JOURNAL OF MATERIALS SCIENCE 19 (1984) 49–56

Low temperature preparation of stabilized zirconia

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The preparation of stabilized zirconia by thermal decomposition of metal alkoxides is reported. Formation of stabilized zirconia takes place at 400° C. The a.c. conductivity of the samples has been measured from 400 to 1000° C. The best conductivity is found in ZrO_2 doped with 15 per cent CaO, which at 400° C is $2.37 \times 10^{-6} \Omega^{-1} cm^{-1}$ and at 1000° C is $1.26 \times 10^{-2} \Omega^{-1} cm^{-1}$, with an activation energy of 1.16 eV. Transport number measurements show that stabilized zirconia prepared by this method is purely an oxygen ion conductor.

1. Introduction

Solid electrolytes which conduct by oxygen ion transport have been of great interest for measurements of thermodynamic and kinetic properties of systems containing oxygen and also for their potential application in energy conversion devices. The greatest activity in the field of oxygen ion conductors has centred around stabilized zirconia [1–4] because this material is a pure ionic conductor over a wide range of oxygen partial pressures.

This property is manifest in ZrO_2, which has the fluorite structure. ZrO_2 is stabilized in this structure by adding divalent oxides such as CaO and MgO or trivalent oxides such as Y_2O_3. This substitution in addition, causes oxygen ion vacancies which are responsible for the enhanced ionic conductivity. Conventionally, this solid solution, e.g. ZrO_2–CaO is prepared by starting from the respective oxides or carbonates through solid state reactions. However, there are many problems associated with these methods of preparation, e.g. high temperature required for the preparation of the powder material as well as for sintering and the associated problem of purity maintenance during the high temperature heating. The reactivity of oxides used for solid state material preparation can be enhanced by using freshly prepared active oxides, submicron size particles and homogeneous mixing.

Ultrafine powders of metal oxides have been prepared by using organometallic compounds and inorganic polymers of the metals of interest [5]. Metal alkoxides have been used to prepare extremely pure and submicron size metal oxides [6–7]. Mazdiyasni *et al.* [8], prepared yttrium oxide stabilized zirconia at 1000° C by hydrolysis of metal alkoxides.

This process has proved to be advantageous over other techniques for the preparation of extremely pure and homogeneous ceramic powders. However, in the above hydrolysis process of alkoxides, some of the advantages associated with the thermal decomposition technique are sacrificed.

We have succeeded in preparing stabilized zirconia by the thermal decomposition technique using zirconium isopropoxide with calcium ethoxide or magnesium ethoxide. The present paper reports the preparation of stabilized zirconia by the above technique and its properties.

2. Experimental details

2.1. Preparation of starting materials

2.1.1. Zirconium isopropoxide

Zirconium isopropoxide was prepared following the method described by Bradley *et al.* [9]. All chemicals used, e.g. ethyl alcohol, isopropyl alcohol and benzene were carefully dried first. Dry HCl gas was passed into a solution of analytical grade zirconium tetrachloride ($ZrCl_4$) in ethyl alcohol (C_2H_5OH) until the solution was saturated with HCl. Dry pyridine (C_5H_5N) was then added

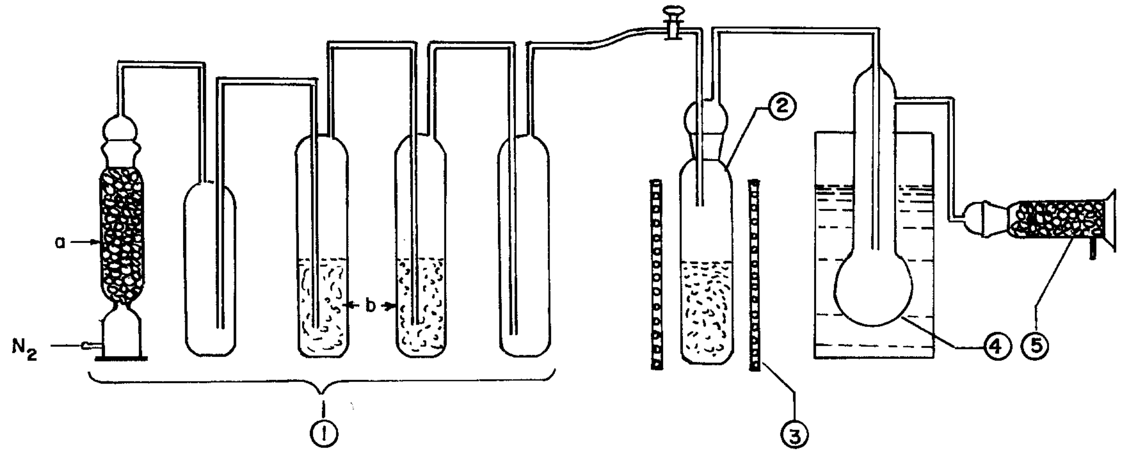

Figure 1 Assembly for the preparation of stabilized zirconia. 1. N_2 drying assembly (a) CaO tower and (b) H_2SO_4 bubbler. 2. Reaction tube. 3. Furnace. 4. Cold trap. 5. Drying tube.

to this solution. A white solid $(C_5H_5N)_2ZrCl_6$ precipitated, which was filtered and dried.

This solution was suspended in a mixture of isopropyl alcohol to give a slurry and dry ammonia gas was passed through this slurry maintained at room temperature. The following reaction is presumed to take place:

$$(C_5H_5N)_2ZrCl_6 + 4C_3H_7OH + 6NH_3 \xrightarrow{\text{Benzene}} Zr(OC_3H_7)_4 + 6NH_4Cl + 2C_5H_5N.$$

The precipitated ammonium chloride was filtered out and zirconium isopropoxide was crystallized from that filtrate by vacuum evaporation of solvent benzene.

2.1.2. Calcium ethoxide

Analytical grade calcium metal was refluxed with dry ethyl alcohol with a trace of iodine to initiate the reaction. When the reaction was complete, as seen from the disappearance of calcium metal, the solid calcium ethoxide was obtained by vacuum evaporation of excess ethyl alcohol.

2.1.3. Magnesium ethoxide

Analytical grade magnesium turnings were refluxed with ethyl alcohol with a trace of iodine. When the reaction was complete, the solid magnesium ethoxide was obtained by vacuum evaporation of excess ethyl alcohol.

The metal alkoxides were characterized by chemical analysis and infrared (IR) spectroscopy.

2.2 Thermal analysis

The thermal analysis was carried out in a Paulik-Paulik and Erdy derivatograph. 200 mg of the alkoxide was placed in a platinum crucible and heated at a rate of 4° C min^{-1}. Finely powdered aluminium oxide was used as a reference material. Mixtures of alkoxides, e.g. zirconium isopropoxide with calcium ethoxide or zirconium isopropoxide with magnesium ethoxide, were also studied. The components were thoroughly mixed in isopropyl alcohol in a ratio such that the final ZrO_2:CaO and ZrO_2:MgO mole fraction was 85 : 15. The mixture was heated at 200° C for two hours to remove alcohol and to partly decompose it in an atmosphere of dry nitrogen and then subjected to differential thermal analysis (DTA), thermogravimetric (TG) and differential thermogravimetric (DTG) analysis.

2.3. Preparation of stabilized zirconia

Zirconium isopropoxide and calcium ethoxide were added in a desired ratio to isopropyl alcohol taken in a quartz tube. The quartz tube reactor which had arrangement for passing N_2 gas was assembled and placed in a vertical furnace (Fig. 1). The tube was heated up to 80° C in an atmosphere of passing nitrogen and was kept at that temperature for half an hour to achieve a homogeneous mixing of alkoxides. The tube was further heated to remove the solvent alcohol. The solid mass of alkoxides obtained after removal of the solvent was further heated to 400° C for complete decomposition. The mixture of oxides obtained was then heated at 700° C in air. The proportion of calcium ethoxide in the mixture was varied to obtain the optimum percentage of CaO required for the stabilization of the cubic zirconia.

Magnesium oxide stabilized zirconia was also prepared similarly using zirconium isopropoxide and magnesium ethoxide.

2.4. Structural analysis

Structural analysis was done by X-ray diffraction. A Philips PW 1730 X-ray diffractometer with Cu*K* radiation was used.

Crystallite size was determined from the X-ray line width using Scherrer's relation [10].

2.5. Conductivity measurement

Stabilized zirconia powder was pressed in the form of a pellet using polyvinyl acetate as a binder. The pellet was sintered in a vacuum furnace at 1600° C for two hours. The pellet turned yellow in colour because of loss of oxygen which on heating in air at 800° C for one hour turned white in colour.

Graphite contacts were made on the pellet by rubbing a pure graphite rod on the two opposite surfaces. Pressure contacts were then applied on these surfaces. It was found suitable for conductivity measurements in vacuum or an atmosphere of dry nitrogen. The sample holder used for conductivity measurements is shown in Fig. 2.

The conductivity was measured from 200 to 800° C using and LCR bridge (Radart make 1203 model).

2.6. EMF measurements

EMF measurements were carried out to determine the transport number of oxygen ions. A galvanic cell was prepared using CaO stabilized zirconia as an electrolyte with Ni–NiO and Cu–CuO electrodes as follows:

$$\mathrm{Cu{-}CuO/Zr_{0.85}Ca_{0.15}O_{1.85}/Ni{-}NiO}.$$

The stabilized zirconia pellet was kept in the centre and the Cu–CuO, Ni–NiO pellets were pressed on the sides. The three pellets were placed in the sample holder used for conductivity measurements. Two platinum foils with platinum leads were pressed on either sides of the above cell with the help of stainless steel springs to provide the necessary connections for measurements.

The EMF was measured at various temperatures, in an atmosphere of purified nitrogen, during the heating and cooling cycles. The cell voltage was measured with a digital multimeter (Yamuna Model 1010).

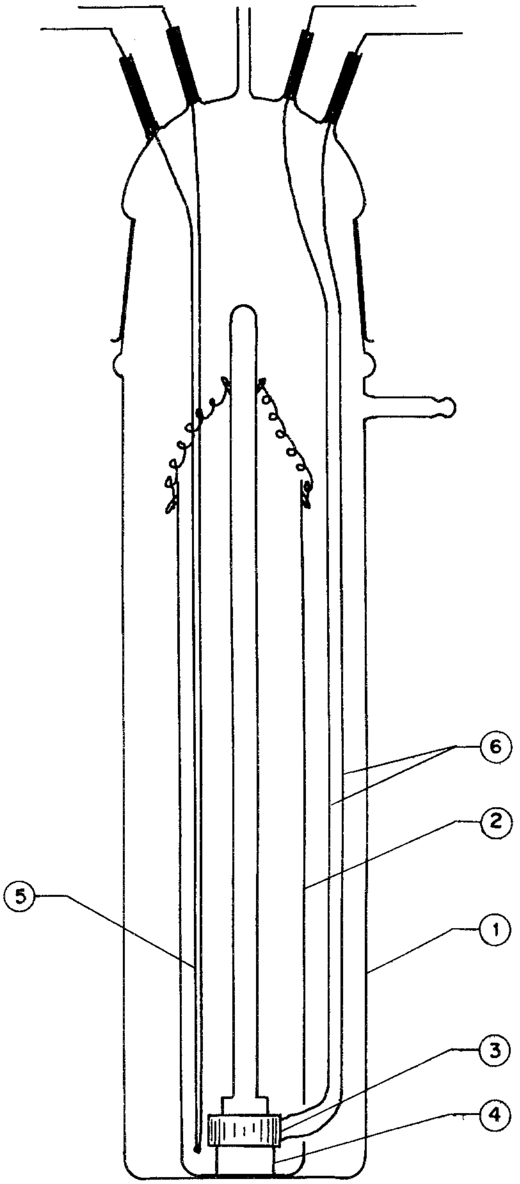

Figure 2 Conductivity measurement assembly. 1. Sample holder enclosure. 2. Sample holder. 3. Sample. 4. Platinum foil. 5. Thermocouple. 6. Platinum wires.

3. Results and discussion

3.1. Thermal analysis

The derivatogram of the mixtures of partly decomposed alkoxides at 200° C are shown in Fig. 3.

It is seen that complete decomposition of magnesium ethoxide and calcium hydroxy ethoxide (obtained from partial decomposition of calcium ethoxide) in the mixtures takes place below 400° C. If the magnesium and calcium ethoxides

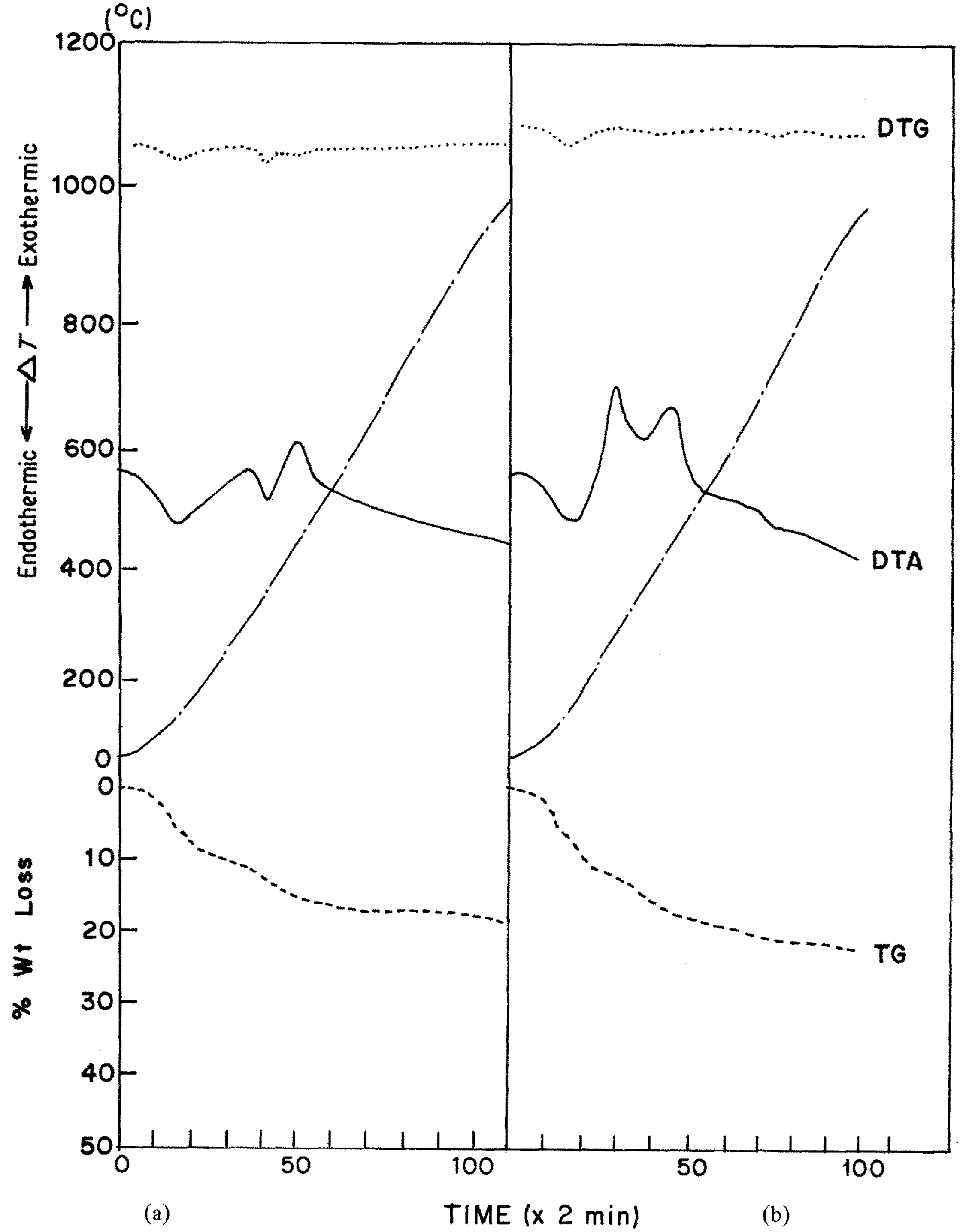

Figure 3 DTA, TG and DTG curves of a mixture of partly decomposed alkoxides. (a) ZrO_2:MgO and (b) ZrO_2:CaO.

are heated individually their decomposition takes place at a higher temperature [11]. The exotherm in the DTA curve in the temperature range of 400 to 500° C in both cases is due to structural changes in the compound. This compound was analysed by X-ray diffraction. The pattern is representative of the cubic form of zirconia. This confirms that zirconia stabilized in the cubic structure forms at 400° C when metal alkoxides are used as the starting meterial.

TABLE I Structural data of (ZrO$_2$:MgO) and (ZrO$_2$:CaO) systems as obtained from X-ray study

MgO:ZrO$_2$ system (prepared at 700° C)			CaO:ZrO$_2$ system			
MgO (mol %)	ZrO$_2$ (mol %)	Structure	CaO (mol %)	SrO$_2$ (mol %)	Prepared at T (° C)	Structure
3	97	Monoclinic zirconia (+ traces of cubic)	4	96	700	Monoclinic zirconia
4	96	predominantly cubic	5	95	700	cubic
5	95	cubic, single phase	10	90	700	cubic
10	90	cubic, single phase	15	85	400, 700 1400	cubic
20	80	cubic, single phase	20	80	700	cubic
30	70	cubic + free MgO	25	75	700	cubic + CaZrO$_3$
50	50	cubic + free MgO	50	50	700	CaZrO$_3$
15	85 (heated at 900° C)	MgO + monoclinic zirconia	15	85	700	cubic

3.2. X-ray results

The structural results obtained by X-ray diffraction technique for ZrO$_2$:CaO and ZrO:MgO system are given in Table I. A typical X-ray diffraction pattern of ZrO$_2$:CaO (85:15 mol %) obtained from metal alkoxides is given in Fig. 4.

The lattice parameter increases with increasing CaO mol % used for stabilization. MgO stabilized zirconia decomposes to MgO and monoclinic zirconia on heating at 900° C.

We have calculated the crystallite size using Scherrer's relationship [10].

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where D is the average crystallite dimension, λ is the X-ray wavelength, β is the full width at half maximum of the peak, θ is the Bragg angle and K is a constant. The calculated crystallite sizes are given in Table II.

It is observed that the crystallite size increases with increase in preparation temperature. The crystallites of (ZrO$_2$:CaO) prepared at 350° C are very small (2.2 nm) and the peaks are very broad

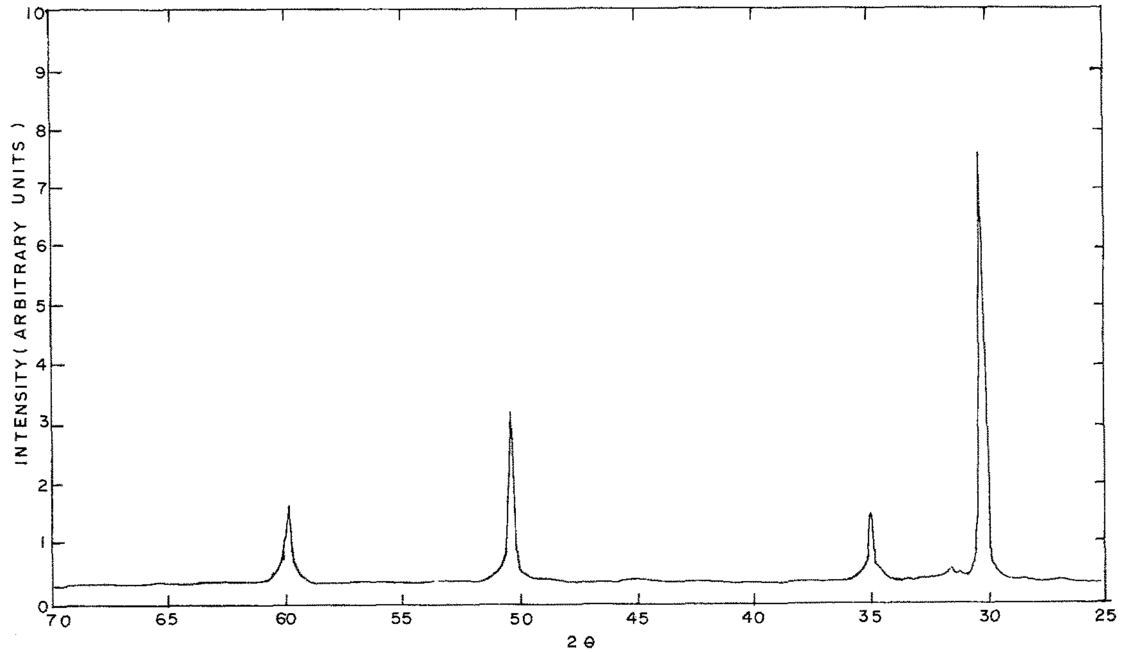

Figure 4 X-ray diffraction pattern of CaO:ZrO$_2$ (15.85 mol %).

TABLE II Crystallite size for ZrO_2:CaO and ZrO_2:MgO system at various temperatures

System	Temperature of preparation (°C)	Crystallite size (nm)
CaO:ZrO_2	350	2.2
	450	5.5
	700	10.0
	1200	60.0
MgO:ZrO_2	400	5.0

as can be seen in Fig. 5. This may be attributed to the growth of the stabilized cubic ZrO_2 crystallites from the amorphous powder at low temperature. In the case of a solid solution, the X-ray peaks are broadened due to inhomogeneity in the sample as well as the finite size of the crystallites. In this case, it is difficult to interpret the results. Although it is difficult to separate the broadening effects due to crystallites and the compositional inhomogeneity in the sample, useful information may be obtained about these solid solutions. For the present investigation the approximate crystallite size can be used to follow up the reactions.

When the preparation temperature is 400° C the X-ray pattern shows well resolved peaks and the crystallite size increases. At higher temperatures (~ 1200° C) the crystallites size increases to 60 nm.

3.3 Electrical measurements

Fig. 6 shows the plot of $\log \sigma$ against $(1/T) \times 10^3$ for various mol% of CaO stabilized zirconia pellets. All the plots are linear and hence conductivity $\sigma(\text{ohm}^{-1}\,\text{cm}^{-1})$ can be expressed in the form

$$\sigma = A \exp(-E/kT)$$

The activation energy E was obtained from the slope of the plot of $\log \sigma$ against $(10^3/T)$. Table III gives the activation energies and electrical conductivity at 1000° C. The density of the pellets was 85% of the theoretical value.

TABLE III Electrical conductivity of stabilized zirconia

mol% of CaO in stabilized ZrO_2	Conductivity ($\Omega^{-1}\,\text{cm}^{-1}$)	Activation energy E (eV)
5	4.0×10^{-5}	0.5
10	2.5×10^{-4}	0.8
15	1.3×10^{-2}	1.2
20	5.3×10^{-3}	1.1
25	1.1×10^{-3}	0.9

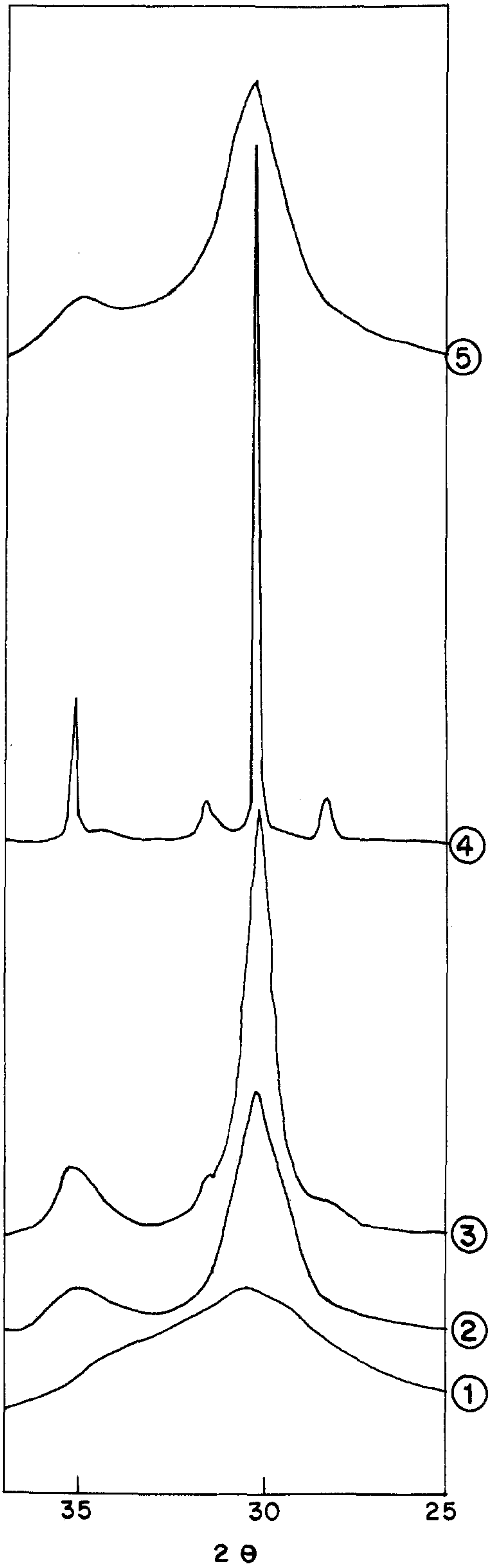

Figure 5 X-ray diffraction peak CaO:ZrO_2 (15:85) heated at 1. 350°C, 2. 450°C, 3. 700°C, 4. 1200°C and 5. MgO:ZrO_2 at 400°C.

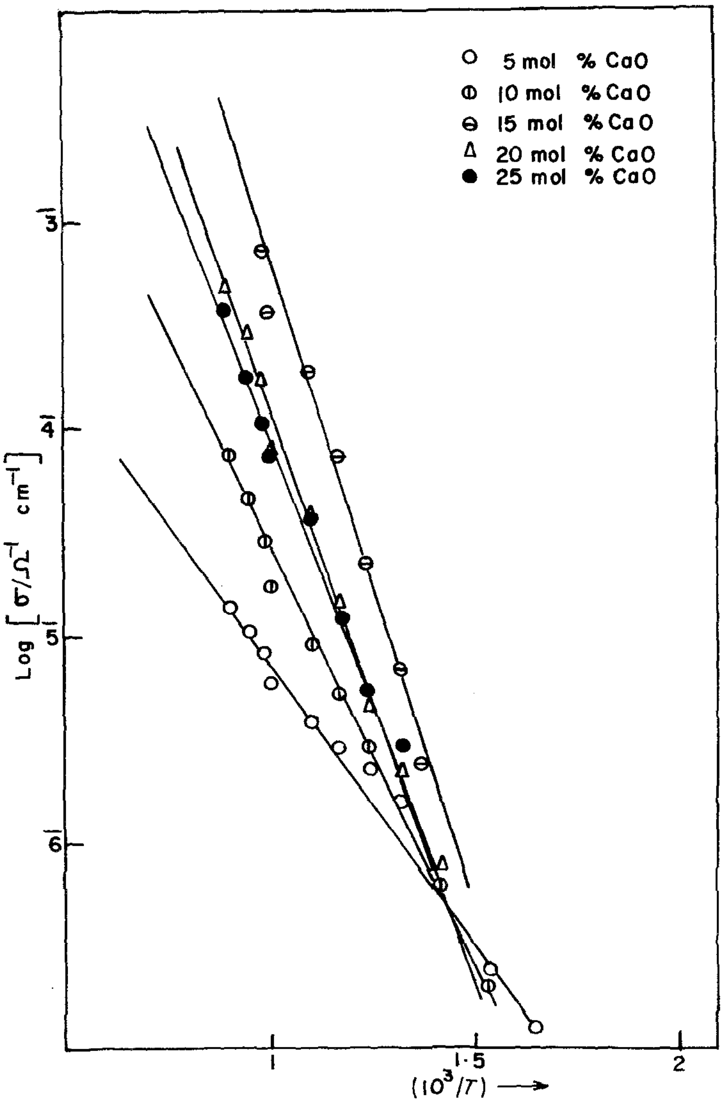

Figure 6 Temperature dependence of conductivity as a function of mol% CaO in stabilized zirconia.

The conductivity results show that σ attains a maximum value at a CaO concentration of 15 mol%. The conductivity σ depends on the number of oxygen ion vacancies which are produced by the replacement of Zr^{4+} by Ca^{2+}. The energy of activation is also low. This supports the hypothesis of Tien and Subbarao [12]. As we increase the CaO content, the concentration of vacancies increases with the increase in Ca^{2+} ions, in the vicinity of Ca^{2+} ions in the lattice. This increases the conductivity. At 20 mol% of CaO the system is binary, i.e. stabilized zirconia and $CaZrO_3$, which decreases the conductivity of the sample.

Our results of the conductivity measurements are in good agreement with the results obtained by Tien and Subbarao [12]. The results of the 15 mol% CaO stabilized zirconia may be compared with those of Hund [13] and of Kingery *et al.* [14]. Our samples were sintered at 1600° C for two hours and have 85% density and still show good conductivity which is comparable to the results of Tien [15] and Kingery *et al.* [14].

The results of the e.m.f. measurements and the thermodynamically calculated values of the e.m.f. are given in Table IV for the cell:

$$C/Cu\text{—}CuO/ZrO_2{:}CaO/Ni\text{—}NiO/C.$$

It is seen that there is good agreement between the measured values of the e.m.f. and the calculated values. From this it may be inferred that stabilized zirconia prepared by this method is

TABLE IV Theoretical and experimental e.m.f. for the cell – C/Cu–CuO/ZrO_2:CaO/Ni–NiO/C

Temperature (K)	e.m.f.	
	Measured (volt)	Calculated (volt)
800	0.29	0.29
900	0.28	0.28
1000	0.26	0.26
1100	0.25	0.25

purely an ionic conductor. The conductivity is attributed to the oxygen ions. These oxygen ions move through the oxygen vacancies created by the introduction of calcium oxide.

4. Conclusion

Stabilized zirconia is obtain at a nominal temperature of 400° C from zirconium isopropoxide and calcium ethoxide or magnesium ethoxide.

In our preparation technique the alkoxides are decomposed thermally and not hydrolytically as reported by Mazdiyasni *et al.* [8]. In case of hydrolytic decomposition, the oxides obtained are hydrated. During drying in air they may possibly get passivated. In the present technique the mixed alkoxides are reacted without exposure to air or moisture. The reactivity of these fine oxide particles is not changed and is apparently responsible for the improved equilibrium conditions required for stabilization of the cubic structure.

The relatively low formation temperature of oxides during decomposition of alkoxides enables them to be obtained in the amorphous or crystalline state with a high degree of purity and homogeneity essential for the solid state reaction.

This method can be used to prepare thin films of metal oxides when deposited from solutions of alkoxides in organic solvents or the gas phase. The use of mixtures of metal alkoxides in the preparation of films from the gas phase involves the problem of different volatilities of the components. In this sense the use of binary alkoxides is very promising. Their solution in organic solvents can be used to obtain composite materials of a given composition over a wide range of concentration.

Thus, we feel that this method of preparation of oxides in the form of powder or thin films has a good potential in the field of ceramic technology which should be explored by further studies.

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Received 26 July 1982
and accepted 22 April 1983