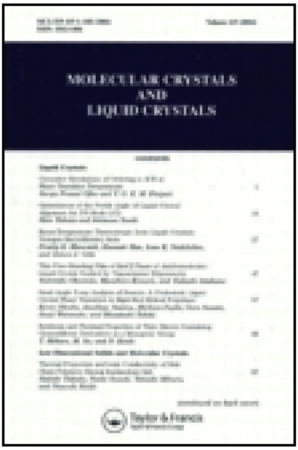

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Spectroscopic Studies of Alkoxide Precursors for the Synthesis of Ba($Mg_{1/3}Ta_{2/3}$)O_3

Duk-Young Jun [a] , Eung Soo Kim [b] , Kyung Hwa Jo [c] & David A. Payne [d]

[a] Department of Chemistry, Sungkyunkwan University, Suwon, 440-746, Korea

[b] Department of Materials Engineering, Kyonggi University, Suwon, 442-760, Korea

[c] Examination Bureau IV, Korean Industrial Property Office, Taejeon, 302-223, Korea

[d] Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, 61801, U.S.A.

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Spectroscopic Studies of Alkoxide Precursors for the Synthesis of $Ba(Mg_{1/3}Ta_{2/3})O_3$

DUK-YOUNG JUN*[a], EUNG SOO KIM[b], KYUNG HWA JO[c] and DAVID A. PAYNE[d]

[a]Department of Chemistry, Sungkyunkwan University, Suwon 440–746, Korea, [b]Department of Materials Engineering, Kyonggi University, Suwon 442–760, Korea, [c]Examination Bureau IV, Korean Industrial Property Office, Taejeon 302–223, Korea and [d]Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, U.S.A

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^1H and ^{13}C Fourier transform-nuclear magnetic resonance (FT-NMR) and mass spectrometric (MS) techniques were used to prove the structures of precursors used in the sol-gel synthesis of the high-frequency dielectric $Ba(Mg_{1/3}Ta_{2/3})O_3$. Various metal methoxyethoxides (MEO) of Ba, Ta, Mg-Ta and Ba-Mg-Ta systems were prepared in 2-methoxyethanol (MeOEtOH). The tantalum and the magnesium-tantalum precursors were determined to be $Ta_2(MEO)_{10}$ and $MgTa_2(MEO)_{12}$, respectively. Similar spectroscopic studies for "$Ba_3MgTa_2(MEO)_{15}$" indicated that the Ba-Mg-Ta alkoxide precursor has a polymer structure of (Ba,Mg,Ta)(MEO) complex and contains the bridging alkoxy groups between Ta and the alkaline earth metals.

Keywords: metals; alkoxide; oxide; perovskite; NMR; Mass spectrometry

INTRODUCTION

Techniques for the formation of inorganic materials, including sol-gel processing, chemical vapor deposition, metal organic decomposition, and molecular beam epitaxy, require metal-organic precursors of molecular building blocks for specific physical and chemical properties [1]. The primary characteristics are generally high vapor pressure and substantial solubility in particular solvents. Design aspects include the synthesis of heterometallic precursors with specific

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* Correspondence Author.

stoichiometries for the desired final material. In this respect, sol-gel synthesis has been used to prepare a variety of complex oxide materials including films, fibers and monolithic ceramics [**2**]. One of the important advantages of the sol-gel process is the convenience of the metal-organic to the metal oxide on heat treatment. Also the advantage of the sol-gel method includes more intimate mixing and control of purity and composition compared with conventional solid state reactions. The chemical sol-gel route leads to lower synthesis processing temperatures, which is important for fabrication of oxide materials.

The metal alkoxides $M(OR)_x$ (M = a metal with oxidation state of x; R = alkyl or aryl group) are good precursors for the preparation of oxide materials. Great interest in preparation of high-Tc superconducting oxides, opto-electronic devices and electrical and magnetic ceramics has led to studies of the chemistry of respective alkoxides [**3**]. Heterometallic alkoxides, which contain two or more different metal atoms linked by bis(μ-OR) bridges could therefore provide convenient precursors for the sol-gel synthesis of multicomponent materials [**4**]. Hydrolysis replaces the alkoxide groups with hydroxyl groups and subsequent condensation (alkoxolation, oxolation and olation) produce M-O-M(or M′) or M(μ-OH)M(or M′) networks.

The mixed-metal perovskite oxide, $Ba(Mg_{1/3}Ta_{2/3})O_3$, has low dielectric loss at microwave frequencies and can be used in microwave resonators and wireless communications [**5**]. The preparation of $Ba(Mg_{1/3}Ta_{2/3})O_3$ dielecetrics by conventional mixed-oxides processing requires high-temperature solid-state reactions (e.g., 1550°C) [**5a**]. Attempts to reduce the densification temperature have included the enhanced ball-milling technique [**5b**], rapid heating [**5c**], and the use of sintering aids, for example, manganese metal [**5d**], $BaTa_2O_6$ [**5e**], $BaWO_4$ [**5f**]. Schnoeller et al. used a chemical method and prepared $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics from a xerogel derived from tantalum ethoxide, barium acetate and magnesium acetate [**5g**] Renoult et al. reported the use of the heterometallic precursor $MgTa_2(OC_2H_5)_{12}$ with hydrated barium hydroxide $Ba(OH)_2{\cdot}8H_2O$ [**5h**]. Katayama et al. proposed $Ba(Mg_{1/3}Ta_{2/3})O_3$ perovskites powders by hydrolysis and refluxed precipitation of alkoxide solutions in ethanolic media [**5i**]. Most of the sol-gel preparations described above were reported without explicit chemical and physical analyses of the precursor solutions.

Our recent investigations [**6**] have involved the preparation of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics from barium metal, anhydrous magnesium acetate and tantalum ethoxide in 2-methoxyethanol. Few studies have reported on the structures of tantalum containing precursors compared with titanates, zirconates, niobates, etc., e.g., $BaTiO_3$ [**7**], $PbTiO_3$, $Pb(Zr,Ti)O_3$,[**8**], $Bi_4Ti_3O_{12}$ [**9**] and $Pb(Mg_{1/3}Nb_{2/3})O_3$ [**10**] systems. In the present study, the soluble precursors of Ba, Ta, Mg-Ta, and Ba-Mg-Ta were isolated and characterized by the FT-NMR and MS methods. FT-NMR spectroscopy gives information on the chemical environment of carbon centers in the alkoxy groups, and analysis of NMR data for solutions in D_2O presents the evolution of species on hydrolysis. MS can also reveal the composition of heterometallic alkoxides, provided they are volatile and stable with respect to disproportionation reactions in the vapor phase. The MS studies allow a first preliminary evaluation of precursors suitable for metal-organic chemical vapor-phase deposition (MOCVD).

EXPERIMENTAL

All manipulations were carried out under dry argon or under flowing dry nitrogen. The following chemicals were used without further purification unless specified otherwise: 2-methoxyethanol (anhydrous, Aldrich Chemical Co., 99+%), barium metal (Alfa Johnson & Mathey, 99.7%), magnesium metal (Alfa Johnson & Mathey, 99.8%), tantalum ethoxide (Aldrich Chemical Co., 99.98%), anhydrous ethanol (McCormick Distilling Co., 99+%). Ethanol was used after dehydration by molecular sieve. The experimental procedures are summarized in Fig. 1.

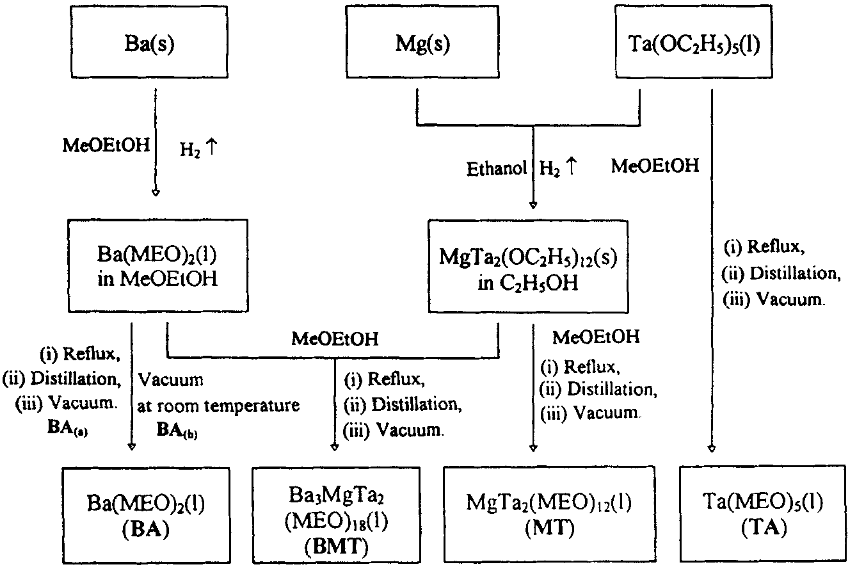


FIGURE 1 Flow diagram of experimental process for **BA**, **TA**, **MT** and **BMT** precursors. The subscripts represent stoichiometric proportions for the mixed metal alkoxide solutions

$Ba(MEO)_2$ (**BA**) was prepared by the combination of excess 2-methoxyethanol with barium metal in a flask cooled in an ice-water bath with stirring. After complete dissolution of the barium metal, the mixture was allowed to warm to room temperature before refluxing at 125°C for 5 minutes. The resulting solution was clear and amber in color. Vacuum distillations were carried out at about 10torr to prepare the $\mathbf{BA_{(a)}}$. Extended refluxing for more than 5 minutes gave a dark brown solution. In addition, the $\mathbf{BA_{(b)}}$ precursor was also prepared after evaporation of hydrogen gas without refluxing. The color of the $\mathbf{BA_{(b)}}$ became darker after evaporation of MeOEtOH by vacuum distillation at room temperature, similar to the color of the aforementioned $\mathbf{BA_{(a)}}$ after refluxing.

A tantalum precursor (**TA**) was prepared by an exchange reaction of tantalum(V) ethoxide with MeOEtOH. The two reactants were combined at room temperature with stirring and refluxed at 70°C for 1h. Ethanol and MeOEtOH were removed by distillation and vacuum evaporation. A clear, viscous, light yellow liquid was obtained.

Magnesium tantalum 2-methoxyethoxide (**MT**) was prepared by an exchange reaction of ethanol in Mg-Ta ethoxide with MeOEtOH. The Mg-Ta ethoxide was obtained by addition of the stoichiometric amounts (Mg:Ta = 1:2) of magnesium powder in a 1*M* solution of tantalum ethoxide in ethanol at room temperature. After evolution of gaseous hydrogen, transparent needle-like crystals formed in the ethanolic solution and the opaque magnesium powder completely disappeared. Excess MeOEtOH was added and the needle-like crystals redissolved at room temperature. After refluxing the resulting solution under dry nitrogen at 125°C for lh, distillations were then carried out to remove the ethanol. MeOEtOH was evacuated and a clear viscous pale yellow liquid was obtained.

The MeOEtOH precursor (**BMT**) containing barium, magnesium and tantalum of 3:1:2 molar ratio was prepared by mixing 10ml of 3*M* Mg-Ta ethoxide in ethanol and 150ml of 0.06*M* $\mathbf{BA_{(b)}}$ in MeOEtOH. Then, the solution was refluxed for 3h, followed by distillation at 125°C and vacuum evaporation of the solvent at room temperature.

^{1}H and ^{13}C FT-NMR spectra were collected on a GE GN300 spectrometer to obtain structural data for the compounds at room temperature. The precursors ($\mathbf{BA_{(b)}}$, **TA, MT** and **BMT**) were diluted in deuterated benzene(1:100 of volume ratio) for NMR experiments. Chemical shifts were internally referenced to proton in deuterated benzene. MS data were obtained on a VG 70-VSE spectrometer using chemical ionization(CI) techniques for identification of molecular species from selected compounds. Viscous samples were injected without dilution into the ionization chamber that was filled with methane ion species.

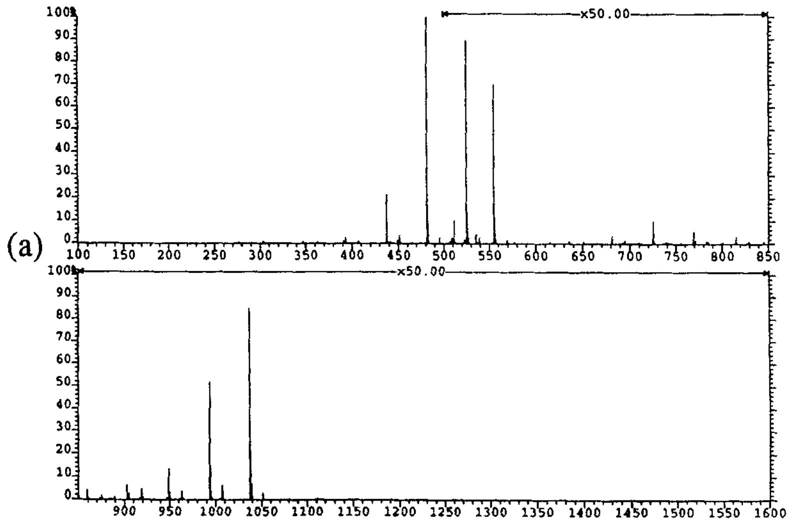
RESULTS AND DISCUSSION

Tantalum precursors

The CI mass spectrum of the tantalum precursor (**TA**), given in Fig. 2a, exhibits peaks at 481. 1 and 1037.3 *m/z* (mass per charge), corresponding to the fragments of $[Ta(MEO)_4]^+$ and $[Ta_2(MEO)_9]^+$, respectively, which results from subtraction of MEO. The mass spectra of **TA** were compared with reference data for alcohol and ether compounds **[11]**. Peaks at 555.2 and 1111.3 *m/z* were also observed, corresponding to molecular ion of $[Ta(MEO)_5\text{-}H]^+$ and $[Ta_2(MEO)_{10}\text{-}H]^+$, respectively. These P-1 (*m/z* of product minus one) peaks with weak intensities are usual for the alcohol compounds, instead of the existence of product ion **[11]**. The peaks at 393.1, 437.1, 525.2, 949.2 and 993.3 *m/z* were attributed to the carbon-carbon bond cleavage next to the oxygen in primary alcohol which gives a general formula $[Ta_x(MEO)_{5x-y}(CH_3O)_y(\text{-}H)_z]^+$ (x=1,2; y=0,1,2; z=0,1). Assigning the molecular fragments is summarized in Table I. Based on similar MS studies for titanium **[8c]** and silicon **[12]** alkoxides, the present MS analysis indicates the molecular formula for **TA** to be $Ta_2(MEO)_{10}$. However, it should be noted that the oligomeric structure of **TA** derived by the MS evidence shows only the structural integrity in the vapor phase. Trimeric species were considered to be absent because of the systematic absence of peaks of higher atomic fragments (>1050 *m/z*) in the mass spectrum. The dimeric model is supported by MS data for tantalum ethoxide which indicate a degree of association of 2, supporting the molecular formula of $Ta_2(OC_2H_5)_{10}$ **[13]**. Tantalum alkoxides may increase in covalency by *inter*molecular bonding, which is opposed by charge repulsion between tantalum cations and by rotational freedom of the alkoxide groups which screen the metal ions. FT-NMR experiments were also carried out to prove the above molecular model. The $^{13}C\{^1H\}$ NMR spectrum of **TA** were compared with that of MeOEtOH. The $^{13}C\{^1H\}$ NMR spectrum of MeOEtOH present 58.8(C_{III}), 61.6(C_I) and 74.0ppm(C_{II}) in C_6D_6, as defined in Fig. 3. The $^{13}C\{^1H\}$ NMR spectrum of **TA** was similar to that of MeOEtOH except for the peak due to the carbon center of C_I, due to the high oxidation state of tantalum. In the $^{13}C\{^1H\}$ NMR spectrum of **TA** (Fig. 2b), peaks could be assigned to the following carbon centers: 58.6 ppm (C_{III}), 71.2 ppm (C_I) and 74.8 ppm (C_{II}). These chemical shifts are comparable with the results (59.33, 75.41 and 73.54 ppm) for $Ti_2(MEO)_8$ **[8c]**, presumably due to the high oxidation states for the titanium and tantalum cations. A broadly overlapped peak was observed for C_{Ia} and C_{Ib}, which was attributed to the various environments for C_I and/or geometrical factors, which make rotation of the carbon chain difficult. The $^{13}C\{^1H\}$ NMR spectrum for $Ta(OC_2H_5)_5$ (Fig. 2c) which was used as the starting material showed a broad peak at 68 ppm corresponding to alkoxy carbon, which represent a different chemical environment. Bradley et al. reported that tantalum alkoxides,

$Ta(OR)_5$ (R=methyl, ethyl, *n*-propyl, *n*-butyl, and *n*-pentyl) were dimeric with six coordinations based on the results of ebulliometric methods and ^1H NMR spectroscopic data **[14]**. We now consider two structural models, (i) one with two bridging alkoxides (Fig. 3b) and (ii) the other with four bridging alkoxides (Fig. 3c). The two bridging configurations would be expected (Fig. 3b) due to a less steric effect. In NMR spectrum for **TA**, the broad peaks at 71.2 ppm and 74.8 ppm are consistent with different chemical environments and steric effects though the two factors described above are effective for both C_{II} and C_I. On the contrary C_{III} would be little influenced by tantalum or geometry because of the long distance from the tantalum cation. Further studies including variable temperature NMR and EXAFS (Extended X-ray absorption fine structure) are now underway to investigate the structure of **TA**.

A $^{13}C\{^1H\}$ NMR spectrum was also obtained for a solution of **TA** in MeOEtOH. A single peak was observed at 61.9 ppm for C_I indicating rapid exchange between ligand and solvent at room temperature. In order to verify complete exchange of MeOEtOH with ethanol in the **TA** precursor solution, hydrolysis with deuterium oxide was carried out for the **TA** solution, where the molar ratio of D_2O to $Ta_2(MOE)_{10}$ was 200:1. The $^{13}C\{^1H\}$ NMR spectrum of the resulting solution (filtrate) gave only three peaks corresponding to MeOEtOD indicating that the MeOEtOH has replaced ethanol completely. A D_2O solution containing MeOEtOH and ethanol was used as a reference. ^{13}C chemical shifts for carbon centers in ethanol were reported as 58.4 ppm and 16.4 ppm **[15]**. Ethanol was not observed for D_2O hydrolyzed solutions of the **TA** precursor under the detection limit of our NMR measurement.



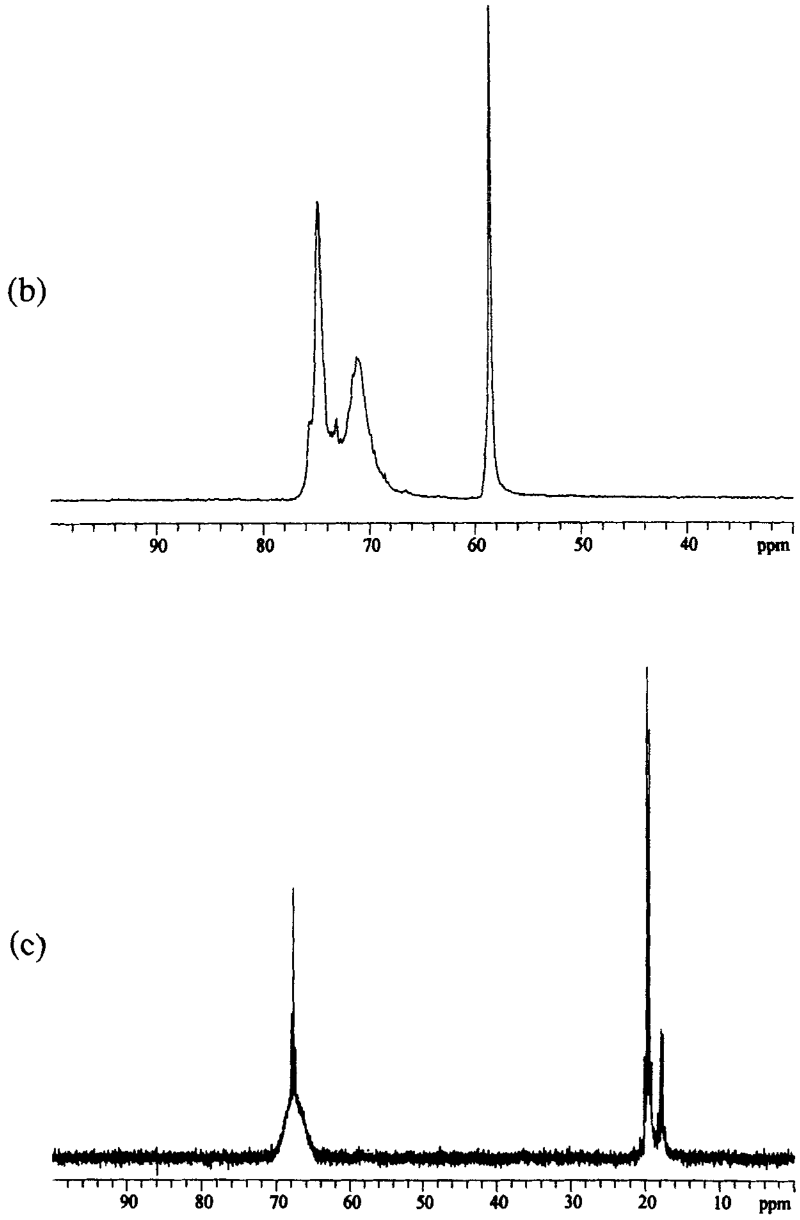


FIGURE 2 (a) Chemical ionization mass spectrum of tantalum precursor, TA. Note the scale multiplied in high *m/z* values. (b) The $^{13}C\{^1H\}$ NMR spectrum for TA in C_6D_6. (c) The $^{13}C\{^1H\}$ NMR spectrum for $Ta(OC_2H_5)_5$ in C_6D_6

TABLE I Experimental mass spectrometric data and assigned fragments[a]

TA		*MT*		*BMT*	
m/z	*[fragments]+*	*m/z*	*[fragments]+*	*m/z*	*[fragments]+*
1112.3	$Ta_2(MEO)_{10}$	655.1	$MgTa(MEO)_6$	1325.3	$BaTa_2(MEO)_{11}$
1037.3	$Ta_2(MEO)_9$	539.1	$Ta(MEO)_5(AO)$-H	1309.2	$BaTa_2(MEO)_{10}(AO)$
993.3	$Ta_2(MEO)_8(MO)$	509.1	$Ta(MEO)_4(AO)_2$	1293.2	$BaTa_2(MEO)_9(AO)_2$
949.2	$Ta_2(MOE)_7(MO)_2$	465.1	$Ta(MEO)_3(AO)_3$	1281.2	$BaTa_2(MEO)_{10}(MO)$
725.1	$Ta_2(MEO)_2(MO)_7$			1265.2	$BaTa_2(MEO)_9(MO)(AO)$
555.2	$Ta(MEO)_5$-H			1249.2	$BaTa_2(MEO)_8(MO)(AO)_2$
525.2	$Ta(MEO)_4(EO)$-H			1237.2	$BaTa_2(MEO)_9(MO)_2$
481.1	$Ta(MEO)_4$			1221.2	$BaTa_2(MEO)_8(MO)_2(AO)$
437.1	$Ta(MEO)_3(MO)$			1205.2	$BaTa_2(MEO)_7(MO)_2(AO)_2$
				1193.1	$BaTa_2(MEO)_8(MO)_3$
			and **TA** fragments		and **TA** fragments

[a] MEO = $CH_3OCH_2CH_2O^-$, EO = $CH_3CH_2O^-$, MO = CH_3O^-, AO = $HCOCH_2O^-$.

Magnesium tantalum precursor

Though the reaction between ethanol and magnesium metal was not evident at room temperature, addition of tantalum ethoxide induced the reaction and the evolution of gaseous hydrogen. The reaction scheme for the preparation of magnesium tantalum ethoxide was suggested as follows,

$$\mathrm{Mg(s)} + 2\mathrm{Ta(OC_2H_5)_5(l)} + 2\mathrm{C_2H_5OH(l)} \rightarrow \mathrm{Mg[Ta(OC_2H_5)_6]_2(s)} + \mathrm{H_2(g)},$$

similar to a method of Goel et al. **[16]**. We obtained colorless needle-like crystals in ethanolic solution without the use of a catalyst $HgCl_2(s)$. The crystals were assumed to be a heterometallic alkoxide, $Mg[Ta(OC_2H_5)_6]_2 \cdot C_2H_5OH$, as in the case of $Mg[Nb(OC_2H_5)_6]_2 \cdot C_2H_5OH$ **[16]** or $MTa_2(OC_3H_7)_{12}$ (M=alkaline-earth metals) **[17]** since the elemental analysis for this crystal confirmed the stoichiometric amount of Mg and Ta. In this study, the heterometallic ethoxide was not isolated during the preparation of the Mg-Ta precursor solution of MeOEtOH. The crystals redissolved in excess alcohol, although magnesium metal generally reacts slowly with ethanol to give insoluble $Mg(OC_2H_5)_2$.

The molecular ion was not shown in the CI mass spectrum (Fig. 4a) for the magnesium tantalum precursor (**MT**). It was interpreted in terms of fragmentation along two parallel paths – one where the tantalum methoxyethoxide group was lost and the other where the magnesium alkoxide group was fragmented,

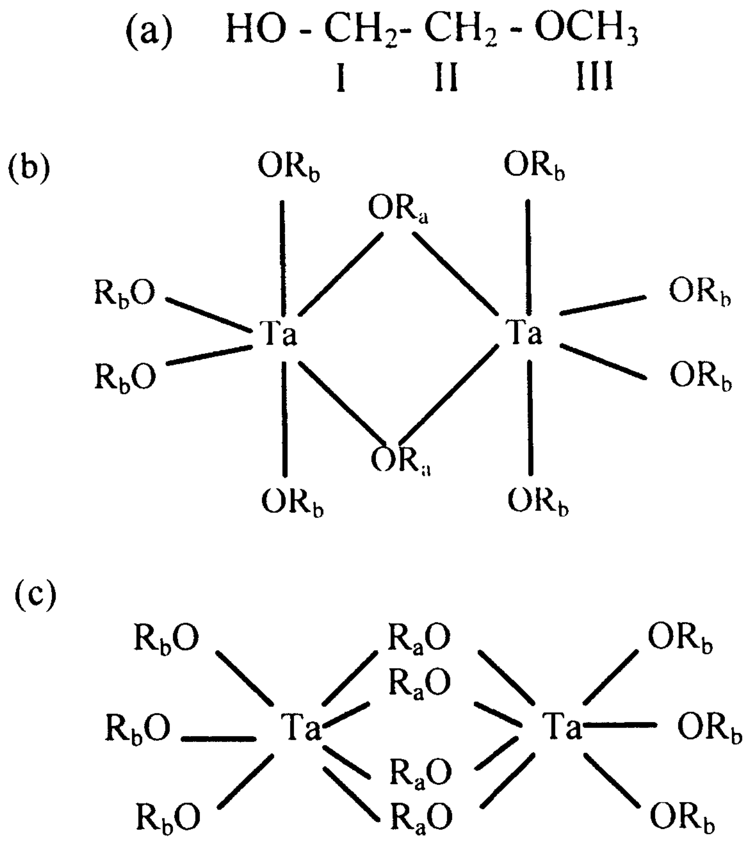
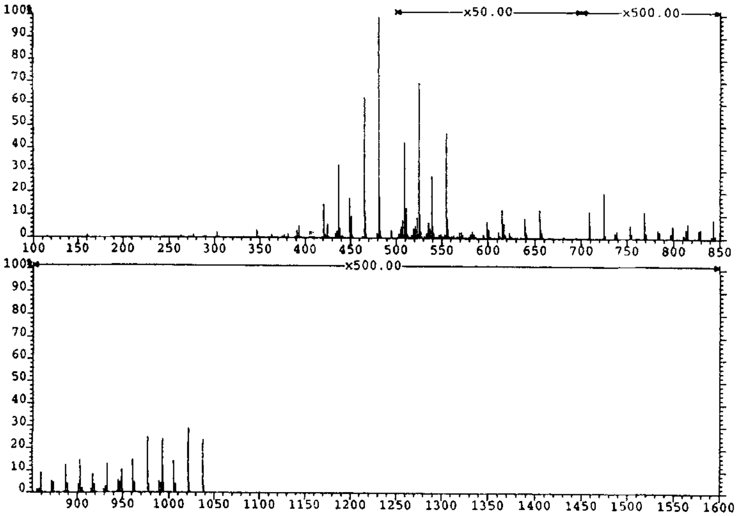


FIGURE 3 (a) Definition of carbon centers for MeOEtOH. (b), (c) Possible molecular structures for the tantalum precursor, **TA**

giving rise to ions with 655. 1 and 1037.2 *m/z*, respectively. Table I summarizes the various assignable ion fragments. The absence of a peak corresponding to the molecular ion $MgTa_2(MEO)_{12}$ was attributed to the decomposition of **MT** during the CI process, presumably resulting from a more volatile magnesium alkoxide species [**17**].

In the $^{13}C\{^1H\}$ NMR spectrum of **MT** (Fig. 4b), peaks could be assigned to the following carbon centers; 58.8 ppm (C_{III}), 75.3 ppm (C_{II}), and three peaks around 68 ppm (C_I). The chemical shift of 68 ppm indicates the averaged induction field applied to C_I by both the tantalum and the magnesium. The three peaks (68.9, 68.6 and 68.3 ppm) correspond to C_{Ic}, C_{Id} and C_{Ie} of a probable structure for the **MT** precursor considered in Fig. 4c. A $^{13}C\{^1H\}$ NMR spectrum of **MT** in

(a)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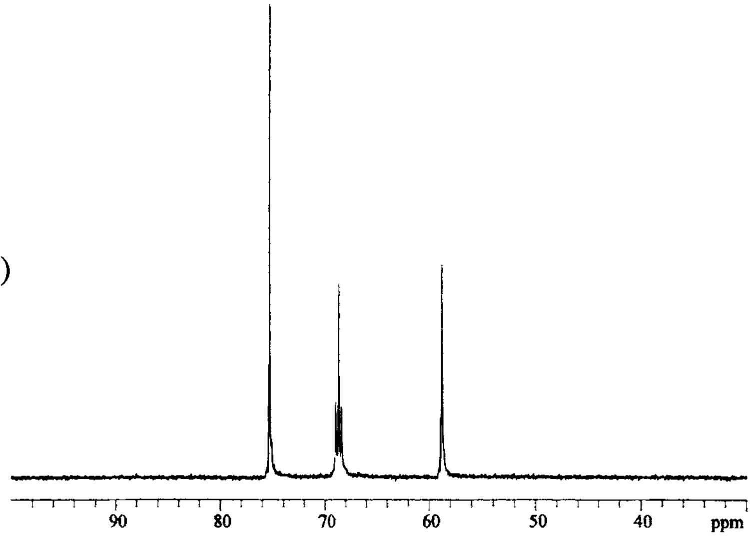
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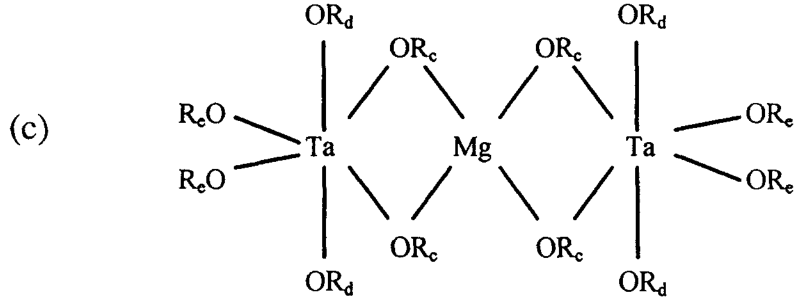


where R = CH_2-CH_2-OCH_3

FIGURE 4 (a) Chemical ionization mass spectrum of magnesium tantalum precursor, **MT**. Note the scale multiplied in high *m/z* values. (b) The $^{13}C\{^{1}H\}$ NMR spectrum of **MT** obtained from magnesium metal. (c) The $^{13}C\{^{1}H\}$ NMR spectrum of **BMTA** prepared from magnesium acetate. The C_6D_6 is used for dilution of samples in the NMR measurements

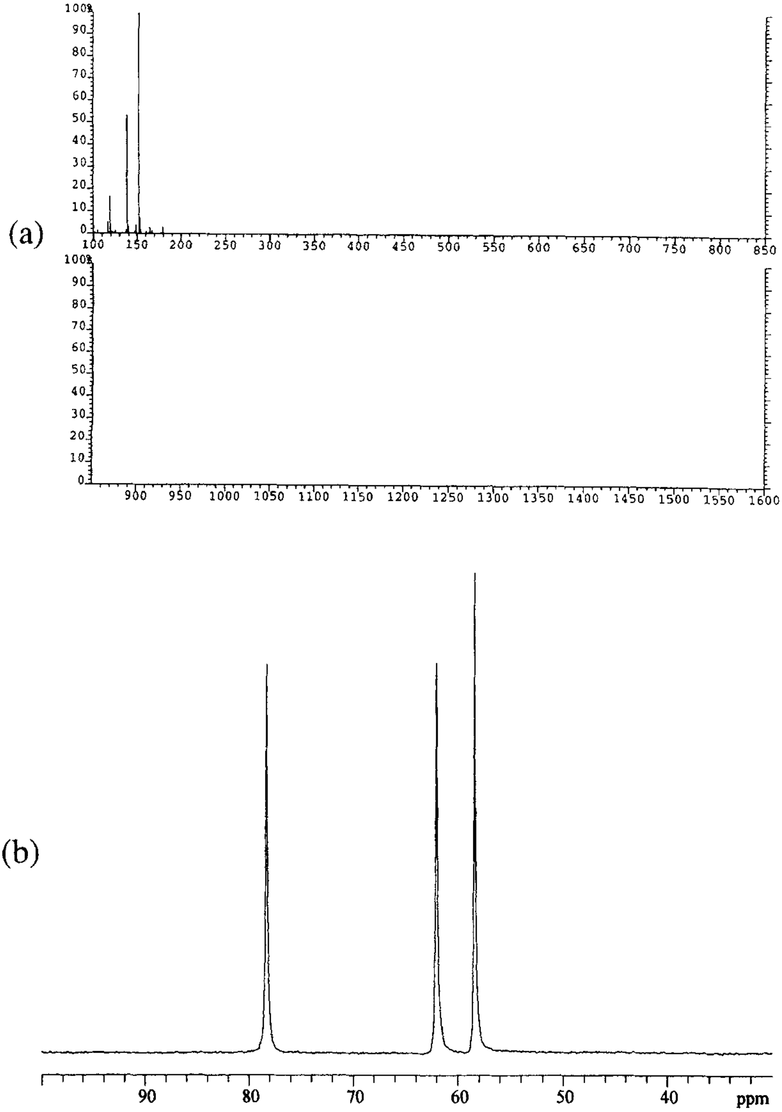
the presence of MeOEtOH gave separate MeOEtOH peaks at 76.3 ppm (C_{II}) and 62.2 ppm (C_I), indicating that *inter*molecular exchange between alkoxide and alcohol was much slower than *intra*molecular exchange. This is in contrast to the behavior of titanium alkoxides which indicate coalescence of alcohol and alkoxide signals by rapid interchange **[14b,8c,8i]**.

If the replacement of ethoxide by methoxyethanol was not completed, the precursor could be $Mg[Ta(OC_2H_5)_{6-x}(MEO)_x]_2$. Terminal groups are expected to be replaced more easily due to the steric effect; for example Goel **[16]** reported that refluxing $Mg[Ta(MEO)_6]_2$ in t-butanol resulted only in the replacement of six (terminal) of the twelve ethoxy groups. However, in the present study, the $^{13}C\{^{1}H\}$ NMR spectrum of MeOEtOD solution in D_2O indicated the absence of any ethanol peaks expected from any remaining magnesium tantalum ethoxide. Thus we conclude that exchange was completed and the MEO group has a similar steric effect with the ethoxy one in the $Mg[Ta(OR)_6]_2$ system.

Barium precursor

The CI mass spectrum of the barium precursor of $\mathbf{BA_{(b)}}$ (Fig. 5a) indicated a molecular fragment at 152.3 *m/z*. corresponding to the dimeric MeOEtOH ($[CH_3OCH_2CH_2OH]_2^{+}$). The absence of any peak for a molecular ion such as $[Ba(MEO)_2]^{+}$ was probably due to decomposition of $\mathbf{BA_{(b)}}$ during chemical ionization and the non-volatile properties of the **BA** precursor.

The $^{13}C\{^{1}H\}$ NMR spectrum for **BA** ($\mathbf{BA_{(a)}}$ and $\mathbf{BA_{(b)}}$) shown in Fig. 5b and Fig. 5c, indicates the chemical environments for the carbon centers in the **BA**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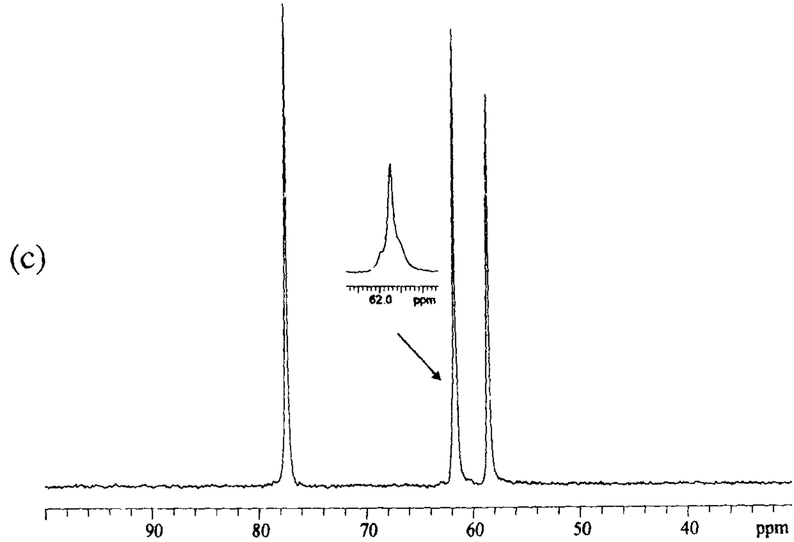


FIGURE 5 (a) Chemical ionization mass spectrum of barium precursor, $\mathbf{BA}_{(b)}$. The $^{13}C\{^{1}H\}$ NMR spectrum of (b) $\mathbf{BA}_{(a)}$, and (c) $\mathbf{BA}_{(b)}$ in C_6D_6

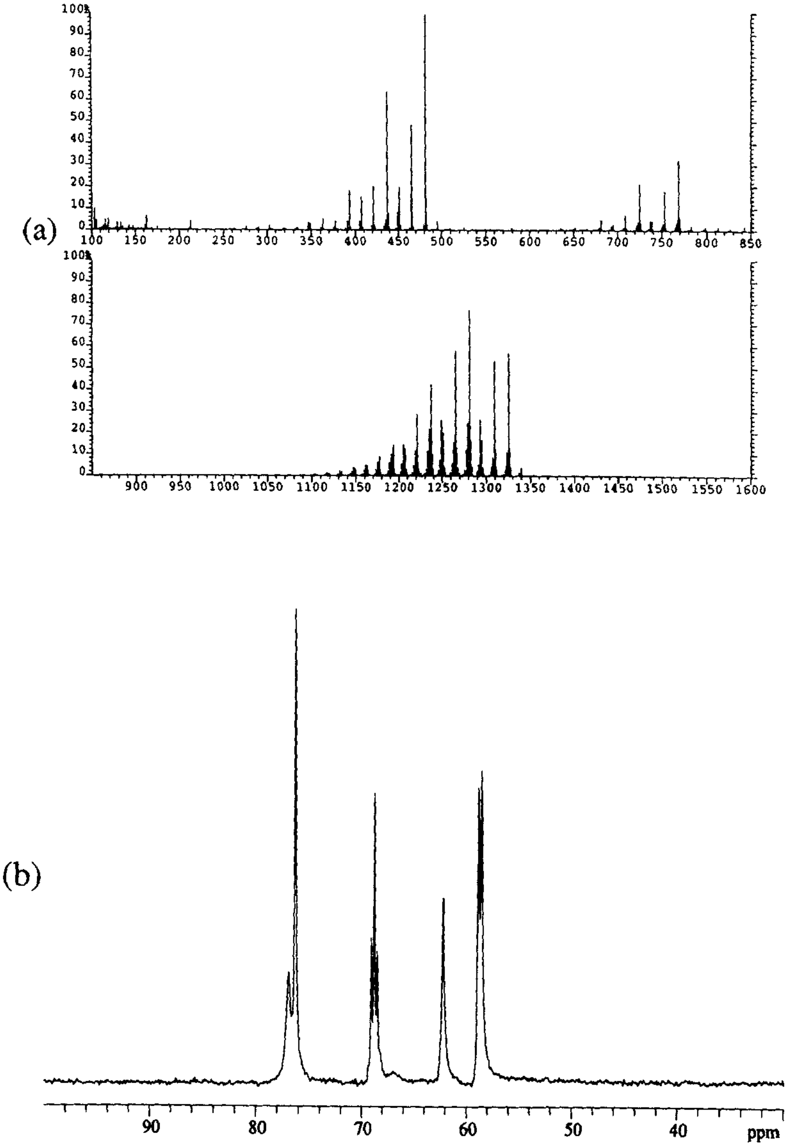
precursor were similar to those of MeOEtOH. It is not unusual that the chemical shifts for $\mathbf{BA}_{(a)}$ (62.1 ppm(C_{I}), 78.4 ppm(C_{II}) and 58.5 ppm(C_{III})) and $\mathbf{BA}_{(b)}$ (61.8 ppm (C_{I}), 78.5 ppm (C_{II}) and 58.5 ppm (C_{III})) are close to those of MeOEtOH **[19]** since barium has a low oxidation state compared to tantalum. Three peaks for $\mathbf{BA}_{(a)}$ are symmetric but the peaks at 61.8 ppm (C_{I}) and 58.5 ppm (C_{III}) for $\mathbf{BA}_{(b)}$ had asymmetric forms indicating various chemical environments for carbon centers in $\mathbf{BA}_{(b)}$. Another possible explanation for the peak overlap is that there are several kinds of chemical species in the $\mathbf{BA}_{(b)}$ precursor. We suggest that the synthesis condition of solution refluxing can have significant influence on the formation of chemical species in the **BA** precursor. After vacuum treatment the resulting products for $\mathbf{Ba}_{(a)}$ (with reflux) gave a dark brown solution and is a more viscous liquid than for $\mathbf{BA}_{(b)}$ (without reflux). The recently reported oligomer $Ba_6H_4(\mu_6\text{-}O)(MEO)_{14}$ **[18a]** and the monomeric $Ba[O(CH_2CH_2O)_nCH_3]_2$ (n=2,3) **[18b]** have similar chemical shifts in solution **[18c]**. The asymmetric NMR peaks for $\mathbf{BA}_{(b)}$ are considered to result from the formation of oligomers **[18,20,21]** such as $Ba_6H_4(\mu_6\text{-}O)(MEO)_{14}$ **[18a]**. However, the alcoholic proton at 7.64 ppm (broad singlet in **[18a]**) was not observed in the ^{1}H NMR spectrum for $\mathbf{BA}_{(a)}$ or $\mathbf{BA}_{(b)}$ solution in C_6D_6. Since the present **BA** precursor showed three separate peaks in the $^{13}C\{^{1}H\}$ NMR spectra for CH_2 and CH_3, a "clam shell" oligomer structure for **BA** as in monomeric

$Ba[O(CH_2CH_2O)_nCH_3]_2$ (n=2,3) **[18b]** was excluded in the used NMR time scale, regarding the optimum hinge length for the shell doors.

Barium magnesium tantalum precursors

The barium magnesium tantalum alkoxide (**BMT**) could have at least three possible structural models. (*i*) A mixture of barium (**BA**) and magnesium tantalum precursor (**MT**) without bridging alkoxy groups between **BA** and **MT**. (*ii*) A mixture of rearranged precursors such as magnesium alkoxide and barium tantalum alkoxide. And *(iii)* a heterometallic alkoxide complex with bridging alkoxy groups such as Ba-μOR-Ta-μOP-Mg bonds, where R is $CH_2CH_2OCH_3$. The mass spectrum and the $^{13}C\{^1H\}$ NMR spectrum for **BMT** are shown in Figs. 6a and 6b, respectively. The model (*i*) was ruled out because simple summation of the molecular fragments for **BA** and **MT** were not observed in the CI mass spectrum of **BMT** (Fig. 6a) and the $^{13}C\{^1H\}$ NMR spectrum (Fig. 6b). The CI mass spectrum of **BMT** gave the fragments corresponding to $BaTa_2(MEO)_{12}$ and $Ta(MEO)_5$ as summarized in Table I, which supports both (*ii*) and (*iii*) models proposed above. Absence of the molecular fragments for $Ba_3MgTa_2(MEO)_{18}$ may be ascribed to easy decomposition of the magnesium alkoxide during the chemical ionization for the mass spectrometric measurements. The $^{13}C\{^1H\}$ NMR data as shown in Fig. 6b indicate that in the **BMT** precursor some alkoxy groups are bonded to tantalum as in the $MgTa_2(MEO)_{12}$ and others are bonded only to magnesium or barium.

Considering these NMR results and high intensities of barium tantalum alkoxide fragments in the CI-MS data (Fig. 6a), both model (*ii*) and (*iii*) are possible. The difference between the two models is the existence of free magnesium alkoxides. According to the $^{13}C\{^1H\}$ NMR data for **BMT**, C_I has a single peak and C_{II} carbon shows two peaks indicating an absence of free magnesium alkoxide. Therefore, model (*iii*) is preferred according to the NMR analysis. All barium and magnesium are bound to tantalum through a alkoxide polymer with a 2- or 3-dimensional repeating unit of a [(barium, magnesium) – O(MEO) – tantalum] as in lead titanate alkoxide **[8c,8j]** This model involves a various ratio of tantalum to total alkaline earth metals, where the alkoxide of Ba(or Mg) remains separately or bridged only on to one side. The composition of $Ba_3MgTa_2(MEO)_{18}$ ((Mg and Ba) : Ta = 2 : 1) presents excess alkaline earth metals to make all the alkoxy groups (MEO) bind to tantalum. The ratio of bonded to non-bonded alkoxides to tantalum for C_I was obtained (2:1) from the integration of peaks at 61.9 ppm and 68.4 ppm in the ^{13}C NMR (^1H-coupled) spectra. The C_{II} center also consists of two peaks of 2:1 ratio. Though the complete structure of the **BMT** precursor is not fully resolved, for now it could be


(a)
100%
90
80
70
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50
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10
0
900
950
1000
1050
1100
1150
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(b)
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50
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ppm

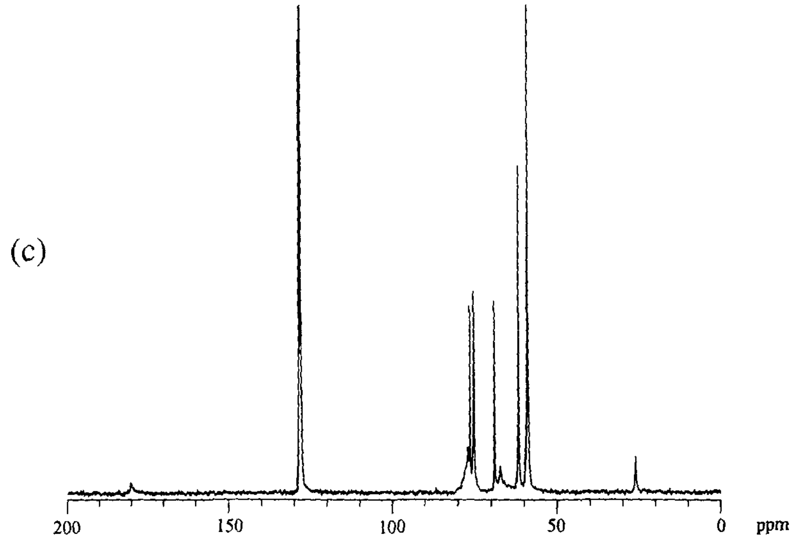

FIGURE 6 (a) Chemical ionization mass spectrum of barium precursor, **BMT**. The $^{13}C\{^1H\}$ NMR spectrum of (b) **BMT** obtained from magnesium metal and (c) **BMTA** from magnesium acetate in C_6D_6

assigned to the complex structure containing the [(Ba,Mg) – O(MEO) - Ta] framework.

When the alkoxide precursor solution of the Ba-Mg-Ta system is prepared by using magnesium acetate anhydrous instead of magnesium metal, a different complex (**BMTA**) was obtained in MeOEtOH solution [**6**]. $^{13}C\{^1H\}$ NMR spectrum for the **BMTA** precursor (Fig. 6c) indicates the MEO ligand of the **BMTA** precursor is the same as that of **BMT**. The peak at 58.3 ppm was assigned to C_I and three peaks at around 78 ppm were due to the C_{II} in MEO ligand. The peak at 61.9 ppm, 68.2 ppm and 69.5 ppm resulted from the C_{II} carbon center (the triplet at 128 ppm corresponds to deuterium of C_6D_6). In addition, $^{13}C\{^1H\}$ NMR spectrum for the **BMTA** precursor (Fig. 6c) indicated the presence of residual amounts of acetate. The concentration of the acetate group was about 1% to MeOEtOH in the peak integration of the ^{13}C (^1H-coupled) NMR spectra. Acetate groups resulting from magnesium acetate were considered to react with the alkoxy groups in the tantalum and barium precursor solutions. Alkoxy and acetate groups produce a bridging oxo(μ_n, n≥2) group [**8d**] and give an ester as the following reaction,

$$M'(OR)_x + Mg(CH_3CO_2)_y \rightarrow$$
$$(OR)_{x-1}M'-O-Mg(CH_3CO_2)_{y-1} + CH_3CO_2R$$

where M'=Ta, Ba; R=$CH_2CH_2OCH_3$. Water molecules are produced in the esterification reaction between acetate and alcohol (from solvent), which also induces partial hydrolysis of hygroscopic barium and tantalum alkoxide precursors. Methyl 3-methoxypropionate resulting from esterification reaction was not observed in NMR in the present study. In this respect, the ester and acetate in the **BMTA** may coordinate to the metals in many possible configurations [**4a**]. Consequently, the **BMTA** has a different structure from the **BMT** precursor, which results in the different morphologies during the sol-gel processing.

CONCLUSION

The **BMT** exclusively containing methoxyethoxide was successfully prepared as a precursor used in the sol-gel synthesis of $Ba(Mg_{1/3}Ta_{2/3})O_3$ dielectric ceramics and thin films. The systematic studies using FT-NMR and MS techniques for **TA**, **MT**, **BA** and finally **BMT** gave the structural evolution of each precursor during the processing. The **TA** precursor was determined to be dimeric and **MT** has bridged alkoxides between Mg and Ta. By comparison of **BMT** with the **BMTA** precursor, magnesium acetate will give a resulting precursor solution with different organic composition. The stepwise monitoring for each precursor is important to identify the molecular structure and chemical environment of metal cations. In this regard, spectroscopic studies give microstructural data on the molecular precursors used for the sol-gel synthesis of $Ba(Mg_{1/3}Ta_{2/3})O_3$.

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