

# Preparation of fine powders with perovskite structure from metal alkoxides

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The preparation of perovskite powders was investigated by the metal alkoxide methods. The complex alkoxide as a precursor was hydrolysed under specific conditions, and submicrometre powders of perovskite compounds differing in composition,  $\text{BaTiO}_3$ ,  $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ,  $\text{PbTiO}_3$ , and  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ , could be obtained. The simultaneous use of a dipolar aprotic solvent, such as acetone, etc., with ethanol was found to be effective for the preparation of the spherical or nearly spherical powders with submicrometre diameter. The submicrometre powders were formed through nucleation–aggregation, but not by the usual nucleation–grain growth. Such powder formation, and the affinity of the solvent for the diffusion layer surrounding the colloidal particle, are important. The powders obtained here could be crystallized to the desired crystalline phase at lower temperatures.

## 1. Introduction

Perovskite compounds such as  $\text{BaTiO}_3$  and  $\text{PbTiO}_3$  have excellent dielectric properties, and are used for electroceramics. These powders are usually prepared by a solid-state reaction among individual powders. Recently, a sol–gel method using metal alkoxides (the metal alkoxide method), has been applied for ceramics powder preparation, by which high-purity and highly sinterable powders are readily obtained. Mazdiyasi and co-workers [1,2] reported the preparation of  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$ , and  $\text{SrZrO}_3$  powders with particle sizes of several nanometres.  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  powders have been obtained by the hydrolysis of mixed alkoxide [3–5] and complex alkoxide solutions [6,7].

The ideal starting material to fabricate reproducible and fine-grained ceramics is a powder with submicrometre particles and narrow size distribution, for achieving a uniform and dense green body. However, in the sol–gel method, control of particle-size distribution is very difficult owing to the rapid hydrolysis rate of metal alkoxides. Sanchez *et al.* [8] found the morphology of a hydrolysis product to be dependent on hydrolysis and condensation rates, and spherical particles to be obtained at a relatively slow hydrolysis rate. According to the sensitivity of metal alkoxides to moisture, the preparation of monodispersed particles from metal alkoxides, except silicon, may be difficult.

To solve the problem of the rapid hydrolysis rate of metal alkoxides, several approaches have been investigated. Barringer and Bowen [9] prepared  $\text{TiO}_2$  powder with a submicrometre particle size by the hydrolysis of a dilute alcoholic solution of

$\text{Ti}(\text{OC}_3\text{H}_7)_4$  or  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ , at  $0.1\text{--}0.2\text{ mol l}^{-1}$ . The hydrolysis of dilute alkoxide solution was reported to be effective for  $\text{ZrO}_2$  [10,11] and  $\text{Ta}_2\text{O}_5$  powders [12]. Jean and Ring [13] indicated monosized  $\text{TiO}_2$  powder generation by hydrolysis with hydroxypropylcellulose (HPC) dispersant. The influence of solvent on hydrolysis has also been studied, such as that with HPC in a mixed solvent of *n*-octanol and aprotic solvent [14,15]. In a multicomponent system, the difference in hydrolysis rates among metal alkoxides is the most important problem. Hardy *et al.* [16] reported that  $\text{SrTiO}_3$  powder with submicrometre particles were obtained from Sr–Ti double alkoxide in *n*-butanol-acetonitrile solution, and by the addition of an organic acid such as *n*- $\text{C}_7\text{H}_{15}\text{CO}_2\text{H}$  to alkoxide solution. Ogiwara *et al.* [4] and Hirashima *et al.* [17,18] reported that, in  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  powder preparation, hydrolysis with refluxing was effective for adjusting hydrolysis rates of individual metal alkoxides.

Our previous papers reported sol–gel processing for perovskite and cordierite powders with submicrometre particles and their crystallization behaviour [19–24]. This study was conducted to find a means for obtaining various submicrometre powders with perovskite structure. The preparation of  $\text{MTiO}_3$  and  $\text{M}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (M: Ba or Pb) powders was investigated. The complex alkoxide as a precursor was hydrolysed under various conditions, and powders with submicrometre particle size were obtained. The morphology of the powders was characterized, and the formation mechanism of the submicrometre powder was discussed.

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## 2. Experimental procedure

### 2.1. Synthesis and hydrolysis of the complex alkoxide

Reagent-grade materials were used to prepare various perovskite powders. The barium system perovskites were prepared by the alkoxide–hydroxide method using barium hydroxide hexahydrate ( $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ). In the alkoxide–hydroxide method, an alkoxide is hydrolysed by crystallization water in the hydrate. Because crystallization water is slowly supplied to the alkoxide solution, homogeneous hydrolysis is possible. Lead system perovskites were prepared by the complex alkoxide method using anhydrous lead acetate ( $\text{Pb}(\text{OAc})_2$ , Ac:  $\text{CH}_3\text{CO}$ ). Metal alkoxides are sensitive to moisture, and thus solvents were dehydrated. Hydrolysis conditions are summarized in Table I.

#### 2.1.1. $\text{BaTiO}_3$

Titanium tetra-iso-propoxide ( $\text{Ti}(\text{OPr}^i)_4$ , 14.21 g) was dissolved in ethanol and the second solvent mixture (50 ml/50 ml). After the addition of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  powder (15.78 g), the solution was vigorously stirred at ambient temperature for 2 h, and refluxed with stirring at 80 °C for 24 h.

#### 2.1.2. $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$

Stoichiometric amounts of magnesium flakes (0.49 g) and niobium pentaethoxide ( $\text{Nb}(\text{OEt})_5$ , 12.87 g) were reacted in ethanol (150 ml) at reflux temperature for 15 h until the magnesium was completely consumed. After the addition of acetone (200 ml), the reaction solution was hydrolysed with  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  powder (19.13 g) following the same method as  $\text{BaTiO}_3$ .

#### 2.1.3. $\text{PbTiO}_3$

Pb–Ti complex alkoxide was synthesized by reaction of  $\text{Pb}(\text{OAc})_2$  anhydrate and titanium tetraethoxide ( $\text{Ti}(\text{OEt})_4$ ).  $\text{Pb}(\text{OAc})_2$  (8.15 g) and  $\text{Ti}(\text{OEt})_4$  (5.71 g)

were refluxed in ethanol (50 ml) for 16 h. Following the addition of the second solvent (50 ml), the Pb–Ti complex alkoxide solution was rapidly hydrolysed with 0.1 M ammonia water of  $\text{H}_2\text{O}/\text{Pb}(\text{OAc})_2$  molar ratio of six, and then refluxed at 80 °C for 24 h with stirring. For comparison, methanol instead of ethanol was used. To obtain  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ , 90% zirconium tetra-normal-propoxide  $\text{Ti}(\text{O}^n\text{Bu})_4$  1-butanol solution instead of  $\text{Ti}(\text{OEt})_4$  was used.

#### 2.1.4. $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$

Pb–Mg–Nb complex alkoxide was synthesized from  $\text{Pb}(\text{OAc})_2$  anhydrate,  $\text{Nb}(\text{OEt})_5$  and magnesium metal flakes.  $\text{Pb}(\text{OAc})_2$  (9.76 g) and  $\text{Nb}(\text{OEt})_5$  (6.36 g) were refluxed in ethanol (60 ml) for 16 h. Cyclohexane (60 ml) and magnesium flakes (0.24 g) were added and the reactant solution was refluxed for 2 h until the magnesium flakes were completely consumed. After the addition of acetone (60 ml), the Pb–Mg–Nb complex alkoxide solution, ethanol/cyclohexane/acetone = 1/1/1, was rapidly hydrolysed with 1 M ammonia water of  $\text{H}_2\text{O}/\text{Pb}(\text{OAc})_2$  molar ratio of five, and then refluxed at 80 °C for 24 h with stirring.

The white powders thus obtained were filtrated and dried at 100 °C. In barium systems, filtration under a nitrogen atmosphere and drying under reduced pressure are necessary to prevent  $\text{BaCO}_3$  formation. For comparison, hydrolysis without the second solvent was conducted. In lead systems, hydrolysis without the second solvent and ammonia water led to greater viscosity of the hydrolysed solution, with consequent formation of a gel-like aggregate.

## 2.2. Characterization

Powder morphology was observed with scanning electron and transmission electron microscopes (SEM and TEM). Particle-size distribution was measured by the centrifugal method (Horiba, CAPA-700). Brunauer–Emmett–Teller (BET) surface area was determined by the single-point nitrogen adsorption method (Quanta

TABLE I Preparation conditions of perovskite powders and their morphology

Compound	Ba or Pb volume (mol)	Ethanol (ml)	Second solvent (ml)	Hydrolysis condition <sup>a</sup>	Morphology
$\text{BaTiO}_3$	0.05	50	Acetone (50)	AH	Powder
$\text{BaTiO}_3$	0.05	50	Acetonitrile (50)	AH	Powder
$\text{BaTiO}_3$	0.05	100	–	AH	Powder
$\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$	0.06	150	Acetone (200)	AH	Powder
$\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$	0.06	300	–	AH	Powder
$\text{PbTiO}_3$	0.025	50	Acetone (50)	0.1 M $\text{NH}_3$	Powder
$\text{PbTiO}_3$	0.025	50	Acetonitrile (50)	0.1 M $\text{NH}_3$	Powder
$\text{PbTiO}_3$	0.025	50	Ethyl acetate (50)	0.1 M $\text{NH}_3$	Powder
$\text{PbTiO}_3$	0.025	50	Benzene (50)	0.1 M $\text{NH}_3$	Gel-like aggregate
$\text{PbTiO}_3$	0.050	100	–	0.1 M $\text{NH}_3$	Translucent gel
$\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$	0.005	20	Acetone (80)	1 M $\text{NH}_3$	Powder
$\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$	0.010	20	Acetone (80)	1 M $\text{NH}_3$	Gel-like aggregate
$\text{PbZrO}_3$	0.005	20	Acetone (80)	1 M $\text{NH}_3$	Powder
$\text{PbZrO}_3$	0.025	30	Acetone (60)	1 M $\text{NH}_3$	Gel-like aggregate
$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$	0.03	30	Acetone-cyclohexane (30/30)	1 M $\text{NH}_3$	Powder
$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$	0.03	60	Cyclohexane (30)	1 M $\text{NH}_3$	Gel-like aggregate

<sup>a</sup> AH indicates the alkoxide–hydroxide method.

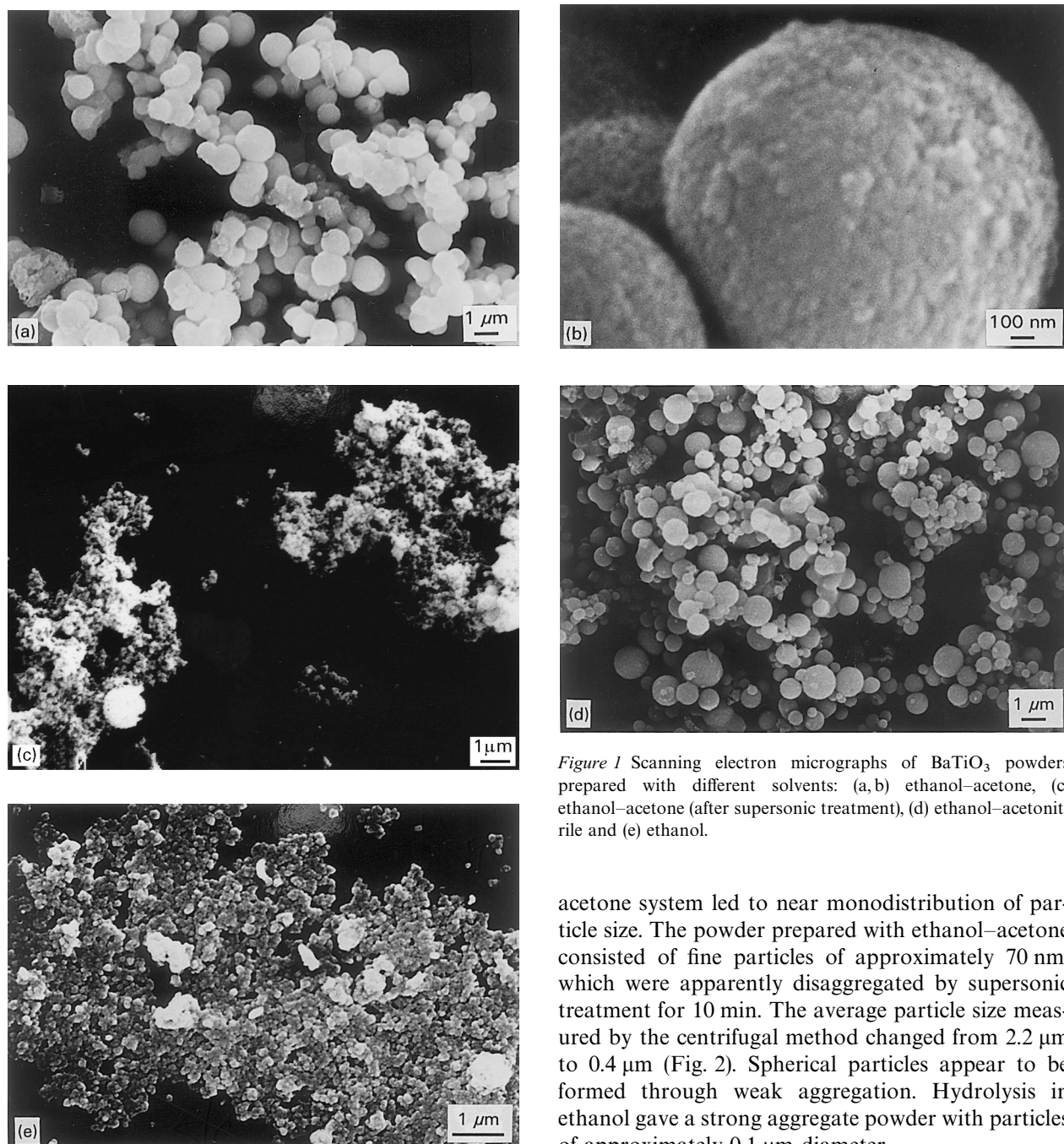


Figure 1 Scanning electron micrographs of BaTiO<sub>3</sub> powders prepared with different solvents: (a,b) ethanol–acetone, (c) ethanol–acetone (after supersonic treatment), (d) ethanol–acetonitrile and (e) ethanol.

chrome, monosorb). Crystalline phases of the powders were identified by the X-ray diffraction method (XRD, RAD-C system, Rigaku Co.).

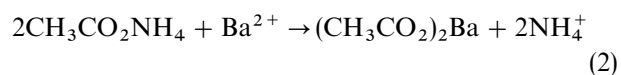
### 3. Results

#### 3.1. BaTiO<sub>3</sub>

BaTiO<sub>3</sub> powder was usually prepared by the hydrolysis of Ba–Ti double alkoxide [1]. In the present study, the alkoxide–hydroxide method using Ba(OH)<sub>2</sub>·8H<sub>2</sub>O was conducted, which permits the use of high metal concentration solution, because crystallization water is slowly supplied to the alkoxide solution. Fig. 1 shows scanning electron micrographs of the resultant BaTiO<sub>3</sub> powders. The kind of organic solvent was found to influence powder morphology. Ethanol–acetone and ethanol–acetonitrile gave powders consisting of spherical particles of 0.7–1.6 and 0.3–1.6 μm diameter, respectively. The ethanol–

acetone system led to near monodistribution of particle size. The powder prepared with ethanol–acetone consisted of fine particles of approximately 70 nm, which were apparently disaggregated by supersonic treatment for 10 min. The average particle size measured by the centrifugal method changed from 2.2 μm to 0.4 μm (Fig. 2). Spherical particles appear to be formed through weak aggregation. Hydrolysis in ethanol gave a strong aggregate powder with particles of approximately 0.1 μm diameter.

X-ray diffraction patterns of the BaTiO<sub>3</sub> powder at various temperatures are shown in Fig. 3. As-prepared powder was cubic perovskite in structure with a crystallite size of 19 nm. A tetragonal structure was assumed at ≥ 1100°C. The crystallite size of the as-prepared powder was dependent on ageing time of the suspension. A carboxylate derivative, such as acetonitrile, is favourable for the preparation of submicrometre powders, but in the presence of Ba<sup>2+</sup> cations, Ba(OAc)<sub>2</sub>, which crystallizes to the perovskite via BaCO<sub>3</sub>, is formed by hydrolysis of acetonitrile, as shown by Equations 1 and 2. The simultaneous use of acetone is thus preferred for perovskite powder containing a strong cationic element.



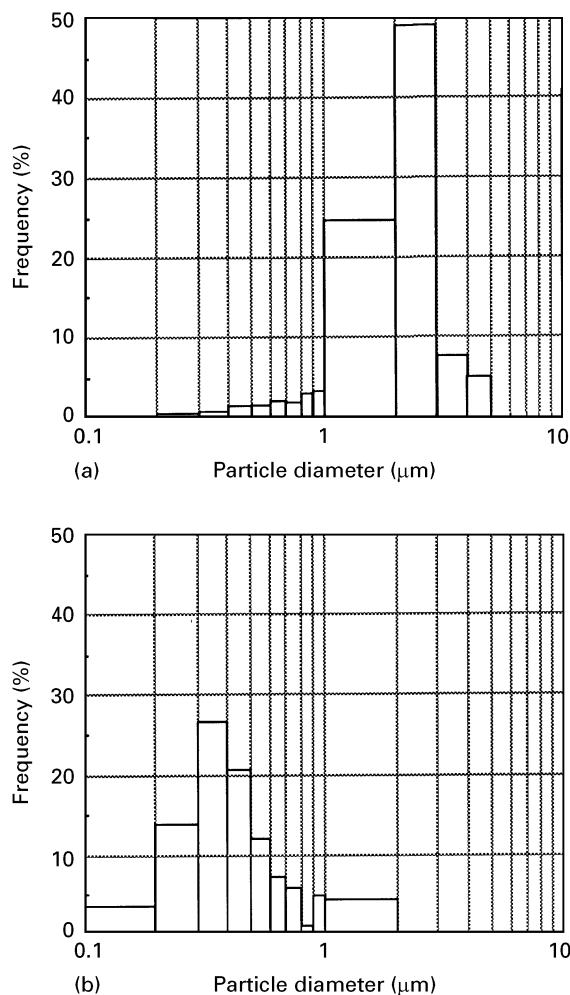


Figure 2 Particle-size distribution of BaTiO<sub>3</sub> powder prepared with ethanol–acetone, (a) as-prepared and (b) after supersonic treatment.

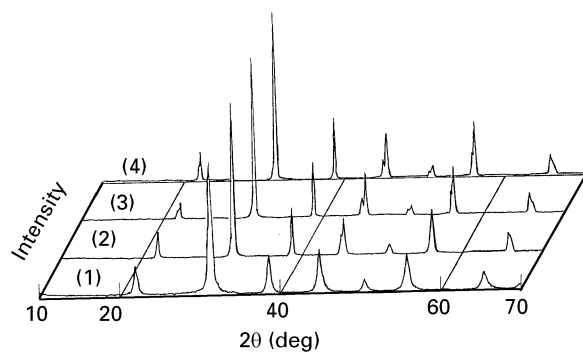


Figure 3 X-ray diffraction patterns of BaTiO<sub>3</sub> powder calcined at different temperatures for 1 h; (1) as-prepared, (2) 900 °C, (3) 1100 °C and (4) 1200 °C.

### 3.2. Ba(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>

Ba(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> (BMN) powder was prepared by the alkoxide–hydroxide method in ethanol–acetone solution. Scanning electron micrographs of the resultant BMN powders are shown in Fig. 4. In the ethanol–acetone system, near spherical powder with particles of approximately 0.55 μm diameter was generated. The surface area of the powder was 156 m<sup>2</sup> g<sup>-1</sup> and BET diameter, 6 nm, and thus the submicrometre powder may possibly be an aggregate of fine BMN

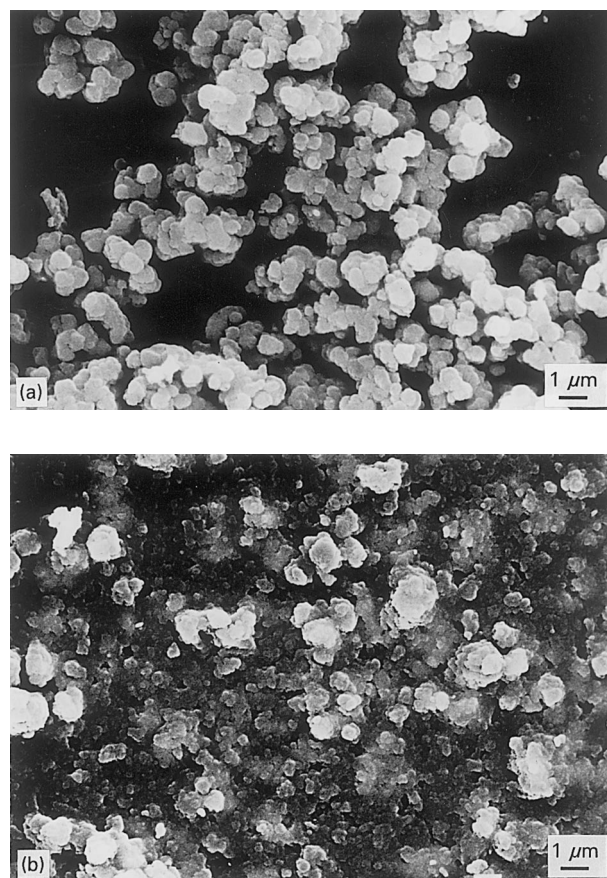


Figure 4 Scanning electron micrographs of Ba(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> powders prepared with different solvents; (a) ethanol–acetone, (b) ethanol.

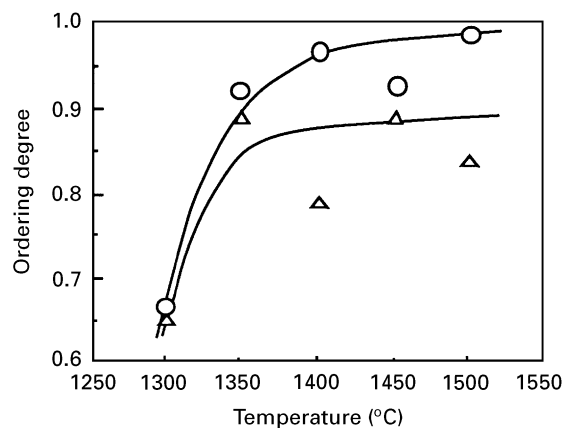


Figure 5 Ordering degree of Ba(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> ceramics sintered at various temperatures for 2 h; (○): ethanol–acetone powder, (△) ethanol powder. The ordering degree,  $S$ , was calculated from  $S = [(I_{100}/I_{110,102})_{\text{obs.}} / (I_{100}/I_{110,102})_{\text{order.}}]^{1/2}$ .

particles, as well as the BaTiO<sub>3</sub> powder. In contrast, hydrolysis without acetone gave an agglomerate powder.

As-hydrolysed powder was amorphous, but crystallized to the cubic perovskite phase with ageing and refluxing for 24 h [21]. For the use of complex perovskite compound as microwave dielectrics, low-temperature ordering in B site ions is one of the most important factors for ceramics preparation. The ordering degree of the present powder increased with sintering temperature:  $\geq 0.9$  at 1350 °C was achieved in this study (Fig. 5). The powder without acetone had a slightly lower ordering degree of 0.8–0.9.

### 3.3. $\text{PbTiO}_3$

In previous papers, the hydrolysis of a mixture of lead, zirconium and titanium alkoxides usually gave high agglomerates consisting of several 10 nm particles in diameter [3, 5], while that of the complex alkoxide from  $\text{Pb}(\text{OAc})_2$  and titanium alkoxide gave gels [6, 7]. Submicrometre  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  powders were obtained only by hydrolysis of the alkoxide mixture with refluxing because the hydrolysis rates of individual alkoxides could be adjusted [4, 17, 18].

In this study,  $\text{PbTiO}_3$  powders of submicrometre diameter (Fig. 6) were successfully prepared by the hydrolysis of the Pb–Ti complex alkoxide in solution containing a second solvent such as acetone, acetonitrile or methyl acetate, using ammonia water. Particle size differed according to solvent combination: ethanol–acetone, 0.4  $\mu\text{m}$ ; methanol–acetone, 0.2  $\mu\text{m}$ ; ethanol–acetonitrile, 0.5  $\mu\text{m}$ ; ethanol–methyl acetate, 0.3  $\mu\text{m}$ . Gel-like aggregates were obtained by hydrolysis with ethanol–benzene, or without the second solvent and ammonia catalysis. For powder preparation, hydrolysis was performed in a dipolar aprotic solvent under basic conditions. Fig. 7 shows transmission electron micrographs of as-prepared  $\text{PbTiO}_3$  powder from ethanol–acetone solution.  $\text{PbTiO}_3$  powder consisted of fine particles of several nanometres. The surface area was  $147 \text{ m}^2 \text{ g}^{-1}$  and BET diameter, 5 nm. These values are consistent with the TEM results. Accordingly, a submicrometre powder is concluded to be an aggregate of fine primary particles. The as-prepared powder was amorphous and contained many hydroxyl or organic residuals on the particle surface. Thus, chemical interactions among primary particles would be strong compared with  $\text{BaTiO}_3$  powder.

$\text{Pb}(\text{Zr}_{1/2}\text{Ti}_{1/2})\text{O}_3$  and  $\text{PbZrO}_3$  powders with particles of approximately 0.25  $\mu\text{m}$  were obtained [20]. The difference in particle size was due to that in hydrolysis rate for  $\equiv\text{Zr}-\text{OR}$  ( $\text{R}: \text{C}_4\text{H}_9$  or  $\text{C}_2\text{H}_5$ ) and  $\equiv\text{Ti}-\text{OC}_2\text{H}_5$  structure and metal concentration, and the present of *n*-butanol (*n*- $\text{C}_4\text{H}_9\text{OH}$ ).

Earlier  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  powders crystallized to the perovskite phase from 450–650°C, depending on Zr/Ti ratio [3–7], and lower temperature crystallization is considered impossible. The present powders crystallized to a perovskite phase, independently of Zr/Ti ratio, at 250°C for 2 h in an oxygen flow [20], and their crystallization behaviour is very interesting.

### 3.4. $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$

No submicrometre powder of  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN) has been reported by the metal alkoxide method, except in this study. Hydrolysis of the Pb–Mg–Nb complex alkoxide in a solution containing acetone using 1 M ammonia water, gave a powder with particles of approximately 0.3  $\mu\text{m}$  diameter (Fig. 8). Without acetone, a gel-like agglomerate was obtained. The surface area of the powder was  $173 \text{ m}^2 \text{ g}^{-1}$  and BET diameter, 4 nm, indicating the powder to be an aggregate formed by a mechanism the same as that of  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  powder. The powder crystallized to the perovskite phase after heating at

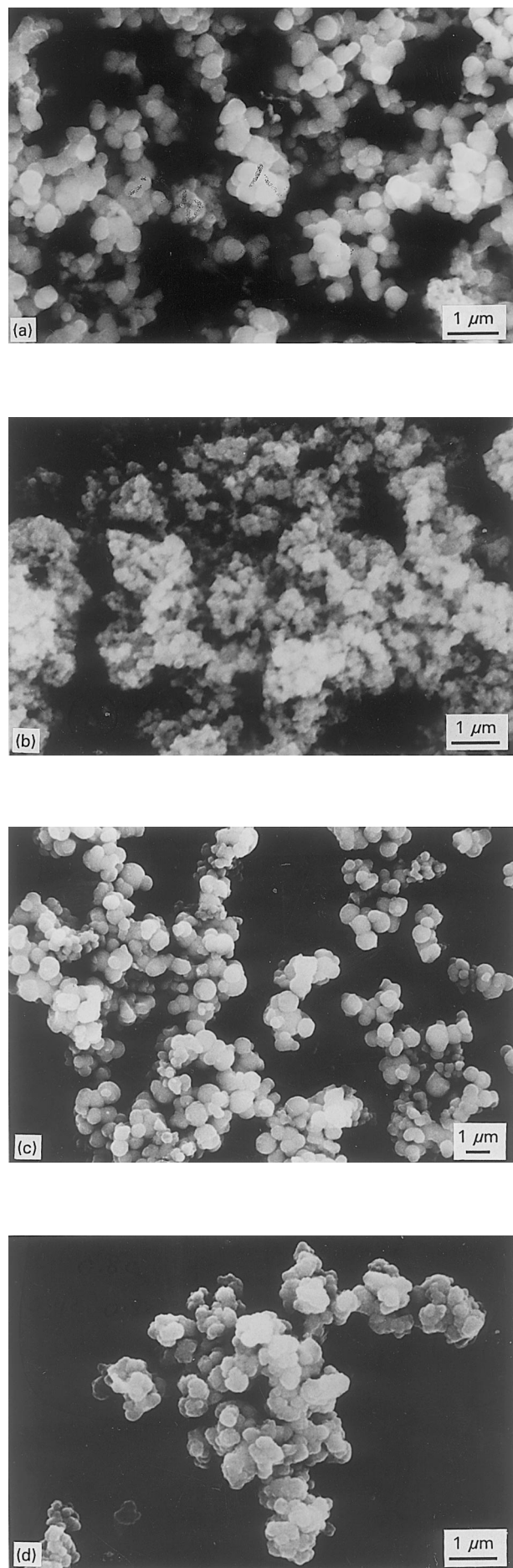


Figure 6 Scanning electron micrographs of  $\text{PbTiO}_3$  powders prepared with different solvents; (a) ethanol–acetone, (b) methanol–acetone, (c) ethanol–acetonitrile and (d) ethanol–methyl acetate.

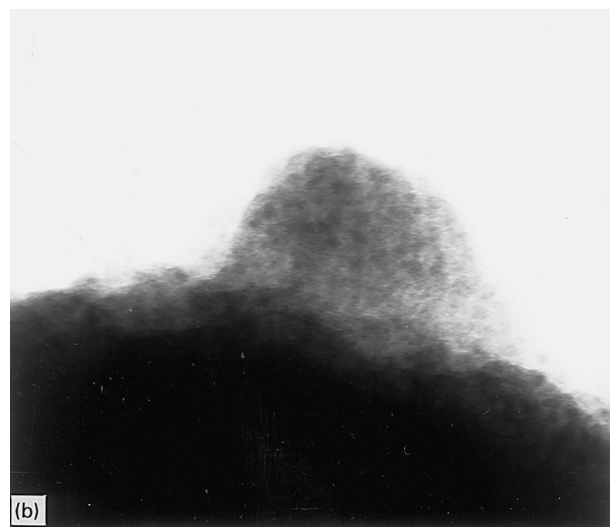
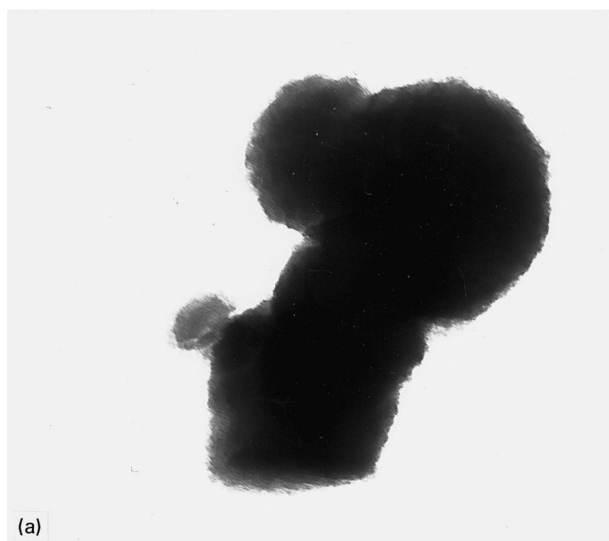


Figure 7 (a, b) Transmission electron micrographs of  $\text{PbTiO}_3$  powders prepared with ethanol-acetone.

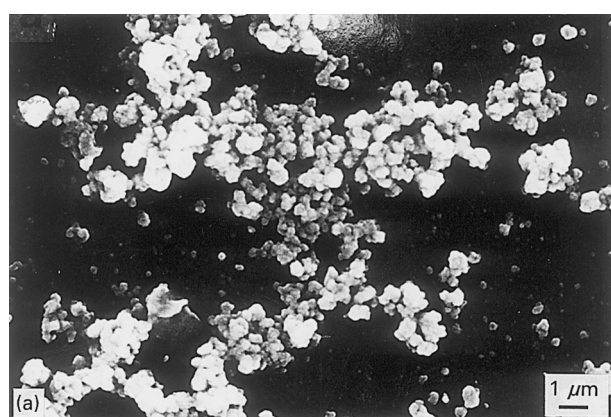


Figure 8 Scanning electron micrographs of  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  powders prepared with different solvents: (a) ethanol-cyclohexane-acetone, (b) ethanol-cyclohexane.

300 °C for 2 h in an oxygen flow, although a slight amount of pyrochlore phase was present [19].

#### 4. Discussion

Monodispersed powder is formed through a nucleation-grain growth mechanism, as demonstrated by La Mehr and Dinegar [25]. Nucleation occurs through dispersed-phase concentration increase and a self-

nucleation area is formed at more than saturated concentration. In this area, nuclei incorporating the dispersed-phase grows accompanied by the formation of new nuclei. In the lower concentration area, grains grow by diffusion, but not nucleation. A monodispersed powder can thus be obtained when the period of nucleation is relatively short. When using metal alkoxides, spherical particles are obtained, provided that the hydrolysis rate is less than that of the condensation rate [8]. Bowen and co-workers [9, 16] prepared  $\text{TiO}_2$  and  $\text{SrTiO}_3$  powders by reducing the hydrolysis rate through lessening the metal concentration or adding an organic acid such as  $n\text{-C}_7\text{H}_{15}\text{CO}_2\text{H}$ . Mizutani *et al.* [14] and Ogiwara *et al.* [15, 26] obtained  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Ta}_2\text{O}_3$ ,  $\text{Nb}_2\text{O}_3$  and perovskite powders [26] by the hydrolysis of alkoxides in *n*-butanol-acetonitrile mixed solution with HPC. Okuyama *et al.* [23] examined hydrolysis conditions of the Mg-Al-Si complex alkoxide as a cordierite precursor for preparing a spherical dense powder with 0.1–0.3 μm diameter. The powder was obtained by rapid hydrolysis alone using aqueous ammonia of pH 13.4, of the iso-butoxyl-substituted Mg-Al-Si complex alkoxide in methanol.

In the present study, hydrolysis conditions, such as the kind of solvent in particular, were observed to influence the morphology of the hydrolysis products. To make the hydrolysis rate less than that of condensation, (1) the use of a polar solvent with high affinity for water (high dielectric constant), (2) the introduction of a bulky alkyl group with a high inductive effect, (3) the use of basic catalysis for accelerating the condensation rate, and (4) using a low viscosity solvent for increasing the diffusion rate of dispersed phase, should prove effective. The above methods of Bowen and co-workers [9, 16], Mizutani *et al.* [14], Ogiwara *et al.* [15, 26] and Okuyama *et al.* [23] satisfy conditions 1–4. The present solvent systems are alcohol-dipolar aprotic solvent systems, analogous to those of Mizutani *et al.* [14] and Ogiwara *et al.* [15, 26]. The present alcohols are high dielectric solvents such as methanol and ethanol. There was no



TABLE II Properties of the solvent used [27]

	Dielectric constant	Vapour-liquid surface tension <sup>a</sup> (10 <sup>-3</sup> N m <sup>-1</sup> )	Viscosity <sup>a</sup> (10 <sup>-3</sup> Pa s)	Boiling point (°C)	Solubility to water <sup>c</sup>
Methanol	32.6 <sup>b</sup>	22.5	0.597	65.0	○
Ethanol	24.6 <sup>b</sup>	22.3	1.19	78.3	○
<i>n</i> -Butanol	17.5 <sup>b</sup>	25.3	2.95	117.3	△
Acetonitrile	37.5 <sup>b</sup>	29.3	–	81.8	○
Acetone	20.7 <sup>b</sup>	24.0	0.322	56.2	○
Ethyl acetate	6.15 <sup>a</sup>	24.0	0.447	77.1	△
Benzene	2.28 <sup>a</sup>	28.9	0.652	80.1	×
Water	78.5 <sup>a</sup>	72.8	1.002	100.0	–

<sup>a</sup> 20 °C.<sup>b</sup> 25 °C.<sup>c</sup> ○, soluble; △, mesosoluble; ×, insoluble.

formation of an alkoxide-solvent emulsion such as noted by Ogiwara *et al.* [15]. The properties of the solvent system and solution thus appear to differ.

BaTiO<sub>3</sub> powder, which disaggregates on supersonic treatment, consisted of fine primary particles (Fig. 1). The surface area of PbTiO<sub>3</sub> powder prepared with acetone was 147 m<sup>2</sup> g<sup>-1</sup> and BET diameter, 5 nm, a value which differs from that shown by SEM observation (Fig. 6), but is consistent with TEM observation (Fig. 7); PbTiO<sub>3</sub> powder also thus consists of fine primary particles. The complex perovskite powders such as BMN (Fig. 4) and PMN (Fig. 8) had similar features but differed in shape from MTiO<sub>3</sub> powders. The formation of the present powders was considered to occur through nucleation-aggregation, but not by nucleation-grain growth.

The following powder formation model is suggested to explain the different morphology of the powders prepared by different solvent systems:

1. nucleation: nuclei of several nanometres in diameter are formed by the hydrolysis-condensation of the metal alkoxide. The nuclei probably would possess hydroxyl groups on the particle surface;
2. solvation: colloidal particles with a diffuse layer of water or alcohol are formed by solvation on initially generated nuclei;
3. aggregation: colloidal particles aggregate with the formation of spherical particles with submicrometre diameters.

When using methanol with a large dielectric constant compared to ethanol, the hydrolysis rate of the alkoxide decreases owing to increased affinity of the solvent for water, with consequent increase in the condensation rate and promotion of the grain growth of primary particles. Increase in the primary particle size decreases the diffusion rate (aggregation rate) of particles, and thus the secondary particle size decreases. For PbTiO<sub>3</sub> powder obtained by the methanol-acetone system, the BET diameter of 29 nm was large compared with that of powder obtained by the ethanol-acetone system. The secondary particle size, approximately 0.2 μm, was small.

The aggregation of colloidal particles would appear to be influenced by the affinity of the solvent for the diffusion layer surrounding the particles. In the presence of a dipolar aprotic solvent, affinity of the solvent

for the diffusion layer slightly decreases compared to that of the simple ethanol. The aggregation of colloidal particles is thought to lead to a lower surface free-energy state, causing the dispersion to be stabilized through the formation of spherical particles. In the ethanol system, colloidal particles are formed by hydrolysis of the Pb-Ti complex alkoxide, and a stable disperse system would be formed. However, with time, dispersed colloidal particles became three-dimensionally agglomerated by the reaction of surface residual groups, resulting in gel-like powder formation.

Spherical or nearly spherical powders of submicrometre diameter were successfully prepared using a relatively high metal concentration solution. The resultant powder possessed not only favourable morphology, but crystallized to the desired crystalline phase at lower temperatures. The simultaneous use of a dipolar aprotic solvent with ethanol was found to be effective for the preparation of perovskite powders.

## 5. Conclusion

The preparation of MTiO<sub>3</sub> and M(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> (M: Ba or Pb) powders was achieved by the metal alkoxide methods. The complex alkoxide, as a precursor, was hydrolysed under specific conditions, and submicrometre powders of perovskite compounds differing in composition were successfully obtained. The simultaneous use of a dipolar aprotic solvent along with ethanol was found to be effective for the preparation of spherical or nearly spherical powders of submicrometre diameter. Submicrometre powders were formed through nucleation-aggregation, but not by the usual nucleation-grain growth. In such powder formation, the affinity of the solvent for the diffusion layer surrounding the colloidal particles is important. The powders obtained here crystallized to the desired crystalline phase at lower temperatures.

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