A New Method for Preparing Monolithic Gels as Precursor for M_xO_y and $SiO_2-M_xO_y$ Glasses ($M=Al, Ti, Zr$) of an Arbitrary Composition

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M_xO_y 及び任意の組成を有する $SiO_2-M_xO_y$ ガラス前駆体としての 均一ゲルの新規合成法

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A new method for preparing gels as a precursor for $SiO_2-M_xO_y$ ($M=Al, Ti, Zr$) glasses of an arbitrary composition was investigated. The gels were formed via polymetalloxanes from hydrolytic condensation of metal chelates of ethyl acetoacetate or condensation polymerization of the chelate with silicic acid. The method permitted to prepare transparent gel plates of M_xO_y and binary $SiO_2-M_xO_y$ component systems.

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1. Introduction

How to control hydrolysis of metal alkoxides is the key point to synthesize monolithic oxide gels by sol-gel process. Especially in binary and ternary systems, the hydrolysis must be controlled precisely because hydrolysis rate of metal alkoxides is different and the reaction will form a mixture of kinds of oxides unless controlled. Since oxide gels are formed by condensation of the hydrolysis intermediates of metal alkoxides, the controlled hydrolysis would more preferably give gels with molecular level homogeneity.

In sol-gel method, hydrolysis of metal alkoxides is controlled by the followings : (1) Reaction molar ratio of water to alkoxides, (2) Preliminary partial-hydrolysis of alkoxide more stable to hydrolysis or hydrolysis of alkoxides in the given order, (3) Hydrolytic condensation through regulated evaporation of solvent. On the other hand, it seems more reasonable to consider the effect of molecular structure on hydrolysis of alkoxide. Recent publications may suggest "chemical modification" of metal alkoxides which is considered to be a way to control the hydrolysis from the following standpoint : (1) Since hydrolysis rate of metal alkoxides decreases with an increase in length of alkyl chain of alkoxy group, metal alkoxides with different alkyl chain and/or

rate appreciably close each other could be used.¹⁾⁻³⁾ (2) Metal alkoxides react with β -diketones, β -ketoesters and diols to give chelate derivatives $(RO)_{v-a}ML_a$ ⁴⁾ where M, R, v, a, and L are metal, alkyl group, valence of metal, degree of substitution and ligand, respectively. The chelates are more stable to hydrolysis than are metal alkoxides, and moreover the group (L) is less reactive to substitution reaction and/or hydrolysis compared with alkoxy groups (OR). Therefore, functionality of these derivatives to hydrolysis is dependent on degree of substitution (a). Actually the papers reported addition of acetylacetone to the reaction system^{5), 6)} and use of chelate derivatives having ligands such as acetylacetone,^{7), 8)} diol,^{5), 9)-11)} and alkanol amine.⁵⁾

In these papers, gels are prepared by cohydrolysis of chelate derivatives and metal alkoxide. However, gels and/or oxide polymers composed of metalloxane bond (metal-oxygen-metal bond) should be provided by copolymerization of component alkoxides and the derivatives. There are many articles on the preparation of $SiO_2-M_xO_y$ ($M=Al, Ti, Zr$) glass system, but the synthetic method is cohydrolysis of metal alkoxides. We found a new method for preparing monolithic gel-like M_xO_y and $SiO_2-M_xO_y$ ($M=Al, Ti, Zr$)

glasses. Gel-like TiO_2 glass has not been obtained, while the preparation of Al_2O_3 ¹²⁾ and ZrO_2 ⁶⁾ glass was reported. However, it seems that Al_2O_3 glass was obtained from hydrolysis of $\text{Al}(\text{OR})_3$ followed by hot-pressing of hydrolysis product. On the other hand, the paper on preparation of ZrO_2 glass describes the effect of acetylacetone as an additive on gel formation.

2. Experimental

According to the previous paper,¹³⁾ 0.85 mol/l silicic acid-tetrahydrofuran (THF) solution was prepared by extracting silicic acid with THF from an aqueous sodium metasilicate solution neutralized with hydrochloric acid. To approximately 6 mol/l concentrated silicic acid solution obtained by addition of hexane to the solution, methanol was added to prepare 3.5 mol/l silicic acid-methanol solution. Bis (ethyl acetoacetato) aluminum isopropoxide (EAP), bis(ethyl acetoacetato) titanium diisopropoxide (ETP) and bis (ethyl acetoacetato) zirconium diisopropoxide (EZP) were synthesized by the method described in the literatures.¹⁴⁾⁻¹⁶⁾

2.1 Preparation of $\text{SiO}_2\text{-M}_x\text{O}_y$ ($\text{M}=\text{Al}$, Ti , Zr) gels

A homogeneous solution was obtained by mixing 3.5 mol/l silicic acid (SA)-methanol solution, metal chelate, 6 N-HCl and methanol in 50 ml polyethylene beaker. The amount of reagents used is listed in Tables 1, 2 and 3. Hydrochloric acid was added as a catalyst on the preparation of $\text{SiO}_2\text{-Al}_2\text{O}_3$ gel containing Al_2O_3 more than

Table 1. Reagents used and chemical compositions of $\text{SiO}_2\text{-Al}_2\text{O}_3$ gels.

SA (ml)	EAP (g)	6N-HCl (ml)	MeOH (ml)	Al_2O_3 mol%
0.3	5.6	1.2	5	88
0.6	5.3	1.2	5	80
1.0	4.8	0.8	5	67
1.7	4.0	0	5	50
2.5	3.0	0	5	33
3.3	2.0	0	5	20
4.0	1.2	0	5	11
4.5	0.6	0	5	5.7
4.7	0.3	0	5	3.0

SA: 3.5 mol/l silicic acid-methanol solution
EAP: bis(ethyl acetoacetato)aluminum isopropoxide

Table 2. Reagents used and chemical compositions of $\text{SiO}_2\text{-TiO}_2$ gels.

SA (ml)	ETP (g)	TiO_2 mol%
0.6	13.9	94
1.1	13.2	89
2.0	11.8	80
3.3	9.9	67
5.0	7.4	50
6.7	5.0	33
8.0	3.0	20
8.9	1.7	11
9.4	0.9	5.7

SA: 3.5 mol/l silicic acid-methanol solution
ETP: bis(ethyl acetoacetato)titanium diisopropoxide

Table 3. Reagents used and chemical compositions of $\text{SiO}_2\text{-TiO}_2$ gels.

SA (ml)	EZP (g)	MeOH (ml)	ZrO_2 mol%
0.3	7.7	10	94
0.6	7.3	10	89
1.0	6.6	10	80
1.7	5.5	10	67
2.5	4.1	10	50
3.3	2.7	10	33
4.0	1.6	10	20
4.5	0.9	10	11
4.7	0.5	10	5.7

SA: 3.5 mol/l silicic acid-methanol solution
EZP: bis(ethyl acetoacetato)zirconium diisopropoxide

Table 4. Preparation of monolithic M_xO_y ($\text{M}=\text{Al}$, Ti , Zr) gels.

Compound	Chelate	6N-HCl (ml)	H_2O (ml)	MeOH (ml)
Al_2O_3	5g ^{a)}	1.0	0	5
TiO_2	5g ^{b)}	0.3	0	0
	5g ^{b)}	0	0.3	0
ZrO_2	5g ^{c)}	1.5	0	5
	5g ^{c)}	0	1.5	5

a) EAP, b) ETP, c) EZP.

fifty percent, while $\text{SiO}_2\text{-TiO}_2$ gels were obtained without use of the catalyst and solvent. The beaker was covered with a polyethylene film with 5 of pinhole of ca. 1 mm diameter to regulate the rate of evaporation of methanol and allowed to stand for three months at room temperatures. Gels were obtained on aging the solution. The time required until gelation took place was highly dependent on metal chelates. The solution containing the aluminum chelate gelled just after prepared.

2.2 Preparation of M_xO_y ($\text{M}=\text{Al}$, Ti , Zr) gels

A homogeneous solution was obtained by mixing metal chelate, 6 N HCl, H_2O and methanol in 50 ml polyethylene beakers. The reagents used are listed in Table 4. These beakers were covered with the film used in the above experiment.

3. Results and discussion

The first and key step on the preparation of gels of M_xO_y and $\text{SiO}_2\text{-M}_x\text{O}_y$ ($\text{M}=\text{Al}$, Ti , Zr) systems is the formation of polymetalloxanes, because it permits to prepare the homogeneous polymer solutions which can form gels extremely easily by additional bond formation on aging the solutions. The reactions are shown by the Eqs. (1), (2), (3) and (4) which represent condensation between silicic acid and chelates (1-2) or between intermediates from hydrolysis of the chelates (3-4). The reaction (2) was confirmed from the results that polytitanosiloxanes with a

ligand of acetylacetone could be isolated.¹⁷⁾

The second step is formation of cross-linked polymers and/or gels by condensation between silanol groups and also between hydroxyl group attached to metals and ligand group, according to the Eqs. (5), (6) and (7). Possibly further condensation followed by hydrolysis of ligand (8) should lead to the formation of gel-like oxide glasses with cross-linked three dimensional network structure during the course of evaporation of solvent on aging.

Gels were obtained on aging a homogeneous solution prepared by mixing silicic acid-methanol solution and chelate in the molar ratio as it is given in Tables 1, 2 and 3. Methanol is best as a solvent for the preparation of gels, for it dissolves polymetalloxanes very well compared with the other solvents. An additional methanol was used in Tables 1 and 3 because the polymers were less soluble than were those in the case of Table 2. In order to obtain round gel plates, the solutions were subjected to controlled condensation by regulating evaporation rate of solvent and allowed to stand at room temperatures for a few months. Gels are formed from the solution on aging for one to seven days, but they are unstable a short while after gel formation and cracks are easily formed when polyethylene film for regulating evaporation of solvent is taken away. However, gels without cracks are obtained by gradual evaporation of solvent for more two months. Geling of the solution is dependent on the concentration of metal chelate and very fast at

Fig. 1. Photograph of Al_2O_3 , TiO_2 and ZrO_2 gel plates.

ca. 30-50 mol%. Furthermore, it also depended markedly on the chelates: At the 1:1 molar ratio of metal chelate to silicic acid, gelling took place immediately after the solution of aluminum chelate was prepared, whereas it occurred after 15 mins' and 10 hs' standing of titanium and zirconium chelate solution, respectively. The tendency of gelling of the metal chelates is in good accordance with that observed on hydrolysis of triethylsiloxo derivatives of aluminum and titanium¹⁸⁾ or hydrolysis in the mixed system of polymerized tetraethoxysilane-aluminum, titanium and zirconium alkoxide.¹⁹⁾ Monolithic gel-like glasses thus obtained were transparent pale-yellow or colorless plates of ca. 30 mm diameter and ca. 4 mm thickness. Tables 1, 2 and 3 clearly indicate that gels of a very wide range of M_xO_y composition are obtained. In addition, monolithic gels of the uni system could be obtained under the conditions listed in Table 4: Al_2O_3 gels are prepared by acid-catalyzed hydrolytic polycondensation of the chelate, whereas TiO_2 and ZrO_2 gels are formed with or without catalyst. Figure 1 shows the photograph of Al_2O_3 , TiO_2 and ZrO_2 gel plates. In these cases, the reactions are shown by the Eqs. (3) and (4) which represent hydrolytic condensation between metal chelates. These results reveal that this method permits to prepare monolithic gel-like glasses of an arbitrary oxide composition.

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