Preparation of CoO-ZnO-Al_2O_3-SiO_2 monolithic gel by sol-gel method

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In recent years, sol-gel technique has emerged as one of the most promising new techniques for the preparation of functional materials with different dimensions: glass monoliths, fibers, nanopowders and thin films or coatings [1, 2]. In comparison with traditional method, the sol-gel method offers the advantages of high purity, good chemical homogeneity and low temperature processing. In sol-gel process, a sol is first prepared by mixing a liquid alkoxide or organic salt precursor. Then the sol transits into glass through the following processes: gelation, drying and firing of the gel. One of the most serious problems encountered in the sol-gel preparation of gel monoliths is fracture and crack formation taking place in the conversion of the wet gel to the dry gel [3]. Many studies about the cracking of the gels have been carried out [4–7]. In general, there are two methods to effectly prevent the crack formation in the course of drying, one is that the gels must be dried quite slowly, the other is to add the drying control chemical additives (DCCA), such as formamide, N,N-dimethylformamide (DMF), to the starting solutions.

The aim of the study was to investigate the preparation conditions of crack-free monolithic ZnO-Al_2O_3-SiO_2-CoO (ZASC) dried gels by a sol-gel method. Co^{2+}-doped $ZnAl_2O_4/SiO_2$ nanocomposites have been obtained by heating ZASC gels and have proved to be a useful functional material due to its absorption and luminescence properties [8]. But it is difficult to obtain large heated monolithic sample because of the cracking during drying and sintering. In this study, an attempt to avoid cracking was made by addition of DMF to the starting solutions. The pore size distributions of the dried gels with or without DMF were studied.

The compositions of the solutions used for preparing dried gels are shown in Table I. The preparation of sol N2 has been described in our previous paper [9]. The experimental procedure of sol D1 is shown in Fig. 1. Firstly, boehmite (AlO(OH)) sol was prepared by hot hydrolysis of $Al(OPr^i)_3$. A mixture of tetraethosilicate (TEOS), DMF, ethanol and water was stirred for 1 hr and was added to the boehmite sols under constant stirring. Then $Zn(NO_3)_2$ and $Co(NO_3)_2$, dissolved in ethanol, were added, followed by stirring for 1 hr to form clear sols by hydrolysis. The solution was placed in glass containers and sealed with plastic film for the reaction. The wet gels were dried at 40 °C in an oven for about one week. Then the temperature was raised to 80 °C, the plastic film was perforated with a few pinholes in order to dry the wet gel.

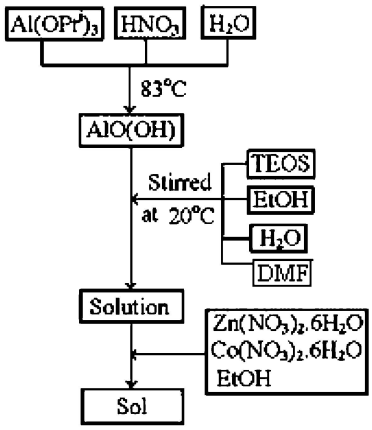

Figure 1 Preparation procedure of ZnO-Al_2O_3-SiO_2-CoO sol containing DMF.

The measurement of pore size distribution was carried out with a OMISORP100-cx physical adsorption analyzer by nitrogen adsorption method. The gel was pulverized and vacuum-treated at 300 °C for 12 hr to degas.

The gelation time and crack formation observed in dried gels are shown in Table I. It is seen from the table that the gelation process of the sol containing DMF is slower than that of the sol without DMF. This behavior could be explained by the higher proportion of solvent that have to be removed compared to sample N2. The dried gel disc of 55 mm in thickness and 2 mm in diameter was produced from the wet gel containing DMF and several cracks are generated during drying of the wet gel when no DCCA is used. Fig. 2 shows the crack and crack-free dried gels after aging for about one month.

TABLE I Composition of the solutions, gelation time and crack formation

Sample	Molar ratio							Drying tem (°C)	Gelation time	Crack fomation in the dried gel
	TEOS	DMF	EtOH	H_2O	$Zn(NO_3)_2$	$Al_2(NO_3)_3$	$Co(NO_3)_2$			
D1	1	2	4	10	0.056	0.067	0.0045	40	7 days	no crack
N2	1	×	4	10	0.056	0.067	0.0045	40	2 days	crack

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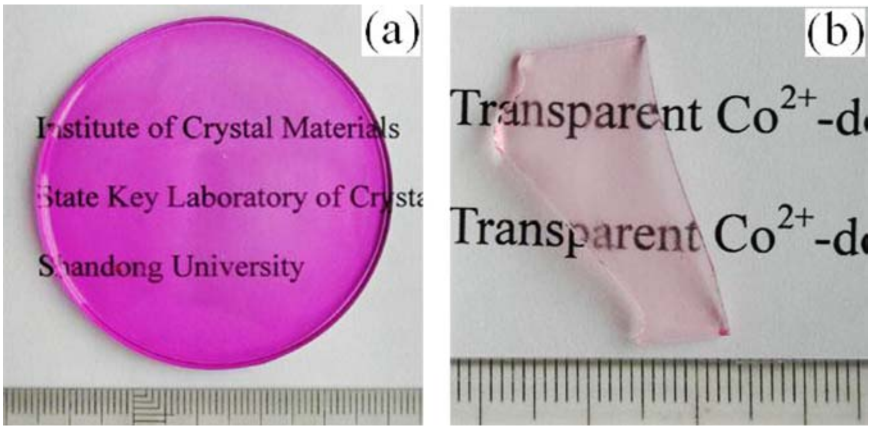

Figure 2 Photographs of the dried gels: (a) D1 and (b) N2.

The pore distribution curves for gels D1 and N2 are shown in Fig. 3. The average pore diameters for D1 and N2 are 7.089 and 3.897 nm, respectively. It is seen that the addition of DMF increased the pore diameter.

The crack formation during drying of wet gels has been attributed to the capillary force generated by the vaporizing liquid in the pores. For a cylindrical capillary of radius r, the capillary force Δp can be expressed by the laplace formula [10]: $\Delta p = 2\nu \cos\theta / r$, where ν, θ and r represent a surface tension of pore liquid, a contact angle of pore liquid to a pore wall and a pore radius, respectively. It indicates that the pressure Δp is proportional to the surface tension ν and inversely proportional to the radius r of the pore. Therefore, it is assumed that the capillary force decreases with decreasing surface tension of the capillary liquid. The effective decrease in the capillary force will result in the formation of crack-free dried monoliths.

TABLE II Surface tensions and boiling points of various liquids

	Surface tension (dyne/cm)	Boiling point (°C)
Ethanol	24.1	78
Water	72.8	100
DMF	36.8	156

From Fig. 3, it has been shown that the crack-free dried gel (sample D1) is characterized by the large pore size, indicating the large pore size decreases the capillary force. The capillary force is also related to the surface tension of liquid. In the wet gels of sample D1, pore liquid is replaced with DMF. It is seen from Table II that the surface tension of DMF is lower than other liquids. During drying of wet gels, the low surface tension liquid remains in the pore, makes the capillary force small, resulting in the formation of crack-free dried gel.

When no DMF is added to the starting solution, ethanol and water fill the pores in the wet gels. As the gel is dried, the vaporization of low boiling point ethanol results in water filling in the pores, the pores shrink

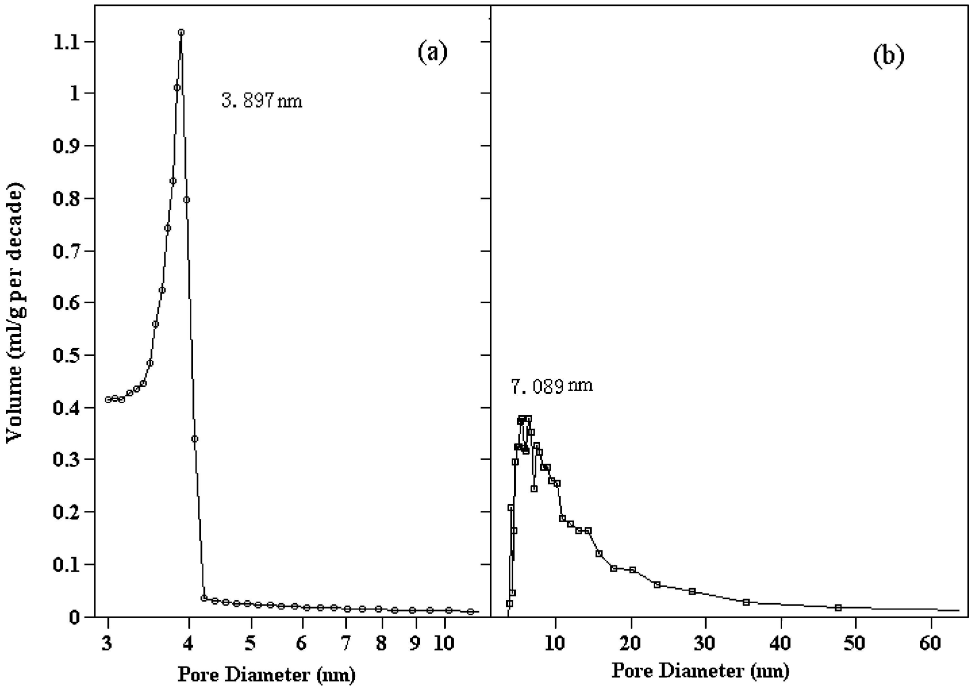

Figure 3 Pore size distribution curves of the dried gels prepared from the solutions: (a) without and (b) with DMF.

as a result of tensile force exerted by the liquid on the gel networks. The resulting smaller pores and the large surface tension of the water-rich liquid cause fracture and crack in the drying gels.

Acknowledgment

This work is supported by grants from the National Natural Science Foundation of China (60178029).

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Received 14 April
and accepted 7 October 2004