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Preparation and Thermal Evolution of Sol–Gel Derived Zirconia and Ceria–Zirconia Precursors

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Precursor powders of pure and 10 mol% ceria doped zirconia have been prepared by physical gelation of zirconium(IV) dichloride oxide, cerium nitrate, and oxalic acid using triple distilled water as solvent at room temperature (ca. 27 °C). Both the zirconium(IV) and doped zirconium(IV) oxalate oxide gels are transparent and are dried at 40 °C. The thermal evolution and crystallization behaviors of the amorphous gels have been investigated by TGA, DTA, and X-ray diffraction analysis. On calcination at 850 °C, zirconia precursor transformed to a monoclinic phase whereas only tetragonal phase has been observed for doped zirconia precursor. Estimation of the surface area and IR characterization have also been carried out for the prepared dried powders.

Zirconia based ceramics are the fascinating materials since the work of Garvie et al.;[1)] and ultimately increasing the demands for such materials because of their pioneering applications such as high temperature refractories,[2)] chemical gas sensors,[3)] coatings,[4)] etc. Several wet chemical routes have been developed for the preparation of zirconia and stabilized zirconia polycrystalline powders; alkoxide,[5—7)] citrate,[8)] chloride,[9,10)] and carboxylate[11,12)] processes have been used successfully. Among the wet chemical methods sol–gel technique has been widely used because of its advantageous such as reduced temperature of preparation, defined shape, porous or dense samples, selective doping, and extreme purity, etc.[13)] Moreover, the sol–gel process has attracted the attention of the industries.[14,15)] Recently Etienne et al.[16)] have prepared zirconium(IV) oxalate oxide using zirconium(IV) chloride and oxalic acid.

Generally, sol–gel process is broadly categorized as 1. Polymerized alkoxides and 2. Colloidal sols. The formation of the sol and gel in the former system is due to the polymerization of alkoxides through the chemical bonding whereas in the latter case the formation of the sol and gel is due to the interaction of various forces acting between the particles. The gelation of the such colloidal sol through the various forces is termed as physical gelation.

The objective of the present work is two fold. One is to extend the oxalate gelation to prepare a transparent, thixotropic, repeptisable 10 mol% ceria doped zirconium(IV) oxalate oxide gel at room temperature (ca. 27 °C) using zirconium(IV) dichloride oxide, cerium nitrate and oxalic acid by physical gelation. Second one is to stabilize the tetragonal phase of zirconia to room temperature by doping of 10 mol% ceria as the cerium nitrate. The repeptised gels have a high zirconia concentration. This preparation route provides a powder forming method for zirconia and tetragonal zirconia polycrystals (TZP).

Experimental

The starting materials were zirconium(IV) dichloride oxide (LR grade, CDH Chemicals), cerium nitrate (AR grade, CDH Chemicals), and oxalic acid (SD fine Chemicals). All the chemicals were used as such without any further purification, except filtration. Triple distilled water had been used throughout the experiments.

1. Preparation of Gels. **a. Zirconium(IV) Oxalate Oxide Gel.** Stoichiometric ratio of 1 M solutions (1 M=1 $\mathrm{mol\,dm^{-3}}$) of zirconium(IV) dichloride oxide and oxalic acid were prepared using water and mixed together at room temperature (ca. 27 °C). Immediately white flocculates were formed and gave a white opaque gel. The gel thus formed yielded a clear sol after stirring/shaking. The sol on being formed was transformed to a transparent thixotropic gel at room temperature by physical gelation. The addition of excess of oxalic acid formed a unclear sol which led to formation of an opaque gel. The gel obtained from the clear sol was oven dried at 40 °C, and the dried gel powder on being mixed with water, again became a clear sol which shows its repeptisable character.

b. Cerium–Zirconium(IV) Oxalate Oxide Gel. Solutions of zirconium(IV) dichloride oxide (1 M) and cerium nitrate (1 M) were stirred together. An appropriate amount of oxalic acid was mixed with the combined solution of zirconium(IV) dichloride oxide and cerium nitrate at room temperature (ca. 27°C). During the gelation, the observed characteristics of the doped gel was the same as those of the zirconium(IV) oxalate oxide gel. The gel was prepared in such a way that the final product of the calcined powder contains 10 mol% CeO_2–ZrO_2.

The prepared gels were dried at 40 °C and crushed in a mortar and pestle. The powders were calcined at 245, 425, 600, 700, and 850 °C for 1 h to estimate the surface area and to study the nature of the crystallization. Thermal behavior and IR studies of the dried gel powders were also conducted.

The following chart (Chart 1) shows the preparation procedure for these gel powders.

Results and Discussion

1. Formation of Gels. As soon as the solutions of oxalic acid and zirconium(IV) dichloride oxide are mixed, white flocculates are formed which give the thick

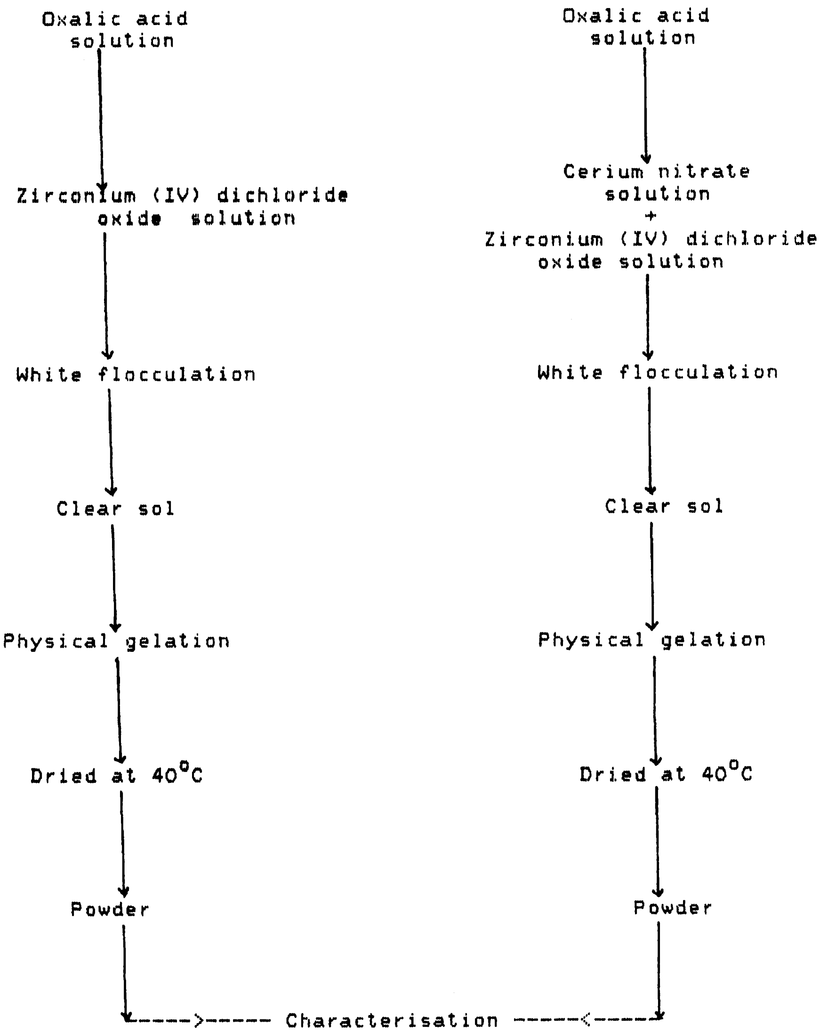

Chart 1.

white gel due to the various forces acting between the particles. After breaking the gel by stirring/shaking, the white gel slowly transforms to a clear sol. This is due to the adsorption of proton on the surface of the colloidal particles and thereby forming the electrical double layer. It has been noticed that the transparency of the sol, gel and the formation of the zirconium(IV) oxalate oxide gel are affected by atmospheric conditions. If the humidity of the atmosphere is more than 95%, the transparent sol and gel are very easily formed at room temperature (ca. 27 °C) and when the humidity is less than 90% both the sol and gel are slightly opaque. This may be due to the variation in the rate of reaction for the formation of zirconium(IV) oxalate oxide.

In the case of the cerium doped zirconium(IV) oxalate oxide gel, the addition of cerium as cerium nitrate results in the formation of transparent sol and becomes gel under the same experimental conditions as that of the pure zirconium(IV) oxalate oxide. The addition of stoichiometric ratio of oxalic acid with mixed solution of cerium nitrate and zirconium(IV) dichloride oxide leads to opaque white gel. But a transparent gel has been observed when the addition of oxalic acid is just sufficient to form the zirconium(IV) oxalate oxide alone. However, the time taken for the formation of clear sol for the doped oxalate is lesser than the pure zirconium(IV) oxalate oxide. The nature of existence of the cerium ions in the sol and gel is not clearly understood. However, Tohge et al.[17)] suggested that the doped ions are located on the surface of the pores in the preparation of the glass. Based on this suggestion, it is assumed that cerium ions would have been uniformly distributed on the pore surfaces of the zirconium(IV) oxalate oxide gel structure. Also, there is a possibility for a part of cerium ions forming cerium oxalate and mixing uniformly in the sol. The calcination temperature above 400 °C, cerium ions substitute zirconium ions in the crystal structure forming stabilized zirconia. For a clear understanding, detailed analysis has to be carried out to study the effect of the temperature, atmospheric humidity, and the concentration of the solution on the formation of the sol and gel.

2. Crystallization Behavior. X-Ray diffraction studies have been employed to analyse the nature of the crystallization of the dried and calcined powders of the gels. Figures 1 and 2 show the powder X-ray pattern of the zirconia and ceria–zirconia precursors dried at 40 °C and calcined at different temperatures for 1 h, respectively. It has been observed that the precursors dried at 40 °C are amorphous in nature. The metastable tetragonal zirconia starts to crystallize when the dried powder of the zirconium(IV) oxalate oxide gel is calcined at 425 °C and it retains the tetragonal phase upto 600 °C. At 700 °C both the tetragonal and monoclinic phases exist. The tetragonal phase has been completely transformed to monoclinic phase when calcined at 850 °C. The tetragonal phase starts to crystallize at 425 °C and the X-ray patterns for 600 and 850 ° show the retention of stabilized tetragonal phase for the doped zirconium(IV) oxalate oxide gel. Similar crystallization behavior has been observed for powders of Y_2O_3–ZrO_2 and Y_2O_3–CeO_2–ZrO_2.[18]

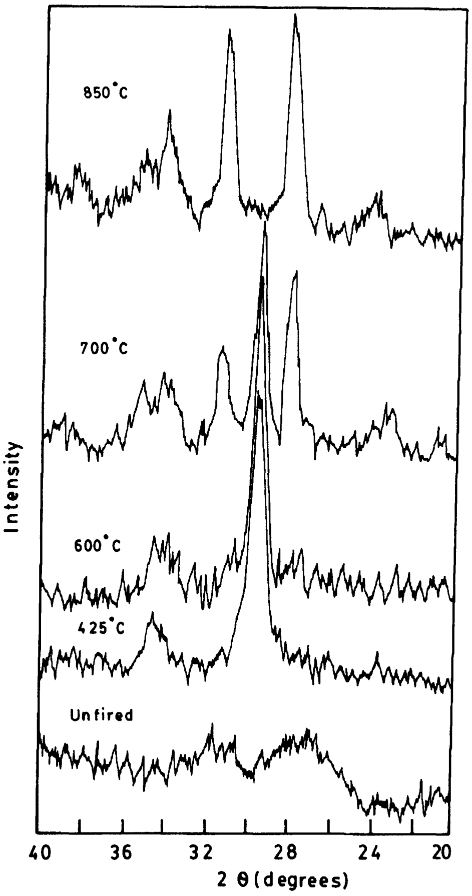

Fig. 1. X-Ray diffraction pattern as a function of heat treatment on dried zirconium(IV) oxalate oxide gel powder (calcination time 1 h).

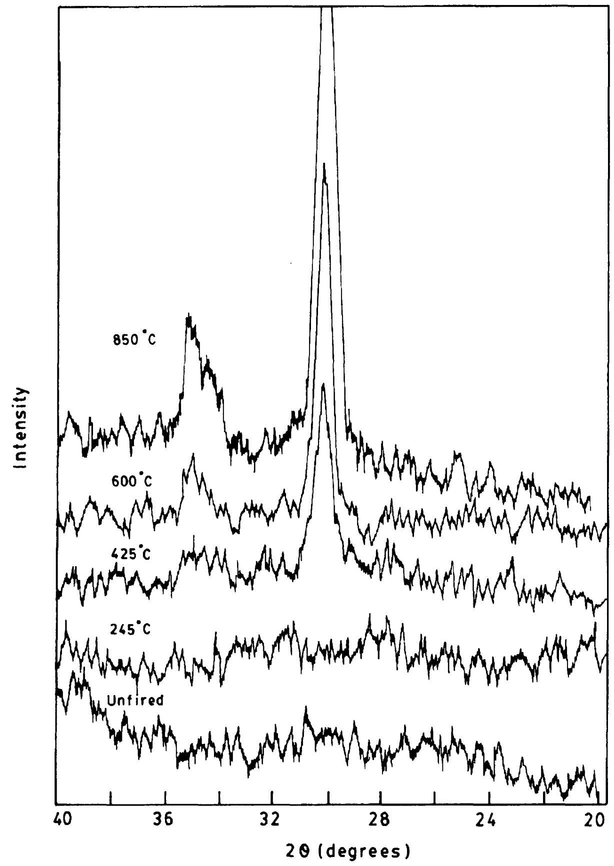

Fig. 2. X-Ray diffraction pattern as a function of heat treatment on dried Cerium–zirconium(IV) oxalate oxide gel powder (calcination time 1 h).

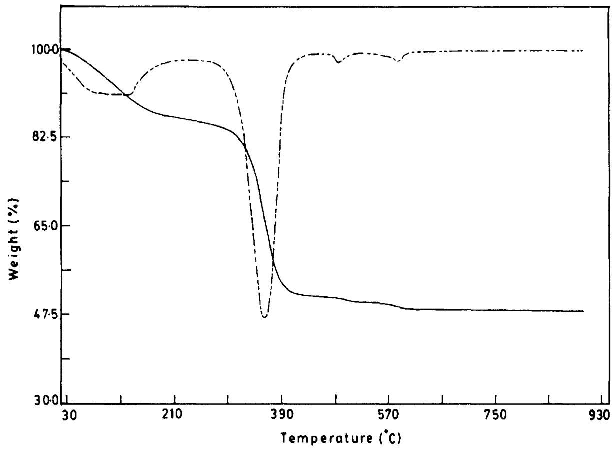

Fig. 3. TGA curve for the zirconium(IV) oxalate oxide gel dried at 40 °C.

3. Thermal Analysis. Weight loss and phase transition behaviors of dried zirconium and doped zirconium(IV) oxalate oxide gels have been carried out by TGA and DTA (For all TGA and DTA, heating rate=10 °C min^{-1}; Atmosphere=Air) studies. Figure 3 shows the TGA from room temperature to 950 °C of the zirconium(IV) oxalate oxide gel dried at 40 °C. It has been observed that there are two major weight losses of 14.23 and 34.64%. First weight loss is due to the dehydration of water and the latter corresponds to the thermal decomposition of organics with the simultaneous formation of amorphous zirconia. The dehydration of water, occurred around 170 °C is represented as

$$ZrOC_2O_4 \cdot 1.5H_2O \rightarrow ZrOC_2O_4 + 1.5H_2O$$

The oxalate decomposition at 348 °C is

$$\mathrm{ZrOC_2O_4 \xrightarrow{Air} ZrO_2 + 2CO_2}$$

There are two more weight losses observed around 480 and 570 °C which may be due to the release of chlorine along with the simultaneous crystallization of zirconia.

From the DTA of the dried zirconium(IV) oxalate oxide gel (Fig. 4), it is seen that there are three peaks in the temperature range 100 to 800 °C. The first peak observed around 170 °C is due to dehydration of water as observed in the TGA curve. The second endothermic peak around 350 °C is due to the decomposition of oxalate which is also observed in the TGA. The amorphous zirconia crystallizes at 441 °C in metastable tetragonal phase and the shoulder around 800 °C may be due to the transformation to monoclinic phase. This displasive phase transformation is a martensitic one which results in a smooth curve rather than a pronounced peak. These phase changes are clearly observed in the X-ray pattern (Fig. 1).

Figure 5 shows the TGA of the doped zirconia precursor dried at 40 °C. It is found that there are four major weight losses of 16.72, 15.61, 15.13, and 3.64%. The first weight loss corresponds to dehydration of water around 170 °C and the second weight loss is due to the burning and release of nitrate around 260 °C which includes the decomposition of the oxalate also. Indeed, the decomposition of oxalate takes place in two steps. The first step overlaps with the nitrate decomposition and the third weight loss corresponds to the decomposition of the second step of the oxalate which starts at 295 °C and comes to an end at 452 °C. The final weightloss may be due to the liberation of chlorine around 570 °C.

Figure 6 shows the DTA of the doped zirconium(IV) oxalate oxide gel dried at 40 °C. It shows one endothermic and three exothermic peaks in the temperature range 30 to 900 °C. The endothermic peak corresponds to the dehydration of water and the first exothermic peak observed around 261 °C is attributed to the burning and release of nitrates as observed in the TGA. The peak observed around 355 °C is due to the decomposition of oxalate which is in agreement with the TGA curve. However, the double step decomposition of oxalate is not resolved in the DTA curve.

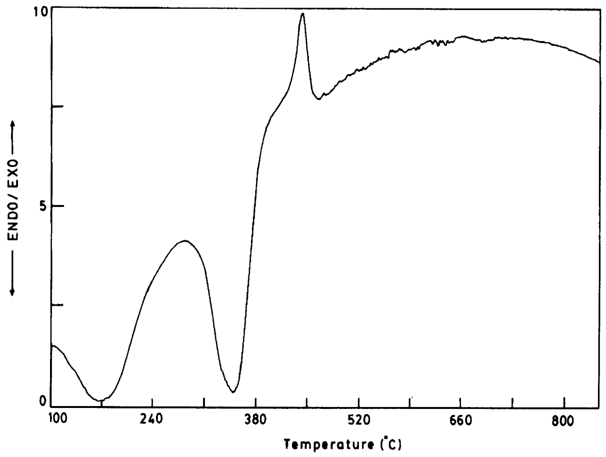

Fig. 4. DTA curve for the zirconium(IV) oxalate oxide gel dried at 40 °C.

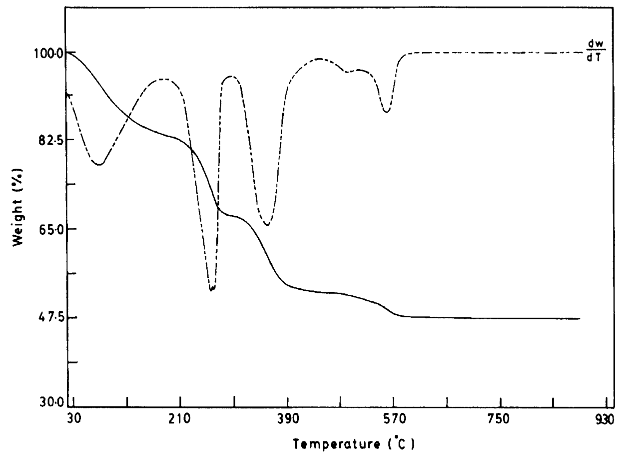

Fig. 5. TGA curve for the cerium–zirconium(IV) oxalate oxide gel dried at 40 °C.

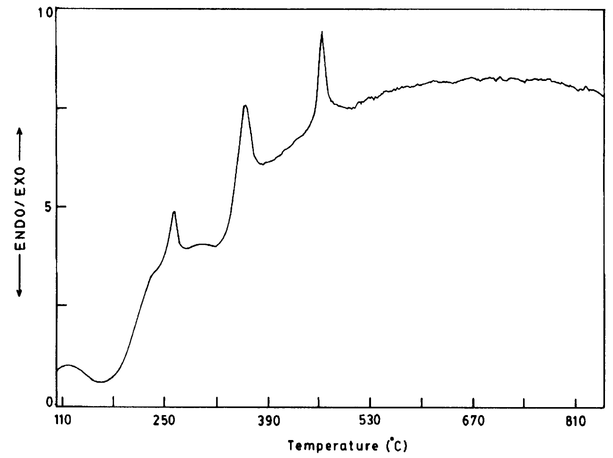

Fig. 6. DTA curve for the cerium–zirconium(IV) oxalate oxide gel dried at 40 °C.

It is interesting to note that in the pure zirconium(IV) oxalate oxide gel the decomposition of oxalate is an endothermic process whereas exothermic peak has been observed for the ceria doped zirconium(IV) oxalate oxide gel. During this process large amount of energy has been liberated for the doped gel. Gangadevi et al.[11,19] studied extensively, the thermal analysis of Zirconium(IV) oxalate oxides. The decomposition of oxalate is an exothermic oxidation of carbon monoxide in air but in vaccum, the decomposition is an endothermic. Based on this suggestion, the release of large amount of energy may be due to the exothermic oxidation of carbon monoxide. During the chemical reaction, part of the cerium nitrate forms the cerium oxalate along with the zirconium(IV) oxalate oxide. The organic decomposition takes place simultaneously for both the oxalates, and the total process becomes exothermic with the release of carbon monoxide and carbon dioxide. The peak at 463 °C corresponds to the crystallization of tetragonal phase of zirconia and is retained above this temperature.

The liberation of chloride ions are not observed in the DTA curve whereas it is observed in the TGA curve around 570 °C. The reason is that the ions may be physically adsorbed on the surfaces of the polycrystalline powders. At the temperatures above 530 °C, the adsorbed chloride ions release smoothly without any exothermic or endothermic energy release from the surfaces of the particles.

In the doped zirconia the crystallization of tetragonal phase takes place at 463 °C, whereas the crystallization of metastable phase is observed at 441 °C in the pure zirconia. The X-ray diffraction patterns clearly show these phase transformations (Figs. 1 and 2).

4. Sol Characterization. The preparation method of sol 1 is clearly given in the experimental procedure. The gel formed by the sol 1 is oven dried at 40 °C. The powder obtained from the dried gel is slowly mixed with water with stirring. The powder slowly dissolves in water and gives a clearer sol, namely sol 2, than the sol 1 and has been successfully repeated a number of times. In the zirconium(IV) oxalate oxide gel the hydrochloric acid that has been formed during the reaction of the reactants plays an important role for the repeptisation of the dried powder and to the formation of clear gel formed by the sol 2. In the case of doped zirconia, it is suggested that in addition to the chloride ions, nitrate ions also come into the picture for the repeptisation of the dried gel powder. The adsorbed positive charges on the surface of the particles are responsible for the repeptisation of the powder.[4]

The different stages of gelation and cycling processes are given in the following chart (Chart 2).

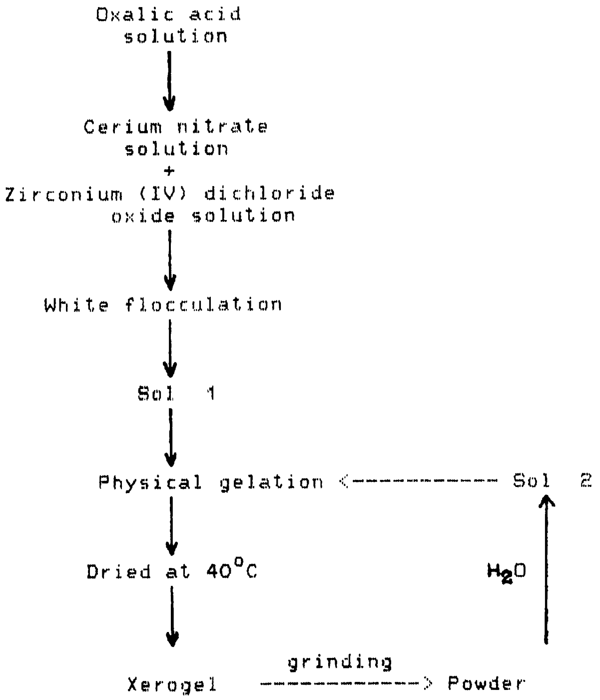

Chart 2.

Figures 7 and 8 show the gelation time as a function of concentration of chloride ions for the sol 1 and sol 2 respectively. Both the sols show the exponential character of gelation time with chloride ion concentration. As the concentration of the oxide powder (chloride ion) increases the gelation time decreases. The concentration of the chloride ions in the sol 2 is estimated by using the Volhard's volumetric method.

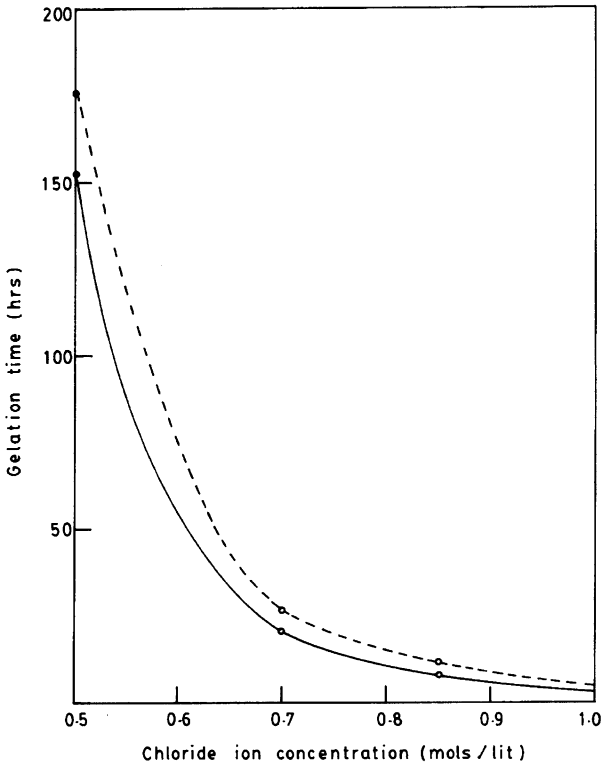

Fig. 7. Gelation time as a function of concentration of chloride ions for Sol 1. ---=zirconium(IV) oxalate oxide, —=cerium–zirconium(IV) oxalate oxide.

The pure and doped zirconium(IV) oxalate oxide gels prepared from the 1 M solutions by the method given in the experimental procedure contain only 6.12 wt% of zirconia and 6.67 wt% of cerium–zirconia powders in water which are gelt within short period of time at room temperature whereas the gels prepared by the gelation of sol 2 contains 10 wt% of the oxide powders after a long period of time. The zirconium(IV) oxalate oxide sol 2 gelt after 26 h and the doped zirconium(IV) oxalate oxide sol 2 gelt after 18 h. The observed large difference in the gelation time for sol 1 and sol 2 may be due to the excess of hydrochloric acid that has been removed during the drying of the gels at 40 °C. The observed shorter gelation time for the doped sol 2 is due to the presence of nitrate ions in addition to the chloride ions in the dried gel powder.

5. IR Characterization. From the IR Spectrum

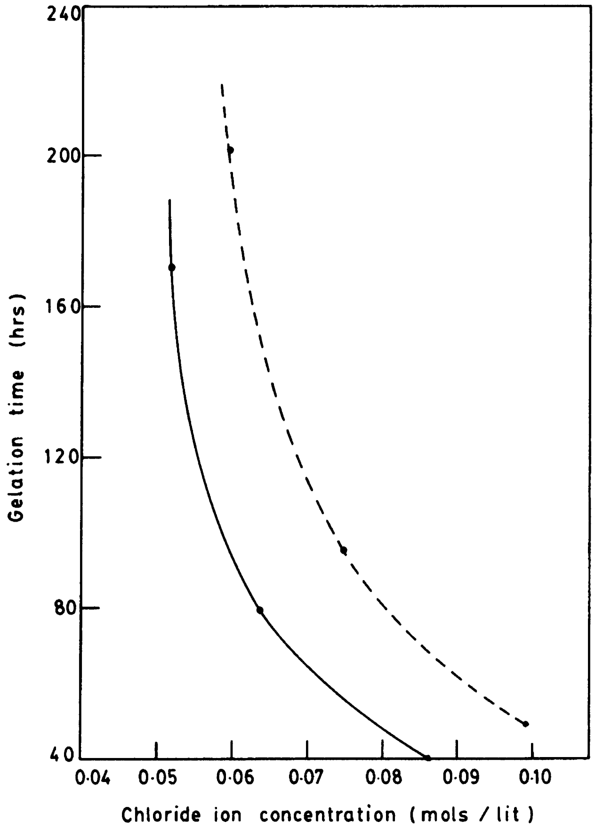

Fig. 8. Gelation time as a function of concentration of chloride ions for Sol 2. ---=Zirconium(IV) oxalate oxide, ——=Cerium–Zirconium(IV) oxalate oxide.

of the dried zirconium(IV) oxalate oxide gel (Fig. 9) powder, it is observed that our results are in agreement with that of Etienne et al.[16] Figure 10 shows the IR spectrum of the ceria doped zirconium(IV) oxalate oxide gel powder dried at 40 °C. The appearance of the peak at 1390 $\mathrm{cm^{-1}}$ may be due to the presence of residual nitrates in the dried doped zirconium(IV) oxalate oxide gel. However, the addition of cerium ion as cerium nitrate does not affect the quadridentate structure of the oxalate with the zirconium ion. As discussed earlier, the location of cerium in the zirconium(IV) oxalate oxide gel is not clear. To understand this, other techniques like Raman, NMR, and Mass spectrometric studies are being carried out. On calcination, the liberation of water and decomposition of oxalate take place as observed in the TGA and DTA results. Table 1 shows the vibrational frequencies of the dried gel powders.

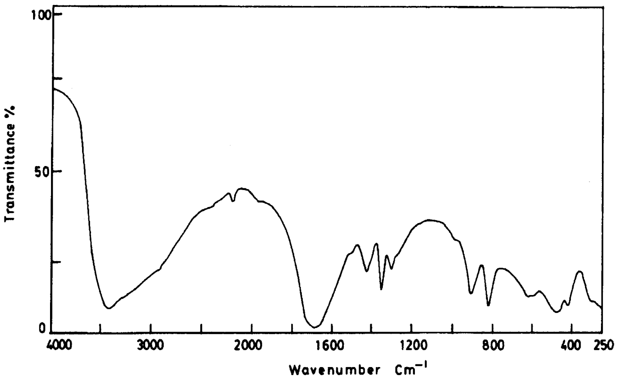

Fig. 9. IR Spectrum for the Zirconium(IV) oxalate oxide gel dried at 40 °C.

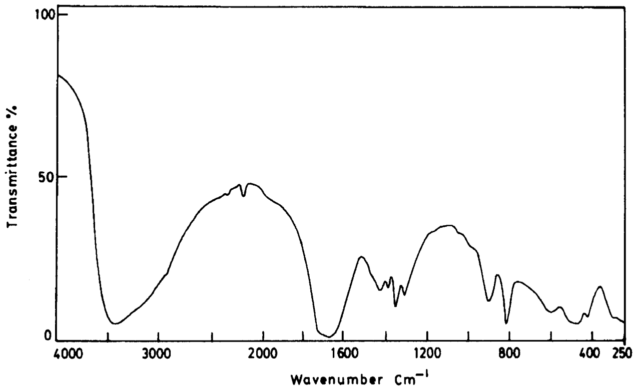

Fig. 10. IR Spectrum for the cerium–zirconium(IV) oxalate oxide gel dried at 40 °C.

6. Surface Area Measurement. Specific surface area of the pure and doped zirconium(IV) oxalate oxide gel powders calcined at different temperatures for 1 h are measured by the BET technique with nitrogen. Assuming the particles are spherical in shape, the average crystallite sizes of the pure and doped zirconia have also been calculated by means of the formula,

$$d=\frac{3}{S\rho},$$

where d is the average particle size (radius) in nm, S is the specific surface area in $\mathrm{m^2\,g^{-1}}$ and ρ is the density of the corresponding calcined powder in $\mathrm{kg\ m^{-3}}$. The results are given in Table 2. From the Table 2 it is observed that the surface area decreases as the calcining temperature increases, since the crystallite size increases with temperature.

Conclusion

In the present work, physical and thixotropic gels of pure and doped zirconium(IV) oxalate oxides have been prepared. The dried powders have a repeptisable character which contain high concentration of metal ions. DTA studies show that the dried zirconium(IV) oxalate

Table 1. Assignment of IR Bands

Vibrational frequencies/cm^{-1}			Group
16)	Zirconyl oxalate	Doped oxalate	
1680	1680	1680	ν_{as}(C–O)
1427	1425	1425	ν_s(C–O) + ν(C–C)
—	—	1390	$\nu(\mathrm{NO_3})^-$
1356	1350	1355	ν_s(C–O) + δ(O–C=O)
899	898	900	ν_s(C–O) + δ(O–C=O)
808	810	815	ν(Zr–O) + δ(O–C=O)
470	470	480	ν(Zr–O–Zr)

Table 2. Variation of Surface Area as the Function of Temperature Measured by BET Technique

	ZrO_2			Doped ZrO_2		
Firing temperature/°C	385	600	850	385	600	850
Specific area/m^2 g^{-1}	90	18	4	16	7	2
Average crystallite size/nm	14	41	94	44	72	159

oxide gel transforms to a monoclinic phase whereas the tetragonal phase has been observed for the doped gel. These have been confirmed by X-ray studies. Since the final weight percent of the dried gel powders are close to 47 wt%, these may be used as precursors for zirconia and ceria–zirconia.

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