



# Reactions of Magnesium and Titanium Alkoxides. Preparation and Characterization of Alkoxy-Derived Magnesium Titanate Powders and Ceramics

M.I. YANOVSKAYA, N.M. KOTOVA AND N.V. GOLUBKO

*Karpov Institute of Physical Chemistry, Vorontsovo Pole St., 10, Moscow 103064, Russia*

N.YA. TUROVA

*Chemical Department of the Moscow State University, Vorobjovy Hills, Moscow 119899, Russia*

*Received March 18, 1997; Accepted June 11, 1997*

**Abstract.** The interaction between magnesium and titanium alkoxides is studied in order to choose the best precursors for synthesis of  $\text{MgTiO}_3$ . No reaction between magnesium and titanium methoxides and isopropoxides occurs. The solubility diagrams for  $\text{Mg}(\text{OR})_2\text{-Ti}(\text{OR})_4\text{-ROH}$ ,  $\text{R} = \text{Et}, n\text{-Bu}$  at  $20^\circ\text{C}$  are studied. Magnesium ethoxotitanates of variable composition  $\text{Mg}_n\text{Ti}_{4-n}(\text{OEt})_{16-2n} \cdot 2n\text{EtOH}$  ( $n = 2.0-0$ ) which are structural analogs of  $\text{Ti}_4(\text{OR})_{16}$  ( $\text{R} = \text{Me}, \text{Et}$ ) are isolated. This is a quite unusual example of statistical distribution of heteroatoms in molecular structures of metal alkoxides. Among the systems of metal alkoxides with simple aliphatic radicals only  $\text{Mg}(\text{OBU})_2\text{-Ti}(\text{OBU})_4\text{-BuOH}$  gives a convenient precursor for the synthesis of  $\text{MgTiO}_3$ . A simple scheme of preparation of magnesium titanate from the alkoxy solutions is suggested. The phase purity of  $\text{MgTiO}_3$  is to a considerable extent dependent on the hydrolysis conditions. The alkoxy-derived magnesium titanate is obtained in the form of a uniform fine powder, it can be sintered into dense ceramics in the temperature range of  $1140\text{--}1220^\circ\text{C}$  which is  $150\text{--}200^\circ\text{C}$  lower in comparison with the conventional powders.

**Keywords:** metal alkoxides, bimetallic alkoxides, oxoalkoxides, precursors, magnesium titanate

## 1. Introduction

Magnesium titanate  $\text{MgTiO}_3$  and its solid solutions or mixtures with alkaline-earth titanates ( $\text{Sr}$ , and  $\text{Ca}$ ) finds extensive applications in high-frequency and microwave capacitors. It is synthesized by conventional solid state reaction of titanium oxide with magnesium carbonate at  $1400^\circ\text{C}$  [1]. However, this material is usually contaminated with magnesium dititanate and other oxides of the  $\text{TiO}_2\text{-MgO}$  system. Coprecipitation from aqueous solutions considerably lowers the synthesis temperature, however the product is never completely free from the admixture of  $\text{MgTi}_2\text{O}_5$  [2].

The hydrolysis of metal alkoxides is frequently used nowadays as a route to high-quality complex oxides.

Nevertheless, there are very few works concerning the preparation of  $\text{MgTiO}_3$  by this method. This is due primarily to the difficulties of synthesis and the low solubility of the magnesium alkoxides [3, 4]. Among all the aliphatic alcohols, only methyl alcohol readily reacts with  $\text{Mg}$ , therefore magnesium methoxide was used by Yamaguchi for synthesis of  $\text{MgTiO}_3$  and  $\text{MgTi}_2\text{O}_5$  [5]. He refluxed the reaction mixture of  $\text{Mg}(\text{OMe})_2$  with titanium isopropoxide in  $\text{MeOH}$  for 20 hours prior to hydrolysis. Hydrolysis of the heterogeneous mixture could hardly guarantee the homogeneity of the future oxide phase on the atomic level.

Schmidt and Feltz suggested an application of metal ethoxyethoxides as precursors which allowed them to have both components ( $\text{Mg}$  and  $\text{Ti}$ ) in solutions

[6]. However, ethoxyethanol (as all  $\text{ROC}_2\text{H}_4\text{OH}$ ) to a considerable extent dissolves hydrated oxides, thus preventing precipitation, this hinders isolation of the precipitates and regulation of the morphology of the oxide powders.

The purpose of the present work was to study the interaction of  $\text{Mg}(\text{OR})_2$  and  $\text{Ti}(\text{OR})_4$  in the corresponding alcohols (with R—simple aliphatic radicals) in order to find a convenient route to synthesize  $\text{MgTiO}_3$ .

## 2. Experimental

All operations on synthesis, isolation and characterization of metal alkoxides were performed in dry argon flow. Alcohols were dehydrated by refluxing for many hours with the corresponding metal alkoxides  $\text{Mg}(\text{OMe})_2$ ,  $\text{Mg}(\text{OEt})_2 + \text{Al}(\text{OEt})_3$ ,  $\text{Al}(\text{OPr-i})_3$ ,  $\text{Mg}(\text{O}i\text{Bu})_2 + \text{Al}(\text{O}i\text{Bu})_3$ . The content of water in alcohols (mass%) determined by Fischer technique was 0.03 in MeOH and *i*-PrOH; 0.05 in EtOH; and 0.02 in BuOH. Magnesium in solutions was analyzed by complexometry after sedimentation of titanium in acidic medium; Ti was analyzed by colorimetry. The sum of Mg and Ti alkoxides in solutions can also be calculated from the weight of the oxide residues after hydrolysis of the samples by acidified distilled water, with further evaporation and annealing at  $800^\circ\text{C}$  till the constant weight. X-ray analysis of metal alkoxides and their thermolysis products was performed with a “DRON-3” instrument ( $\text{CuK}_\alpha$ -radiation, Ni-filter).

$\text{Ti}(\text{OMe})_4$  was obtained at room temperature in the form of a white precipitate by the exchange reaction of titanium butoxide with MeOH.

$\text{Ti}(\text{OEt})_4$ ,  $\text{Ti}(\text{OPr-i})_4$ ,  $\text{Ti}(\text{O}i\text{Bu})_4$  were used in the form of the freshly distilled colorless liquids.

$\text{Mg}(\text{OMe})_2$  was used in the form of its solution in MeOH obtained by direct dissolution of Mg in MeOH.

$\text{Mg}(\text{OEt})_2$  was obtained in the form of white powder insoluble in organic solvents by prolonged refluxing of Mg with excess EtOH.

“ $\text{Mg}(\text{O}i\text{Bu})_2$ ” was obtained in the form of white amorphous powder on refluxing of Mg with excess BuOH, no catalyst was used for the reaction [4]. On cooling of the reaction mixture to room temperature colorless gel-like precipitate was formed, which was dried under vacuum after decantation of alcohol. Despite quite good agreement of the chemical analysis data with the calculated values for  $\text{Mg}(\text{O}i\text{Bu})_2$  pronounced  $\nu_{\text{OH}}$  band of solvating alcohol at  $\approx 3720\text{ cm}^{-1}$

was registered in the IR spectra, therefore as it frequently occurs it is impossible to distinguish by chemical analysis between magnesium butoxide and magnesium oxobutoxide solvated by BuOH.

$\text{Mg}_2\text{Ti}_2(\text{OEt})_{12} \cdot 4\text{EtOH}$ . Mg (0.40 g, 16.5 mmol) was introduced into the solution containing  $\text{Ti}(\text{OEt})_4$  (3.76 g, 16.5 mmol) in 46.51 g of anhydrous EtOH. The reaction mixture was heated, dissolution of Mg began at the temperature  $>60^\circ\text{C}$ ; after refluxing of the reaction mixture for 1–2 hours Mg dissolved completely. On cooling of the solution to room temperature crystals precipitated. Anal. Calcd. for  $\text{C}_{32}\text{H}_{84}\text{Mg}_2\text{O}_{16}\text{Ti}_2$ : C, 44.2; H, 9.7. Found: C, 43.6; H, 9.9.

$\text{Mg}_{1.2}\text{Ti}_{2.8}(\text{OEt})_{13.6} \cdot 2.4\text{EtOH}$  (I). Mg (0.13 g, 5.3 mmol) was introduced into the solution containing  $\text{Ti}(\text{OEt})_4$  (4.83 g, 21.2 mmol) in 37.71 g of anhydrous EtOH. Reaction was performed as described in the previous case, precipitation however occurred in 20–30 min after cooling of the solution. Single crystals for X-ray diffraction study were chosen from the precipitate, then the mother liquor (which contained 4.12% of  $\text{Ti}(\text{OEt})_4$  but no Mg) was decanted and the precipitate was carefully dried in vacuo. The yield of the crystals was 4.01 g. Anal. Calcd. for  $\text{C}_{32}\text{H}_{82.4}\text{Mg}_{1.2}\text{O}_{16}\text{Ti}_{2.8}$ : C, 43.4; H, 9.3; Mg, 3.3; Ti, 15.1. Found: C, 42.1; H, 9.4; Mg, 3.3; Ti, 15.3.

The attempt to desolvate crystals (I) by evacuation of the melt resulted in their decomposition: the glassy residue did not crystallize on cooling.

$\text{MgTiO}_3$ .  $\text{Ti}(\text{O}i\text{Bu})_4$  (36.50 g, 107.4 mmol) was dissolved in 140 g of BuOH, the solution was refluxed for 1.5 hours; after cooling Mg (2.61 g, 107.4 mmol) was introduced in the solution. Dissolution of the metal accompanied by vigorous hydrogen evolution began on heating of the reaction mixture to  $80^\circ\text{C}$  and was completed in an hour. When the dark green solution thus formed was cooled in a flow of dry air it bleached. The colorless transparent solution was hydrolyzed at room temperature on stirring by addition of 23 g of distilled water dissolved in BuOH ( $[\text{H}_2\text{O}] : [\text{Ti}(\text{O}i\text{Bu})_4] = 12$ ). After decantation of aqueous butanol, the white precipitate formed was dried at  $60^\circ\text{C}$  in a vacuum oven, then calcined at  $800^\circ\text{C}$  for 1 hour; 10.3 g of  $\text{MgTiO}_3$  (yield 98%) was obtained.

## 3. Results and Discussion

Titanium methoxide  $\text{Ti}(\text{OMe})_4$  is insoluble in MeOH. The equilibrium solubility of  $\text{Mg}(\text{OMe})_2 \cdot 4\text{MeOH}$  at

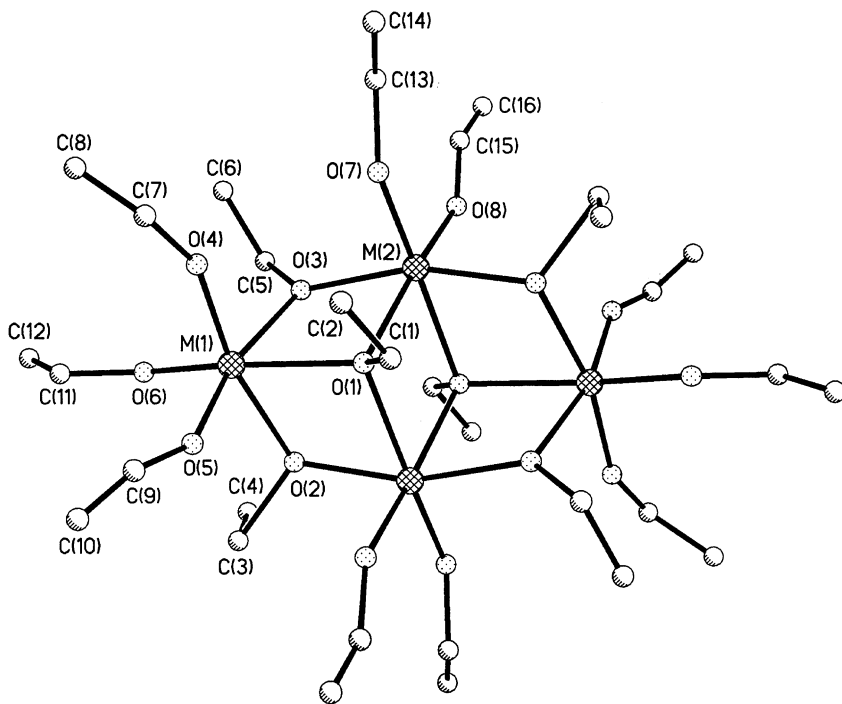


Figure 1. Molecular structure of  $\text{Mg}_{1.2}\text{Ti}_{2.8}(\text{OEt})_{13.6} \cdot 2.4\text{EtOH}$  (I). Positions labeled as M(1) and M(2) are occupied by both Ti and Mg atoms.

$20^\circ\text{C}$  is 10.5 mass% [3]. Titanium methoxide did not dissolve in magnesium methoxide solutions. This fact was also confirmed by the X-ray patterns of the products of thermolysis of the solutions: they contained only peaks corresponding to MgO. Therefore no reaction between magnesium and titanium methoxides occurred.

$\text{Mg}(\text{OEt})_2$  is insoluble in EtOH; solubility of  $\text{Ti}(\text{OEt})_4$  in EtOH at  $20^\circ\text{C}$  was 76 mass% [7]. Agitation of magnesium ethoxide with solutions (with concentration 2.5–60 mass%) of freshly distilled  $\text{Ti}(\text{OEt})_4$  for a few hours resulted in decrease of the concentration of the latter to 0–25 mass% respectively. Reaction of  $\text{Ti}(\text{OEt})_4$  solutions with Mg metal was performed with the variation of the  $[\text{Mg}] : [\text{Ti}(\text{OEt})_4]$  ratio from 2 : 1 to 1 : 6. On heating Mg readily reacted with the  $\text{Ti}(\text{OEt})_4$  solutions in EtOH with intensive hydrogen liberation to give colorless solutions. However on cooling precipitation from the solutions occurred. No Mg was found in solutions while concentration of  $\text{Ti}(\text{OEt})_4$  decreased in different experiments from 6–40 to 1–10 mass% respectively, practically in the same range as in its reactions with  $\text{Mg}(\text{OEt})_2$ . Well-shaped crystals were obtained from solutions with the ratio of the components

$[\text{Mg}] : [\text{Ti}] = 1 : 4$ . Their composition calculated from the results of X-ray structural analysis corresponded to  $\text{Mg}_{1.2}\text{Ti}_{2.8}(\text{OEt})_{13.6} \cdot 2.4\text{EtOH}$  (I) and was in good agreement with the results of the chemical analysis (see Section 2). Single crystals X-ray diffraction study of I was performed [8]. The crystals contain tetranuclear molecules analogous to those formed by titanium methoxide and ethoxide  $[\text{Ti}_4(\text{OR})_{16}]$  (Fig. 1) [9, 10]. However, in the molecule (I) positions corresponding to metal atoms may be statistically occupied by Ti and Mg atoms which in fact reflects the superposition of molecules with the same M-O skeleton but different compositions viz.,  $\text{Ti}_4(\text{OEt})_{16}$ ,  $\text{Ti}_3\text{Mg}(\text{OEt})_{14}(\text{EtOH})_2$  and  $\text{Ti}_2\text{Mg}_2(\text{OEt})_{12}(\text{EtOH})_4$  (with the general formula  $\text{Mg}_n\text{Ti}_{4-n}(\text{OEt})_{16-2n}(\text{EtOH})_{2n}$ ,  $n = 0, 1, 2$ ). Although this is a well-known structural motif to our knowledge this is the first example of the structure with statistical distribution of heteroatoms, involving metals as different as Mg and Ti, in molecular structures of metal alkoxides.

XRD-pattern of I was indexed in the triclinic unit cell parameters found in the course of single crystal X-ray structural study ( $a = 9,946$ ;  $b = 11,842$ ;  $c = 12,243$  Å;  $\alpha = 90,05$ ;  $\beta = 112,14$ ;  $\gamma = 111,78$ ; space group P1;  $Z = 1$ ). No other peaks were registered

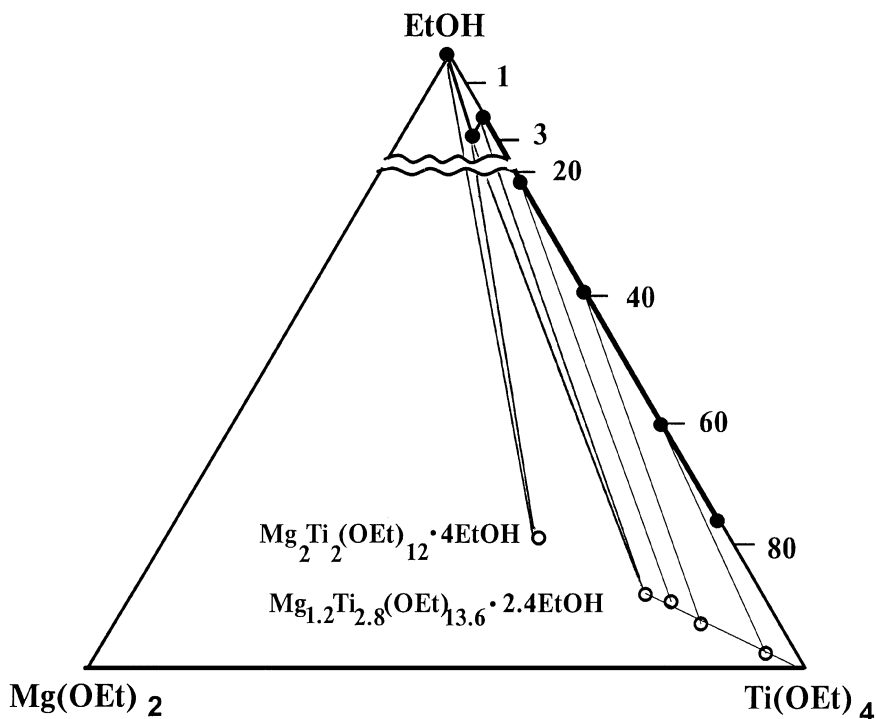


Figure 2. Solubility diagram for the system  $\text{Mg}(\text{OEt})_2\text{-Ti}(\text{OEt})_4\text{-EtOH}$  at  $20^\circ\text{C}$ , mass%.

in crystalline precipitates obtained from solutions with  $\text{Mg} : \text{Ti} \leq 1 : 2$ . The X-ray pattern changes for the precipitates with the  $\text{Mg} : \text{Ti}$  ratio of  $1 : 1$ , which allows us to suggest that besides the above described complex I there exists also the complex with  $\text{Mg} : \text{Ti}$  ratio of  $1 : 1$ . Unfortunately, we did not succeed in isolating of this complex as single crystals suitable for X-ray structural analysis. The system contains a homogeneity region in the solid phase which stretches from I to  $\text{Ti}(\text{OEt})_4$ . The solubility diagram for the system is presented in the Fig. 2.

Interaction between magnesium and titanium isopropoxides could not be studied directly, as magnesium isopropoxide in spite of numerous attempts had not so far been isolated in the individual form [4]. Mg metal does not react with solutions of  $\text{Ti}(\text{OPr-i})_4$  in *i*-PrOH either. In the alcoholic exchange reactions of the above described magnesium ethoxotitanates with isopropyl alcohol, gradual substitution of the ethoxide groups by the isopropoxide groups occurred, however it could not be lead to completion. On refluxing of the reaction mixture for a few hours, complexes were partially decomposed with dissolution of titanium isopropoxide.

Titanium butoxide, magnesium metal or “ $\text{Mg}(\text{OBu})_2$ ” synthesized by reaction of metal with BuOH were used as starting materials for the study of solubility in the system  $\text{Mg}(\text{OBu})_2\text{-Ti}(\text{OBu})_4\text{-BuOH}$ . Magnesium butoxide is insoluble in BuOH,  $\text{Ti}(\text{OBu})_4$  can be mixed with BuOH in any proportion. After the saturation of  $\text{Ti}(\text{OBu})_4$  solutions of different concentrations by magnesium butoxide for 2–3 hours the solutions were decanted and analyzed. The solubility diagram is presented in the Fig. 3.

In all the cases the solid phase “ $\text{Mg}(\text{OBu})_2$ ” did not undergo any changes, no considerable content of Ti was found in the precipitate after its reaction with  $\text{Ti}(\text{OBu})_4$  solutions (the X-ray patterns of the pyrolysis product also corresponded to pure  $\text{MgO}$ ). After evaporation of the solvents from solutions with the compositions corresponding to the solubility branch on the diagram, viscous liquids with  $\text{Mg} : \text{Ti} = 1 : 1$  were obtained (thermolysis product corresponded to  $\text{MgTiO}_3$ ). The same product was prepared by saturation of  $\text{Ti}(\text{OBu})_4$  without solvent by magnesium butoxide.

Reaction of Mg metal with solutions of  $\text{Ti}(\text{OBu})_4$  ( $\text{Mg} : \text{Ti} = 1 : 1$ ) of various concentrations in anhydrous BuOH begins at  $80^\circ\text{C}$  and is accompanied by vigorous

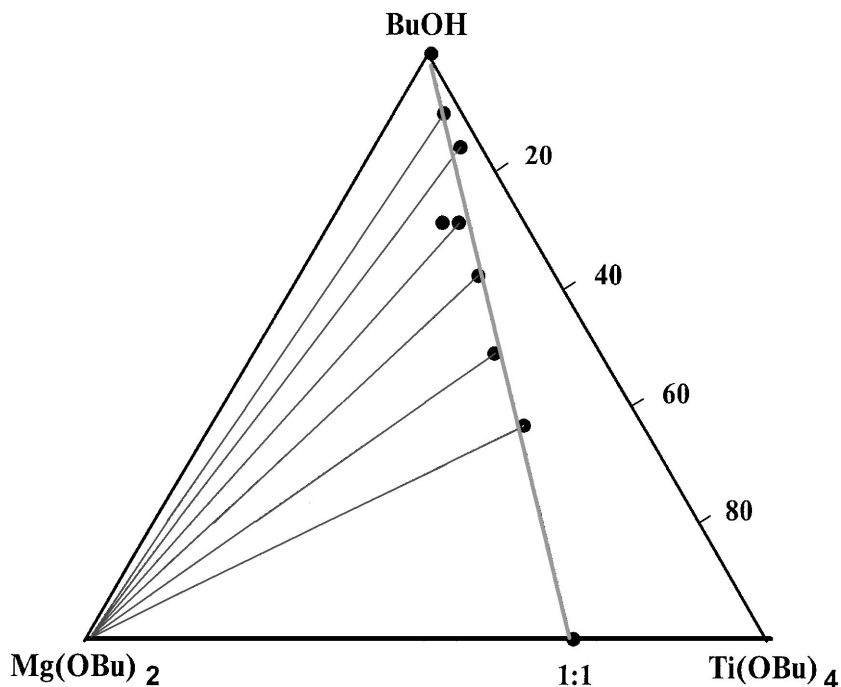


Figure 3. Solubility diagram for the system “Mg(OBu)<sub>2</sub>”-Ti(OBu)<sub>4</sub>-BuOH at 20°C, mass%.

evolution of hydrogen. The solution turns dark green (as a result of partial reduction of Ti(OBu)<sub>4</sub> with formation of complexes with the mixed oxidation state Ti(III,IV)), green precipitate is formed which is presumably a bimetallic Mg-Ti(III,IV) butoxide. This complex does not dissolve in BuOH if the reaction mixture is cooled under argon flow with precautions against oxidation by air. In the presence of dry air the precipitate dissolves completely with oxidation which leads in accordance with [11] to appearance of Ti=O groups. If the Mg : Ti ratio in reaction is >1 magnesium butoxide in the form of white solid precipitates on cooling from the colorless solutions until the Mg : Ti ratio in solution is 1 : 1 (Fig. 3). Therefore the position of the solubility branch of “Mg(OBu)<sub>2</sub>” testifies according to criteria [12] to the formation of the bimetallic complexes with the composition of Mg : Ti = 1 : 1. The question of the true composition of this bimetallic complex as well as the content of oxo-groups in it remains open: the data of chemical analysis of the viscous liquid do not allow us to distinguish between the two compositions—MgTiO<sub>n</sub>(OR)<sub>6-n</sub> · xROH and MgTi(OR)<sub>6</sub>.

Reaction of magnesium metal with the solution of Ti(OBu)<sub>4</sub> in BuOH is extremely sensitive to the content

of moisture in the alcohol, especially when dilute solutions are used. Thus if concentration of Ti(OBu)<sub>4</sub> is lower than 10 mass%, dissolution of Mg occurs only if the water content in BuOH is lower than 0.02 mass%, while 50% solutions of Ti(OBu)<sub>4</sub> react with Mg even at water content of 0.1 mass%. The rate of Mg dissolution may be enhanced if the solution of Ti(OBu)<sub>4</sub> in aqueous BuOH is refluxed for 2–3 hours prior the introduction of Mg: this procedure leads to formation of titanium oxobutoxide TiO<sub>n</sub>(OBu)<sub>4-2n</sub> with higher “acidity”, and consequently higher reactivity in comparison with Ti(OBu)<sub>4</sub>.

It is especially interesting to compare the results for Mg(OR)<sub>2</sub>-Ti(OR)<sub>4</sub>-ROH system with the solubility data for other systems M<sup>II</sup>(OR)<sub>2</sub>-Ti(OR)<sub>4</sub>-ROH (where M<sup>II</sup> = Ca, Ba), in which quite stable complexes with the composition M<sup>II</sup>Ti<sub>4</sub>(OR)<sub>18</sub> are formed. The latter exist in solutions, crystalline and even gaseous states [13]. Such complexes presumably cannot be formed in the case of Mg because of its small atomic radius and therefore its inability to form complexes with high coordination numbers (=8) characteristic of alkaline-earth metals. Nevertheless, in all the studied systems bimetallic oxoalkoxides with the 1 : 1 stoichiometry are real precursors of the corresponding complex oxides.

Solutions for hydrolysis were prepared by reaction of Mg in solutions of  $\text{Ti}(\text{OBu})_4$  in BuOH with the concentration of  $\sim 25$  mass%. After the completion of reaction and cooling, the colorless transparent solution was hydrolyzed by aqueous BuOH (concentration of water in BuOH varied in the range from 1.3 to 17.6 mass%). Different conditions of hydrolysis were studied. Hydrolysis was performed on vigorous stirring in one or in two steps, at different temperatures from 20 to  $80^\circ\text{C}$ ; the water to alkoxide ratio  $[\text{H}_2\text{O}] : [\text{Ti}(\text{OBu})_4]$  varied in the range from 9.5 to 17.5. White precipitate was usually formed directly in the course of hydrolysis, mixing was continued for 30–60 minutes, then the mother liquor which contained aqueous BuOH was decanted; the residue was washed by ethyl alcohol and acetone and dried at  $110^\circ\text{C}$ .

The yellowish amorphous precipitate was annealed at  $800^\circ\text{C}$  for 1 hour,  $\text{MgTiO}_3$  without any admixtures of other crystalline phases crystallized on thermal treatment. Typical scanning electron micrograph of the powder is presented in the Fig. 4. Powders consist of very fine particles ( $< 0.1 \mu\text{m}$ ) without any pronounced tendency to agglomeration. It is quite unusual that the morphology of the particles practically did not change with the variation of the alkoxide concentration and the  $[\text{H}_2\text{O}] : [\text{Ti}(\text{OBu})_4]$  ratio. Usually different investigators registered considerable changes in the particle sizes with the variation of the hydrolysis conditions [14, 15].

The temperature of hydrolysis and application of aqueous butanol as a hydrolyzing agent proved to be very important conditions for preparation of the powder without admixtures of the foreign phases. Hydrolysis of the reaction mixture by water at enhanced

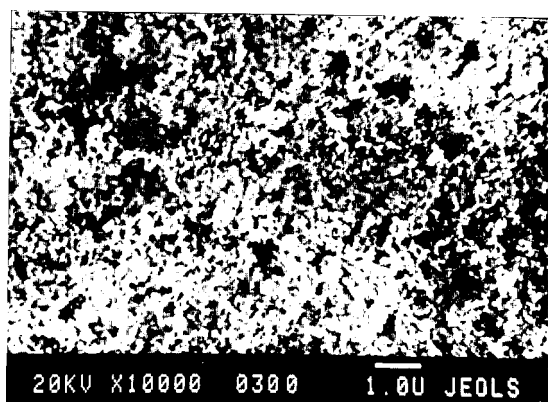
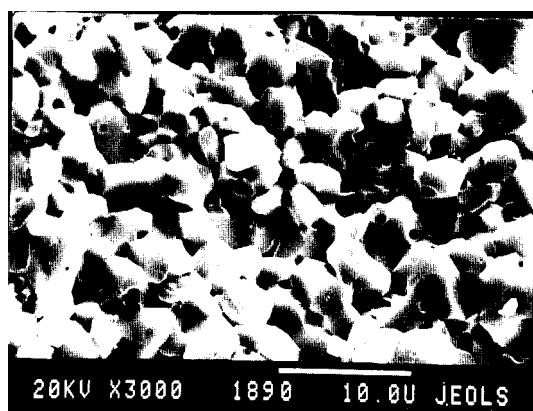


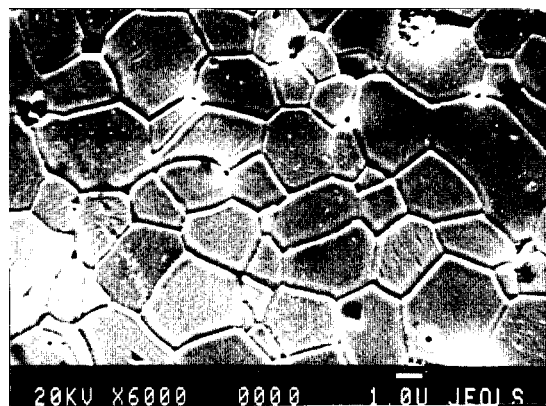
Figure 4. Typical scanning electron micrographs of the alkoxy-derived  $\text{MgTiO}_3$  powders.

temperature, e.g., on refluxing of the reaction mixture resulted in amorphous precipitates which crystallized on thermal treatment to  $\text{MgTiO}_3$  containing considerable admixture of  $\text{MgTi}_2\text{O}_5$ . Presumably  $\text{MgTiO}_3$  itself is hydrolyzed by the excess of water at enhanced temperature. Thus, hydrolysis of magnesium oxobutoxotitanate solutions at room temperature by aqueous BuOH suggests a simple and efficient technique for preparation of  $\text{MgTiO}_3$ .

Alkoxy-derived powders were used for sintering of ceramics without any mineralizing agents in the temperature range of  $1140$ – $1220^\circ\text{C}$ , which is  $150$ – $200^\circ$  lower than for the conventional  $\text{MgTiO}_3$  synthesized from oxides or by precipitation from aqueous solutions. Ceramic bodies were dense, with the porosity of 2–3% and the mean crystallite size from 2 to  $4 \mu\text{m}$ . Scanning electron micrographs (Fig. 5) testify to high uniformity of the sintered bodies. Dielectric



(a)



(b)

Figure 5. Scanning electron micrographs of the alkoxy-derived ceramics  $\text{MgTiO}_3$  sintered at  $1180^\circ\text{C}$  ((a) fracture surface; (b) surface polished and further etched by thermal treatment).

permittivity of the ceramics was 17.8–18.5,  $tg\delta < (3-9) \cdot 10^{-5}$  ( $f = 1$  MHz); the temperature coefficient of the dielectric constant was  $+(110-135) \cdot 10^{-6} \text{C}^{-1}$  and practically did not change up to 300°C.

#### 4. Conclusions

The results of the present work testify to different character of interaction between Mg and Ti alkoxides with different R: no reaction occurs in the case of  $R = \text{Me}$ , unusual complexes of varying composition were registered in the case of  $R = \text{Et}$ , only in the case of  $R = \text{Bu}$  complex with  $\text{Mg}:\text{Ti} = 1:1$  is formed. Easy synthesis of the latter together with its 1:1 stoichiometry and high solubility makes this complex an ideal precursor for sol-gel synthesis of  $\text{MgTiO}_3$ . Application of metal alkoxides suggests an easy and convenient way to synthesis of  $\text{MgTiO}_3$  fine powders with good sintering properties.

#### Acknowledgments

The authors would like to thank Prof. L.M.Kovba for fruitful discussions. The research was partially supported by INTAS (grant 94-771) and Russian Foundation for Basic Research (project N 96-03-33553).

#### References

1. B.A. Wechsler and A.J. Navrotsky, *Solid State Chem.* **55**, 165 (1984).
2. I.A. Kudrenko, V.N. Trosheva, and A.E. Skudnova, *Izv. AN SSSR, Ser. Neorg. Mater.* **12**, 679 (1976) (Russian).
3. N.Ya. Turova, B.A. Popowkin, and A.W. Nowoselowa, *Z. Anorg. Allg. Chem.* **365**, 100 (1969).
4. N.Ya. Turova, V.A. Kozunov, E.P. Turevskaya, and A.V. Novoselova, *Russ. J. Inorg. Chem.* **18**, 327 (1973).
5. O. Yamaguchi, S. Yamamoto, and K. Shimizu, *Ceram. International* **7**, 73 (1981).
6. F. Schmidt and A. Feltz, *Z. Anorg. und Allg. Chem.* **573**, 208 (1989).
7. E.P. Turevskaya and N.Ya. Turova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1977**, 1380.
8. A.I. Yanovsky, F.M. Dolgushin, Yu.T. Struchkov, N.M. Kotova, M.I. Yanovskaya, and N.Ya. Turova, *Russ. J. Inorg. Chem.* **42**, 385.
9. D.A. Wright and D.A. Williams, *Acta Cryst.* **24B**, 1107 (1968).
10. J.A. Ibers, *Nature* **197**, 686 (1963).
11. A.N. Nesmeyanov, O.V. Nogina, and R.Kh. Freydlina, *Izv. AN SSSR Ser. Khim.* **1956**, 373 (Russian).
12. N.Ya. Turova, *Soviet J. Coord. Chem.* **10**, 644 (1984).
13. A.I. Yanovsky, E.P. Turevskaya, M.I. Yanovskaya, V.G. Kessler, N.Ya. Turova, A.P. Pisarevsky, and Yu.T. Struchkov, *Russ. J. Inorg. Chem.* **40**, 399 (1995).
14. N.M. Kotova, S.G. Prutchenko, and M.I. Yanovskaya, *Inorganic Materials* **30**, 367 (1994).
15. E.A. Barringer and H.K. Bowen, *Commun. American Ceram. Soc.* **1982**, 199.