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A Simple Mixing Study for Perovskite Ceramics:

Comparing Lancaster Products K1 Series High Shear Mixer with Conventional Ball Milling

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Findings from a recent research project commissioned
by Lancaster Products and developed under the aegis of
Dr. Steven Mercurio / H&M Analytical, LLC.

Introduction

In the field of ceramic processing, mixing is an important, but often neglected step. The mixedness of the components in typical mixed element oxide composition can influence the resultant mechanical properties and behaviors of the system. While this fact is well known within the industry, the efforts that must be taken to ensure well mixed systems often require extended times as the primary solution. In today's age of increasing energy costs and tighter demands on production timelines, having more innovative methods would prove advantageous for many applications.

The Lancaster Products K-Series High Shear Counter-Current mixer can offer such benefits. In this simplified study, the performance of the Lancaster K1 mixer for mixing the oxide components of a solid-state sintering ceramic system, $CaTiO_3$ (Perovskite) was compared to ball milling, a simple, commonly used process for ceramic processing. Often employed to reduce particle size, ball milling is also widely used to mix components. It offers simple scalability to large sizes and is widely available.

However, ball milling is not without disadvantages. It requires as long as 8 – 24 hours of time, even for mixing tasks that do not have the specific goal of particle size reduction. These operations require heavy energy usage, and also have issues with the material drying, sticking to surfaces and/or clumping and therefore not being subjected to the proper mixing/milling. Also, there can be contamination from the chipping or breakage of the milling media.

It is advantageous to productivity to have a mixer design that simplifies, accelerates, and optimizes the process, such as a high shear counter-current mixer. Lancaster Products K-Series Mixers combine a high-speed mixing tool with a counter-rotating pan to facilitate continuous movement of materials, with no dead zones, throughout the mixing cavity.

A simple study was designed to help establish the feasibility of the K-Series mixer as a replacement for ball milling and to evaluate the advantages referenced above including its reduced processing times. For this comparison of mixing methods, a simple model ceramic system of $CaTiO_3$ was chosen. This is a typical ceramic system which can be synthesized through wet chemistry and other methods, but most commonly through the mixed oxide route where the components are mixed, milled, reacted and/or heat treated.

By taking a batch of powders through both the K1 mixing and the ball milling routes at different times, a comparative evaluation of the mixed capability of high shear, counter-current mixing can be established.

Materials & Methods

The CaO and TiO_2 phase diagram was referenced to choose a composition using $CaCO_3$ and TiO_2 powders where $CaTiO_3$ formation was thermodynamically favored. Although reaction kinetics and temperatures may prevent complete reaction under the simple conditions used in this study, by subjecting the same mix to each of the processing routes, the comparative results will still be informative.

The starting $CaCO_3$ and TiO_2 powders were tested by XRD in order to establish the phase purity and phases present. These powders were also tested for particle size by using laser diffraction to indicate the starting particle sizes. The proper amounts of $CaCO_3$ and TiO_2 were weighed out and gently combined by hand in a large container. This initial mix served as the 0-mix data point, and then was divided into separate sets of material that were taken for processing by either a ball mill or Lancaster K1 mixer.

The ball mill sample set was mixed in a laboratory scale (1 kg batch size) alumina ball mill jar with 1 mm size alumina media. The ball mill was operated at a medium speed setting for either 3, 6, 12, or 24 hours of milling time. The powder was then removed from the jars and set aside for further processing. During the 12- and 24-hour milling times, some amount of material was observed to be caked on the jar openings and other surfaces, and not likely to be as involved in the milling process over the lengthy processing times.

The other batch of selected material was sent to Lancaster Products for mixing using the K1 laboratory scale (2 kg) batch scale mixer. The powder was mixed for 30 minutes total, with samples pulled for analyses every 2 minutes.

Results

Phase Conversion

The yielded mixed powders from both routes, as well as the 0-mix batch, were heat treated at 1100°C for 1 hour to react the oxides into $CaTiO_3$. XRD testing of the reacted powders at the various time intervals from each processing method are shown below in Figure 1.

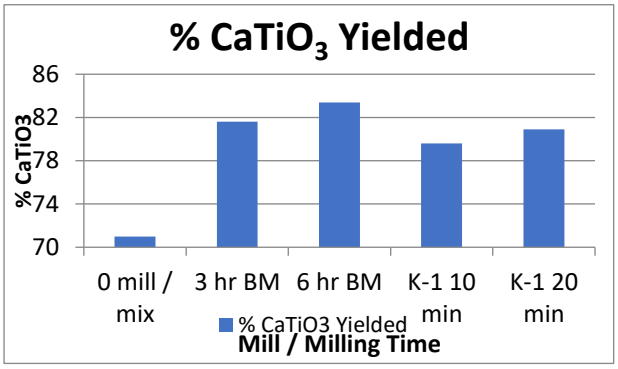


Figure 1

It is clear that mixing is an important step in providing the intimate powder contact required for improved reactivity in solid state sintered powders such as these. Both routes yielded – at any mixing time studied - improved $CaTiO_3$ powder yields versus the 0-mix data. The graph shows that 10 or 20 minutes of mixing time in the K1 series mixer yielded phase conversation results comparable to 3 and 6 hours of ball milling.

Neither process yielded complete or nearly complete conversions, but this is not unexpected with the simplified thermal treatments and conditions of this study. The reaction temperature utilized was lower than ideal but was the maximum temperature possible using the available furnace. Other literature indicates improved results from the higher temperatures, as well as cycles of heating and grinding, or more active heat treatment methods such as fluidized bed, etc., to better expose unreacted powder surfaces. Still, as a comparative study not focused on optimization, the lower temperature was suitable for this purpose.

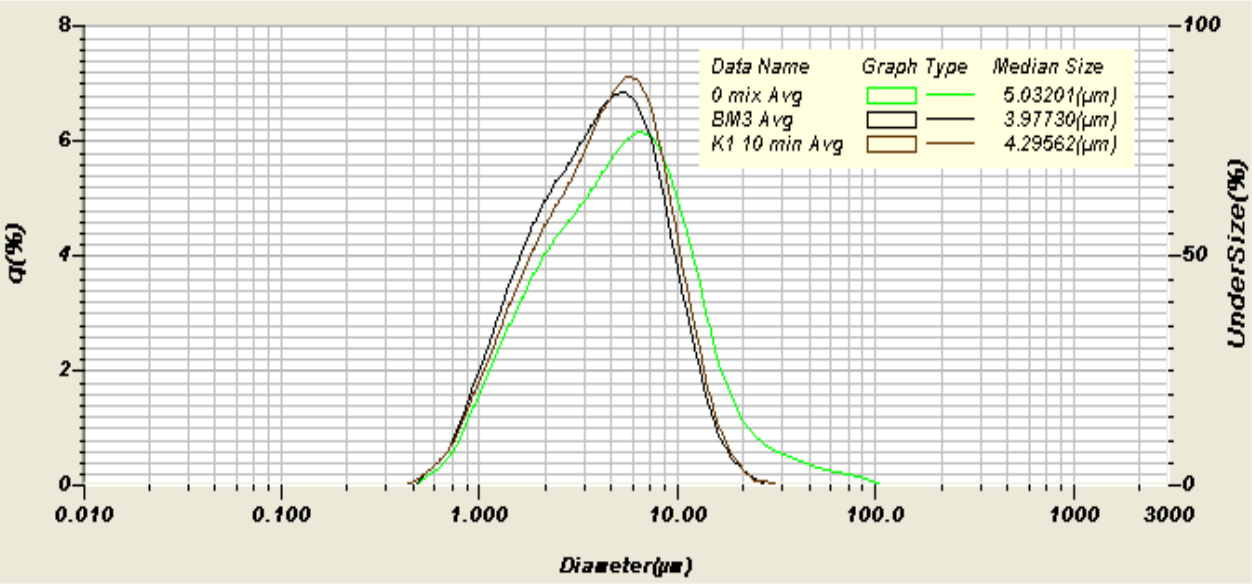
The XRD data indicates that 20 minutes of mixing time in the K1 series mixer is comparable to much longer ball milling times of 3 or 6 hours. There are also advantages relative to the constant motion of the high-speed rotor, plow and counter-rotating pan that keep the material from clumping or sticking.

Particle Size

While a process may be primarily concerned with mixing, the reduction of particle size can be the focus, or a consequent result, during processing in a ball mill. An understanding of the changes in particle size for these processing routes was also desired.

Particle size measurements of the starting powders, 0-mix batch, and the mixed powders from the ball mill and K1 mixing evaluations, before the firing for the reaction, were undertaken using laser diffraction. The starting powders had median particle size values of around 3 microns for the $CaCO_3$ and 8 microns for the TiO_2.

The 0-mix batch data reflects the combination of these two distributions and demonstrated a bimodal distribution with a median at 5.03 microns.



Evaluation of the samples after the milling process revealed a reduction in particle for both the ball milled and K1 mixed powders. The particle size comparisons for 3 hours of ball milling and 10 minutes in the K1 mixer are shown as an overlay with the 0-mix batch data in Figure 2.

You can observe the distribution shape remains roughly the same, but with a reduction in the extended coarse tail and an overall lower median. The median values for the ball milled powders at 3 hours were 3.98 microns while at 6 hours the reduction was to 3.38 microns. In 10 minutes of time in the K1 mixer, the median was 4.29 microns, while at 20 minutes the median particle size was 3.95 microns.

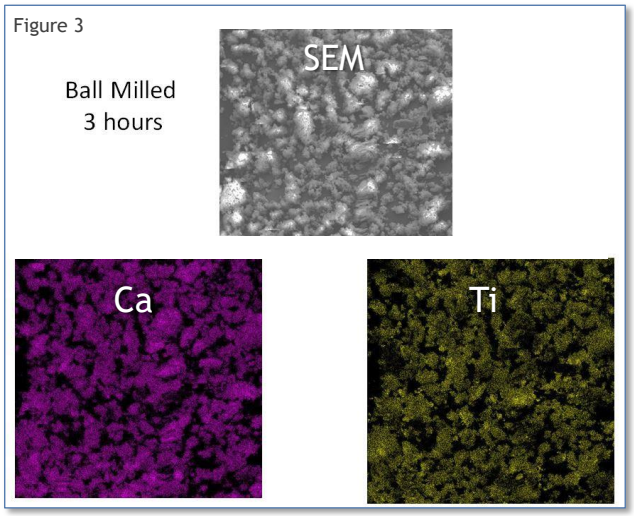
The K1 mixer was shown to be effective at reducing the particle size to almost the same median value in only 20 minutes of time versus the 3 hours of time in the ball mill. This represents a significant advantage in time efficiency versus ball milling for applications where heavy milling is not the primary goal.

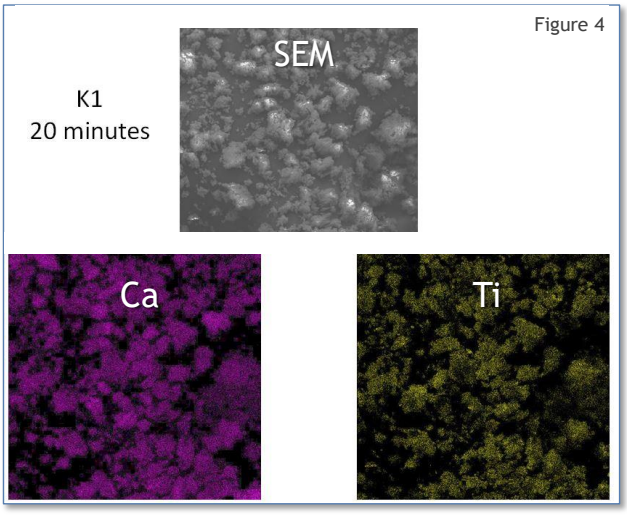
Compositional Mapping

As another method of evaluating the mixing quality of the samples prepared from the different mixing routes, the reacted powders were examined in the scanning electron microscope (SEM) using the energy dispersive spectroscopy (EDS) to generate compositional maps of the major elements present. At this initial stage, the maps were generated for the powders only.

Examining polished surfaces is more advantageous for this kind of study but requires dense samples that can be properly polished or the addition of special steps for preparing and imaging porous green bodies. These methods may be explored in later studies.

Elemental maps, along with an image of the sample region the maps are taken from, are shown in Figures 3 and 4 below.





Visually, the powders appear similar in shape and size, which correlates with the particle size data. The bright areas present in these images are artifacts due to charging from insufficient sample preparation.

These maps indicate comparable composition between the reacted samples from both processing routes. There are no large regions of elemental clusters in either sample which would indicate poor local mixing.

Conclusion

The objective of this experiment was to compare the two methods of mixing—traditional ball milling versus high shear, counter-current mixing in the Lancaster Products K1 High Shear Mixer. A ceramic system with mixed oxide powders was prepared in a large batch and then processed using each mixing method at increasing time increments.

The findings reveal that in this case, high shear, counter-current mixing is highly comparable to ball milling but requires significantly shorter mixing times. This is advantageous for these types of ceramic systems for many reasons, including but not limited to, reduced contamination, increased efficiency, reduced energy usage, reduced equipment footprint and improved/simplified batch planning.

In an analysis of the particle size, a reduction in the median particle size was achieved in a shorter amount of time with the K1 mixer. Good compositional mapping showed a comparable final product.

Overall, the data supports the thesis that the Lancaster K-Series High Shear Counter-Current Mixer produces a comparable product, for a ceramic such as calcium titanate – in much less time - in comparison with the standard ball milling process.

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