A straight way toward phase pure complex oxides

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Abstract

Great majority of the electroceramic materials to date are complex oxides. Phase purity, high crystallinity and small grains with narrow size distribution are almost always required. Quick nucleation and limited growth are essential for that purpose. The author concentrates himself on a straight way toward this goal by taking three components into account, i.e. (1) active nucleation sites in high concentration, (2) short diffusion path for growth and (3) achievement of kinetic stabilization. Soft-mechanochemical synthesis is one of the best shortcuts to the goal. The main spirit is the incipient chemical reaction at the boundary between dissimilar particles through homogenization of the starting mixture by exerting as small mechanical energy as possible. Case studies are devoted to the syntheses of various complex perovskites, recently carried out in the author's own laboratory.
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1. Introduction

Since great majority of the electromagnetic properties of the materials rest upon the rationalized long-range atomic arrangement, control of crystallographical and morphological properties of the starting particulate materials is by far the most important issues for electroceramists. Various non-conventional processes have been applied for this purpose.[1] Typical processes with precision control like hydrothermal, sol–gel, solution or soft-chemical ones are attractive enough. But they are not free from various kinds of drawbacks. For a solid-state process, often coined as a "ceramic process" or "shake and bake", on the other hand, a number of possibilities to overcome stereotyped criticism, i.e. inhomogeneity, low reactivity and associated necessity of high temperature. Firing at high temperature is to be avoided, not only to save energy but, more importantly, to suppress troublesome grain growth, which easily leads to abnormal ones and hence to product inhomogeneity.

Present overview deals, therefore, with the effort to make solid-state reaction paths toward complex metal oxides more attractive and pave the way to fabrication of advanced electroceramic materials. Emphasis is laid on the methods and consequences of making the starting mixtures as homogeneous as possible, in conjunction with the optimization of a fabrication process for phase pure electroceramic materials.

2. Homogenization of the starting mixture by mechanical stressing

Everybody in the electroceramic community is aware of importance of homogeneity in the starting materials since it is reflected on the various steps in the entire fabrication process and, finally, homogeneity of the products. Notorious abnormal grain growth, for instance, is generally understood as a consequence of inhomogeneity. It has seldom been identified, however, what kind of inhomogeneity was explicitly responsible for a particular trouble. Even less attention has been paid to objectively and quantitatively evaluate the different kinds of inhomogeneity.

To obtain a homogeneous powder mixture, engineers tend to use almost instinctively a ball mill, mostly, in a wet state. In conjunction with the increasing demands for finer particles down to nanometer regime, various types of mills made their debut on the market in the last two decades. Intensive milling certainly brings about smaller particles and in most cases,

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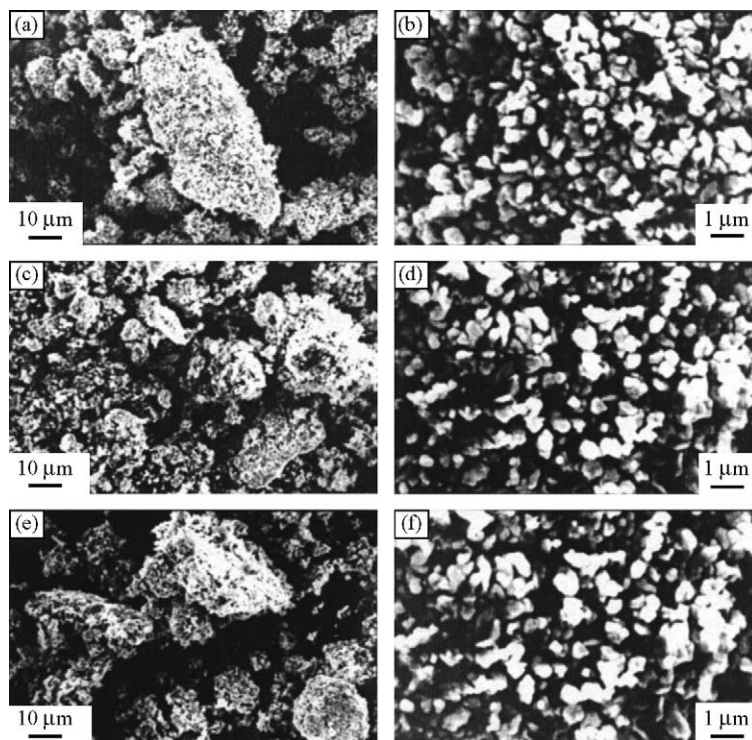 *E-mail address:* senna@applc.keio.ac.jp.

Fig. 1. Scanning electron micrographs of the reaction mixture for PMN–xPT: Left and right columns; before and after mechanical homogenization, respectively. (a) and (b) $x = 0$; (c) and (d) $x = 0.1$; (e) and (f) $x = 0.2$.

more intimate mixing. This does not mean, however, to get a mixture appropriate for the present purpose. High intensity milling is quite often troublesome, not only due to their high initial and running costs or low energy efficiency, but, even more seriously, due to serious contamination and stoichiometry loss. It is therefore very important to exert mechanical stress as sparingly as possible by knowing what is absolutely beneficial by virtue of mechanical stressing. Importance and charm of the mechanical stressing under the concept, coined as soft-mechanochemical processing, are established.[2–11]

A soft-mechanochemistry process is now introduced by citing our first case study on the complex perovskite, Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN) with and without coexistence of TiO$_2$. (PMN–xPT with $x = 0$, 0.1 or 0.2).[12] In the case study, we have paid as much attention as possible to increase the homogeneity of the starting mixture, i.e. a stoichiometric one comprising respective oxides with an exception of Mg(OH)$_2$, being a stable hydroxide, instead of MgO.[12] It is to be emphasized that appropriate milling of the starting mixture brings about homogenization in various categories.

As shown in Fig. 1, degree of agglomeration of the starting mixture substantially decreases after milling with a multi-ring mill[13] for 60 min. While total deagglomeration by powder processing is generally not possible, size distribution of the aggromerates always narrows toward homogenization in 100 nm regime. Homogeneity in the nanometer regime was also quantified by using the standard deviation of the local atomic ratio from the overall nominal one determined by EDX installed in the transmission electron microscope.[12]
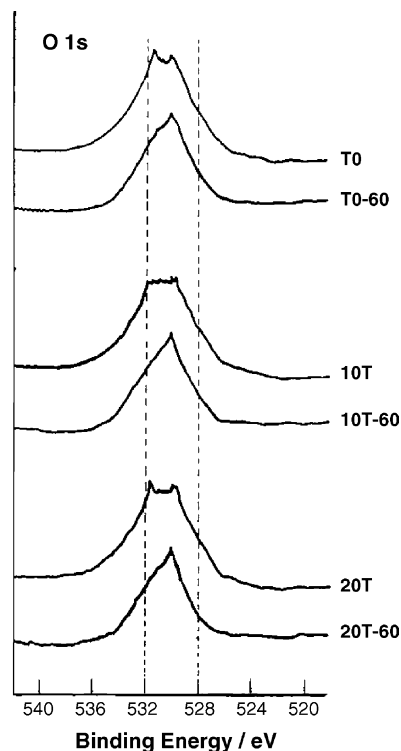

Fig. 2. X-ray photoelectron spectra of the reaction mixture for PMN–xPT. T0, T10 and T20 denote, $x = 0$, 0.1 and 0.2, respectively. Extention–60 denotes mechanically milled for 60 min.
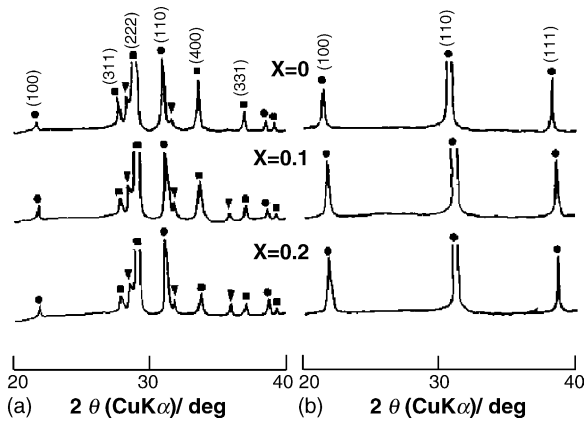
Fig. 3. X-ray diffraction profiles of PMN-xPT after firing at 850 °C for 4 h. Columns (a) and (b) correspond to the starting materials without and with mechanical homogenization, respectively.

Fig. 5. Lattice parameter, a and average grains size of PMN–xPT after firing at 850 °C for 4 h.

3. Consequences of homogenization

3.1. PMN–PT

As we calcined the mechanically homogenized mixtures mentioned in the previous section at 850 °C for 4 h, we obtained always phase pure perovskite, as shown in Fig. 3.[12] From an intact, inhomogeneous mixture, in contrast, we always observed coexistence of the unreacted unitary oxides and pyrochlores as second phases. As shown in Fig. 4, morphology of the calcined powders is also much more uniform when we started from homogenized mixture. The lattice constant decreased linearly with x, as shown in Fig. 5,

It is however, more important to notice that the mixture is chemically homogenized as well. As shown in Fig. 2, oxygen 1s XPS spectra changes from the multimodal one reflecting those of individual starting materials to that of the solid solution, i.e. the end product. The increase in the relative intensity of Pb–O-multi component B-site ions by mechanical treatment is attributed to the formation of new chemical bonds as a result of chemical interactions between dissimilar components.
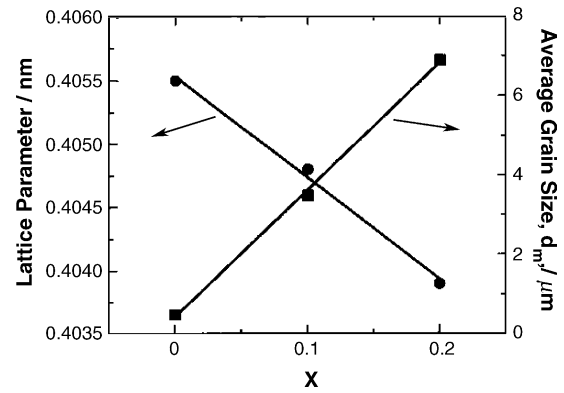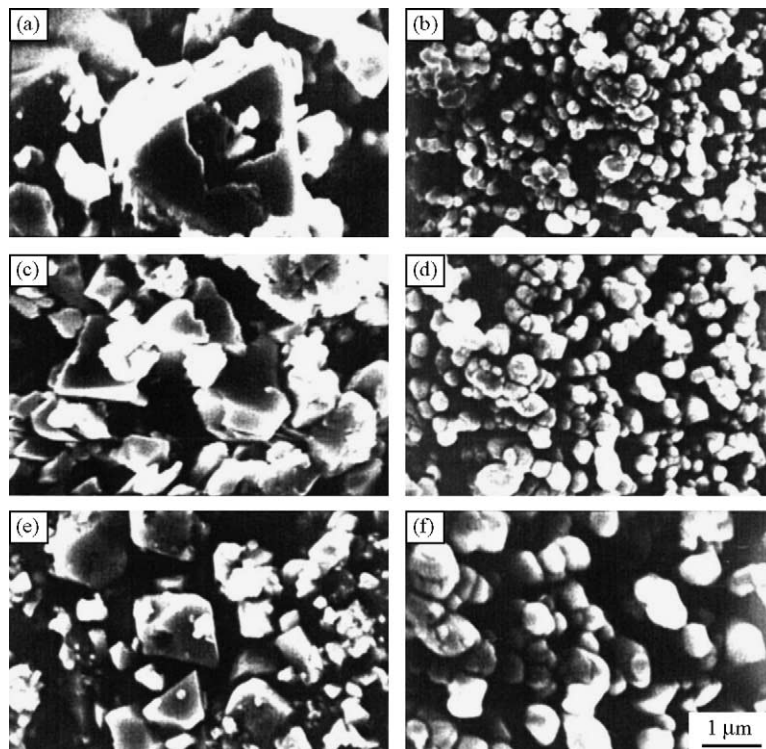

Fig. 4. Scanning electron micrographs of PMN–xPT after firing at 850 °C for 4 h. Left and right columns; before and after mechanical homogenization, respectively. (a) and (b) $x = 0$; (c) and (d) $x = 0.1$; (e) and (f) $x = 0.2$.
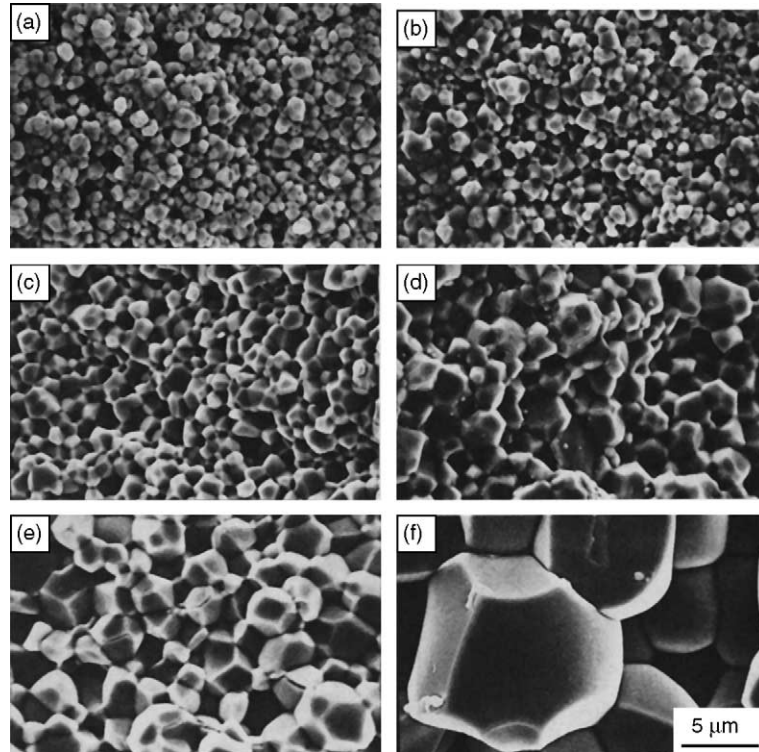
Fig. 6. Fracture surface of the PMN–0.1PT starting from homogenized samples after sintering for 2 h at temperatures: (a) through (f) at 1000, 1050, 1100, 1150, 1200 and 1250 °C, respectively.
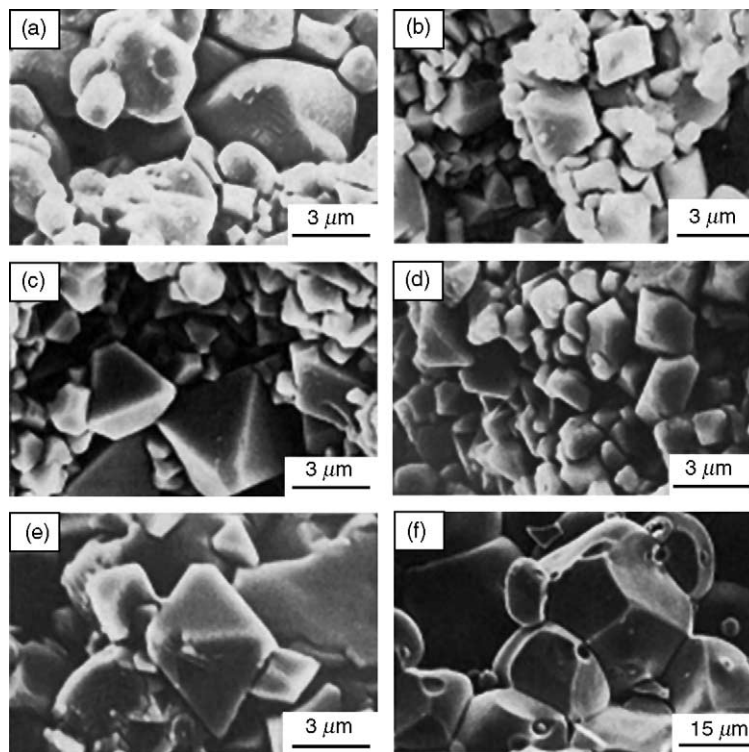

Fig. 7. Fracture surface of PMN–0.1PT starting from non-homogenized samples after sintering for 2 h at temperatures: (a) through (f) at 1000, 1050, 1100, 1150, 1200 and 1250 °C, respectively.

indicating the formation of uniform PMN–PT solid solution.

Calcined powers were subjected to the conventional ceramic process by compressing at 250 MPa with 5 mass% PVA and fired for sintering up to 1250 °C. As shown in Fig. 6, the fracture surface of the sintered ceramics exhibits the clearly edged and well-developed perovskite grains. This makes a sharp contrast to those starting from intact mixture, as shown in Fig. 7, where octahedral pyrochlore grains surrounded by the lowest energy (1 1 1) surfaces are observed up to the sintering temperature 1200 °C. As expected, dielectric properties exhibit large difference, with typical characteristics of the relaxer in the case of starting from the homogenized mixture, as shown in Fig. 8. The obvious superiority of the mechanically pretreated products is primarily attributed to the elimination of the second phase, pyrochlore.

3.2. PMN–PZN

Even more difficult than PMN is to synthesize PZN, where Mg in PMN is substituted by Zn. Difficulty is chiefly attributed to the thermodynamic instability of PZN. It is therefore important to achieve kinetic stability, i.e. to arrive at the crystalline state as rapidly as possible and quench before decomposition or further phase transformation takes place.

PbO, $Mg(OH)_2$, Nb_2O_5 and $2ZnCO_3 \cdot 3Zn(OH)_2 \cdot H_2O$ were mixed in a desired stoichiometry.[14] A compound $2ZnCO_3 \cdot 3Zn(OH)_2 \cdot H_2O$ was chosen as a zinc source because of its higher basicity than any other commercially available Zn salts in a powdery form.

It is to be emphasized that while PbO transforms from massicot to litharge and peaks for $Mg(OH)_2$ and Nb_2O_5 disappear, a set of new XRD peaks corresponding to perovskite appear from early stages of milling, i.e., after milling for only 30min. Relative intensity of perovskite peaks increases with milling time, indicating gradual formation of perovskite solely by milling. Similar tendency was observed for mixtures with different x values, even those without MN, i.e., pure PZN.
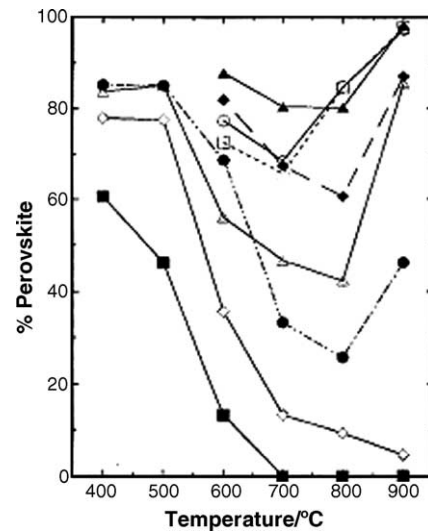
Fig. 9. Plots of percent perovskite against firing temperature for mixtures milled for 180 min. Different curves corresponding different x varying from top to bottom: 0 (PMN), 0.2, 0.4, 0.6, 0.7, 0.8, 0.9 and 1.0 (PZN).

On subsequent heating up to 400 °C and quenching, perovskite became a sole crystalline phase. As shown in Fig. 9, percent perovskite, f_p, decreases and again increases after showing a minimum at temperatures 700–800 °C for the mixtures up to $x = 0.8$. Increase or recovery of perovskite phase is obviously attributed to the incorporation of PMN into PZN by an increased ionic mobility and hence restabilization of the perovskite phase. As a matter of fact, no recovery of perovskite is observed for the components with $x = 0.9$ and $x = 1.0$ (pure PZN).

Instability of perovskite PZN is mainly attributed to unfavorable ionic states for rational packing, including lower coordination state and the bulge due to lone pair electrons to make ions non-spherical.[15,16] It has been theoretically calculated that substitution of Pb(II) at A-site by Ba up to 10 mol % or Zn at B-site by Mg up to 7.4 mol% will stabilize PZN.[16,17] In actual fact, however, additive concentration as high as 40 mol % Mg to PZN ($PZ_xM_{1-x}N$ with $x = 0.6$) was necessary for phase pure perovskite.[18] This means instability of perovskite $PZ_xM_{1-x}N$ is much higher than what is theoretically expected.

We attribute successful synthesis in our study by using mechanically activated precursor mainly to the kinetic stabilization, i.e., rapid formation of a $PZ_xM_{1-x}N$ solid solution at relatively low temperatures where lattice strain is still accommodated to tolerate the perovskite structure. As a matter of fact, continuous increase in the X-ray diffraction peak breadth of perovskite was observed with increasing the fraction of PZN, x, as shown in Fig. 10.

3.3. BMN–BZN with additional homogenization technique

By the same token, it was quite easy to prepare phase pure BMN–BT which is similar to PMN–PT just mentioned
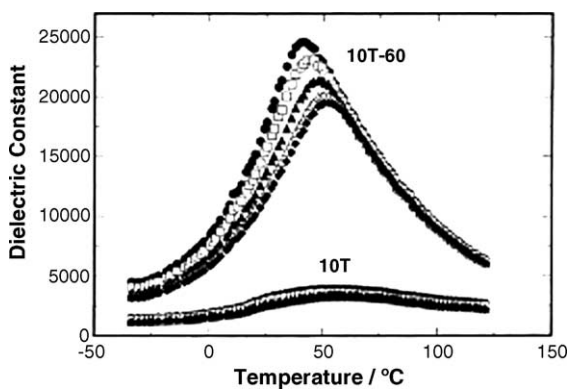
Fig. 8. Frequency dependence of the dielectric constant of PMN–0.1PT after sintering at 1200 °C for 2 h. Extension–60 denotes homogenized for 60 min.
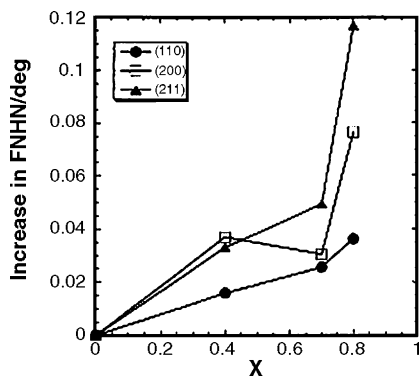
Fig. 10. Increase in the full-width at half-maximum of XRD peaks with fraction of PZN, x, for mixtures milled for 180 min and fired at 1100 °C for 1 h.

above with only one exception of replacing lead with Ba. As we began a serial research with this concept, we added a new component in the entire processing, i.e. mechanical deagglomeration between mechanical activation and calcinations. This brought about further homogenization of the starting mixture and is reflected to the homogeneity of the fired product. It is noteworthy that there is a high correlation between the homogeneities of the samples before and after calcination, as shown in Fig. 11. We presume the decrease in the diffusion distance as a primary component of the favorable results by mechanical deagglomeration.

4. Micrograined barium titanates for MLCC

BaTiO$_3$ (BT) has been mass-produced by a conventional solid-state reaction (SSR), taking advantage of its properties, among others, low cost with high efficiency and precision control of composition. For down sizing of the product particulates, however, SSR has been regarded as inappropriate. Here again, merit of a soft-mechanochemical process turned out to be quite useful.

Well-dispersed BT particles with their average size less than 0.2 µm and tetragonality as high as 1.01 were obtained from SSR by preliminary dry mechanical processing.[19,20] We
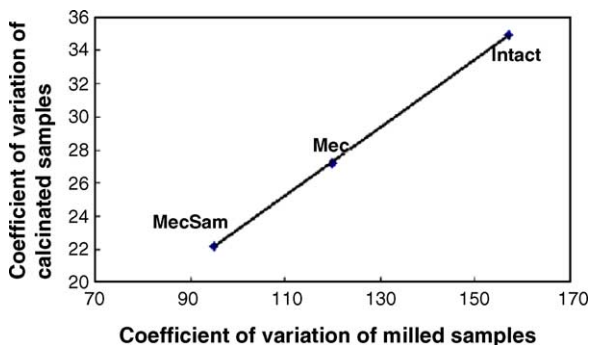

Fig. 11. Correlation between the coefficients of variation of the samples before and after firing the mixture, 0.5BMN–0.5BZN.

attribute these favorable effects to the complex consequences of milling a powder mixture to enhance nucleation of BT and its growth with shorter diffusion path to suppress excessive grain growth. We confirmed these items from various experiments, i.e.: (i) down sizing of individual particulates without causing agglomeration from microscopy; (ii) increase in the homogeneity in a few micrometer regime as confirmed by electron probe microanalysis; and (iii) mechanochemical bridging bond formation across the solid-solid boundary of dissimilar particles detected by X-ray photoelectron spectra.

Starting from fine powders of BaCO$_3$ and TiO$_2$, we have prepared various kinds of starting mixtures. Samples S and W, with and without agitation milling, respectively, were obtained by freeze-drying the respective slurry. We subsequently milled the mixture by a laboratory vibration mill for n-hours, as denoted Sb-nh or Wb-nh, respectively. Homogeneity of the reactant mixture was defined by the coefficient of variation, i.e. the ratio, σ/x, where σ and x denote the standard deviation and the average value, respectively, of X-ray intensity of Ti, determined from electron probe microanalysis (EPMA).

Breakdown of the primary particles in a starting mixture, especially BaCO$_3$, took place by dry ball milling. Larger number density of BaCO$_3$–TiO$_2$ contact points supplies larger number of nucleation sites for BT and reduces the diffusion path length toward the reaction completion. Simultaneously, BaCO$_3$ particles are highly activated to facilitate CO$_2$ release. Partially decomposed BaCO$_3$ reacts more easily with TiO$_2$. For these reasons, a large number of BT-nuclei were formed swiftly at about 550 °C. Nucleation of BT at lower temperature brought about fully-grown BT particles with narrow particle size distribution when fired at 1000 °C.
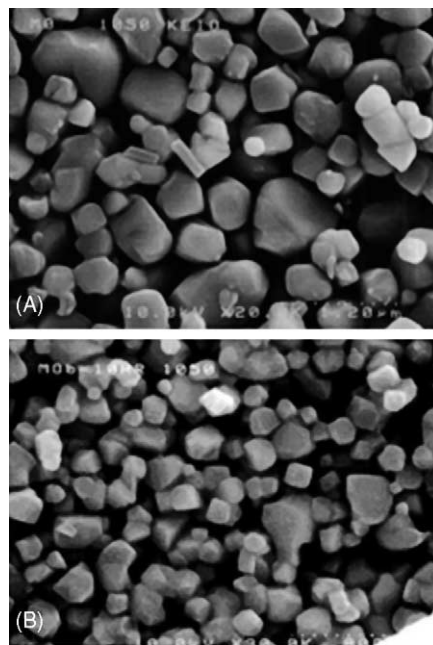

Fig. 12. Scanning electron micrographs of the BT grains obtained from firing W (A) and Wb-10 h (B) at 1050 °C for 2 h.
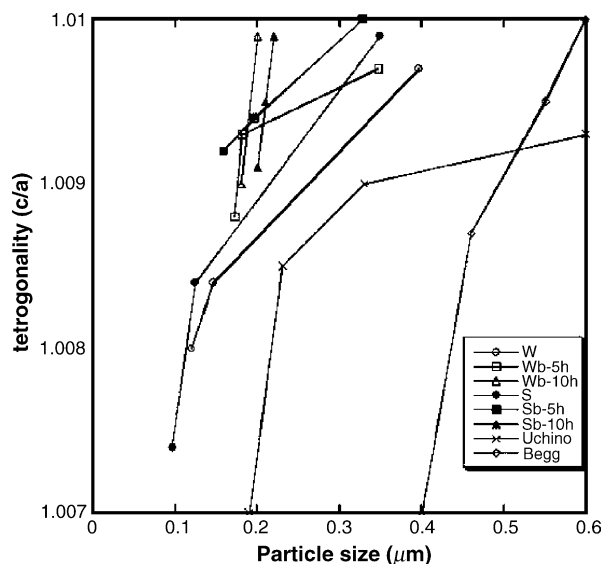
Fig. 13. Relationship between particle size and tetragonality of BT. Small particles with high tetragonality was obtained from Wb-10 h or Sb-10 h.

As shown in Fig. 12, significant suppression of grain growth and with narrower particle size distribution was observed when we start from mechanically activated reactants. We attribute the suppression to significant relaxation of excess free energy by nucleation at lower temperature, reducing the driving force of grain growth by subsequent heating up to higher temperature. Exact mechanisms of grain growth suppression by mechanical activation are yet to be elucidated. One of the most important consequences is the maintenance of high tetragonality, as shown in Fig. 13. This is only possible by assuming very small amount of lattice imperfection. All the results shown above consistently suggest the enormous merit of mechanical activation for small-grained $BaTiO_3$. The success of the technology is largely attributed to the significant incipient chemical interaction during milling, without causing any significant agglomeration.

5. Concluding remarks

Importance of the homogeneity of the starting mixture is emphasized in this overview. Homogeneity is diverse from atomic level (10^{-10} m~) to the agglomerates and grains ($\sim 10^{-3}$ m). We have to pay efforts to control so many different factors simultaneously.

For successful fabrication of composite oxides, it is very important to bridge the dissimilar solid species across the solid boundary to create bridging bonds (HBBs), centered by an oxygen atom. Oxygen-abridged HBBs are formed across the solid/solid interface when OH groups with different polarity are present. This is just what we acquire during mechanical homogenization, or milling a starting mixture. Scientific details of these processes were given elsewhere.[2,3,5,6,9] Confirmation by computational route was also made.[10,11]

While bridging bond formation during mechanical stressing on the starting mixture facilitates the nucleation and to maintain stoichiometry, intimate and well dispersed mixing increases the number of nucleation sites and reduces the diffusion path. The latter, in turn, increases the probability to reach the state of final product without passing through intermediates. This is one of the most important aspects to avoid formation of second phases. All these contribute toward phase purity, higher homogeneity and grain micronization, which we absolutely prefer for electroceramics.

Acknowledgement

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