

Preparation of cubic alumina and scandia doped zirconia and its thin film fabrication by pulsed laser deposition technique

MUTHUKKUMARAN KARTHIKEYAN*

College of Natural Sciences, Department of Physics, Hawassa University, Hawassa, Ethiopia

Alumina and scandia doped zirconia was prepared through a soft chemistry synthesis route and sintered at 1873 K. X-ray diffraction patterns indicate a pure cubic phase for the composition of $0.88\text{ZrO}_2-0.112\text{Sc}_2\text{O}_3-0.008\text{Al}_2\text{O}_3$. Thin films were fabricated on Al_2O_3 <0001> substrates using pulsed laser deposition technique. Dense films of $0.941\ \mu\text{m}$ thickness were obtained at 873 and 1023 K substrate temperatures at an oxygen partial pressure of 15 Pa. The ionic conductivity of both thin film and sintered pellet was measured using ac impedance spectroscopy in air. The conductivity values are higher for thin films compared to that of sintered pellets.

Keywords: *alumina and scandia doped zirconia; thin film; pulsed laser deposition; ionic conductivity*

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1. Introduction

There is a growing need for more environmentally friendly and efficient means of energy conversion. At the forefront of this search is the solid oxide fuel cell (SOFC). The most advanced SOFCs are those based on yttria-stabilized zirconia (YSZ) with the solid electrolyte operating around 1173 K [1]. Although there are advantages of high temperature operation, it does place severe constraints on material selection and on the lifetime of the fuel cell. Lowering the operating temperature to 873 K would permit a use of oxidation-resistant metallic alloys as the interconnect material. It would also enhance the reliability and life of the cell, minimize the electrode/electrolyte interactions, permit more frequent cycling and reduce the operating cost. This can be achieved by using dense pore free thin films of material having superior oxide ion conductivity to that of YSZ, as the solid electrolyte. The two most promising materials are strontium and magnesium doped LaGaO_3 , $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-(x+y)/2}$ (LSGM) as well as alumina and scandia doped zirconia [2–5]. Thin dense pore free films of LSGM of various com-

positions were synthesized using pulsed laser deposition (PLD) [6, 7] and electrophoretic deposition (EPD) [8]. There are no reports on the synthesis of alumina and scandia doped zirconia thin films by PLD. Here, we report the synthesis of Al_2O_3 and Sc_2O_3 doped ZrO_2 through soft chemistry route and fabrication of thin films by pulsed laser ablation.

2. Experimental

2.1. Material preparation

X-ray single-phase $0.88\text{ZrO}_2-0.112\text{Sc}_2\text{O}_3-0.008\text{Al}_2\text{O}_3$ sample was prepared using a novel solution combustion technique. Appropriate amounts of zirconyl nitrate (99.99 %), scandium nitrate (99.99 %) and aluminium nitrate (99.99 %) were dissolved in distilled water. The solution was then saturated at 353 K over a hot plate. Then a saturated solution of urea was added to the solution as fuel and complexant. The urea was added in the amount that is required to consume completely the excess oxygen in the nitrate mixture (so called stoichiometric amount) [9, 10]. The resultant solution was then refluxed for 10 min and introduced into an open muffle furnace maintained at 873 K. At this temperature the excess water is removed

*E-mail: muthuk29@gmail.com

Table 1. Typical deposition parameters.

Laser:	KrF Excimer (248 nm)
Pulse duration:	30 ns
Repetition rate:	10 Hz
Laser energy:	200 mJ/pulse
Energy density:	2 – 3 J/cm ²
Target:	0.88ZrO ₂ –0.112Sc ₂ O ₃ – 0.008Al ₂ O ₃
Substrate:	Al ₂ O ₃ <0001>
Substrate temperature:	873, 1023 K
Target-substrate spacing:	45 mm
Oxygen partial pressure:	15 Pa

from the solution, resulting in the formation of a gel and its simultaneous combustion. The resulting fine powder was then calcined at 823 K for 30 min. The single – phase character of the product was then confirmed by powder XRD. The powder was then compacted to pellets of 15 mm diameter and sintered at 1873 K for 6 h. The sintered pellets were then used for pulsed laser deposition.

2.2. Thin film fabrication

The deposition of Al₂O₃–Sc₂O₃ doped zirconium oxide thin films was carried out using a KrF excimer laser of 248 nm wavelength (Compex 205 from Lambda Physik) and a turbo pumped deposition system. The typical deposition conditions were laser repetition rate of 10 Hz and energy density of 2 – 3 J/cm² at the target. A sintered pellet of 0.88ZrO₂–0.112Sc₂O₃–0.008Al₂O₃ and Al₂O₃ <0001> with the size of 10 mm x 5 mm was used as a target and a substrate respectively. In this experiment, the excimer laser was focused onto the target at an angle of incidence of 45°. During deposition the target was rotated and oscillated to avoid pitting. The deposition parameters used are given in Table 1.

2.3. Characterization

Structural characterization of bulk samples and thin films were carried out using powder and glancing incidence X-ray diffraction, respectively. Philips PW1730 was used for this purpose. Thin film surface morphology characterization was per-

formed using atomic force microscopy (AFM). AFM images of thin films were taken in the tapping mode (DFM mode using SPA400, Seiko Instruments Inc). The root-mean square roughness and grain sizes were also obtained from the images.

Ac conductivity (SOLARTRON impedance/gain phase analyzer model no: SI-1260) of the pellets and thin films was measured using two-probe impedance spectroscopy. Platinum paste was applied to both sides of the pellets, fired at 873 K for 60 min and sandwiched between two platinum foils connected with platinum leads. Measurements were made at 100 K interval in air over the temperature range of 773 to 1073 K with an accuracy of ±1 K. The frequency range from 0.01 Hz to 32 MHz was used.

In case of thin films, the electrical contacts were made using platinum paste and wires. Two platinum wires of 100 µm diameter were kept on two ends of the film and adhered to it by applying platinum paste, with a mask at the center of the film to avoid any direct contact between the two electrodes. This was then heated at 873 K for 60 min so that the paste settled to hold the contacts firmly on to the film.

3. Results and discussion

The compound 0.88 ZrO₂–0.12 Sc₂O₃ has a rhombohedral structure at room temperature and undergoes transformation to cubic fluorite structure around 923 K. The cubic phase can be stabilized down to room temperature by substituting a small portion of Sc³⁺ with Al³⁺ [4]. For the compositions synthesized in this study the crystal structure obtained is cubic. The XRD pattern corresponding to the composition 0.88ZrO₂–0.112Sc₂O₃–0.008Al₂O₃ is shown in Fig. 1. The ionic radii of Sc³⁺ and Zr⁴⁺ are almost similar, therefore in the same co-ordination, the entropy gain on randomization of the cations (configurational entropy) is relatively small. When the ions are of different size, in the same co-ordination, the configurational entropy is greater and hence, more driving force for randomization is available. Since the difference in ionic radii of Al³⁺ and Zr⁴⁺ is greater than that of Sc³⁺ and Zr⁴⁺, the introduc-

tion of small amount of Al^{3+} into the cation sublattice increases the configurational entropy. This additional configurational entropy is the extra driving force for randomization which decreases the number of micro-domains (crystallite seeds) of the low temperature rhombohedral phase.

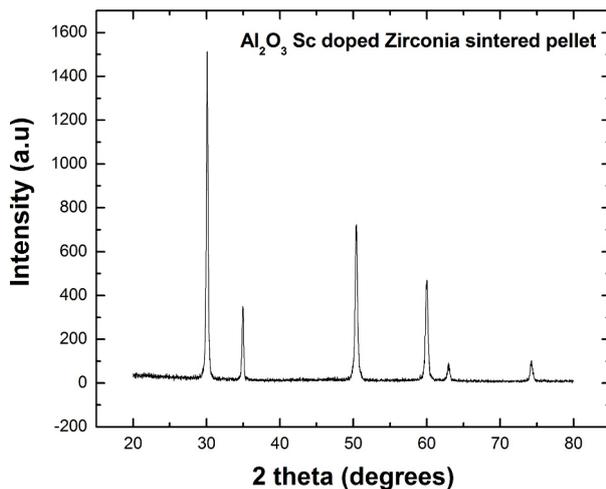


Fig. 1. Powder XRD pattern of $0.88\text{ZrO}_2-0.112\text{Sc}_2\text{O}_3-0.008\text{Al}_2\text{O}_3$ sintered target material.

For the various compositions synthesized in this study, assuming that the thermo chemical reaction occurs with the stoichiometric quantity of the fuel, the balanced combustion reaction can be written as (1).

The product of rapid combustion has resulted in very fine powders due to the large amount of gases evolved during reaction (1). About 16 moles of gases are evolved for each mole of stabilized zirconia. The low processing temperature required for the formation of the cubic phase, when the material is synthesized via the solution route, results from the effective homogeneous mixing (randomization) of cations, on atomic level, achieved in a liquid solution. Formation of a metal-urea complex and its

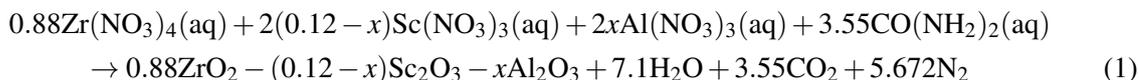
ignition take place simultaneously so that the random distribution of cations achieved in the solution is retained until ignition. Moreover, although the furnace temperature is kept below 873 K, the particle attains a temperature in excess of 1273 K during combustion. This is inferred from the color of the flame (colorless in this case).

The powders obtained by combustion as well as after high temperature (1873 K) sintering and cooling at 5 K/min rate were found to be of cubic crystal structure upon XRD analysis

XRD patterns of thin films deposited at substrate temperatures of 873 and 1023 K at an oxygen partial pressure of 15 Pa on $\text{Al}_2\text{O}_3 \langle 0001 \rangle$ are shown in Fig. 2. The AFM pictures, both two- and three-dimensional, of the thin films grown on sapphire substrate are shown in Fig. 3. It is clear from the AFM pictures that the films are dense and free of pores. The thickness of the films, measured using Dektak-3010 surface profilometer, was found to be $0.941 \mu\text{m}$.

Though the films were grown at temperatures where the rhombohedral phase is stable, a cubic phase was obtained as evidenced by XRD studies. This is because of Al_2O_3 doping as well as the completely random distribution of ions, atoms and molecules in the vapour and plasma phases formed during the ablation and their extremely rapid condensation on the substrate followed by nucleation and growth.

The Nyquist plot obtained for the sintered material at 1073 K is given in Fig. 4. The contribution due to grain boundary is clearly visible. The sintered pellet conductivity values obtained from the ac impedance study at various temperatures are given in Fig. 5. The corresponding values for YSZ obtained from literature [11, 12] are also shown for comparison.



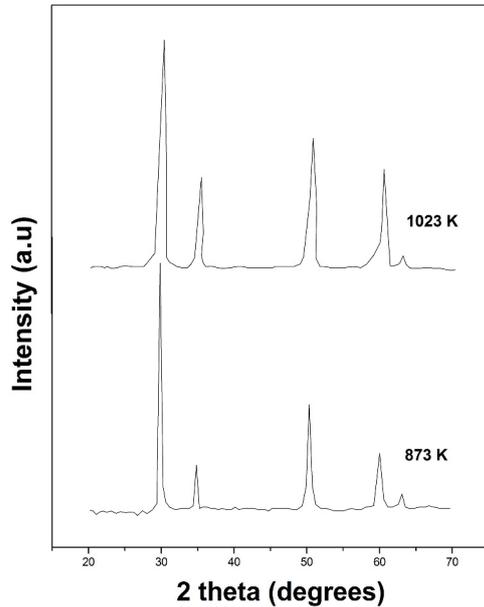


Fig. 2. XRD pattern of thin films of $0.88\text{ZrO}_2-0.112\text{Sc}_2\text{O}_3-0.008\text{Al}_2\text{O}_3$ prepared at 873 and 1023 K on (0001) Al_2O_3 at an oxygen partial pressure of 15 Pa.

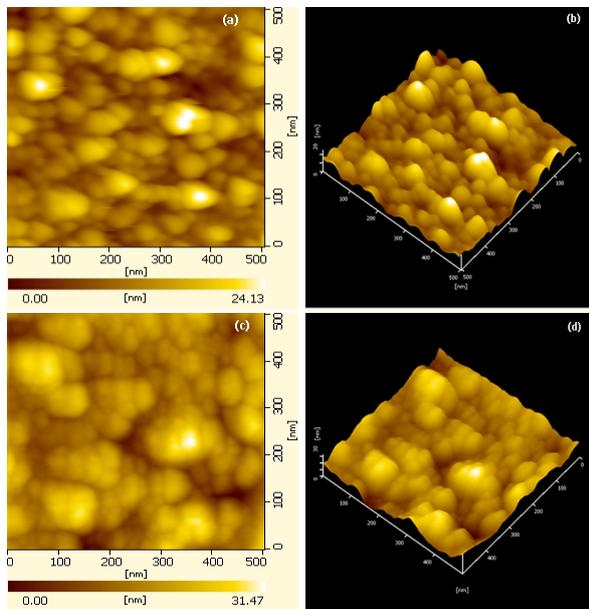


Fig. 3. The 2D and 3D AFM images of thin films prepared at different substrate temperatures (a), (b) 873 K and (c), (d) 1023 K.

The Nyquist plot obtained for the thin films at 1073 K is shown in Fig. 6. The contribution from

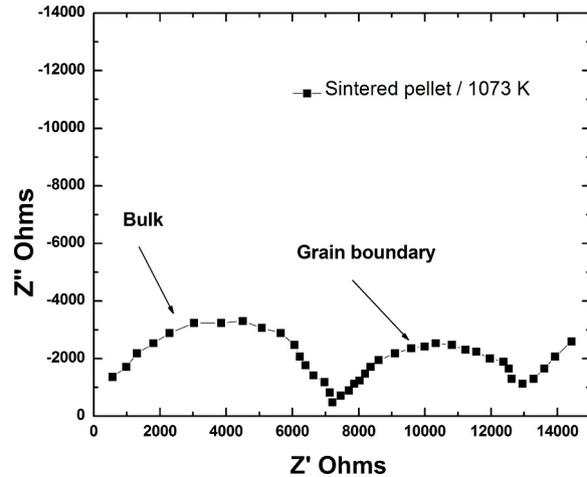


Fig. 4. Nyquist plot of $\text{Al}_2\text{O}_3-\text{Sc}_2\text{O}_3$ doped zirconia pellet measured at 1073 K.

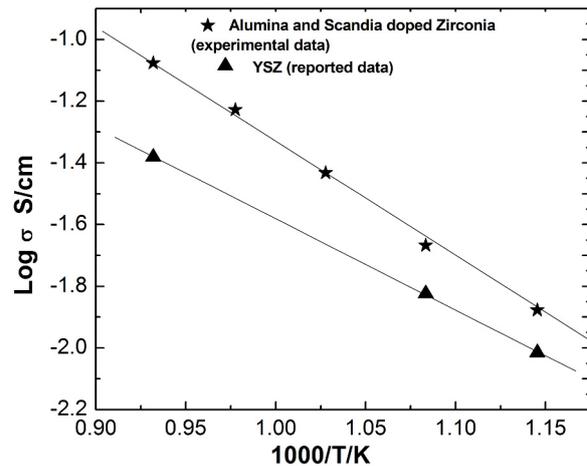


Fig. 5. Arrhenius plots of electrical conductivities of sintered $\text{Al}_2\text{O}_3-\text{Sc}_2\text{O}_3$ doped zirconia and reported conductivity value of YSZ.

the grain boundary is not as clearly visible as in the sintered material. This is because in the sintered pellet there is segregation of Al_2O_3 at the grain boundaries above an Al_2O_3 concentration of 0.006 mol% [13], which is not detected by XRD, whereas the solubility of Al_2O_3 in the thin film is greater than that in the sintered material because of the vapour and plasma phases formation prior to condensation and growth of the film. The conductivity values for the thin films are given in Fig. 7. The conductivity values are higher for the thin films compared to that of sintered pellets.

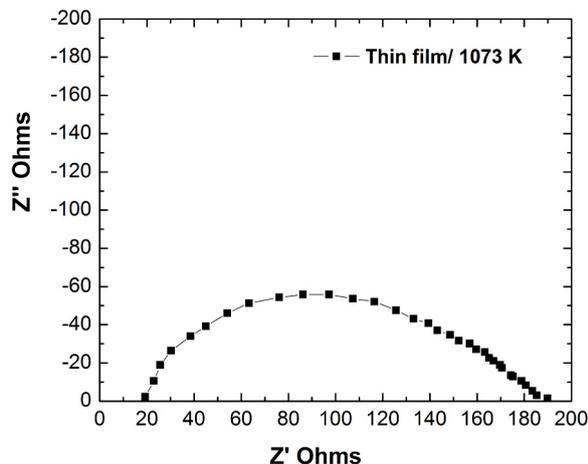


Fig. 6. Nyquist plot of $\text{Al}_2\text{O}_3\text{-Sc}_2\text{O}_3$ doped zirconia thin films on (0001) Al_2O_3 substrates deposited at 873 K at an oxygen partial pressure of 15 Pa, measured at 1073 K.

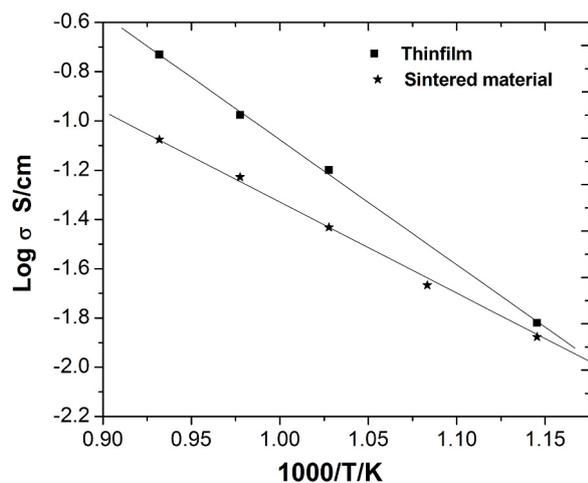


Fig. 7. Arrhenius plots for electrical conductivities of $\text{Al}_2\text{O}_3\text{-Sc}_2\text{O}_3$ doped zirconia thin films prepared on (0001) Al_2O_3 at 873 K and an oxygen partial pressure of 15 Pa. Sintered material values are shown for comparison.

4. Conclusion

Dense, single-phase thin films of alumina doped scandia stabilized zirconia were fabricated by PLD. The conductivity of the thin film was found to be greater than that of the sintered pellet. The contribution from the grain boundary was clearly seen for the sintered material but it was overlapped with the bulk contribution in thin films.

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References

- [1] MINH N. Q., *J. Am. Ceram. Soc.*, 76 (1993), 563.
- [2] ISHIHARA T., MATSUDA H., TAKITA Y., *J. Am. Chem. Soc.*, 116 (1994), 3801.
- [3] FENG M., GOODENOUGH J.B., *Eur. J. Sol. State Inor.*, 31 (1994), 663.
- [4] ISHII T., *Solid State Ionics*, 78 (1995), 333.
- [5] MATHEWS T., RABU N., SELLAR J.R., MUDDLE B.C., *Int. J. Self-Propag. High-Temp. Synth.*, 9 (2000), 15.
- [6] MATHEWS T., MANORAVI P., SELLAR J.R., MUDDLE B., *Chem. Mater.*, 12 (2000), 917.
- [7] MATHEWS T., MANORAVI P., ANTONY M.P., SELLAR J.R., MUDDLE B.C., *Solid State Ionics*, 135 (2000), 397.
- [8] MATHEWS T., RABU N., SELLAR J.R., MUDDLE B.C., *Solid State Ionics*, 128 (2000), 111.
- [9] PATIL K.C., ARUNA S.T., EKAMBARAN S., *Curr. Opin. Solid St. M.*, 2 (1997), 158.
- [10] MATHEWS T., *Mater. Sci. Eng. B*, 78 (2000), 39.
- [11] INABA H., TAGAWA H., *Solid State Ionics*, 83 (1996), 1.
- [12] WAKABAYASHI N., YAMAMOTO O., *Solid State Ionics*, 28 – 30 (1988), 1510.
- [13] BASTOW T.J., MATHEWS T., SELLAR J.R., *Solid State Ionics*, 175 (2004), 415.

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