - The β'' phase content in precursor powders with different amounts of NiO doping.

Table 2 - Some calculated parameters and measured properties of the sinters with different amounts of NiO doping

Fig. 1 TG and DSC curves of the specimen with 0.15wt% NiO

Fig.2 XRD spectra of precursor powders with different amounts of NiO doping

Fig. 3 XRD spectra of the sinters with different amounts of NiO doping

Fig.4 The cross section micrograph of the sinters with different amounts of NiO doping

Fig.5 The measured and relative densities of the sinters with different amounts of NiO doping

Fig.6 The impedance spectra of the sinters with different amounts of NiO doping at 350°C

Fig.7 Equivalent circuits at different NiO contents

Fig.8 Arrhenius plot of resistivity data for the sinters with different amounts of NiO doping

Fig. 1 TG and DSC curves of the specimen with 0.15wt% NiO

Fig.2 XRD spectra of precursor powders with different amounts of NiO doping

Fig. 3 XRD spectra of the sinters with different amounts of NiO doping

Fig.4 The cross section micrograph of the sinters with different amounts of NiO doping

Fig.5 The measured and relative densities of the sinters with different amounts of NiO doping

Fig.6 The impedance spectra of the sinters with different amounts of NiO doping at 350°C

Fig.7 Equivalent circuits at different NiO contents

L1: Inductance due to platinum wire and silver electrode; R0: Lead wire resistance;

Rg: Grain resistance; CPEg: Grain capacitance; Rgb: Grain boundary resistance;

CPEgb: Grain boundary capacitance; CPEDl: a double layer capacitance;

Rct: Charge transition resistance

Fig.8 Arrhenius plot of resistivity data for the sinters with different amounts of NiO doping

Table 1 The β'' phase content in precursor powders with different amounts of NiO doping

NiO wt%	0	0.01	0.05	0.1	0.15	0.25	0.5	1	1.5
β'' phase content (%)	77.8	78.6	81.54	81.67	81.74	82.54	79.91	79.43	78.75

Table 2 Some calculated parameters and measured properties of the sinters with different amounts of NiO doping

NiO wt%	0	0.01	0.05	0.1	0.15	0.25	0.5	1	1.5
β'' phase content (%)	92.28	94.49	95.04	95.33	96.75	98.91	98.47	98.12	96.98
Bending strength(MPa)	194	228	253	256	286	296	208	201	177
σ at 350 °C (S cm ⁻¹)	0.015	0.018	0.024	0.035	0.038	0.066	0.029	0.023	0.012
Ea(eV)	0.205	0.192	0.187	0.182	0.171	0.166	0.186	0.205	0.208