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ELECTRICAL CONDUCTIVITY, DEFECT STRUCTURE AND DENSITY IN THE CERIA - GADOLINIA SYSTEM

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Abstract. Previous studies on the ceria-gadolinia system have mainly been done on oxides rich in ceria. The purpose of the present work is therefore to establish how the conductivity, density and structure depend on the gadolinia content especially at high doping levels.

Five different compositions were examined: $Ce_{1-x}Gd_xO_{2-x/2}$ with $x = 0.1, 0.3, 0.5, 0.7$ and 0.9. Oxide powders of these compositions were prepared by homogeneous precipitation of carbonates by hydrolysis of urea followed by calcination in air. Specimens were prepared by pressing and sintering in air at 1550°C.

Conductivity measurements on discs cut from the sintered specimens in the temperature range 400 - 900°C showed that the oxygen-ion conductivity decreases with increasing gadolinia content with a corresponding increase of the activation enthalpy for oxygen-ion migration. A model describing the variation of the theoretical density in this system is presented. From this model the densities of the sintered specimens was found to be in the range 93-99% TD.

(Continued on next page)

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Finally X-ray diffraction on the calcined powders showed that fcc single-phase material exists up to about x = 0.4 after which a bcc phase is formed

INIS Descriptors: ACTIVATION ENERGY; CERIUM OXIDES; CRYSTAL DEFECTS; DENSITY; DOPED MATERIALS; GADOLINIUM OXIDES; IONIC CONDUCTIVITY

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SUMMARY

Gadolinia-doped ceria is one of the best oxygen-ion conductors known today. The ionic conductivities obtained for these oxides at low dopant concentrations (4 - 8 mole% $GdO_{1.5}$) are considerably higher than those obtained for the doped zirconium oxides and they are therefore of interest for low-temperature (500 - 600°C) oxygen sensors, fuel cells and electrolyzers. The defect responsible for the high conductivity in these oxides is, as for the doped zirconium oxides, oxygen vacancies formed by doping with oxides with aliovalent cations of a lower valence than that of the host cations. In the case of high doping levels (50% or higher), however, the situation is reversed. Here the system can be considered as ceria-doped gadolinia in which the predominant defect is interstitial oxygen. Previous studies on these oxides have mainly been on oxides rich in ceria whereas, to the knowledge of the authors, no systematic studies have hitherto been done on oxides with a high gadolinia content. The purpose of the present work is therefore to establish how the conductivity, density and structure depend on the gadolinia concentration especially at high doping levels.

Five different compositions were examined. If the stoichiometric formula of oxides in this system is expressed as $Ce_{1-x}Gd_xO_{2-x/2}$, the compositions covered in the present work correspond to $x = 0.1, 0.3, 0.5, 0.7$ and 0.9. Powders of doped oxides were prepared by homogeneous precipitation of carbonates by hydrolysis of urea followed by calcination in air. Specimens were prepared by pressing and sintering in air at 1550°C. EDAX measurements showed that a good homogeneity was obtained by this process. The structure of the specimens was determined by X-ray diffraction, whereas the electrical properties were determined in air in the temperature range 400 - 900°C by 2-probe ac-measurements on discs cut from the sintered specimens. Finally, the densities of the sintered specimens were determined by buoyancy measurements, and from a model describing the

variation of the theoretical density in this system the percentage of the theoretical densities obtained could be determined.

The results obtained in this work indicate: (a) that the oxygen-ion conductivity decreases with increasing gadolinia content. The interstitial oxygen formed at higher doping levels thus cannot contribute to the conductivity probably due to geometrical factors; (b) that the activation enthalpy for oxygen-ion migration increases with increasing gadolinia content (c) that the process developed for the fabrication of specimens can give sintered densities in the range 93 - 99% TD, and finally (d) that fcc single-phase material exists up to about $x = 0.4$ after which a bcc phase is formed. The monoclinic Gd_2O_3 phase could only be detected for $x > 0.95$.

This work is part of Mr. Heggestad's thesis research for his Master degree at the Technical University of Trondheim, Norway. It was presented as a poster at the Euchem Conference on Solid State Chemistry and Electrochemistry, Oxford, March 1984. This poster is reproduced in the present report.

BACKGROUND

The purpose of this work is to develop alternatives to stabilized zirconia as oxygen ion conductors. Ceria has several advantages compared to zirconia:

- *Recent works show that ceria doped with approximately 5 mole% gadolinia has a better conductivity than stabilized zirconia at temperatures lower than 800°C*

- *Ceria needs less doping than zirconia to achieve optimal conductivity.*

- *Pure ceria possess the fluorite structure and can accommodate large amounts of doping. This is an advantage for the study of defect interactions as a function of doping level.*

- *The electrical properties of compositions with more than 50 mole% gadolinia have not been fully investigated before. The conductivity drops as the gadolinia content increase towards 50 mole%. Our aim is to see if this trend continues throughout the system.*

THEORY

It is convenient to divide the system into three parts:

-CeO_2 doped with $GdO_{1.5}$.

All compositions up to about 40 mole% $GdO_{1.5}$ keep the fluorite structure of pure CeO_2. The defect reaction is:

$$2GdO_{1.5} \rightarrow 2Gd'_{Ce} + 3O_O + V_O^{\cdot\cdot}$$

Oxygen vacancies are the charge carriers.

-$GdO_{1.5}$ doped with CeO_2.

It is here reported (see below), that compositions with more than 75 mole% $GdO_{1.5}$ have the cubic gadolinia structure. The defect reaction suggested is:

$$2CeO_2 \rightarrow 2Ce^{\cdot}_{Gd} + 3O_O + O''_i$$

In this case the interstitial oxygen is the charge carrier.

-Compositions containing between 40 and 75 mole% $GdO_{1.5}$ consist of two phases; one with 40 mole% $GdO_{1.5}$, the other with 75 mole% $GdO_{1.5}$.

THEORY

The electrical conductivity can be expressed by the general equation:

$$\sigma = A/T \exp(\Delta S/k) \exp(\Delta H/kT)$$

A, ΔS and ΔH will depend on the degree of defect interactions. Table I and II lists the three terms for V_o and O_i respectively. In both tables it is assumed either complete defect association or -dissociation.

The defect interaction equation in the two cases is, for V_o and O_i respectively:

$$V_o^{\cdot\cdot} + Gd'_{Ce} = [V_o Gd_{Ce}]^{\cdot}$$
$$O_i'' + Ce_{Gd}^{\cdot} = [O_i Ce_{Gd}]'$$

Table I: V_o

	A (K/ohm cm)	ΔS (eV)	ΔH (eV)
Dissoc. def:	$e^2 a_0^2 \nu_0 n_0/2k$	ΔS_m	ΔH_m
Assoc. def:	$e^2 a_0^2 \nu_0 N_{Ce}/4k$	$\Delta S_m + \Delta S_D$	$\Delta H_m + \Delta H_D$

Table II: O_i

	A (K/ohm cm)	ΔS (eV)	ΔH (eV)
Dissoc. def:	$e^2 a_0^2 \nu_0 n_0/8k$	ΔS_m	ΔH_m
Assoc. def:	$e^2 a_0^2 \nu_0 N_{Gd}/16k$	$\Delta S_m + \Delta S_D$	$\Delta H_m + \Delta H_D$

m=migration, D=dissociation.

MODEL FOR CALCULATION OF THEORETICAL DENSITY IN THE SYSTEM.

The model is based on the general equation:

$$d=1.66020\,\Sigma A/V$$

ΣA: weight sum of all atoms in the unit cell.
V: volume of unit cell (Å^3)
1.66020: converts amu/Å^3 to g/ccm.

This is applied in the two one-phase regions:

Region 1: $Ce_{1-x}Gd_xO_{2-x/2}$. $x=0-0.4$
The term ΣA for this region is:

$$\Sigma A=((1-x)A_{Ce}+xA_{Gd})4+(1-x/4)A_o 8$$

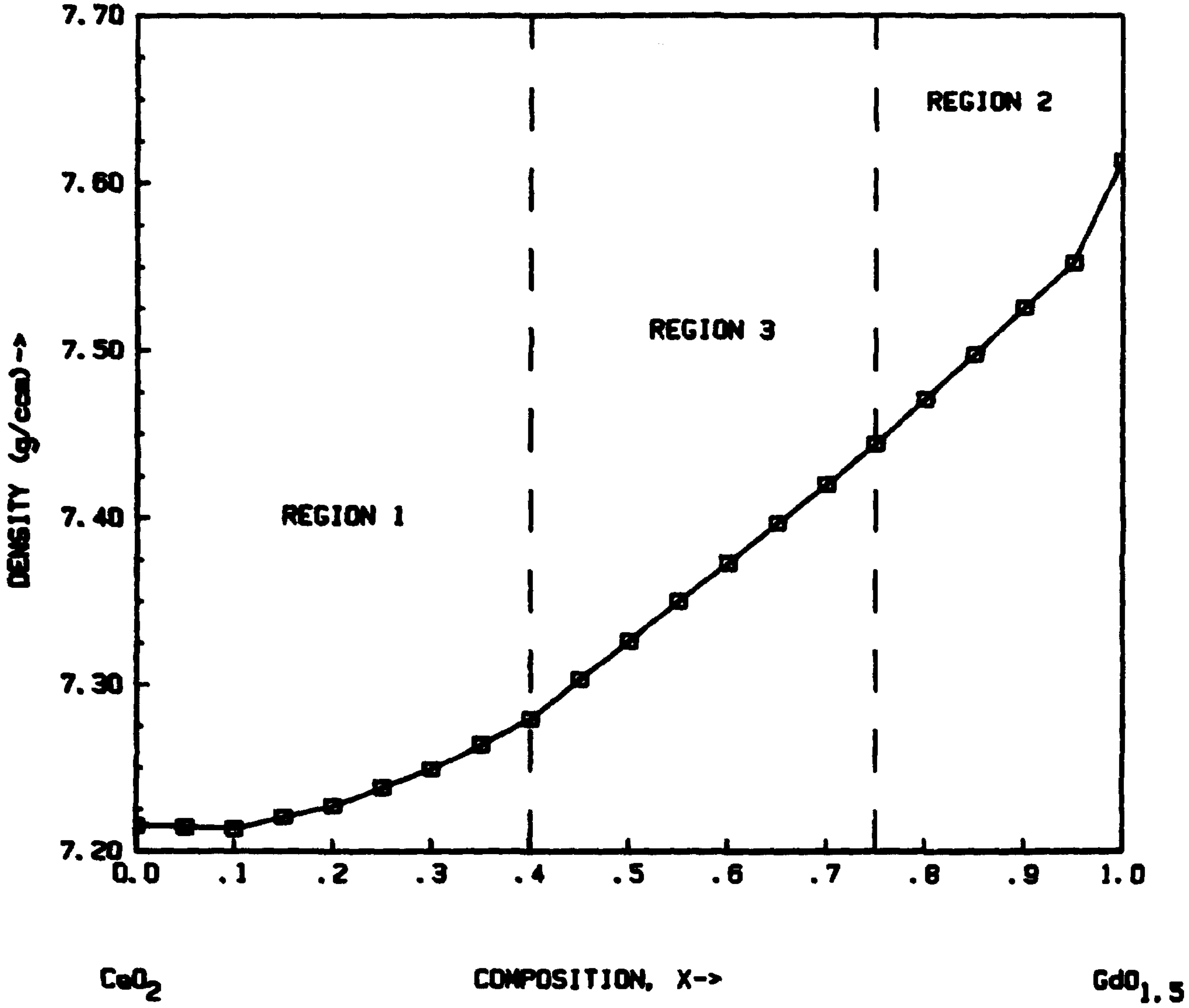
Region 2: $Gd_{1-y}Ce_yO_{1.5+y/2}$. $y=0-0.25$

$$\Sigma A=((1-y)A_{Gd}+yA_{Ce})4+(1+y/3)A_o 6$$

Region 3: The model assumes a linear increase in the 75 mole% $GdO_{1.5}$ phase from 0 to 100% in the two-phase region. The density is:

$$d=d_{0.75}C+d_{0.40}(1-C)$$

C is fraction of the 75 mole% $GdO_{1.5}$ phase.



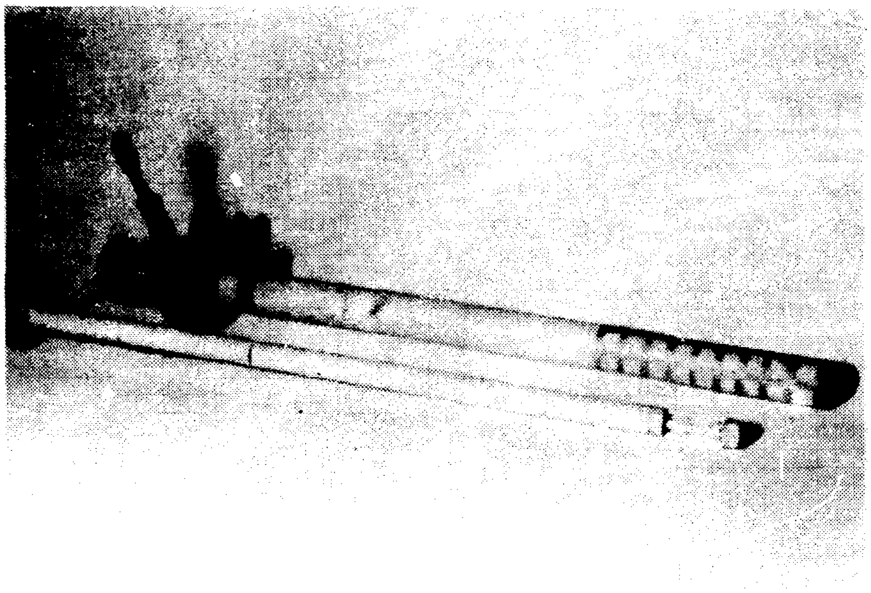
Theoretical density in the system, according to the model presented in this work.

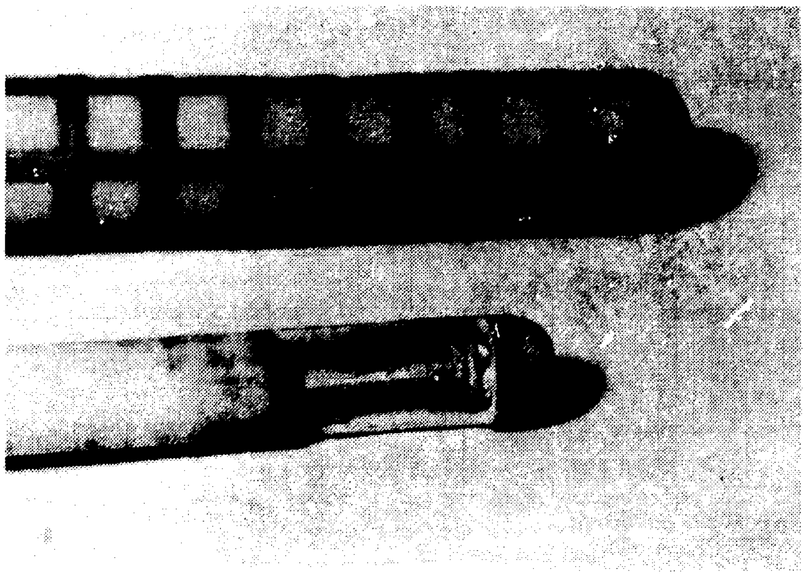
EXPERIMENTAL

- 5 compositions were prepared containing 10, 30, 50, 70 and 90 mole% $GdO_{1.5}$ respectively. The precipitated powder was calcined at 800°C overnight and pressed to pellets at 3tons/cm^2 pressure. The pellets were sintered at 1600°C for 1 hour. Three samples were cut of each composition; the lengths being approximately 0.75, 1.0 and 1.5mm. The samples were cut from the same sintered pellet. Each sample was coated with platinum paste and fired at 900°C.

- The frequency dependent impedance was measured using a 1250 Solartron Frequency Response Analyser. The measurements were all within the frequency range 65kHz-100mHz, and the temperature range 350-900°C.

- The two photos show the sample holder.





HOMOGENEOUS PRECIPITATION

This method is based on the hydrolysis of urea, which provide carbonate ions for the precipitation of the metal carbonates. The hydrolysis can be expressed by the following equation:

$$H_2NCONH_2 + 2H_2O \rightarrow 2NH_4^+ + CO_3^{2-}$$

The advantage is that the precipitation takes place simultaneously in the whole reaction volume. This is because the hydrolysis does not occur at room temperature, but requires heating. This means that the urea and the metal nitrates may be dissolved together, and then heated. Precipitation starts when the solution reaches the boiling point, at approximately 103°C.

In this work the precipitation time was 6hrs, and the yield was between 93 and 97% of the theoretical.

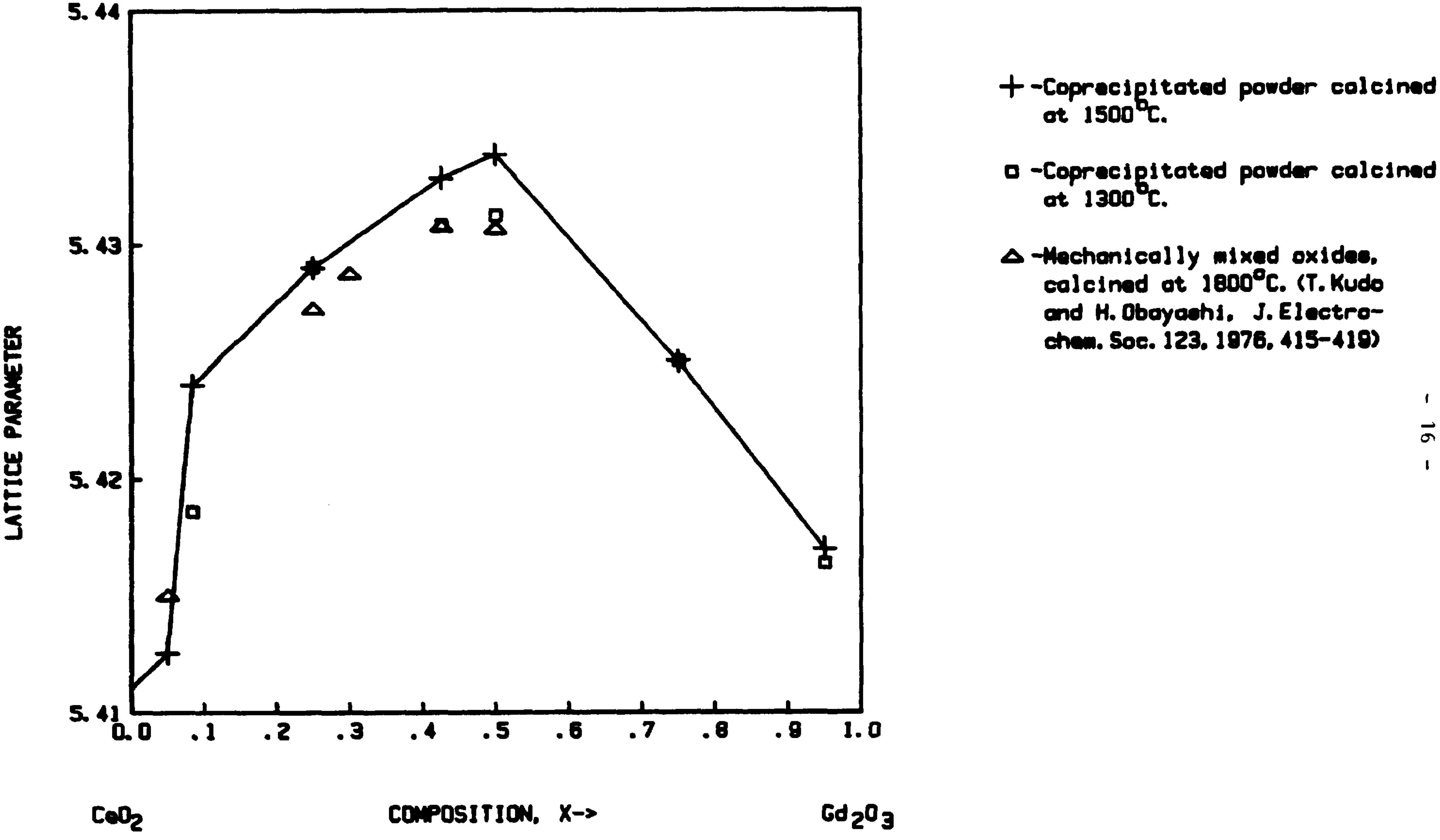
STRUCTURE OF $(Ce_{1-x}Gd_x)O_{2-x/2}$ SOLID SOLUTIONS.

X-ray analysis at room temperature showed:

$0=x$	fcc
$0<x<0.4$	fcc, single phase.
$0.4<x<0.75$	fcc+bcc, two phases.
$0.75<x<0.95$	bcc, single phase.
$0.95<x<1$	bcc+monoclinic, two phases.
$x=1$	monoclinic (high temp.), single phase.

LATTICE PARAMETER OF $(Ce_{1-x}Gd_x)O_{2-x/2}$ SOLID SOLUTIONS

The lattice parameters were determined by extrapolation using the Nelson & Riley method. The unit cell for the cubic structure of $GdO_{1.5}$ consists of eight fcc cells (cation lattice). Only half of the lattice parameter of this large cell is shown here.


5.44
5.43
5.42
5.41
LATTICE PARAMETER
0.0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
CeO_2
COMPOSITION, X->
Gd_2O_3
+ -Coprecipitated powder calcined at 1500°C.
□ -Coprecipitated powder calcined at 1300°C.
△ -Mechanically mixed oxides, calcined at 1800°C. (T. Kudo and H. Obayashi, J. Electrochem. Soc. 123, 1976, 415-419)

RESULTS

- TABLE I. Densities given in percent of theoretical value (%TD):

mole% $GdO_{1.5}$:	10	30	50	70	90
%TD :	98.6	95.8	92.9	98.4	98.5

- TABLE II. Activation enthalpy H for the five compositions. Two values are listed for the specimens containing 10 and 30 mole% $GdO_{1.5}$. These represent stage II and III respectively. H is calculated from the regression line and is valid within ±0.5 in the final digit.

mole% $GdO_{1.5}$	H (eV)	
10	0.35 (st. II)	0.70 (st. III)
30	0.53 (st. II)	1.08 (st. III)
50	1.38	
70	1.56	
90	1.68	

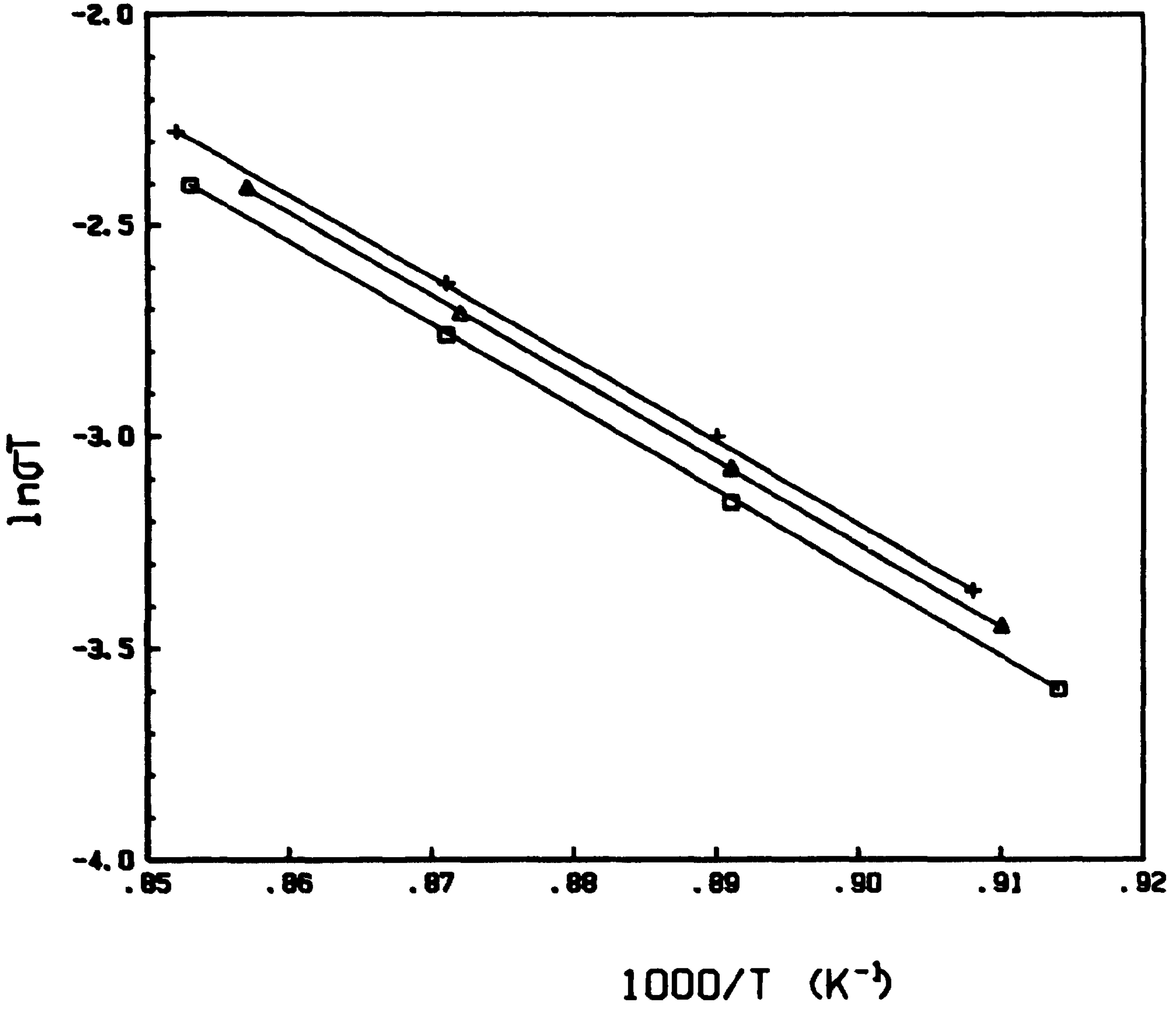
DISCUSSION

The figure shows the Arrhenius-plot for the three samples of the composition with 90 mole% $GdO_{1.5}$. The sample length is 0.75mm(E1), 1.0mm(E2), and 1.5mm(E3). As can be seen from the figure the conductivity seems to increase with the length, and this effect is observed for all compositions. It is assumed that this is caused by a low degree of porosity in the electrodes, resulting in an inhomogeneous current flow near these. With the approximation that the electrodes of the samples are equal one sees that this effect becomes less important with increasing sample length. The Solartron sees the current inhomogeneity caused by lack of triple points as an extra resistance in the material.

To compensate for this a 'true conductivity' has been calculated. The formula used is:

$$1/\sigma'_t = (l_2\rho_2 - l_1\rho_1)/(l_2 - l_1)$$

l means sample length, ρ is resistivity and σ'_t is the true conductivity. The subscript indicates the sample number with increasing length 1->3. Changing the subscripts 2 by 3 gives σ''_t, and the average of these two σ'_ts is taken as the true conductivity.



Arrhenius-plot for the three samples of composition E, 90 mole% $GdO_{1.5}$.

□ - sample E(1)

△ - sample E(2)

+ - sample E(3)

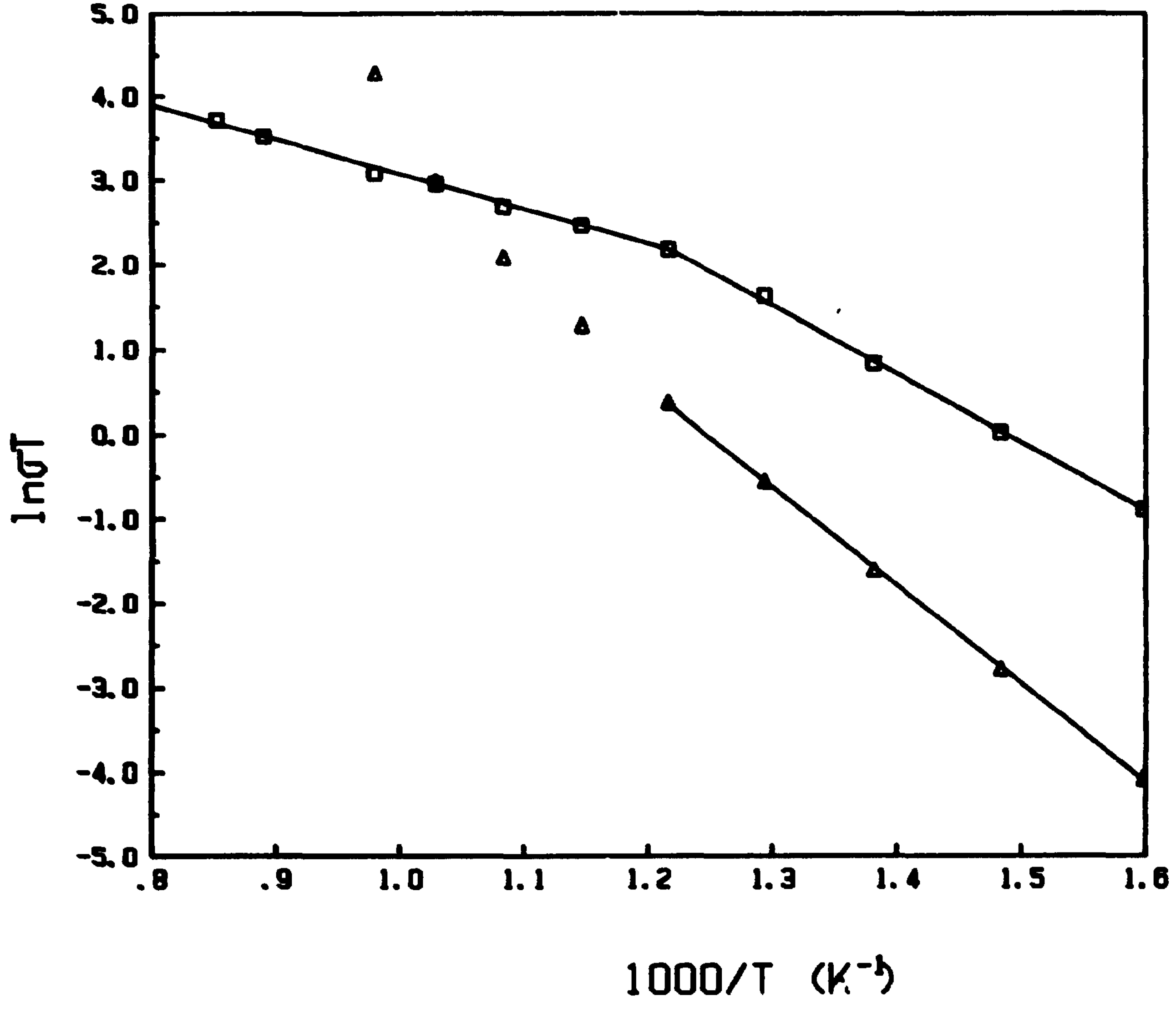
DISCUSSION

The figure shows the Arrhenius-plot for one of the samples of the 10 mole% $GdO_{1.5}$ composition. This plot contains all the typical features for the 10 and 30 mole% $GdO_{1.5}$ compositions.

- The lattice conductivity show two linear regions within this temperature range, the higher called stage II and the lower stage III. Stage II is connected with dissociated defects, hence the activation enthalpy for migration is lower than in stage III, the defect association range.

- This plot has a relatively well defined break point between stages II and III. This transition region usually covers a wider temperature interval.

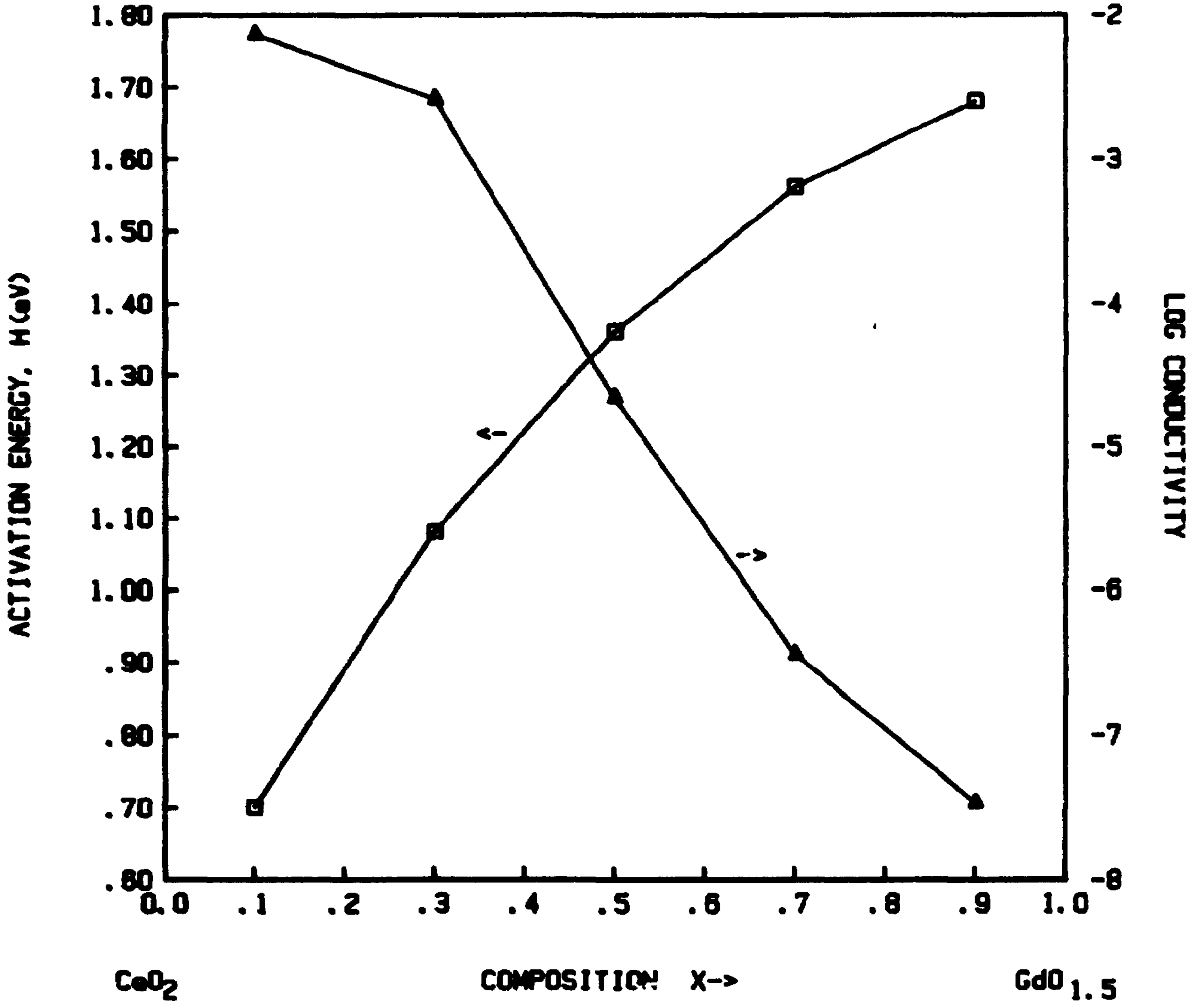
- The grain boundaries give a considerable contribution to the total conductivity. As can be seen from the plot it is the dominating factor below 700°C for this specimen. The grain boundary conductivity increases from 10 to 30 mole% $GdO_{1.5}$. For the other compositions, no grain boundary effect occur. Thus it seems that the lattice- and the grain boundary conductivity, varies inversely with composition.



Arrhenius-plot for one sample of the composition A, 10 mole% $GdO_{1.5}$.

□ - lattice conductivity

Δ - grain boundary conductivity



Activation energy and conductivity (500°C) vs composition. Note that the conductivity scale is logarithmic.

CONCLUSIONS

- It is confirmed that doped ceria has a ionic conductivity that rivals that of stabilized zirconia at lower temperatures (down to 550-600°C).

- The ionic conductivity decrease monotonously in the range 10 to 90 mole% $GdO_{1.5}$.

- The correspondance between activation enthalpy and conductivity previously observed is verified in this work. It is not possible here to decide the optimal conductivity.

- Considering the high densities of the sintered pellets, it can be concluded that preparation of powders by homogeneous precipitation is a very attractive method.

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Title and author(s)

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Abstract

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