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## CeO<sub>2</sub> thin films by flash evaporation

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### Abstract

Oxide ion conductors have received special attention during the last 20 years for their applications in high temperature fuel cells and sensors. Cerium oxide based solid electrolytes have one of the lowest activation energies among the fluorite type oxide ion conductors. We present a methodology for obtaining cerium oxide thin films by flash evaporation. The films were characterized using X-ray diffraction, optical absorption, and AC conductivity. The results show the ionic nature of the electrical conductivity.

**Keywords:** Cerium oxide; Thin films; Ion conductivity – oxide; Flash evaporation; Electrolyte

### 1. Introduction

Solid electrolytes based on cerium oxides have attracted considerable attention particularly during the last 20 years, owing to their applications, e.g. to fuel cells and sensors [1–3]. Cerium oxide is an interesting material because of its high ionic conductivity when it is doped with divalent and/or trivalent cations, even at dopant concentrations as low as 1% mole percent [4,5]. The defect chemistry of these materials is a consequence of the replacement of the host cations by aliovalent ions with compensation by oxygen vacancies. The conductivity

is produced by the rapid transport of vacancies as a conventional hopping mechanism [6].

In the use of solid electrolytes, thin films have practical advantages for device fabrication because their apparent resistance can be reduced, and because of their improved reliability, size decrease, cost and electrical consumption [7]. Preparation of ionic conductor films by several techniques has been reported [8–13].

In our work the flash evaporation technique was used for the preparation of CeO<sub>2</sub> thin films followed by a thermal annealing in order to obtain crystalline films with good adherence. In this paper we report a technical procedure for the preparation of cerium oxide based solid electrolyte thin films by flash evaporation. The films were characterized using X-

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ray diffraction (XRD), optical absorption (OA) and real part AC-conductivity (ACC).

## 2. Experimental

Powders of cerium oxide ( $< 100$  m), provided by the Department of Chemical Technology of the Center of Applied Researches for the Development of Nuclear Energy, were used as the starting material. Purity of 99% was determined by atomic spectroscopy with the majority impurities consisting of La 0.5%, Nd 0.2%, 0.1%, Th 0.1%. The aliovalent impurities were considered as dopants.

The films were deposited by flash evaporation in a vacuum chamber. The system was pumped down to a pressure of  $10^{-6}$  torr by an oil-diffusion pump and then a pre-evaporation was performed to clean the surface of the crucible. The powder feeding frequency was adjusted to get an evaporation rate of 2.6 m/h. The boat-to-substrate distance was varied between 4.5 and 5.5 cm. Some evaporated films were annealed for 12 h in air at 300°C.

Two types of substrate were used for the evaporations: glass and alumina (99%) sheets. Both substrates were also cleaned with trichloroethylene, acetone, deionised water rinse, chemical cleaning, deionised water again and dried using nitrogen flow. The chemical cleaning for the glass was done with  $H_3PO_4$ , and for the alumina substrates, with a mixed solution of HCl,  $H_2O$  and  $H_2O_2$ .

XRD patterns were recorded in a TUR M 62 diffractometer, using Cu  $K\alpha$  radiation ( $\lambda = 1.54178$  Å) at 30 kV and 30 mA, the scanning rate was  $1^\circ \text{ min}^{-1}$  in the  $2\theta$  range from 25 to  $60^\circ$ . The  $2\theta$  values were calibrated using a Si external standard.

Optical absorption data were determined from optical transmittance in the energy range 2–3.4 eV. A SF-26 Lomo UV–visible spectrometer was used for the optical transmittance measurements.

The AC conductivity was measured in the temperature range 423–723 K in air. A phase sensitive lock-in amplifier (Scitec Instruments) was used for the measurement of the real part of the AC electrical conductivity in the frequency range 25–100 kHz, with an applied voltage of 0.1 V. Bio Rad (Microscience Division) silver paste was used as the electrode. The configuration for the electrical measurements is presented in Fig. 1.

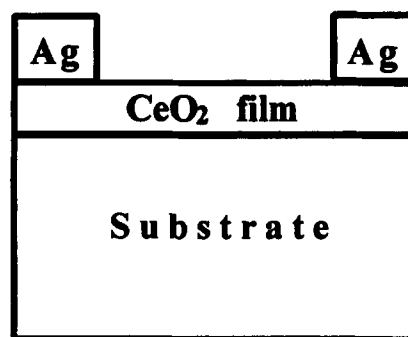


Fig. 1. Configuration of substrate/ $CeO_2$  thin film/Ag samples for the AC conductivity measurements.

## 3. Results and discussion

Fig. 2 shows a typical XRD pattern of  $CeO_2$  film deposited on a glass substrate, which received thermal treatment. It can be concluded that the film is crystalline and second phases are not present. The cell parameter, 5.417 Å, is in good agreement with the reported value, 5.417 Å, for bulk  $CeO_2$  [14]. However, the relative intensities of peaks 200, 220 and 311 are significantly lower (6, 18, and 9%) than those reported for bulk material (30, 52 and 42%); this fact could be due to a preferable orientation, such as has been seen by other authors in  $CeO_2$  thin films [15].

The optical absorption results are shown in Fig. 3 for annealed and as-grown films. The linear response of the square of the absorbance vs. photon energy indicates that permitted direct transitions are present [16], as Sundaran et al. have found for  $CeO_2$  films [17]. The absorption edge does not show significant

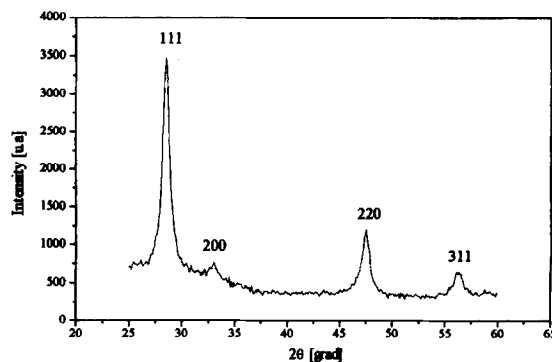
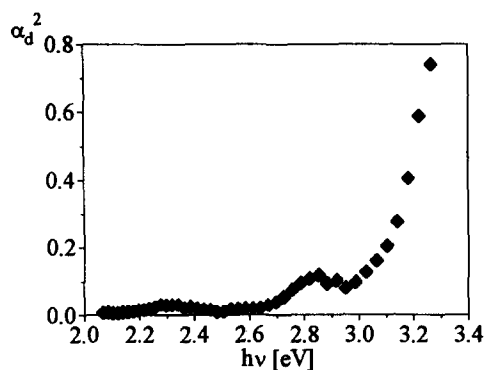
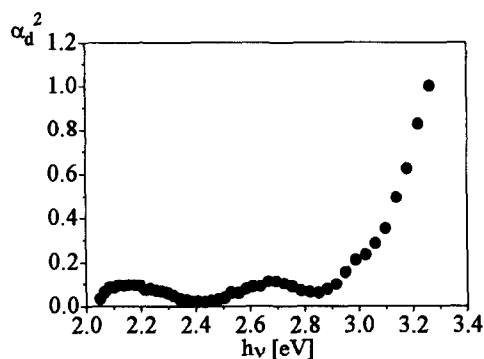


Fig. 2. DRX pattern of a deposited film.



a)



b)

Fig. 3. Optical absorbance of the  $\text{CeO}_2$  films: (a) without annealing, (b) annealed.

differences in all the samples and lies between 3.04 and 3.11 eV, but it is important to say that the film adherence improves with the thermal annealing. The thicknesses of the films were estimated from the interference oscillations of the transmittance, knowing the refractive index of  $\text{CeO}_2$  [18]. The calculated values are in the interval 0.6–0.9  $\mu\text{m}$ .

Fig. 4 shows a typical film after heat treatment. The pattern of circles corresponds with homogenous thickness zones. Note that homogeneous circles of 12 mm in diameter are evaporated.

The real part AC conductivity vs. frequency is presented in Fig. 5. The ACC for disordered systems [19], including ionic conductors [20], follows a power law for high frequencies. In our case, for temperatures above 523 K, the curves show almost no dependence on the frequency, corresponding to a DC conduction mechanism in this frequency interval.

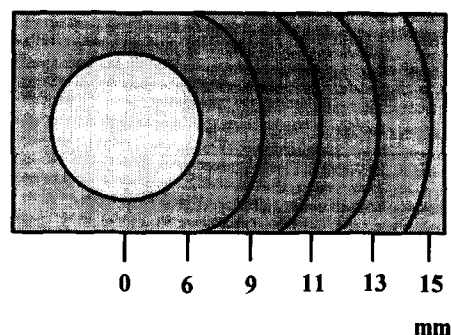


Fig. 4. Circles patterns showing the homogeneity of the film thickness.

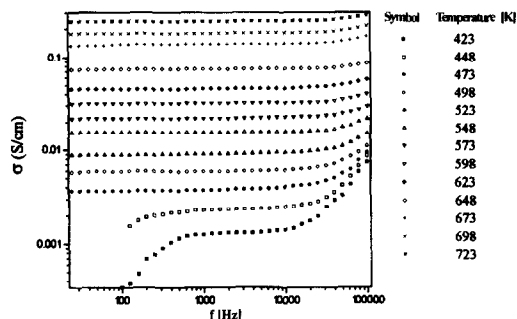


Fig. 5. AC conductivity vs. frequency at different temperatures. Note that for temperatures of 423 and 448 K a strong dispersion occurs at low frequencies. This dispersion has been attributed to a capacitance effect of the electrodes, but it disappears for higher temperatures, so changes the type of electrode from blocking to non-blocking electrode.

Even for temperatures lower than 523 K the development of a power law divergence in the frequency window is not enough to determine the power value.

The electrical response of the systems at different temperatures shows a very interesting behavior. Note that for temperatures of 423 and 448 K a strong dispersion occurs at low frequencies. This dispersion has been attributed to a capacitance effect of the electrodes [21], but it disappears for higher temperatures, thus changing the type of electrode from a blocking to a non-blocking electrode. If the conduction was electronic, this behavior was not present since the electrode has (Ag) metallic origin. However, it could be well understood on the basis of the blocking effect of the silver paste at these temperatures, which blocks the oxygen dissociation and hence gives a capacitive response. For higher tem-

Table 1

DC conductivity (taken at 1 kHz from the AC conductivity) for each temperature

Temperature [K]	DC conductivity [ $\sigma \text{ cm}^{-1}$ ]
423	0
448	0
473	0
498	0.01
523	0.01
548	0.02
573	0.02
598	0.03
623	0.05
648	0.07
673	0.14
698	0.18
723	0.24

peratures the oxygen dissociation increases leading to a non-blocking electrode.

The values of the DC conductivity were taken at 1 kHz, because this frequency belongs, for all temperatures, to the frequency independent interval of the ACC. These values are recorded in Table 1. The Arrhenius activation energy calculated from the DC conductivity is  $0.51 \pm 0.02$  eV, which is in good agreement with the values for oxygen vacancy diffusion in fluorite type oxides [4,5,22–24], but is lower than the values of heavy doped oxides [4,5,25]. It indicates that the vacancies are free, not forming clusters due to the low dopant concentration in the films. The values of conductivity and activation energy show that these films are suitable for use in chemical sensor technology. Studies of morphological, crystallographic and transport dynamics aspects in samples with controlled dopant concentrations are left for future work.

#### 4. Conclusions

CeO<sub>2</sub> was deposited using flash evaporation and then thermally treated, getting films with good adherence. The films are cerium oxide films as shown by the DRX and optical absorption results. The films have a wide electronic band gap ( $\sim 3$  eV), and a DC conductivity mechanism of lower activation energy ( $\sim 0.5$  eV), together with the blocking

and non-blocking effect of the electrodes indicates the ionic nature of the charge transport.

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#### References

- [1] E.C. Subbarao and H.S. Maiti, *Solid State Ionics* 11 (1984) 317.
- [2] T.J. Kirk and J. Winnick, *J. Electrochem. Soc.* 140 (1993) 3494.
- [3] B.C.H. Steele, *Solid State Ionics* 75 (1995) 157.
- [4] P. Sarkar and P.S. Nicholson, *Solid State Ionics* 21 (1986) 49.
- [5] D.Y. Wang, D.S. Park, J. Griffiths and A.S. Nowick, *Solid State Ionics* 2 (1981) 95.
- [6] C.R.A. Catlow, *Philos. Mag. A* 64 (1991) 1011.
- [7] M. Balkanski (Ed.), *Microionics* (North-Holland, Amsterdam, 1991).
- [8] A.C. Tan and P.S. Nicholson, *Solid State Ionics* 67 (1993) 131.
- [9] V.E.J. van Dielen and J. Schoonman, *Solid State Ionics* 57 (1992) 141.
- [10] R.E. Klingler, *Solid State Ionics* 52 (1992) 1.
- [11] R. Creus, J. Sarrandin and M. Ribes, *Solid State Ionics* 53–56 (1992) 641.
- [12] C. Julien, A. Khelifa, N. Benramdane, J.P. Guesdon, P. Dzwonkoski, I. Samaras and M. Balkanski, *Mater. Sci. and Eng. B* 23 (1994) 105.
- [13] E. Caudron, G. Baud, J.P. Besse, M. Jacquet and G. Blondiaux, *Solid State Ionics* 57 (1992) 189.
- [14] PDF 34-394, *Nat. Bur. Stand. (U.S.), Monogr.* 20 (1983) 38.
- [15] T. Inoue, H. Kudo, T. Fukusho, T. Ishihara and T. Ohsuna, *Jpn. J. Appl. Phys.* 33 (1994) L139.
- [16] R.H. Bube, *Photoconductivity of Solids* (John Wiley, New York, 1960).
- [17] K.B. Sundaram and P.F. Wahid, *Phys. Stat. Sol. B* 161 (1990) K63.
- [18] K.B. Sundaram, P.F. Wahid and P.J. Sisk, *Thin Solid Films* 221 (1992) 13.
- [19] A.K. Jonsher, *Dielectric Relaxation in Solids* (Chelsea Dielectric Press, London, 1983).
- [20] K. Funke, *Philos. Mag. A* 64 (1991) 1025.
- [21] J.R. Macdonald (ed), *Impedance Spectroscopy Emphasizing in Solid Materials and Systems* (John Wiley, New York, 1987).
- [22] C.R.A. Catlow, *J. Chem. Soc. Faraday Trans.* 86 (1990) 1167.

- [23] F.R. Requejo, A.G. Bibiloni, C.P. Massolo and K. Freitag, *Modern Phys. Lett. B* 8 (1994) 329.
- [24] R. Wang, J.A. Gardner, W.E. Evanson and J.A. Sammers, *Phys. Rev. B* 47 (1993) 638.
- [25] O.T. Sorensen, O. Johannessen and K. Clausen, in: *Transport–Structure Relations in Fast Ion and Mixed Conductors*, F.W. Poulsen, N.H. Andersen, K. Clausen, S. Skaarup and O.T. Sorensen (eds.) (Risø, 1985, p. 93).