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Smart soft-mechanochemical syntheses of well-crystallized pure phase fine particulates of mixed oxides for electroceramics

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Abstract

Optimum preparation of starting materials or precursors of mixed oxides via solid-state reaction is discussed with a goal of phase pure, well-crystallized fine particulates. After discussion on general condition on good precursors including the role of additives, results of ongoing case studies are displayed, including the systems, $BaBi_2Ta_2O_9$ (BBT), $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT), and $Li_4Ti_5O_{12}$ (LT). Particular emphasis is laid on the importance of appropriate mechanical activation and choice of starting materials.

Keywords: Milling; Grain size; Reactivity; Perovskites; Functional applications

1. Introduction

While quality upgrade and device downsizing continue in the community of electronic industry, we are simultaneously obliged to cope with different kind of difficulties, among others, cost-push and environmental problems. Tactics to surmount the hurdles will be argued in the present study from the viewpoints of solid-state chemistry. Based on these incompatible requirements simultaneously, a so-called ceramic process should be reconsidered, since it seem much more promising than any other apparently more sophisticated processes including sol–gel or solution chemistry.[1,2]

High calcination temperature to bring the reaction to completion is one of the most serious rebuttals against a ceramic process. To maximize the reactivity of starting mixtures is, therefore, of paramount importance. Mechanical activation is recognized to be one of the most promising methods to meet the requirement. Countless efforts have, therefore, been paid in this area. Stochastic nature of grinding or milling, contamination and low energy efficiency are, however, stereotyped demerits of mechanochemical processes. This is why we now prefer “soft” mechanochemical processes.[3–9]

Most of the works in this area, however, are still very phenomenological and the contemporary state is still far from process optimization. It is, therefore, a good opportunity to reconsider the factors necessary to optimize starting mixtures, which we call “precursors” under their extended definition. We should focus our efforts to: (1) choose appropriate starting species or compounds, (2) maintain stoichiometry as exactly as possible and (3) elevate reactivity of the reactant mixture. Since most of the modern electroceramics are mixed oxides, we have to think about the choice between metal oxide anhydrides, hydrated oxides and hydroxides prior to prepare a physical mixture further to be pretreated.

We would, therefore, discuss here about some general concepts of precursor optimization. Role of additives will also be discussed in this context. Several on-going case studies are then presented, i.e. on the systems: $BaBi_2Ta_2O_9$ (BBT), $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) and $Li_4Ti_5O_{12}$ (LT).

2. Optimizing starting mixtures

2.1. General requirements

In order to fulfill the requirements given above, a soft-mechanochemical process was refined in an attempt to obtain electroceramic materials with lowest possible size dimension and highest possible crystallinity and phase purity.

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Downsizing of the particles of the starting materials and homogenization of the mixing state increase the number of nucleation sites and decrease the diffusion path so that they doubtlessly contribute to decrease the firing temperature. While decreasing firing temperature guarantees smaller grains of the products, it is not always compatible with higher crystallinity, which is indispensable for most of the electroceramic materials.

Most of the reaction processes to complex oxides are multistep. We recognize that mechanical activation of the starting mixture is effective for the initial step to the intermediate, but rarely to the final product. Mechanical activation on the intermediate is, therefore, to be taken into account. Maintenance of the stoichiometry is indispensable for phase purity. Once an intermediate compound is sufficiently stable, a new starting mixture from the intermediates to the final goal may well be "off-stoichiometry" at least in a scale of, say, 10 μm × 10 μm area regime. While mechanical stressing is indispensable to realize basic concepts of soft-mechanochemistry, it should be given as sparingly as possible in order, mainly, to reduce possible contamination during stressing, apart from the energy saving, which by itself is certainly important in the era of high petroleum price. We therefore should pay more efforts to make the solid-state synthetic process smarter to surmount problems mentioned above.

2.2. *Role of additives*

In order to make the preparation process of the starting mixture, design of the apparatus is to be refined, which is discussed elsewhere.[10] Apart from these mechanical aspects, however, role of different additives is not to be underestimated. One of the most important functions of the organic additives is the coordination of organic additives to the ingredient metallic ions (e.g. Ba), easing the decomposition of the compounds (e.g. $BaCO_3$).[8] Once the main diffusing species (e.g. Ba) is liberated in the intimately admixed starting materials, substantial decrease in the reaction temperature is guaranteed. However, there are another important factors dominating nucleation of the new phase. When the process is divided into several substeps, it is often the case that the reaction eventually stops at the stage of relatively stable intermediate phase. This might be avoided by the selection of additives and optimizing heating conditions.

Functions of additives could be categorized as: (1) to promote decomposition of the starting mixture, e.g. carbonates of alkaline earth metals, (2) to promote nucleation of the products of addition reaction, (3) to reduce agglomeration, (4) to increase the homogeneity of the mixture in mesoscopic or macroscopic scale, and (5) to reduce grain growth and/or coalescence of the products.

Since it is generally not appropriate to have the rest of additives in the final product, we prefer organic additives to inorganic ones. In our serial studies, we found that some of the amino- or amide-containing compounds are effective as additives with their functions given above.[8,9] Some of the latest results will be given below as well.

3. $BaBi_2Ta_2O_9$ (BBT) and $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT)

We have examined to prepare ferroelectric relaxors with simple or layered perovskite structures by a solid-state reaction via a soft-mechanochemical route. Those compounds are demanded particularly due to their lead-free composition for microwave dielectrics.[11,12] A number of synthetic methods were explored.[13–15] For the synthesis of BBT, $BaCO_3$, in this work, Bi_2O_3 and Ta_2O_5 were selected as starting materials. The stoichiometric mixture was milled with nylon balls in vibratory mill for 3 h and was calcined for 1 h in air at temperatures between 850 and 1000 °C. A sample without milling was also prepared for comparison. As for BMT, $BaCO_3$ and $Mg(OH)_2$ were used as Ba and Mg source and either Ta_2O_5 or $Ta_2O_5 \cdot 3.8H_2O$ was used as Ta source. Milling and calcination processes are the same as that of BBT. $Ta_2O_5 \cdot 3.8H_2O$ used here was prepared as follows: 5 g of $TaCl_5$ was dissolved into 10ml ethanol. This solution was then added into 5 mol/l NH_3 aqueous solution. Obtained precipitation was separated from the solution by a centrifuge and was dried for 3 days 50 °C. The molar amount of hydrated water per mole of Ta_2O_5 was determined to be 3.8 by thermogravimetry.

Fully crystallized, fine particulate BBT was obtained by firing the mechanically activated starting mixture at 900 °C. The resultant particles are rather uniform with their average grain size as small as 400 nm, as shown in Fig. 1. In the case of $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT), in contrast, similar success was only reached by using hydrated sample, $Ta_2O_5 \cdot 3.8H_2O$, in place of anhydrous Ta_2O_5. As shown in Fig. 2, the second phase, $BaTi_2O_4$, was almost disappeared, if not completely, by using mechanically activated mixture with $Ta_2O_5 \cdot 3.8H_2O$, as shown in Fig. 2(b). Note that the remarkable effect of milling is obvious here, again, by comparing the calcined products starting from the intact mixture with $Ta_2O_5 \cdot 3.8H_2O$, as shown in Fig. 2(c).

In Fig. 3(A), O 1s XPS profiles are displayed for (a) Ta_2O_5-derived mixture, (b) sample (a) after milling for 3 h, (c) $Ta_2O_5 \cdot 3.8H_2O$-derived mixture, (d) sample (c) after milling for 3 h, and (e) BMT obtained by calcining sample (d) at 900 °C, respectively. A second peak appeared in curves (c) at the lower binding energy is ascribed to the hydrated water aid is disappeared after milling. We attributed this to the consumption of hydrated water due to the formation of bridging bonds, Ba–O–Ta and Mg–O–Ta across the boundary of dissimilar particle species. As for the binding energy of Ta 4f, it is particularly noteworthy by referring Fig. 3(B), where curves (a–e) correspond to those of Fig. 3(A), that the profile of the curve (d), after milling the $Ta_2O_5 \cdot 3.8H_2O$-derived mixture is very close to that of well-crystallized BMT (curve (e)), implying the electronic state of Ta being already very close to the final product in the mechanically activated precursor.

The difference in the availability of pure-phase BBT and BMT is attributable to the difference in the easiness of bridging bond formation under mechanical stressing. BBT is layered perovskite, in which $(Bi_2O_2)^{2+}$ and $(BaTa_2O_9)^{2-}$ layers line along *c*-axis and metal–O–metal' bridging bonds in BBT perovskite structure are mainly Ta–O–Ba. On the other hand, BMT

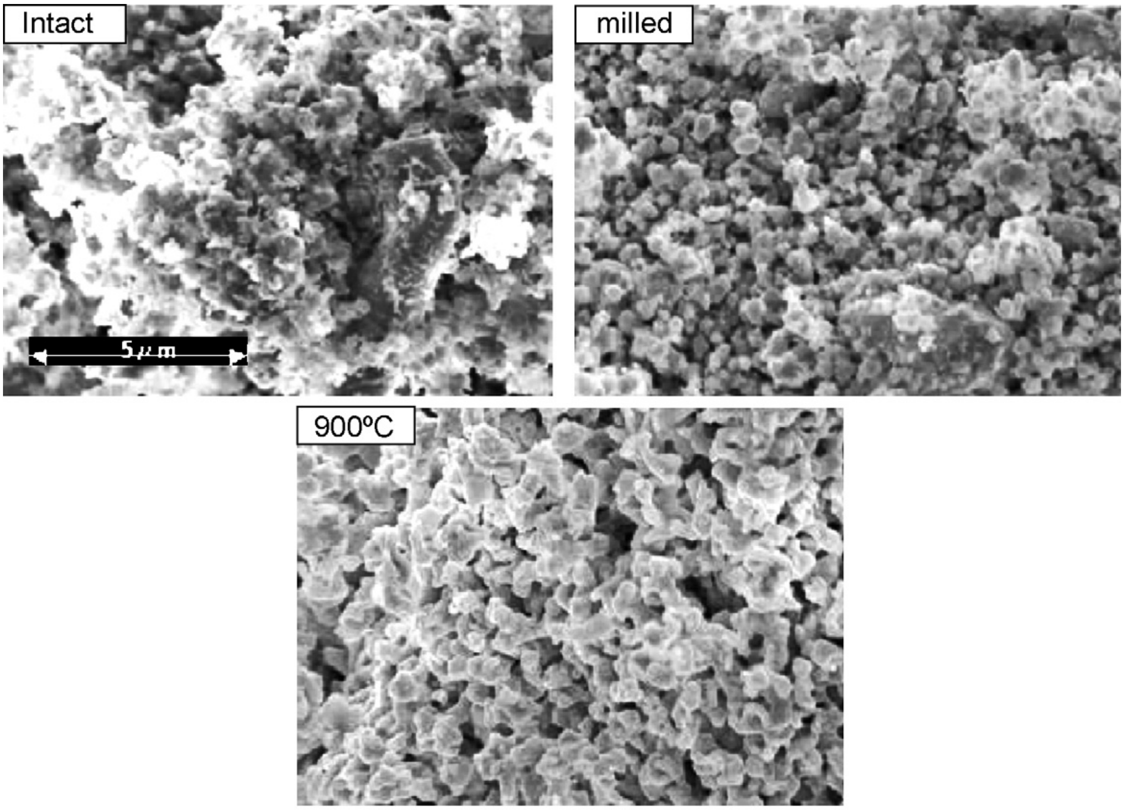

Fig. 1. Scanning electron micrographs of the starting mixture without milling (intact), milled by a laboratory sized vibration mill for 3 h (milled) and subsequently calcined at 900 °C for 1 h.

is complex perovskite in which Ba occupies A site and Mg and Ta occupy B site. In this case, Ta–O–Ba and Ta–O–Mg bonds coexist within a perovskite unit cell. In view of the acid–base reaction across the boundary of solid particles, Ta–O–Ba is easier to form than Ta–O–Mg, because of the higher basicity of Ba than Mg. These speculations are yet to be verified.

4. $Li_4Ti_5O_{12}$ (LT)

We further challenged to synthesize phase pure particulates of a spinel phase, $Li_4Ti_5O_{12}$, with smallest possible grains via a solid-state reaction route. Its good cycle stability and zero-dilation-shrinkage during charge–discharge processes

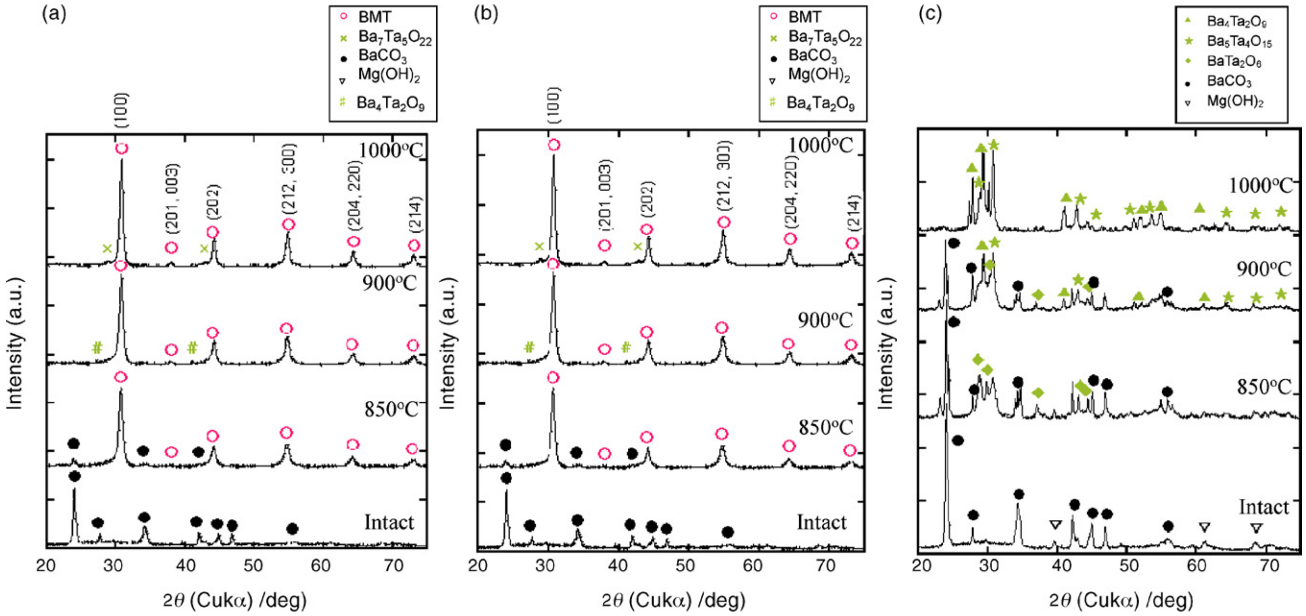

Fig. 2. X-ray powder diffractograms for BMT calcined at varying temperatures derived from the mixtures containing (a) Ta_2O_5, milled for 3 h, (b) $Ta_2O_5{\cdot}3.8H_2O$ milled for 3 h and (c and b) $Ta_2O_5{\cdot}3.8H_2O$ without milling.

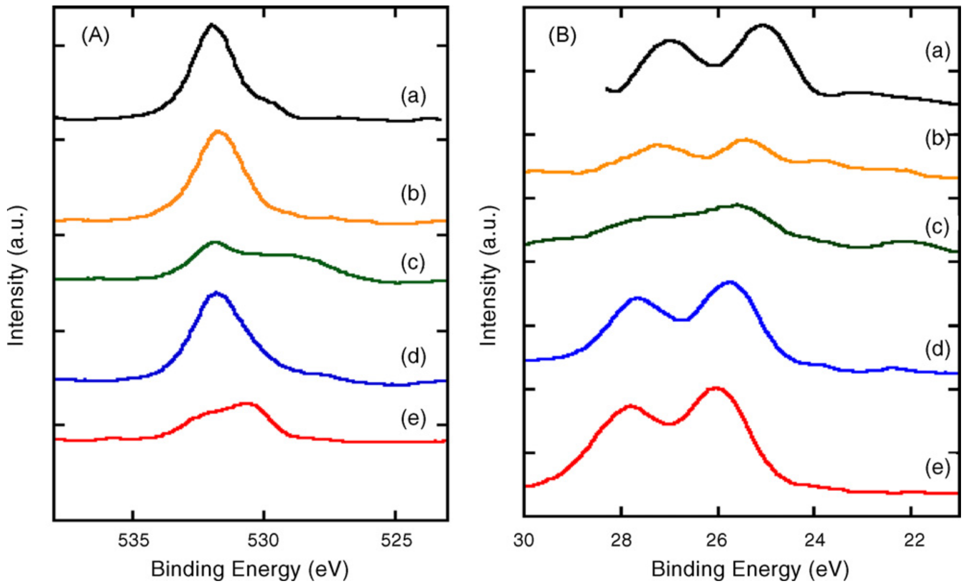

Fig. 3. XPS profiles of (A) O 1s and (B) Ta 4f. Curves denote: (a) Ta_2O_5-derived mixture, (b) sample (a) after milling for 3 h, (c) $Ta_2O_5 \cdot 3.8H_2O$-derived mixture, (d) sample (c) after milling for 3 h, and (e) BMT obtained by calcining sample (d) at 900 °C.

makes it one of the best candidates of anodic materials for Li-ion battery, in spite of its potential lower than that of graphite. Julien et al. obtained phase pure spinel by firing the ball-milled mixture in air at 850 °C for 12 h, with its mean particle size ca. 600 nm.[16,17] $Li_4Ti_5O_{12}$ is also used as electrochromic materials.[17] We here tried to apply mechanical activation after choosing appropriate candidate compounds as starting materials.

As shown in Fig. 4(a), we obtained quasi phase pure spinel by firing the stoichiometric mixture comprising Li_2CO_3 and TiO_2 (anatase, BET surface area 150 m^2/g) at 950 °C for 1 h. At lower temperatures, we always observe Li_2TiO_3 as a second phase. When we go up to 1050 °C, stoichiometry is lost due to vaporization of Li component to obtain $Li_2Ti_3O_7$ as a second phase to a significant extent. As we activated the same mixture by a multi-ring-type mechanical activator, Mechanno-Micros®, Nara Machinery, we obtained similar quasi phase pure spinel by firing at 850 °C for 1 h, as shown in Fig. 4(b).

Appropriate choice of the starting material is another very important issue of the ceramic processes. In the case of Li compounds, it is noteworthy that when we substituted Li_2CO_3

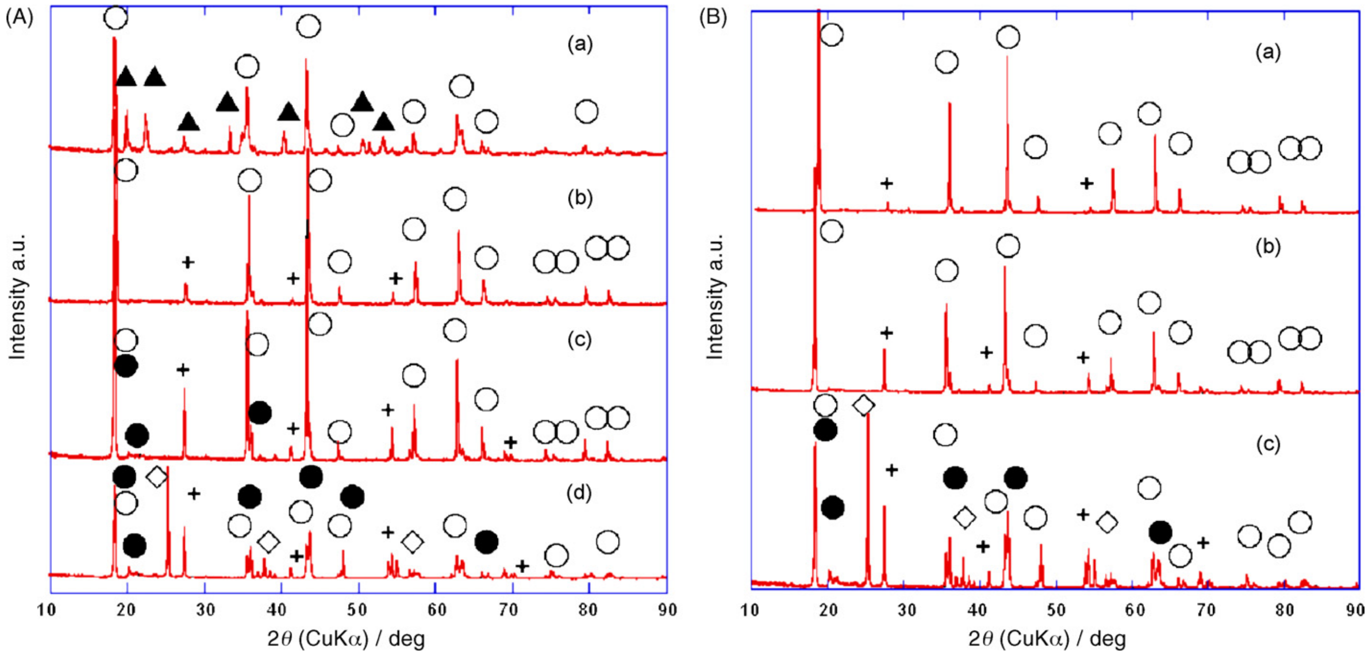

Fig. 4. X-ray powder diffractrograms of Li–Ti–O system, starting from the stoichiometric mixtures for $Li_4Ti_5O_{12}$, comprising Li_2CO_3 and TiO_2, (A) without milling, calcined at (a) 1050 °C, (b) 950 °C, (c) 850 °C and (d) 750 °C; (B) after milling for 30 min by M-MIC and calcined at (a) 950 °C, (b) 850 °C and (c) 750 °C. Calcination was carried out in air for 1 h (○, $Li_4Ti_5O_{12}$; ●, Li_2TiO_3; ▲, $Li_2Ti_3O_7$; +, TiO_2 (rutile); ◇, TiO_2 (anatase)).

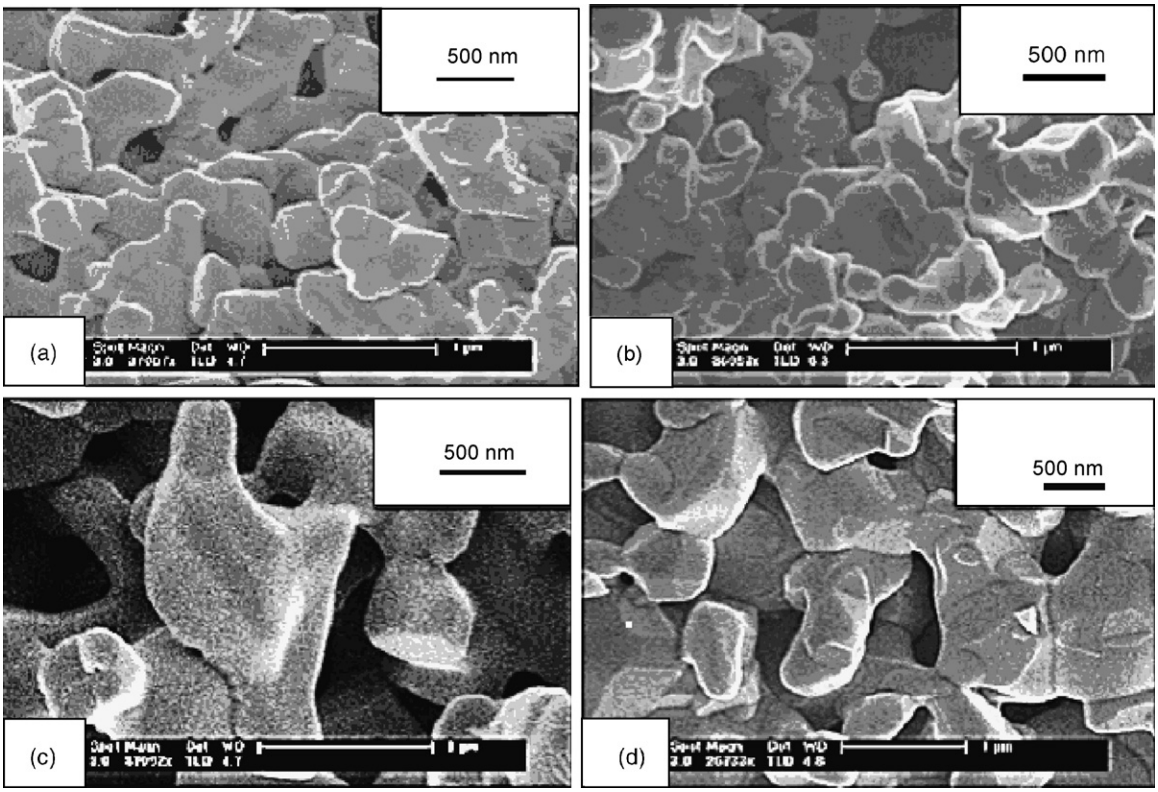

Fig. 5. Scanning electron micrographs of the calcined $Li_4Ti_5O_{12}$. (a) Intact, 850 °C, (b) milled for 30 min, 850 °C, (c) intact, 950 °C, and (d) milled for 30 min, 950 °C.

with $LiNO_3$ and titania with 50 m^2/g in place of 150 m^2/g, we obtained quasi phase pure at 750 °C even without milling. This is attributed to the particularity of the nitrate, which melts at 261 °C. We obtain similar results by using lithium acetate, whose melting temperature is as low as 70 °C. At this stage, we almost always observe excess titania after it has been transformed to rutile, in spite of starting from an exactly stoichiometric mixture. This is most probably an indication of incomplete reaction, with a small amount of Li_2TiO_3, which is indistinguishable due to overlap of the diffraction peaks of the main phase, $Li_2Ti_3O_7$.

As for the particulate properties, we observe remarkable differences, particularly with respect to the grain size and specific surface area. As shown in Fig. 5, grain sizes are significantly smaller by staring mechanically activated precursor. The average particle size of quasi phase pure $Li_4Ti_5O_{12}$ obtained from mechanically activated precursor with Li_2CO_3 is ca. 500 nm, which coincides with the value calculated from BET surface area under the assumption of homogeneous spheres, 460 nm. By using $LiNO_3$ and 750 °C we observe even smaller grains, i.e. ca. 250 nm, which agrees well with the BET diameter, 240 nm, from the specific surface area, 7.18 m^2/g.

Most of the mixed oxides have different crystallographical phases other than the final targeted one. As mentioned in the introduction, stabilization at the metastable intermediate impedes the phase pure synthesis. We therefore tried to mechanically activate the intermediate, Li_2TiO_3, in the course of phase pure synthesis of $Li_4Ti_5O_{12}$. By combining this intermediate grinding process with appropriate additives, we very recently surmounted the incompletion of the phase purity of $Li_4Ti_5O_{12}$.[18] By milling the mixture preliminarily calcined at 500 °C and calcined further at temperatures higher than 500 °C brings about better results, particularly when we combine this with the addition of some amino acids including glycine, mentioned above. This was judged from the X-ray diffractometry, i.e. sharpening of the peaks from $Li_4Ti_5O_{12}$ and hence disappearance of the intermediate, Li_2TiO_3, and the rest of the peaks of rutile.

5. Concluding remarks

As far as we wish to stay at the forefront of electroceramic community, it is absolutely necessary to fulfill the apparently incompatible requirements mentioned at the beginning of introduction. It is absolutely necessary to decrease the calcination temperature to bring the solid-state reaction to completion, in order to obtain finest possible grains with high crystallinity. Elevation of the reactivity requires higher atomic mobility at the near surface region, which simultaneously enhances grain growth. Although milling a mixture is versatile to obtain a good precursor, this should be done as sparingly as possible, particularly when we use smaller starting particulates. For the best choice of machine and conditions of milling, we have to start from the best choice of the compounds involved in the reactant mixture. Change in the chemical states in the course of mechanical activation should be monitored as carefully as possible. Multiple roles of additives are yet to be explored, since appropriate incorporation of organic additives improves the properties of precursors and changes the reaction processes during calcination toward smaller grains with higher crystallinity.

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