

Synthesis of Some New Sol–Gel Derived Metal–Organic Compounds and Their Hydrolysis–Condensation Reactions

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(Received February 8, 1999)

This work comprised the following parts: a) hydrolysis of $\text{Ti}(\text{OEt})_4$ and $\text{Zr}(\text{OPr})_4$ with different amounts of water, b) complexation of the same alkoxides with varying amounts of 2-methylbutanoic and 3-methylbutanoic acids, and c) hydrolysis of complexation products with varying amounts of water.

All reactions were carried out at room temperature. The complex products were $[\text{Ti}(\text{OEt})_{3.2}(\text{2-MBA})_{0.8}]$, $[\text{Ti}(\text{OEt})_{3.2}(\text{3-MBA})_{0.8}]$, $[\text{Zr}(\text{OPr})_{2.5}(\text{2-MBA})_{1.5}]$, and $[\text{Zr}(\text{OPr})_{3.3}(\text{3-MBA})_{0.7}]$ (2-MBA: 2-methylbutanoate, 3-MBA: 3-methylbutanoate). The products were characterized by ^1H NMR, FT-IR, and elemental analysis. While $\text{Ti}(\text{OEt})_4$, $[\text{Ti}(\text{OEt})_{3.2}(\text{2-MBA})_{0.8}]$, and $[\text{Ti}(\text{OEt})_{3.2}(\text{3-MBA})_{0.8}]$ were hydrolyzed with 1.30, 1.28, and 1.30 mol of water, $\text{Zr}(\text{OPr})_4$, $[\text{Zr}(\text{OPr})_{2.5}(\text{2-MBA})_{1.5}]$, and $[\text{Zr}(\text{OPr})_{3.3}(\text{3-MBA})_{0.7}]$ were hydrolyzed with 2.0, 0.96, and 1.10 mol of water, respectively. These products were characterized by gas chromatography (GC), Karl–Fischer coulometric titrations, and thermal analysis.

The manufacturing of advanced technological materials from commercially available metal alkoxides by the sol–gel process has received increased interest recently.^{1–7} This can be attributed to the successful development of better materials or completely new products.^{8–19} The sol–gel method, in general, offers the advantages of carrying out the reactions at ambient temperature and pressure with very simple apparatus and within considerably shorter times. Metal alkoxides, the starting materials of the sol–gel process, are known for their relatively high reactivity, especially toward water. However, they acquire considerable stability if they are modified with chelating ligands, such as acetylacetone, allyl acetoacetate, diols, and organic acids.^{20–23} The carboxylate groups of organic acids may coordinate to the metal as monodentate, bidentate chelating ligands or bidentate bridging ligands, about which detailed infrared analyses have been reported by Thiele and Panse.³⁴ The hydrolysis of metal alkoxides is a fundamental reaction that converts alkoxides into oxides.²⁴ Although modification by organic acids increase the stability of the alkoxides, it is still necessary to maintain a slow rate of hydrolysis to obtain the desired oxides. Condensation is always a follow-up reaction of hydrolysis in these processes, along with the release of either water or alcohol.^{25,26} Products obtained from metal alkoxides by the sol–gel process lead to the development of new glass and ceramic materials, a wide range of protective coatings, various electrodes as sensors, metal-ion adsorbents and some gas adsorbents.^{27–30}

In this work, acid derivatives of metal alkoxides were obtained by complexing, titanium(IV) ethoxide, and zirconium(IV) propoxide with 2-methylbutanoic and 3-methylbutanoic acids. Alkoxide groups of Ti and Zr alkoxides were partially exchanged with 2-methyl and 3-methyl butanoate groups.

Although chelating ligands, such as those mentioned above, have been used to modify metal alkoxides, to the authors' knowledge, the modification of $\text{Ti}(\text{OEt})_4$ and $\text{Zr}(\text{OPr})_4$ with 2-methylbutanoic or 3-methylbutanoic has not been reported. Furthermore, the use of two isomeric acids could be helpful to understand the influence of the position of the methyl groups on how the acids are attached to the metal atoms. Thus, hydrolysis–condensation reactions of $\text{Ti}(\text{OEt})_4$, $\text{Zr}(\text{OPr})_4$, and their butanoate complexes were studied in some detail. The compounds that were synthesized in this work are potentially useful materials for the removal of certain industrial organic and inorganic contaminants; the authors are currently investigating the adsorptive properties of these compounds.

Experimental

Materials and Measurements. Titanium(IV) ethoxide (Fluka) and zirconium(IV) propoxide (Fluka) were used as received. 2-Methylbutanoic acid (2-MBAH) (Aldrich), 3-methylbutanoic acid (3-MBAH) (Aldrich), chloroform (Merck) and ethyl methyl ketone (MEK) (Merck) were stored over molecular sieves (Fluka, 3 ÅXL8) for a 24-h period before use.

In the hydrolysis reactions, a Mettler DL 18 Model Karl–Fischer Coulometric titrator was used to measure the amount of unreacted water, and a Beckman 2120 Model Gas Chromatograph was employed to determine the amount of alcohol released using calibration curves, prepared with known alcohol concentrations in the solvent. Ethyl methyl ketone was used as an internal standard.

The infrared spectra of the hydrolysis products (using KBr pellets) and the butanoate complex products (dissolved in CHCl_3) were recorded with a Mattson 1000 Model FT-IR spectrophotometer over the 400–4000 cm^{-1} region. The ^1H NMR spectra of butanoate complexes dissolved in CDCl_3 at room temperature were recorded on a 60 MHz Perkin–Elmer spectrometer. The hydrolysis–conden-

sation products of $\text{Ti}(\text{OEt})_4$, $\text{Zr}(\text{OPr})_4$, and butanoate complexes of these alkoxides were dried in a vacuum sterilizer at 40 °C, and their thermal analyses were carried out by a Setaram TG-DTA A 24 Model Thermal Analyzer. Elemental analyses of these products were performed on ICP Perkin–Elmer 5500 and Carlo Erba EA 1108 Model Elemental Analyzers.

Synthesis of Butanoate Complexes of $\text{Ti}(\text{OEt})_4$ and $\text{Zr}(\text{OPr})_4$.

$\text{Ti}(\text{OEt})_4$ (0.01 mol) was dissolved in 5 mL of CHCl_3 and stirred for 10 min. To this solution, 0.6 mol of 2-MBAH was added per mol of $\text{Ti}(\text{OEt})_4$, at a rate of one drop for every 3 s. Faster addition of the acids yielded a jelly-like product, due to the remarkably exothermic character of the reaction. The reaction was complete after an hour of stirring the mixture at room temperature. When the solvent and the liberated alcohol were removed under a vacuum, a yellow viscous liquid was obtained. The hitherto described procedure was also carried out for 0.7, 0.8, 1.0, 1.2, 1.4, 1.5, 1.6, 2.0, and 2.5 mol of 2-MBAH, per mol of $\text{Ti}(\text{OEt})_4$, respectively. Another series of such experiments was performed by using 3-MBAH instead of 2-MBAH; finally, the whole set of experiments was repeated by substituting $\text{Zr}(\text{OPr})_4$ for $\text{Ti}(\text{OEt})_4$. By using GC, ^1H NMR, FT-IR measurements and elemental analyses, the compounds corresponding to the products were characterized as $[\text{Ti}(\text{OEt})_{3.2}(\text{2-MBA})_{0.8}]$, $[\text{Ti}(\text{OEt})_{3.2}(\text{3-MBA})_{0.8}]$, $[\text{Zr}(\text{OPr})_{2.5}(\text{2-MBA})_{1.5}]$, and $[\text{Zr}(\text{OPr})_{3.3}(\text{3-MBA})_{0.7}]$, respectively.

Hydrolysis Reactions. In all hydrolysis reactions of the compounds, water was added drop by drop. In preliminary experiments, on the other hand, it was observed that the product was an extremely light powder (thus posed problems in all steps of handling) when all water was added instantaneously. The amounts of alcohol liberated in the hydrolysis-condensation reactions of $\text{Ti}(\text{OEt})_4$, $\text{Zr}(\text{OPr})_4$, and their butanoate complexes remained constant after 30 min. Thus, a reaction period of 30 min was adopted for the hydrolysis-condensation reactions of these compounds. All hydrolysis reactions throughout this work were performed without using a catalyst.

Hydrolysis of $\text{Ti}(\text{OEt})_4$ and $\text{Zr}(\text{OPr})_4$. The hydrolysis of $\text{Ti}(\text{OEt})_4$ (0.01 mol) was effected by adding, drop by drop, 1, 2, 3, and 4 mol of water per mol of $\text{Ti}(\text{OEt})_4$ in MEK (5 mL), stirring for 30 min at room temperature. The percentage of unreacted water was measured with a Karl–Fischer coulometric titrator, and the amount of alcohol released was determined by gas-chromatography. The same procedure was duplicated for the hydrolysis of $\text{Zr}(\text{OPr})_4$. The colloidal mixture, which formed immediately after the addition of water, turned into a gel as the hydrolysis-condensation reaction proceeded. A solid product was obtained upon removing the solvent and the liberated alcohol under vacuum.

Hydrolysis Reactions of Butanoate Complexes. The hydrolysis of Ti and Zr alkoxide-butanoate complexes was carried out using 1, 2, 3, and 4 mol of water (added drop by drop) per mol of alkoxides. After stirring the solution for 30 min at room temperature, the amount of unreacted water was measured with a Karl–Fischer coulometric titrator. The gelation was observed within 10 to 15 min after the addition of water. Removal of the liquid phase under vacuum yielded solid products. Both the metal alkoxides [Ti (

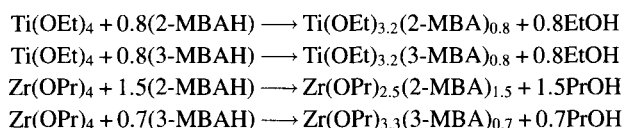
$\text{OEt})_4$, $\text{Zr}(\text{OPr})_4$] and the hydrolysis-condensation products of their butanoate complexes were dried in a vacuum sterilizer at 40 °C, before they were analyzed by a thermal analyzer.

Results and Discussion

Complexation Reactions of $\text{Ti}(\text{OEt})_4$ and $\text{Zr}(\text{OPr})_4$.

The stoichiometry of the complexation reactions can be determined by monitoring the amount of alcohol released in these reactions, since by stoichiometry, one mol of alcohol should be released for each mol of acid reacting with the alkoxide. Gas-chromatography measurements revealed that the maximum amounts of liberated ethanol was 0.8 mol when 1.0 to 2.5 mol of 2-MBAH or 3-MBAH was treated with one mol of $\text{Ti}(\text{OEt})_4$. The maximum amounts of 1-propanol released in complexation of $\text{Zr}(\text{OPr})_4$ with these acids, however, were 1.5 and 0.7 mol, respectively. Furthermore, the amount of alcohol released in the complexation reaction remained constant after one hour, indicating that these reactions reach an equilibrium state after this period.

In the FT-IR spectra of all complexes, the $\text{C}=\text{O}$ bands of the unreacted acids were not observed unless the amount the acid exceeded the combining ratio found by the GC measurements. Thus, it has been confirmed that the stoichiometry of the complexation reactions is as follows:



Furthermore, the frequency separations ($\Delta\nu$), which are the difference between $\nu_{(\text{COO})\text{asym}}$ and $\nu_{(\text{COO})\text{sym}}$, show that 2-MBAH and 3-MBAH were bonded to metal atoms as bidentate chelating ligands (Chart 1).³⁴ The frequency separation ($\Delta\nu$) data of all complexes are given in Table 1.

M : Ti; R : Et

M : Zr; R : Pr

OOCR' : 2-methyl butanoate or 3-methyl butanoate

^1H NMR spectral data of all complexes are shown below and consistent with the structure of these complexes.

$\text{Ti}(\text{OEt})_{3.2}(\text{2-MBA})_{0.8}$: ^1H NMR δ = 4.2 (q; 6.4H; OCH_2CH_3), 2.3 (br q; 0.8H; $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{COO}$), 1.9—

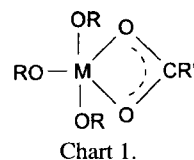


Chart 1.

Table 1. The Frequency Separation ($\Delta\nu$) Data of All Complexes

Complex	$\nu_{(\text{COO})\text{asym}}$	$\nu_{(\text{COO})\text{sym}}$	$\Delta\nu$ (cm^{-1})
Titanium(IV) ethoxide-2-methylbutanoate	1557	1455	102
Titanium(IV) ethoxide-3-methylbutanoate	1565	1484	81
Zirconium(IV) propoxide-2-methylbutanoate	1560	1474	86
Zirconium(IV) propoxide-3-methyl butanoate	1560	1464	96

1.4 (q; 1.6H; $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{COO}$), 1.5—0.8 (m; 14H; OCH_2CH_3 and $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{COO}$).

Ti(OEt)_{3.2}(3-MBA)_{0.8}: $^1\text{H NMR}$ δ = 4.0 (q; 6.4H; OCH_2CH_3), 2.2 (br d; 1.6H; $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{COO}$), 1.7 (m; 0.8H; $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{COO}$), 1.3—0.8 (m; 14H; OCH_2CH_3 and $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{COO}$).

Zr(OPr)_{2.5}(2-MBA)_{1.5}: $^1\text{H NMR}$ δ = 3.6 (t; 5H; $\text{OCH}_2\text{CH}_2\text{CH}_3$), 2.3 (br t; 1.5H; $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{COO}$), 1.8—1.3 (m; 8H; $\text{OCH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{COO}$), 1.1—0.7 (m; 16.5H; $\text{OCH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{COO}$).

Zr(OPr)_{3.3}(3-MBA)_{0.7}: $^1\text{H NMR}$ δ = 3.5 (t; 6.6H; $\text{OCH}_2\text{CH}_2\text{CH}_3$), 2.2 (br d; 1.4H; $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{COO}$), 1.8—1.4 (m; 7.3H; $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{COO}$ and $\text{OCH}_2\text{CH}_2\text{CH}_3$), 1.1—0.7 (br t; 14.1H; $\text{OCH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{COO}$).

Elemental-analysis data for the complexation products, given in Table 2, also support the findings mentioned above.

Hydrolysis Reactions. Table 3 gives the maximum amounts of water consumed and the amounts of liberated alcohol in the hydrolysis reactions of these compounds, as determined by Karl–Fischer titrations and GC measurements.

It can be seen from the data in Table 3 that the amounts of liberated alcohol in hydrolysis-condensation are greater than that of water consumed on the mol basis. Thus, it is clear that condensation reactions are involved by the elimination of alcohol. The amounts of the alcohol formed in the condensation reactions are given in Table 4.

Thus, hydrolysis-condensation reactions of the six compounds can be shown as follows (Schemes 1, 2, 3, 4, 5, and 6):

It should be noted that the amount of alcohol liberated in the condensation reaction is much less than that formed in the hydrolysis reactions. This can be reasoned as follows. The amount of alkoxide bonded to the metal before hydrolysis is greater than that of the hydrolysis product. Alcohol released in hydrolysis reaction is likely to form hydrogen bonds with the hydroxide group on the metal, and this makes condensation reaction more difficult. It is seen that the amount of water used up in the hydrolysis increases as the alkoxide chain becomes longer, but generally decreases if the group bonded to the metal is both branched and of chelate property, as with methyl butanoate.

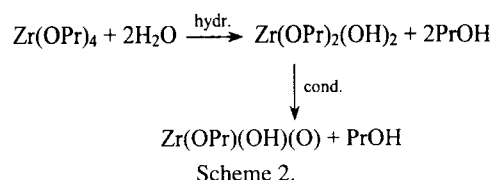
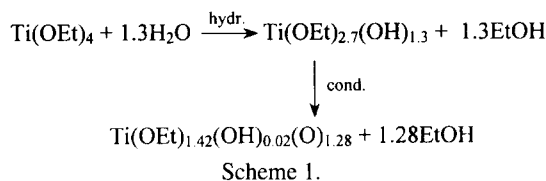
In metal alkoxide-methyl butanoate complexes, the chelating bonds are expected to be stronger than that of the alkoxide bonds towards hydrolysis and condensation reactions due to delocalization. Delocalization is well known to stabilize

Table 3. Maximum Amounts of Water Consumed and Amounts of Liberated Alcohol in the Hydrolysis Reactions

Compound	Amounts of water consumed	Amounts of liberated alcohol
	mol/mol metal	mol/mol metal
Ti(OEt) ₄	1.30	2.58
Zr(OPr) ₄	2.00	3.00
Ti(OEt) _{3.2} (2-MBA) _{0.8}	1.28	2.15
Ti(OEt) _{3.2} (3-MBA) _{0.8}	1.30	1.72
Zr(OPr) _{2.5} (2-MBA) _{1.5}	0.96	1.90
Zr(OPr) _{3.3} (3-MBA) _{0.7}	1.10	1.85

Table 4. Amounts of Alcohol Formed in the Condensation Reactions

Compound	Amount of alcohol (mol/mol metal)
Ti(OEt) ₄	1.28
Zr(OPr) ₄	1.00
Ti(OEt) _{3.2} (2-MBA) _{0.8}	0.87
Ti(OEt) _{3.2} (3-MBA) _{0.8}	0.42
Zr(OPr) _{2.5} (2-MBA) _{1.5}	0.94
Zr(OPr) _{3.3} (3-MBA) _{0.7}	0.75

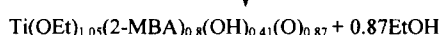
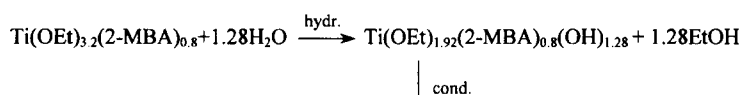


carboxylate modified metal alkoxides.²⁰

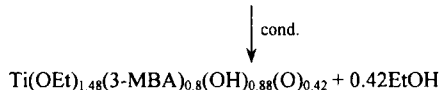
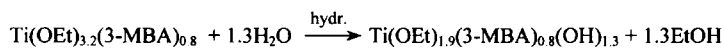
After the formation of hydrolysis-condensation products at room temperature, their thermal stabilities were studied by thermogravimetry (TG). In general, the products show one major weight loss at elevated temperature, which is attributed to thermal decomposition of the organic groups. This decomposition ends up with the formation of metal oxides. The thermal analysis and elemental analysis data of all the hydrolysis-condensation products are given in Table 5.

Table 2. The Elemental Analysis Data of the Compounds Synthesized

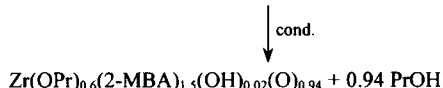
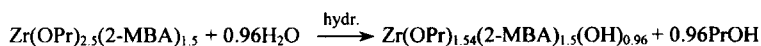
Compound	Found / %				Calculated / %			
	C	H	Ti	Zr	C	H	Ti	Zr
Ti(OEt) _{3.2} (2-MBA) _{0.8}	45.88	8.59	17.70	—	45.76	8.57	17.56	—
Ti(OEt) _{3.2} (3-MBA) _{0.8}	45.81	8.60	17.68	—	45.76	8.57	17.56	—
Zr(OPr) _{2.5} (2-MBA) _{1.5}	45.33	8.15	—	24.47	45.50	8.18	—	24.68
Zr(OPr) _{3.3} (3-MBA) _{0.7}	45.00	8.31	—	25.71	45.08	8.29	—	25.55



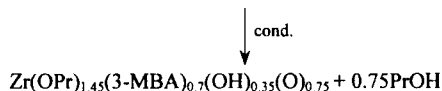
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

Table 5. Thermal and Elemental Analysis Data of the Hydrolysis-Condensation Products of $\text{Ti}(\text{OEt})_4$, $\text{Zr}(\text{OPr})_4$, $\text{Ti}(\text{OEt})_{3.2}(2\text{-MBA})_{0.8}$, $\text{Ti}(\text{OEt})_{3.2}(3\text{-MBA})_{0.8}$, $\text{Zr}(\text{OPr})_{2.5}(2\text{-MBA})_{1.5}$, and $\text{Zr}(\text{OPr})_{3.3}(3\text{-MBA})_{0.7}$

Compound	TG Weight loss (%)	Elemental analysis							
		Calculated %				Found %			
		TiO_2	Ti	ZrO_2	Zr	TiO_2	Ti	ZrO_2	Zr
a	24.00	76.00	45.56	—	—	71.90	42.30	—	—
b	15.52	—	—	84.48	62.54	—	—	84.90	62.80
c	37.70	62.30	37.35	—	—	62.48	38.10	—	—
d	42.50	57.50	34.47	—	—	57.42	34.23	—	—
e	35.10	—	—	64.90	48.04	—	—	65.13	47.22
f	40.50	—	—	59.50	44.05	—	—	58.72	44.25

a: $\text{Ti}(\text{OEt})_{1.42}(\text{OH})_{0.02}(\text{O})_{1.28}$, b: $\text{Zr}(\text{OPr})(\text{OH})(\text{O})$, c: $\text{Ti}(\text{OEt})_{1.05}(2\text{-MBA})_{0.8}(\text{OH})_{0.41}(\text{O})_{0.87}$, d: $\text{Ti}(\text{OEt})_{1.48}(3\text{-MBA})_{0.8}(\text{OH})_{0.88}(\text{O})_{0.42}$, e: $\text{Zr}(\text{OPr})_{0.6}(2\text{-MBA})_{1.5}(\text{OH})_{0.02}(\text{O})_{0.94}$, f: $\text{Zr}(\text{OPr})_{1.45}(3\text{-MBA})_{0.7}(\text{OH})_{0.35}(\text{O})_{0.75}$.

Conclusion

New metal alkoxides that are stable towards hydrolysis were synthesized and characterized. Titanium and zirconium alkoxides can be modified with different organic acids, such as 2-methyl and 3-methylbutanoic acids. IR studies show that carboxylate groups are bonded to metal atoms as bidentate chelating ligands.³⁴ As is evident from the data in Table 3, butanoate-modified alkoxides are more stable towards hydrolysis than the unmodified counterparts. It is believed that suitable adsorbents for various organic contaminants can be prepared by a thermal treatment and reduction to an adequate particle size of these new metal alkoxides. Our findings in our yet unpublished adsorption experiments indicate that chances are notably good in this respect.

References

- 1 J. D. Mackenzie, *J. Non-Cryst. Solids*, **100**, 162 (1988).
- 2 M. Nandi, J. A. Conklin, L. Salvati, Jr., and A. Sen, *Chem. Mater.*, **3**, 201 (1991).
- 3 K. Lato, *J. Mater. Sci.*, **27**, 1445 (1992).
- 4 M. Nabavi, S. Doeuff, C. Sanchez, and J. Livage, *J. Non-Cryst. Solids*, **89**, 153 (1987).
- 5 U. Schubert, E. Arpaç, W. Glaubitt, A. Helmerich, and C. Chau, *Chem. Mater.*, **4**, 291 (1992).
- 6 J. Livage, C. Sanchez, M. Henry, and S. Doeuff, *Solid State Ionics*, **32**, 633 (1988).
- 7 M. J. Munoz-Aguado, M. Gregorkiewitz, and A. Larbot, *Mater. Res. Bull.*, **27**, 87 (1992).
- 8 H. Sayilkan, Ş. Şener, and E. Arpaç, *J. Inorg. Organomet. Polym.*, **4**, 301 (1994).
- 9 H. Sayilkan and E. Arpaç, *Chim. Acta Turc.*, **22**, 63 (1994).
- 10 H. Sayilkan, Ş. Şener, and E. Arpaç, *Doğa-Tr. J. Chem.*, **17**,

- 75 (1993).
- 11 M. Dejneka, E. Snitzer, and R. E. Riman, *J. Non-Cryst. Solids*, **202**, 23 (1996).
 - 12 J. M. Miller, B. Dunn, J. S. Valentine, and J. I. Zink, *J. Non-Cryst. Solids*, **202**, 279 (1996).
 - 13 L. Chu, M. W. Daniels, and L. F. Francis, *Chem. Mater.*, **9**, 2577 (1997).
 - 14 J. Zhang, S. Luo, and L. Gui, *J. Mater. Sci.*, **32**, 1469 (1997).
 - 15 J. V. Crivello and Z. Mao, *Chem. Mater.*, **9**, 1562 (1997).
 - 16 D. A. Loy, E. M. Russick, S. A. Yamanaka, and V. M. Baugher, *Chem. Mater.*, **9**, 2264 (1997).
 - 17 J. V. Crivello and Z. Mao, *Chem. Mater.*, **9**, 1554 (1997).
 - 18 Y. Yan, Y. Hoshino, Z. Duan, S. R. Chaudhuri, and A. Sarkar, *Chem. Mater.*, **9**, 2583 (1997).
 - 19 T. Gacoin, L. Malier, and J. P. Boilot, *Chem. Mater.*, **9**, 1502 (1997).
 - 20 H. Sayilkan, E. Arpaç, and E. Şener, *Synth. React. Inorg. Met.-Org. Chem.*, **27**, 1437 (1997).
 - 21 H. Sayilkan, E. Ekinici, and E. Arpaç, *J. Sci. Res. Found.*, **1**, 79 (1996).
 - 22 H. Sayilkan and E. Arpaç, *Chim. Acta Turc.*, **22**, 213 (1994).
 - 23 A. Kayan, Thesis (Master degree), İnönü University, Malatya, Turkey (1992).
 - 24 K. Tokutome and T. Yamaguchi, *J. Ceram. Soc. Jpn. Inter. Ed.*, **97**, 568 (1989).
 - 25 H. Sayilkan, Thesis (Ph. D. degree), İnönü University, Malatya, Turkey (1992).
 - 26 J. Wen, B. Dhandapani, S. T. Oyama, and G. L. Wilkes, *Chem. Mater.*, **9**, 1968 (1997).
 - 27 R. Nass, E. Arpaç, W. Glaubitt, and H. Schmidt, *J. Non-Cryst. Solids*, **121**, 370 (1990).
 - 28 H. Sayilkan, E. Ekinici, and E. Arpaç, *Doğa-Tr. J. Chem.*, **17**, 196 (1993).
 - 29 M. Eyal, R. Gvishi, and R. Resfeld, *J. De Phys.*, **48**, 471 (1987).
 - 30 A. Aydin, U. Koklu, and S. Taşcıoğlu, *Chim. Acta Turc.*, **15**, 91 (1987).
 - 31 H. Meing, "Handbuch des Umweltschutzes," Umweltbundstand, Berlin (1987).
 - 32 F. Kircil, *Koll. Z.*, **77**, 146 (1936).
 - 33 "Ullmann Enzyklopädie der Technischen Chemie, 21. Band," Verlag Chemie, Weinheim (1982).
 - 34 V. K. H. Thiele and M. Panse, *Z. Anorg. Allg. Chem.*, **144**, 23 (1978).
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