A straight way toward phase pure complex oxides

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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 fast 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. A soft-mechanochemical process 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 given based on the experimental studies done recently in the author's own laboratory on the syntheses of various complex perovskites.

High intensity milling is quite often troublesome, not only due to their high energy cost or low energy efficiency, but also 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 of soft-mechanochemical processing are 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).

As we calcined the mechanically activated stoichiometric mixtures of (hydr)oxides at 850^{o}C for 4h, we obtained always phase pure perovskite. From an intact, inhomogeneous mixture, in contrast, we always observed coexistence of the unreacted unitary oxide and pyrochlores as second phases. Morphology of the calcined powders is also much more uniform when we started from homogenized mixture. The lattice constant decreased linearly with x, indicating the formation of uniform PMN-PT solid solution.

Calcined powers were subjected to the conventional ceramic process and fired for sintering up to 1250^{o}C. 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, where octahedral pyrochlore grains surrounded by the lowest energy (111) surfaces are observed up to the sintering temperature 1200^{o}C. As expected, dielectric properties exhibit large difference, with typical characteristics of the relaxer in the case of starting from homogenized mixture.

After introducing further case studies on PZN-PMN and BMN-BZN, more practical examples on $BaTiO_3$ (BT) for MLCC are given. Well-dispersed BT particles with their average size less than 0.2μm and tetragonality as high as 1.01 were obtained from a solid-state process by preliminary dry mechanical processing. We attribute the 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.

Finally, importance of bridging bond formation during preparation of starting mixture is emphasized by referring some basic mechanisms. While bridging bond formation during mechanical stressing on the starting mixture serves to facilitate 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.