BRIEF COMMUNICATION

Homogenization and Particle Size Reduction of PbTiO₃ by Ball-Milling of Precursor Gels

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Ball-milling of mixed gel derived from a simple mixing of component alkoxides increased the compositional microhomogeneity, judged quantitatively by high-resolution microprobe chemical analysis. At the same time, the particle size of PbTiO₃ obtained after calcination at 1023 K for 2 hr in air decreased, approaching those of oxide fine particles delivered from a bidentate alkoxide through an identical thermal treatment. © 1994 Academic Press, Inc.

INTRODUCTION

In our previous reports (1, 2), we showed that homogenization during heating is remarkably promoted by a preliminary ball-milling of the inhomogeneous Pb–Ti–O hydrogel mixtures from inorganic salts. By taking advantage of short-range ionic diffusion during mechanical stressing, the present study attempts to improve the compositional fluctuation due to inhomogenous hydrolysis, without passing a complex way of preparing bidentate alkoxides (3–5).

EXPERIMENTAL

Individual and coprecipitated sols were prepared from $Ti(O^iC_3H_7)_4$ and $Pb(O^iC_3H_7)_2$. Bidentate alkoxides were synthesized from $Ti(O^iC_3H_7)_4$ and $Pb(OCOCH_3)_2$ after Budd *et al.* (4). We used gels starting from complex alkoxide, mixed alkoxide, and mixed sol, as summarized in Table 1. Samples were ball-milled by a method described elsewhere (1, 2). The gels with and without ball-milling were subsequently heated to 1023 K at 10 K min⁻¹ in an air flow of 500 cm³ min⁻¹, held at 1023 K for 2 hr, and cooled in air to room temperature. Particle size distribution was determined by a direct photocounting method.

RESULTS

According to the transmission electron micrographs of gels, a number of agglomerates comprising primary particles in a single nanometer regime were observed. After ball-milling, microhomogeneity, H, for MS(A)-gel increased, while the degree of agglomeration increased and the specific surface area, S_A, decreased, as shown in Fig. 1 and Table 1.

The binding energies of the oxygen 1s electron for $3PbO \cdot H_2O$, TiO_2 gel, and $PbTiO_3$, being associated with Pb–O–Pb, Ti–O–Ti, and Pb–O–Ti, respectively, were 531.4, 530.7, and 529.4 eV. On ball-milling MS(A)-gel, the binding energy of the peak top shifted from 531.2 to 530.0 eV and the relative intensity of the O 1s peak around 530 eV increased, as shown in Figs. 2a and 2b. A similar tendency was also observed for MA-gel, as shown in Figs. 2c and 2d.

Broadening of the O 1s peaks shown in Fig. 3a for CA-gel suggests the plurality of the states of oxygen, i.e., due to Pb–O–Ti and acetyl groups. The latter was confirmed from IR spectroscopy. The higher O 1s binding energy for CA-gel was close to that of lead acetate, as seen from comparison of Figs. 3a and 3c. After ball-milling for 3 hr, the relative intensity due to Pb–O–Ti decreased, as shown in Fig. 3b. Taking the particle size of a few nanometer regime into account, all the XPS information is reasonably assumed to represent the properties of entire specimens and is not restricted to those from the surface.

Exothermic DTA peak due to crystallization was observed at 790 and 795 K for CA- and MA-gels, respectively. These peaks remained unchanged on ball-milling for 3 hr. In contrast, the broad exothermic peak around 785 K for MS(A)-gel became sharper on ball-milling for 24 hr. When the precursor gels were calcined at 1023 K for 2 hr and cooled to room temperature, tetragonal perovskite with the exact stoichiometry was observed.

As shown in Fig. 4 and Table 1, the average particle size, d_{av}, of calcined powders from nonground gels decreased in the order of MS(A) > MA > CA. The broadness of particle size distribution, σ_p, also decreased in the order of MS(A) > MA > CA. On ball-
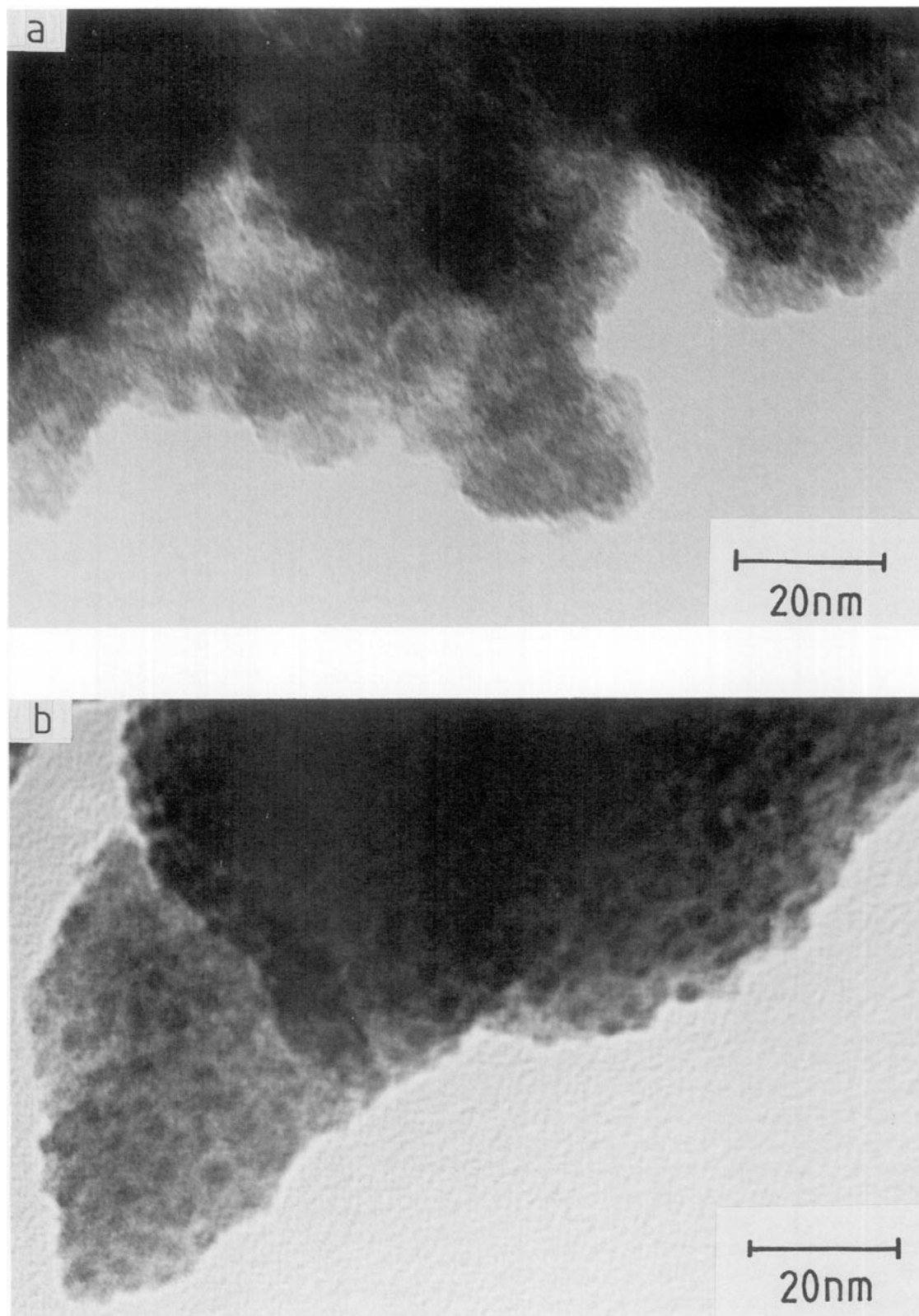
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FIG. 1.   Transmission electron micrographs. (a) MS(A)-gel and (b) MS(A)–R24-gel.

TABLE 1

The Degree of Compositional Homogeneity, H, and the Specific Surface Area, S_A, for Precursor Gels, and the Average Particle Size, d_{av}, and the Standard Deviation of Particle Size Distribution, σ_p, for the Calcined Powders

Sample	Preparation method	Gel		Oxide	
		H^a	S_A (m^{2}g^{-1})	d_{av} (μm)	σ_p
CA	Complex	0.998	150	0.13	0.06
CA–R3	alkoxide	0.999	70	0.23	0.11
MA	Mixed	0.997	125	0.50	0.37
MA–R3	alkoxide	0.999	48	0.31	0.15
MS(A)	Mixed	0.885	97	2.18	1.45
MS(A)–R24	sol	0.991	1^b	1.72	0.90

^{a} $H = 1 - \sigma^2/\sigma_0^2$, $\sigma^2 = \Sigma|(\overline{X}_{Pb} - X_{Pb})(\overline{X}_{Ti} - X_{Ti})|/n$, $\sigma_0^2 = \overline{X}_{Pb}\,\overline{X}_{Ti}$. σ, standard deviation of mole fraction; X_i, mole fraction of species i; $\overline{X}_i$, mean mole fraction of species i; n, number of analyzed points. ($n > 10$.)

^{b} With relatively larger error than other values because of small absolute value.

milling the precursor gels, d_{av} and σ_p for calcined MA and MS(A) decreased, while those of calcined CA increased.
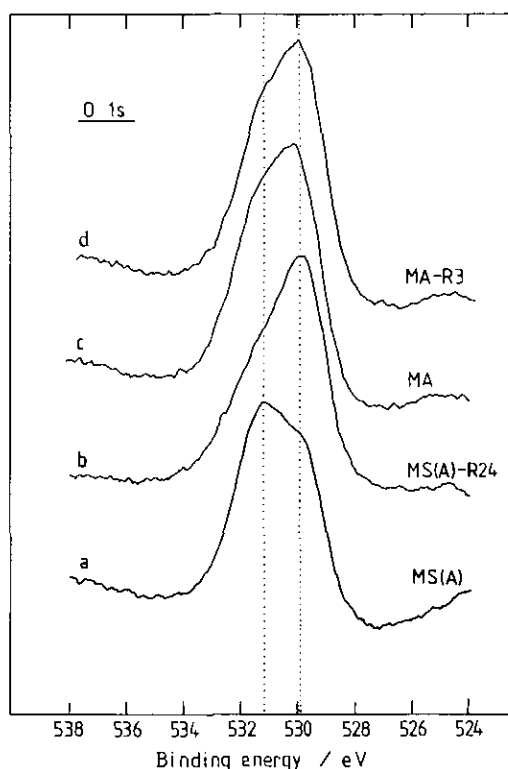

FIG. 2. X-ray photoelectron spectrograms of oxygen 1s. (a) MS(A)-gel, (b) MS(A)–R24-gel, (c) MA-gel, and (d) MA–R3-gel.
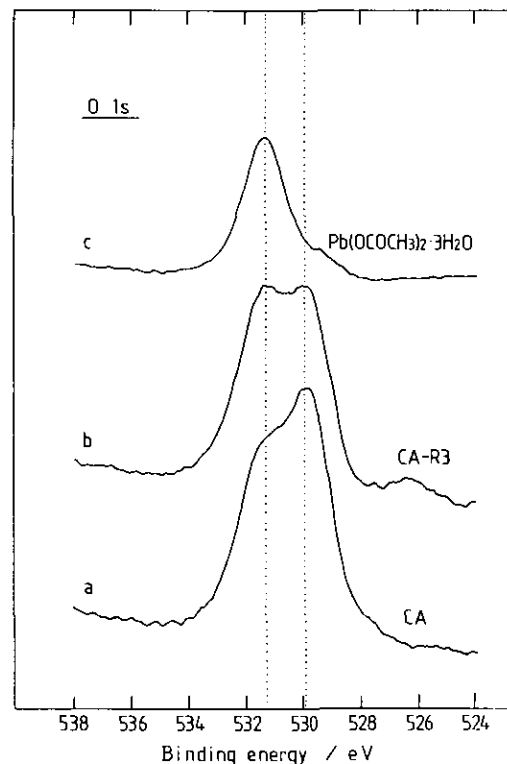

FIG. 3. X-ray photoelectron spectrograms of oxygen 1s. (a) CA-gel, (b) CA–R3-gel, and (c) Pb(OCOCH$_3$)$_2$ · 3H$_2$O.

DISCUSSION

Ball-milling of precursor gels derived from a simple mixing of alkoxides or sols brought about microhomogenization with simultaneous enhancement of chemical interaction. The microhomogeneity based on the elemental distribution and the chemical state for starting precursor gels seems to be reflected in the particle sizes of complex oxides obtained after calcination.

An encounter of Pb^{2+} and Ti^{4+} is necessary for the nucleation of PbTiO$_3$. Higher homogeneity, together with the collapse of the internal voids, gives a larger probability of juxtaposition for dissimilar metallic atoms and hence a larger number of nucleation sites. A larger number of nuclei, in turn, causes a reduction in particle size after subsequent calcination, unless the heating condition is too severe to allow abnormal grain growth.

In contrast to the case of alkoxide- or sol-mixing, the index of homogeneity, H, for CA-gel derived from complex alkoxide remained unchanged, and the relative intensity of the oxygen 1s peak due to Pb–O–Ti bond decreased after ball-milling CA-gel, as shown in Fig. 3. It is therefore concluded that mechanical stress on a priori very homogeneous precursors can only bring about inhomogenization due to the local breakage of –Pb–O–Ti–O–Pb– regular
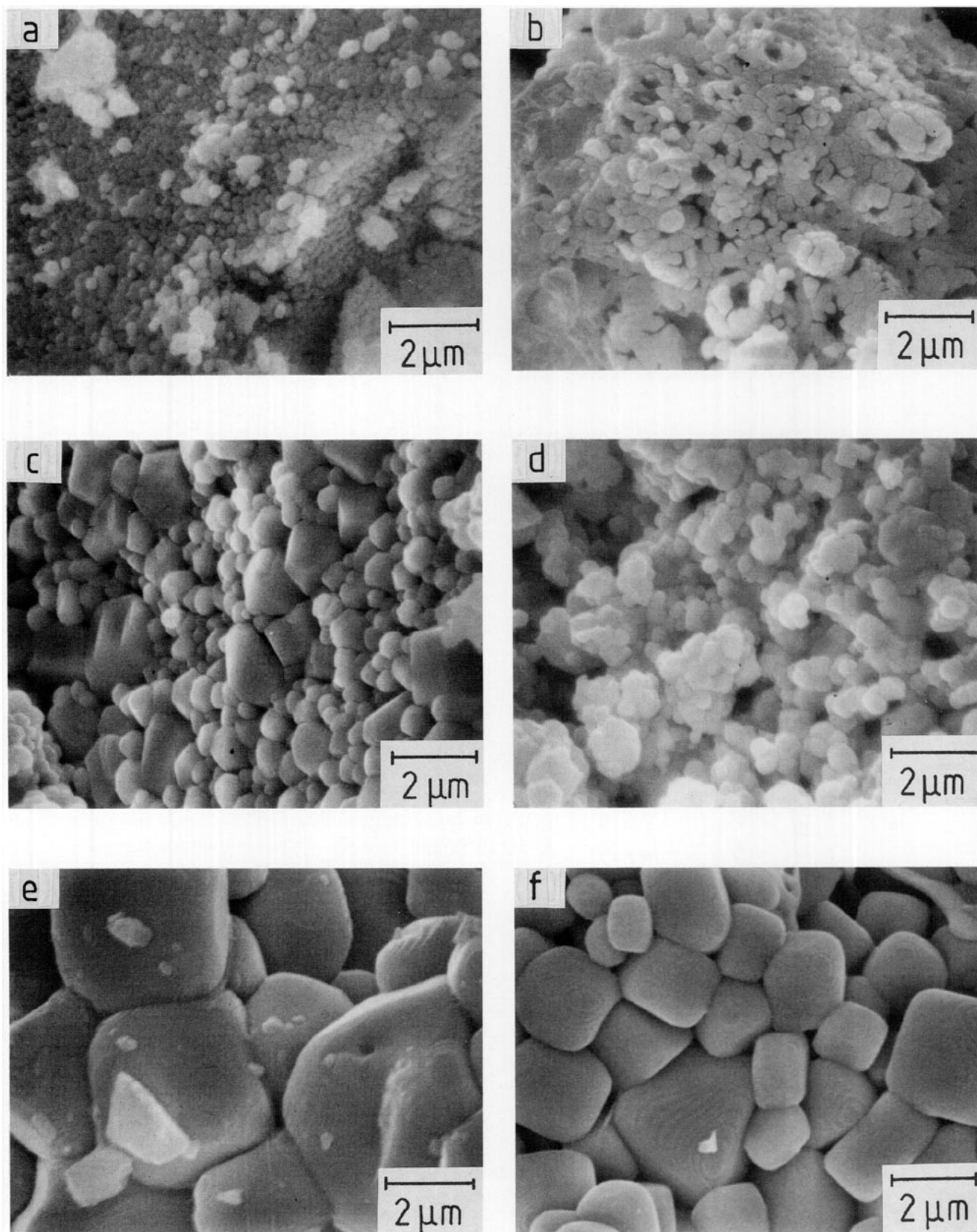
BRIEF COMMUNICATION

FIG. 4. Scanning electron micrographs of the samples, obtained by calcining the gels at 1023 K for 2 hr. (a) CA, (b) CA–R3, (c) MA, (d) MA–R3, (e) MS(A), and (f) MS(A)–R24.

networks. This kind of inhomogenization only reduces the site and frequency of nucleation. This explains the increase in the particle size and its distribution width after calcination.

It is also to be noted that several large particles appeared for the ball-milled gels, as observed by electron microscopy. They are likely to be agglomerates of complex oxides with undeveloped crystallinity. Mechanical stress with its density exceeding a certain critical value may directly result in nucleation, because the activation energy for nucleation can also be surmounted by the energy supplied in the form of mechanical stress, provided the atomic couples necessary for the nucleation are abundant.

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