JOURNAL OF MATERIALS SCIENCE **35** (2000) 2763 – 2767

Influence of solution composition on the formation of SiO_2/LaF_3 composites in the sol-gel process

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Influence of starting solution composition on the formation of SiO_2/LaF_3 composites was examined in the sol-gel process of tetramethylorthosilicate, methanol, water and *N,N*-dimethylformamide. Trifluoroacetic acid (TFA) and lanthanum acetate were used as chemical sources for LaF_3. Microcrystals of LaF_3 with a size of 10 nm were formed in silica matrix by heating dried gels above 300°C. Colorization, crack formation and fragmentation during drying and heating gels were greatly dependent on the amount of TFA. It was possible to suppress fragmentation of the heated gels by using lanthanum trifluoroacetate gels as precursor in preparing the starting solutions.

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1. Introduction

The sol-gel synthesis of oxide glasses involves various chemical and physical processes [1]. Factors are concerned such as starting materials, compositions, pH values, type of catalysts, drying and heating patterns, etc. The optimal conditions for silica alone should be altered to obtain silica-based composites because constituents of sols increase in number and compositions become diversified. It is important to understand the role of each constituent and try to simplify the process.

In preparing fluoride glasses or silica/fluoride composites by the sol-gel process, HF and F_2 are generally used as a fluorine source, which makes the process complicated. For example, Rywak and Burlitch [2] reported sol-gel-derived SiO_2/MgF_2 composites through the preparation of an MgF_2 sol from methanolic H_2O_2, $Mg(OCH_3)_2$ and HF and the mixing of the MgF_2 sol and a silicon alkoxide sol. Recently, we have used trifluoroacetic acid (CF_3COOH, TFA) as a fluorine source to prepare SiO_2/LaF_3 composites [3]. LaF_3 microcrystals were formed in silica matrix through a usual drying/heating process from tetramethylorthosilicate (TMOS), methanol, water, *N,N*-dimethylformamide (DMF), nitric acid, lanthanum acetate and TFA. The addition of lanthanum acetate and TFA to usual silicon alkoxide systems caused problems such as colorization of dried gels, crack formation and fragmentation during heating, and inhomogeneous optical transmission of the heat-treated gels with high LaF_3 concentration. TFA can act in the process as the fluorine source for LaF_3, an acid catalyst for hydrolysis and polycondensation reactions, and a generator of gases in the formation of LaF_3. It is necessary to know how TFA affects the processing of the SiO_2/LaF_3 composites.

In the present work, we have examined effects of solution compositions on the formation of the SiO_2/LaF_3 composites. The TMOS-methanol-DMF-water system was selected as a basic composition with regard to silica, which is suitable for preparing monolithic silica gels [4]. Nitric acid was not used in this study. The amount of water, DMF and TFA was varied. It was revealed that TFA has the greatest influence on the colorization and fragmentation of the samples. Minimization of the amount of TFA by alternating the sol preparation process led to the formation of monolithic samples.

2. Experimental procedure

2.1. Preparation of sols

Reagent grade chemicals were employed for TMOS, methanol, DMF, lanthanum acetate and TFA. DMF was used as a drying control chemical additive (DCCA) to keep gels monolithic [4, 5]. Two sets of experiments were performed in the preparation of sols as shown in Fig. 1. In one set of experiments (denoted by "method I", hereafter), effects of starting compositions were examined. TMOS-DMF solutions and methanol-water-lanthanum acetate-TFA solutions were prepared by mixing each chemical. The latter solutions were dropped into the former solutions, and sequentially the resultant solutions were stirred for 30 min at room temperature. $1TMOS\cdot 2.2CH_3OH\cdot 1DMF\cdot 10H_2O\cdot 0.5TFA\cdot 0.1(La(CH_3COO)_3\cdot nH_2O)$ in mol was adopted as a basic composition. The composition, $1TMOS\cdot 2.2CH_3OH\cdot 1DMF\cdot 10H_2O$, was chosen because monolithic silica gels were expected to be obtained [4]. The amount of DMF, water and TFA was independently varied as

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TABLE I Compositions of the starting solutions and appearance of the dried and heat-treated gels

		Composition (mole ratio)						Appearance of the dried gels		Fragmentation[a] after heating at 500°C
Method	Sample series	TMOS	CH_3OH	DMF	H_2O	TFA	$La(CH_3COO)_3\cdot nH_2O$	Fragmentation[a]	Colorization	
I	Basic	1	2.2	1	10	0.5	0.1	B	Reddish brown	C
	[DMF]/[TMOS]	1	2.2	0.5	10	0.5	0.1	B	Reddish brown	C
		1	2.2	1.5	10	0.5	0.1	B	Reddish brown	C
	$[H_2O]$/TMOS]	1	2.2	1	6	0.5	0.1	B	Reddish brown	C
		1	2.2	1	8	0.5	0.1	B	Reddish brown	C
		1	2.2	1	11	0.5	0.1	B	Reddish brown	C
		1	2.2	1	12	0.5	0.1	B	Reddish brown	C
	[TFA]/TMOS]	1	2.2	1	10	0.3	0.1	B	Pale yellow	C
		1	2.2	1	10	0.4	0.1	B	Pale brown	C
		1	2.2	1	10	1	0.1	B	Reddish brown	C
		1	2.2	1	10	1.5	0.1	B	Reddish brown	C
II	Basic (except TFA)	1	2.2	1	10	(0.3)	0.1	B	None	A

[a] A, no fragmentation; B, one or a few pieces; C, many small pieces.

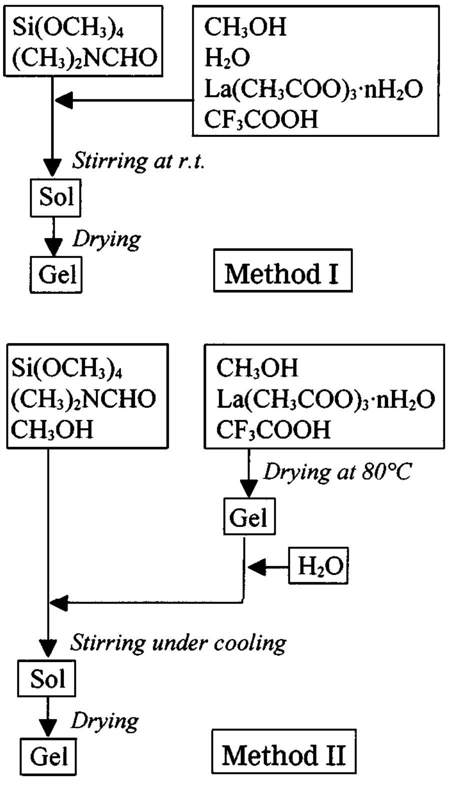

Figure 1 Flow diagram of the preparation of sols by method I and II.

[DMF]/[TMOS] = 0.5, 1, 1.5, $[H_2O]$/[TMOS] = 6, 8, 10, 11, 12, and [TFA]/[TMOS] = 0.3, 0.4, 0.5, 1, 1.5. The compositions of the solutions are summarized in Table I.

In the other set of experiments (denoted by “method II”, hereafter), the preparation process of sols was altered. Lanthanum acetate was dissolved in methanol and TFA. The resultant solution was dried at 80°C to be gelled. The dried lanthanum trifluoroacetate gel was dissolved in water, and added to TMOS-DMF-methanol solutions. Water was added further to the solutions and the composition was adjusted to $1TMOS\cdot 2.2CH_3OH\cdot 1DMF\cdot 10H_2O$. The ratio of La/TMOS was 0.1. Finally the solutions were stirred for 30 min under water cooling.

2.2. Gelation, drying and heating

The same gelation, drying and heating process were carried out for the sols prepared by method I and II. The solution was placed in a polymethylpentene container, sealed with aluminum foil, and kept at 45°C for gelation. The resultant wet gel was aged by raising the temperature from 45 to 80°C in 48 h. Some holes were made in the foil when the temperature reached 80°C. Then the temperature was kept at 80°C for 120 h, further raised to 150°C in 96 h, and kept there for 24 h to obtain the dried gel.

The dried gels were heated at a rate of 20°C/h up to 200, 300, 400, 500 or 800°C and kept there for 2 h. The heat-treatment was done in air.

2.3. Characterization

The pH value of the solutions was measured by a pH meter (F-21, Horiba, Japan). Colorization and crack formation of the dried and heat-treated gels were visually observed. Thermogravimetry-differential thermal analysis (TG-DTA) of the gels was performed in air at a heating rate of 10°C/min (TG-DTA2020S, MAC Science, Japan). Crystalline phases precipitated in the heat-treated gels were identified by X-ray diffraction (XRD) method using CuKα radiation (RAD-C diffractometer, Rigaku, Japan). The size of the LaF_3 crystallites in the composite was estimated using the Scherrer’s equation:

$$D = 0.9\lambda/(\beta\cos\theta) \qquad (1)$$

where D is the crystal size, λ the X-ray wavelength, β the broadening of the diffraction peak and θ the diffraction angle.

3. Results and discussion

3.1. Variation of solution compositions

Appearance of the dried gels prepared by method I is shown in Table I. Although the samples had a few cracks after the completion of the drying process, bulk gels of 5–10 mm in diameter were obtained for all the compositions as a result of minor fragmentation. No remarkable change in shape of the gels was observed among the compositions with the various amounts of DMF, water and TFA. The dried gels were basically tinged with reddish brown. Only the [TFA]/[TMOS] series gels exhibited change in depth of color, which decreased with reducing [TFA]/[TMOS] ratio. No difference in color was observed among the gels with varied [DMF]/[TMOS] and [H_2O]/[TMOS] ratio. This result suggests that TFA affects the evolution of gel structures and pores, which are responsible for vaporization manner of the solvents.

Initial pH values of the solutions with [TFA]/[TMOS] of 0.3, 0.4 and 0.5 were 2.67, 1.26 and 1.03, respectively. TFA can work as acid catalyst for hydrolysis reaction of TMOS. The colorization of the gels is due to organic residue. Paler colors of the gels with increased pH values indicate that the gel structure changes with the amount of TFA. The structure, porosity and pore size of silica gels are also affected by the kind of acid catalysts which provide not only H_3O^+ but anions such as Cl^-, NO_3^- and CH_3COO^- [6, 7]. The present system contains CH_3COO^- and CF_3COO^- which may have influence on the gelation process. Especially, TFA seems to play an important role in the evolution of the gel structure. The cracks were caused by the vaporization of constituents such as methanol, trifluoroacetic acid, H_2O, acetic acid and DMF with the boiling point of 64.7, 72.4, 100, 118 and 153°C, respectively. Since no difference was observed for the crack formation among the gels with the various compositions, other factors such as addition of NH_4OH [4] should be considered to obtain crack-free gels.

The dried gels were heat-treated at temperatures between 200 and 800°C. The formation of LaF_3 crystals in silica was confirmed with XRD for all the compositions. Diffraction peaks due to LaF_3 started to be observed by heating at 300°C. At temperatures between 300 and 800°C, only the LaF_3 peaks were observed without those of any other crystalline phases. Fig. 2 shows the XRD patterns of the gels in the [TFA]/[TMOS] series after heating at 500°C. The intensity and width of the peaks hardly change with different [TFA]/[TMOS] ratio. This means that the almost equivalent amount of starting lanthanum acetate was used for the formation of LaF_3 regardless of the [TFA]/[TMOS] ratio. The size of the LaF_3 crystallites in any heat-treated gels was estimated to be about 10 nm using the Scherrer's equation. The dried gels with any of the compositions underwent fragmentation to small pieces when it was heated at 200°C. Heating at higher temperatures led to the same results. When DMF is used as DCCA in an appropriate composition with addition of NH_4OH, dried gel monoliths can be converted to silica glass monoliths without crack formation or bloating [4]. However, fragmentation could not be avoided in spite of the variety of [DMF]/[TMOS], [H_2O]/[TMOS] and [TFA]/[TMOS] ratio in the present case.

Fig. 3 shows the TG-DTA curve of the dried gel with the basic composition. Two exothermic peaks are observed around 320 and 350°C after large weight loss between 250 and 340°C. This behavior was also observed in our previous work for the different solution composition [3]. The peak at the lower temperature can be explained by the crystallization of LaF_3 [3, 8] and that at the higher temperature is assigned to the crystallization of La_2O_3 [3]. Since no diffraction peak of La_2O_3 was detected in the XRD analysis, the amount of La_2O_3 is probably much smaller than that of LaF_3. The formation reaction of LaF_3 is accompanied by generation of gases as follows [3, 9],

$$La(CF_3COO)_3 \rightarrow LaF_3 + (CF_3CO)_2O + CO_2 + CO \quad (2)$$

The residual TFA in the gel is also thought to generate these gases. Moreover, the decomposition of acetic acid cannot be negligible. However, we cannot understand influence of gas generation on the conversion of the

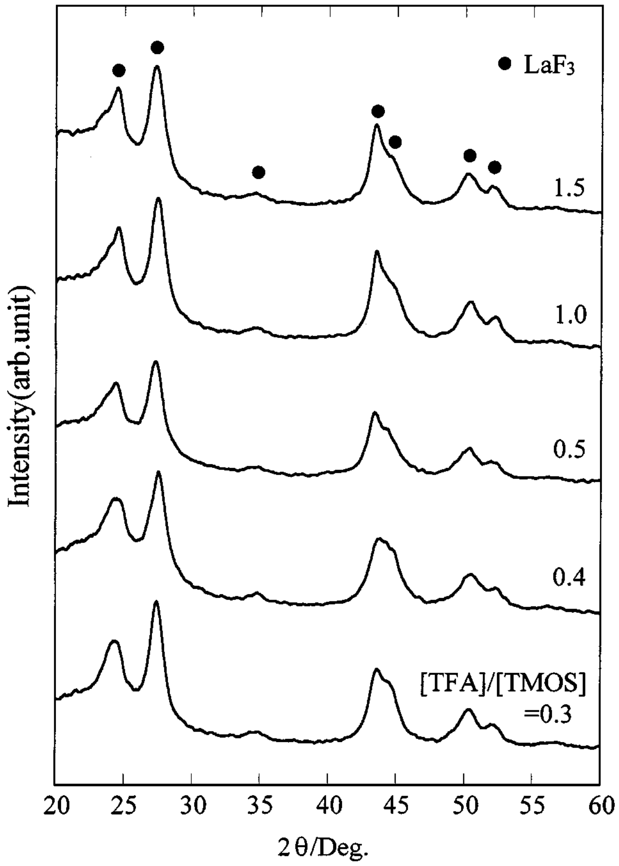

Figure 2 The XRD patterns of the [TFA]/[TMOS] series gels after heating at 500°C.

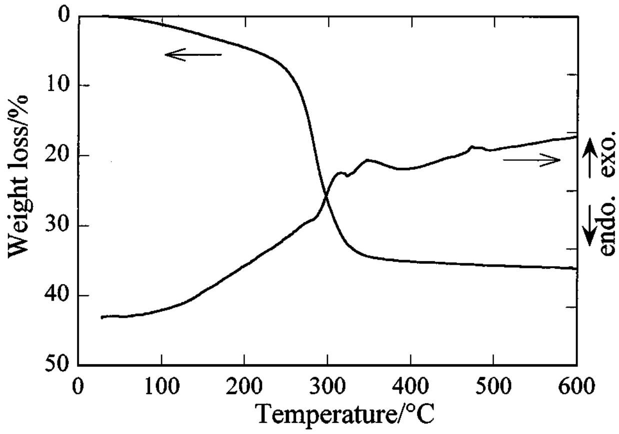

Figure 3 TG-DTA curve of the dried gel with the basic composition prepared through method I.

dried gels to the SiO_2/LaF_3 composites at temperatures higher than 300°C since fragmentation took place at the lower temperature of 200°C.

For a comparative study, we prepared a sample of a basic composition without TFA. No fragmentation was observed after the heat treatment at 500°C. This indicates the greater influence of TFA than acetic acid on fragmentation of the gel during heating. Therefore, the amount of TFA should be minimized to produce the bulk SiO_2/LaF_3 composites.

3.2. Improvement of sol preparation process

On the basis of above discussion, the other preparation process, method II, was contrived to obtain better samples. This process includes preparing lanthanum trifluoroacetate (La/TFA) precursors beforehand as shown in Fig. 1. The basic composition, $1TMOS\cdot 2.2CH_3OH\cdot 1DMF\cdot 10H_2O$, was adopted. The excessive amount of TFA can be removed from the sols through the process. When the aqueous solution of the La/TFA precursor was dropped into the TMOS-DMF-methanol solution at room temperature, gelation was accomplished within 5 minutes. Cooling the system could retard the gelation and give enough time for stirring. This might be related to a higher pH value of the solution, which was measured to be 5.6. Appearance of the dried gel is shown in Table I. A gel body of 10 mm in diameter was obtained after the completion of the drying process as a result of minor fracture. No colorization was observed for this sample.

Fig. 4 shows the TG-DTA curve of the dried gel. Differences are clearly seen from that in Fig. 3. Only one exothermic peak is observed around 310°C accompanying large weight loss between 280 and 310°C. This is attributed to the crystallization of LaF_3. The temperature range where the weight loss occurs is narrower for the present gel as compared with the gel prepared by method I. It is thought that acetic acid is hardly contained in this case as suggested by absence of the exothermic peak at the higher temperature. These results indicate that $La(CF_3COO)_3$ is formed in the precursor and La^{3+}–CF_3COO^- coordination is sustained in the sols and dried gels.

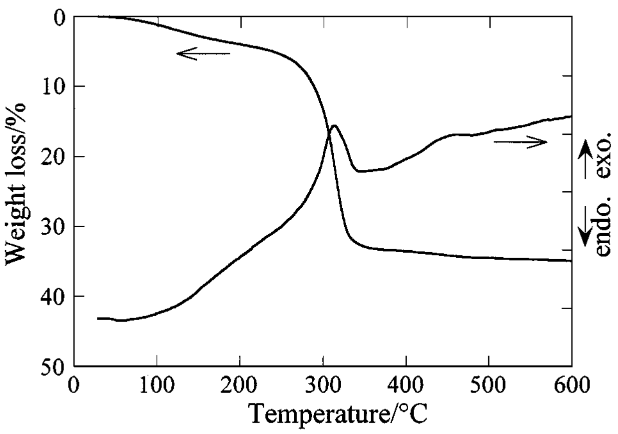

Figure 4 TG-DTA curve of the dried gel through method II.

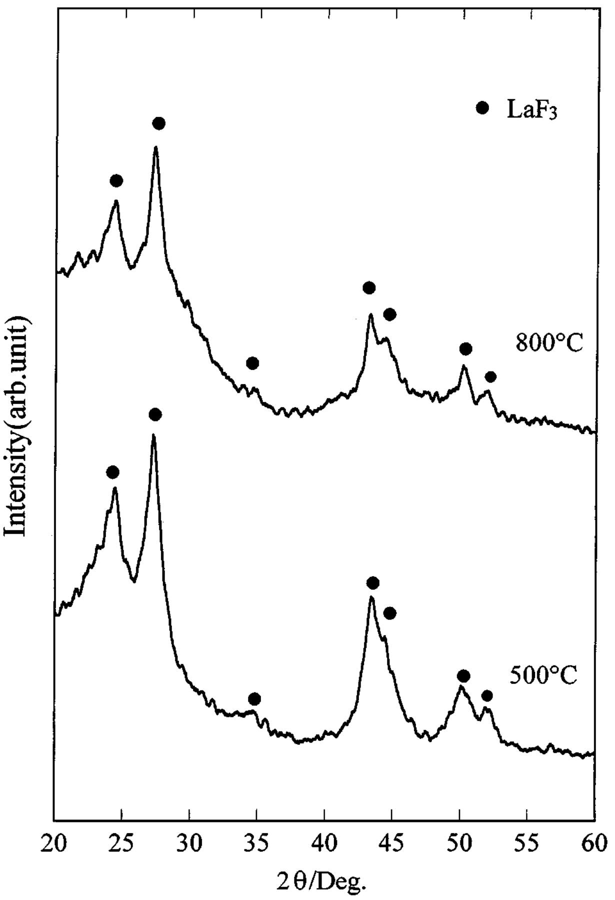

Figure 5 The XRD patterns of the gels through method II after heating at 500 and 800°C.

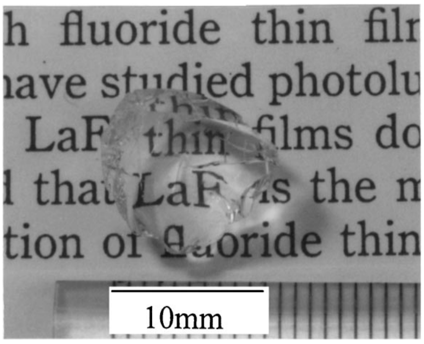

Figure 6 Appearance of the gel through method II after heating at 500°C.

The XRD patterns of the gels heated at 500 and 800°C are shown in Fig. 5. Only the LaF_3 peaks are observed for both the samples. The size of the LaF_3 crystallites was determined to be about 10 nm using the Scherrer's equation. The fact that the grain growth of LaF_3 does not proceed at the elevated temperatures indicates the homogeneous distribution of the microcrystals in the silica matrix. Fig. 6 is the photograph of the gel heat-treated at 500°C. It keeps high transparency, which evidences the nano-scale size of LaF_3. The shape is just like the pre-heated gel. Only a few cracks are observed in the surface. The different result between method I and II is attributable to change of the gel structure. Probably stronger bondings between silica sol particles are obtained through method II. Further work is ongoing to investigate evolution of the silica gel structures in preparing the SiO_2/LaF_3 composites.

In the previous work [3], we met a problem that the heat-treated gel with La/Si = 0.1 ratio had an inner translucent part and an outer transparent part. The evolution of two parts was considered to result from difference in refractive index of the silica or in the size of the LaF_3 crystals. Also the number of the LaF_3 crystals distributed in the silica matrix might be different. This problem can also be removed in the present work by altering the preparation process.

4. Conclusions

The effects of solution compositions on the formation of the SiO_2/LaF_3 composites by the sol-gel process were examined. Among constituents of the sol, TFA exhibited great influence on colorization and fragmentation of the gels during the drying process and the heat treatment. Minimization of the amount of TFA was effective in preparing the SiO_2/LaF_3 composites. Nano-scale LaF_3 crystals were formed in the monolithic silica matrix by using lanthanum trifluoroacetate gels as precursor in preparing starting solutions.

Acknowledgement

S. Fujihara thanks Nippon Sheet Glass Foundation for Materials Science and Engineering (20th, 1998) for their financial support.

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Received 30 March
and accepted 22 November 1999