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Sol-gel synthesis of Na^+ beta-Al_2O_3 powders

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Abstract

Powders of general formula $Na_{1+x}Al_{11}O_{17+x/2}$ with $x=0$, 0.2 and 0.57 have been obtained by hydrolysis and condensation of metal alkoxides. X-ray diffraction investigations showed the crystallization of β-alumina peaks at 1100 °C, confirmed by DTA/TG measurements. The same phase was revealed for pellets sintered in air at 1400 °C. Densities up to 97% of the theoretical value were reached. Electrical performances of pellets of $x=0.2$ and 0.57 compositions were investigated by Dielectric Analyzer (DEA) at various frequencies. The measured values confirmed the good conductivity and activation energy performances of the material.

Keywords: Na^+ beta-Al_2O_3; Ionic conductivity; Sintering; Sol-gel process; X-ray methods

1. Introduction

Sodium beta-alumina ceramics are a family of oxides that exhibits a fast-ionic conductivity. This property makes the material one of the best solid electrolytes known today and suitable for use in modern electronic devices. Charge transport is determined by the structure of Na^+ beta-alumina in which two-dimensional conduction planes partially occupied by Na^+ ions are separated by crystalline Al_2O_3 spinel blocks.[1,2] Activation energy values for ion transport in the conduction plane are low, between 0.12 and 0.27 eV,[1,3] because of the correlated movement of interstitial Na^+ pairs, instead of a standard vacancy mechanism.

Various methods have been developed for processing beta alumina ceramics,[3–8] which range from simple mechanical mixing of oxides to sol-gel techniques.

Samples obtained were single crystal or polycrystalline ceramics with different electrical properties. In fact β-alumina single crystals are anisotropic because of the two-dimensional structure. In the case of polycrystalline ceramics the electrical behaviors are also related to grain-sizes, and the conduction in sintered polycrystalline samples is limited by the contribution of the grain boundary and is generally isotropic and lower than in the single crystal.[1]

In this paper we report the synthesis of sol-gel β-alumina powders at low temperatures and the electrical characterization of pellets sintered at 1400 °C.

2. Experimental

Powders from xerogels evaporated in air at room temperatures have been obtained by the sol-gel method. Sol-gel solutions were prepared by hydrolysis and condensation of Aluminum tri-*sec*-butoxide $[C_2H_5CH(CH_3)O]_3Al$ and sodium ethoxide (NaOEt) in ethanol under ambient water vapour.

Aluminum butoxide was added to the ethanol when the solvent reached the boiling point, while NaOEt was added at room temperature. Precursors were allowed to react under stirring for some minutes. Samples with Na_2O/Al_2O_3 =1:11; 1:9 and 1:7 molar ratios (corresponding to $Na_{1+x}Al_{11}O_{17+x/2}$ with $x=0$, 0.2 and 0.57 respectively) were prepared. Xerogels were obtained leaving the clear final sols for a week at room temperature in an open vessel. The water humidity favors the transformation process of the sol in gel. Powders obtained from the xerogel were calcined for 30 minutes at temperatures between 700 and 1200 °C. The thermal evolution of the ligands and the structure of powders were observed by IR spectra using a Perkin Elmer 2000, between 400 and 4000 cm^{-1}. The transformation of the material during heat treatment was studied by DTA/TG measurements with an STA 409/429 Netzsch instrument at a rate of 10 °C/min up to 1400 °C. The crystallization was confirmed by X-ray diffraction (XRD) using a Philips diffractometer

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operating at 40 KV and 40 mA. The average crystallite size was calculated from the Scherrer equation after fitting the experimental profiles using the method described in Ref. 9.

Pellets of 1.9 cm diameter were obtained with powder calcined at 1200 °C for 1 h, pressed at 100 bar and sintered in air at 1400 °C for 2 h (heating rate 5 °C/min) . The density of sintered pellets was measured by Archimedes principle in distillate water at room temperature.

Electrical performances of $x=0.2$ and 0.57 pellets were investigated by TA Instruments Dielectric Analyzer (DEA) 2970 at frequencies from 10^{-2} to 10^5 Hz and at temperatures from 25 to 400 °C. Measurement involves placing a sample between two gold electrodes under a pressure of 400 N and exposing it to an alternating electrical field.

3. Results and discussion

Hydrolysis and condensation of the precursors took place without the inclusion of water and catalyst, that usually are fundamental compounds of a sol-gel process. The water originating from the atmosphere is sufficient to initiate the polymerization during the xerogel formation, moreover NaOEt acts as a base catalyst.

TGA–DTA curves were similar for $x=0$, 0.2 and 0.57. In Fig. 1 is reported the resulting spectra for the $x=0.2$ composition. Large mass losses of the sample were observed at temperatures between 50 and 650 °C, accompanied by an endothermic peak around 150 °C due to the evaporation of physiosorbed water or residual solvent and two exothermic peaks were seen between 350 and 650 °C due to the removal of residual organic groups. The exothermic peak at about 1100 °C, not accompanied by weight losses, is due to the crystallization of β-alumina. XRD analyses performed on powder heated over the same schedule confirmed these behaviors.

In order to clarify the effect of the calcination temperature on the ligands, IR measurements were carried out on powders treated at different temperatures. Even in this case the IR spectra were similar for all the reported compositions. Fig. 2 shows IR curves for powders treated at 60 and 1200 °C. A broad peak centered at 3410 cm^{-1} is assigned to the H–OH vibrational signal and to organic substances such as ethanol, while peaks at 1640 and 1400 cm^{-1} were consistent with water coordination of aluminum ions and to C-H vibration of residual organic groups, respectively.[10,11] These peaks almost disappear at 1200 °C, indicating a densification of the gel powder. The peak around 1050 cm^{-1} is due to the Al–O stretching vibration.[11] In the region of the spectrum that defines the alumina structure (between 600 and 1000 cm^{-1}), several broad and undefined bands are observed at low temperatures, probably because alumina is still amorphous. At 1200 °C these bands are well defined, indicating the crystallization of alumina.[11]

Fig. 3 shows the XRD patterns of $x=0.2$ composition powder. The results were similar for all compositions of powders and confirmed the crystallization of the β-alumina phase at 1100 °C. An α-alumina impurity phase was detected only in powders with the lowest content of sodium ($x=0$). As already observed by Takahashi et al.,[3] this is due to the volatilization of sodium oxide that for samples with lower sodium contents results in the formation of sodium-free alumina phases.

The mean diameter of β-alumina crystallites in powders, estimated from the linewidth of the <002> reflection, increases with heating temperature (from 24 nm at 1100 °C to 27 nm at 1200 °C for $x=0$; from 22 to 27 nm for $x=0.2$; from 20 to 22 nm for $x=0.57$) indicating a crystal growth of the phase.

The choice of the sintering temperature is important in order to obtain pellets with good electrical performances. Sintering temperatures up to 1550 °C have been reported.[1,3,12,13] The sol-gel technique permits the production of very fine and reactive powders that can ensure a good densification even at lower sintering temperatures, limiting the loss of Na_2O during the heating process with a consequent lowering of the ionic con-

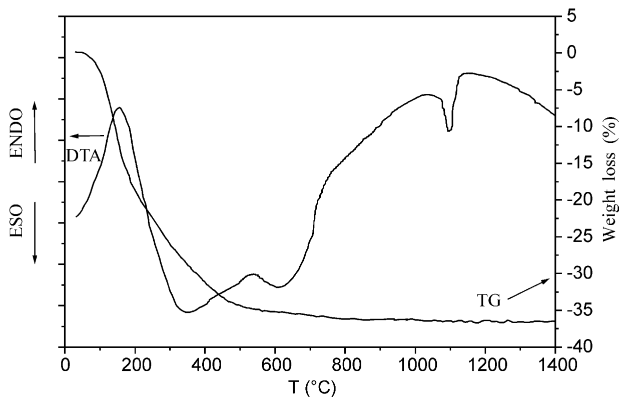

Fig. 1. DTA–TGA curves.

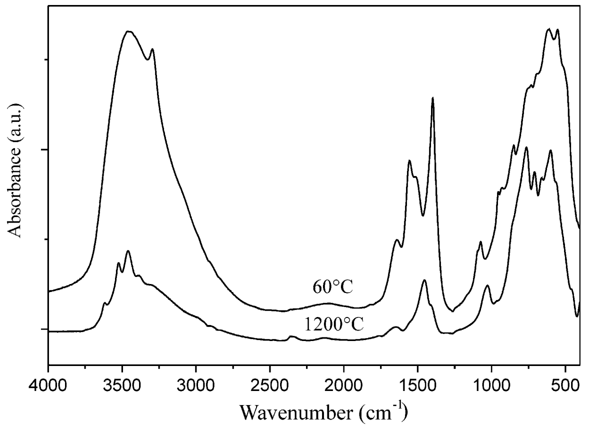

Fig. 2. FTIR spectra of $Na_{1+x}Al_{11}O_{17+x/2}$ powders with $x=0.2$, heated at different temperatures.

ductivity. In this work pellets sintered at 1400 °C showed a density up to 97% of theoretical one (3.26 g/cm^3). XRD measurements performed on pellets sintered at 1400 °C confirmed the β-alumina phase stability.

Conductivity measurements and activation energy values are summarized in Fig. 4 and Table 1. The experimental results are fitted using the Arrhenius equation modified for taking into account the frequency of the applied voltage:[14]

$$\sigma = [(2\pi\upsilon\sigma_0)/T]\exp(= E_a/k_bT)$$

where σ is the measured ionic conductivity, ν is the frequency, T is the temperature in K, k_b is the Boltzman constant and σ_0 and E_a (activation energy) are determined by the intercept and slope of the line in a log σT vs $1/T$ plot, respectively.

For a simple hopping conductivity process and in the absence of long-rate interactions, the conductivity is expected to be independent of the frequency, as a single ion is presumed to move along an infinite lattice of identical potential walls. In general, however, interactions between unassociated defect species are expected leading to a frequency-dependent conductivity.[15] In fact the presence of interactions has been used to explain the observed frequency dispersion in the conductivity of a number of solid electrolyte seen by many authors.[16]

Also, in our samples, we observed a frequency dependent behavior of the ionic conductivity and we found that the activation energy changes between high and low frequencies. For example for $x = 0.2$ the activation energy was about 0.65 eV for high frequencies and 0.32 eV for frequencies lower than 10^2 Hz. A similar trend was also found for samples with $x = 0.57$ and the activation energy was around 0.70 and 0.44 eV for high and low frequencies respectively. Studies are in progress to understand this behavior.

It is quite difficult to compare these results with values reported by other authors because of the variations in the composition, diverse techniques and conditions by which conductivity has been measured, as already pointed by Stevens et al.[13] Anyway, conductivity in the order of 10^{-4} ohm^{-1}cm^{-1} have been reported[8] for polycrystalline β-alumina, which confirmed the good conductivity performances of the material obtained by the sol-gel method presented in this work.

A value of apparent activation energy of 0.27 eV at a frequency of 100 kHz[3], comparable to the values for the

Table 1
Activation energy (E_a) and ionic conductivity at 400 °C (σ) of $Na_{1+x}Al_{11}O_{17+x/2}$ ($x = 0.2$ and 0.57) pellets at different frequencies (ν)

	$x = 0.2$		$x = 0.57$	
ν (Hz)	E_a (eV)	σ (400 °C) (Ω^{-1}cm^{-1})	E_a (eV)	σ (400 °C) (Ω^{-1}cm^{-1})
10^5	0.65	1.3×10^{-4}	0.67	1.7×10^{-4}
10^4	0.69	9.4×10^{-5}	0.73	1.4×10^{-4}
10^3	0.65	4.9×10^{-5}	0.69	7.1×10^{-5}
10^2	0.49	1.3×10^{-5}	0.50	1.5×10^{-5}
10^1	0.32	2.0×10^{-6}	0.45	3.0×10^{-6}
10^0	0.32	4.7×10^{-7}	0.44	7.3×10^{-7}
10^{-1}	0.35	1.2×10^{-7}	0.44	1.6×10^{-7}
10^{-2}	–	–	0.42	4.2×10^{-8}

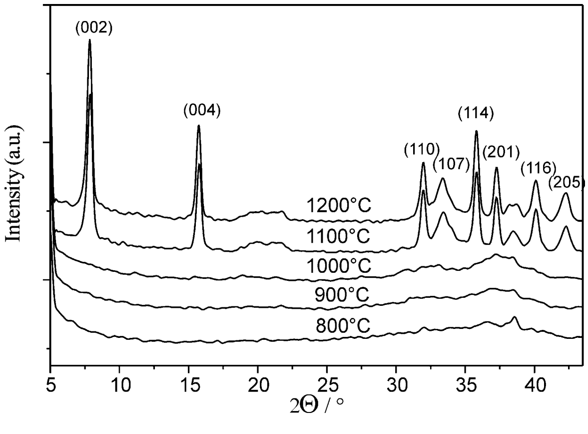

Fig. 3. XRD spectra of powders heated at different temperatures. Indexed peaks belong to β-Al$_2$O$_3$ phase.

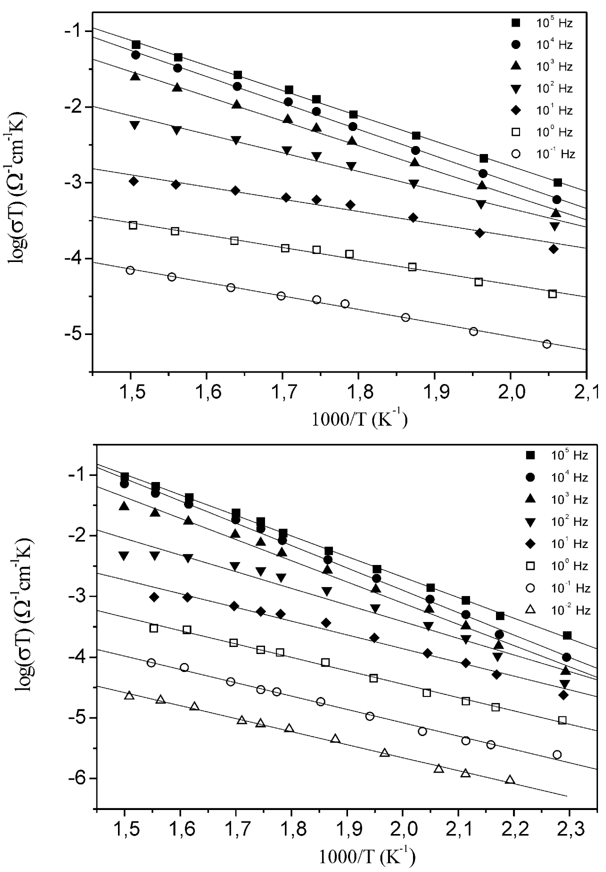

Fig. 4. Arrhenius plot of β-alumina pellets sintered at 1400 °C with nominal composition $Na_{1+x}Al_{11}O_{17+x/2}$: $x = 0.2$ (top) and $x = 0.57$ (bottom). Lines correspond to linear fit of the experimental values.

polycrystalline specimens,[1] were reported, on the contrary we measured an activation energy of about 0.4 eV.

4. Conclusions

A sol-gel synthesis of $Na_{1+x}Al_{11}O_{17+x/2}$ with $x=0$, 0.2 and 0.57 powders was performed. β-alumina crystallizes at 1100 °C. The fine powder obtained allows sintering of dense pellets at temperatures as low as 1400 °C. Ionic conductivity measurements confirmed the good performances of polycrystalline β-alumina pellets.

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