



PARTICLE SIZE OF ELECTRONIC CERAMIC POWDERS

Particle size analysis plays a crucial role in the manufacture of electronic materials for dielectric applications. These materials include single-phase powders such as barium titanate as well as formulations that contain many different oxide phases. In all cases, the particle size distribution has a great impact on their processing and performance.

Introduction

Electronic ceramic powders include a wide variety of mixed metal oxide compounds and formulations. These materials are based primarily on barium titanate (BaTiO_3). One of the most common applications is in multilayer ceramic capacitors (MLCC's). Because of their ability to store relatively large amounts of energy in a very small volume, MLCC's are found by the hundreds in cell phones, computers and other consumer electronics. For this reason, production rates at a large capacitor manufacturing facility can exceed 1 billion pieces/month. Fig. 1 illustrates a typical MLCC structure. A typical MLCC is comprised of multiple layers of ceramic separated by metal electrode layers made of silver/palladium or nickel depending on the application. Each ceramic layer is 10 μm to less than 1 μm thick. Some of today's capacitors can contain upwards of 500 layers.

BaTiO_3 is ferroelectric and undergoes reversible structural changes upon heating above about $\sim 130^\circ\text{C}$ (the Curie temperature or T_c). Above T_c , the unit cell has a cubic structure. Upon cooling below T_c , the unit cell transforms to tetragonal symmetry (see Figure 2). The change in structure is a result of the spontaneous displacement of the Ti^{4+} ion. The displacement causes a lengthening and polarization of the unit cell and the polarization imparts the large dielectric constant. Figure 3 shows the effect that the transformation

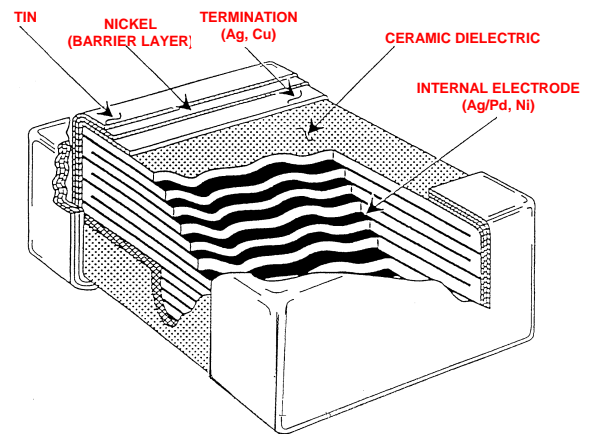


Figure 1

has on dielectric constant. At T_c , the dielectric constant is at a maximum and decreases on either side. Two more transformations take place below room temperature but are less significant in terms of the change in dielectric constant.

For use in MLCC's, pure BaTiO_3 is doped with small amounts ($<5\text{wt}\%$ of BaTiO_3) of other oxides, which impart variations in the electrical characteristics of the capacitor. These "dopants" primarily alter the temperature stability of the dielectric constant and flatten out the curve shown in Figure 3 [1].

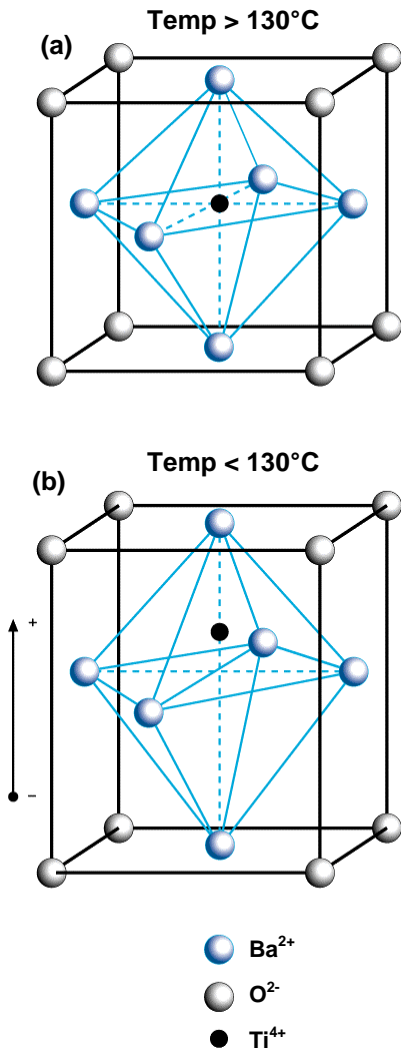


Figure 2

The Importance of Particle Size

While chemical composition is primarily responsible for electrical performance, particle size plays a critical role as well, having significant effects on the physical construction, processing, and electrical performance of a MLCC. In terms of construction, a powder with a very narrow particle size distribution is required so that each layer of the capacitor contains similar numbers of particles. Figure 4 is an image of a single ~1.5 μm layer. The presence of

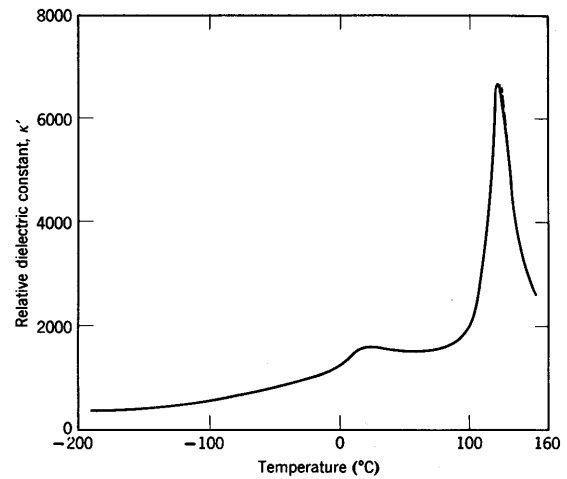


Figure 3

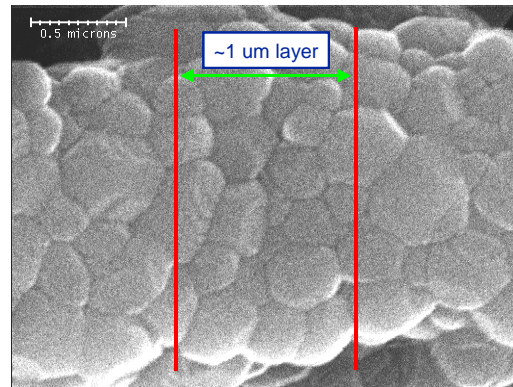


Figure 4

large particles (of only ~1-2 μm!) in such a layer can severely affect the voltage breakdown strength and reliability of the entire capacitor. Among the steps involved in processing an MLCC are: mixing the BaTiO₃ with dopants, casting tape, laminating, and high temperature sintering. All of these steps can be affected by the particle size distribution of the powder. The final composition is a mixture whose optical properties are not well defined yet whose particle size must be known to a high degree of certainty. This can



present a challenge in itself. From the above, it should be apparent that the tails of the distribution are especially important. The problems with an unknown large particle population have already been discussed. Fine particles,

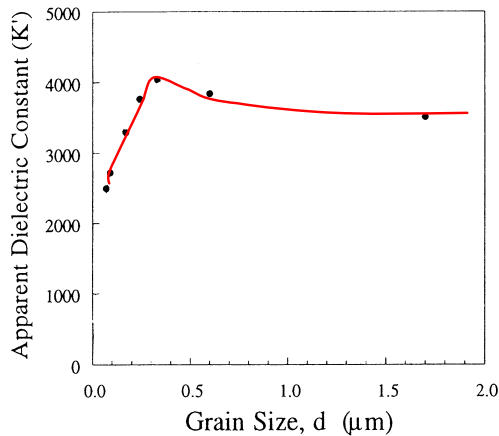


Figure 5

less than ~100 nm for example, are also important in processing. A distribution that contains too many fines will be very sensitive to firing conditions. Sintering rate is related to particle radius, r , as follows [1]:

$$\text{Rate} \propto r^{-2/3}$$

Therefore, fine particles sinter faster and are more reactive, causing excessive shrinkage, grain growth and formation of unwanted phases. This can also cause shrinkage mismatch issues with the metal electrodes. Particle size also affects electrical performance. The structural change from cubic to tetragonal discussed previously generates internal stresses that are relieved through the formation of domains within each particle where the dipoles (elongated unit cells) are aligned in the same direction. At a particle size of ~1 μm, domain formation becomes less energetically favorable so the stress can no longer be relieved. A stressed particle will have a

higher dielectric constant than an unstressed one. Therefore, an increase in dielectric constant is observed as the particle size decreases. However, as shown in Figure 5 [2], a point is reached where the stresses are great enough to reduce the polarization of the unit cell. This effectively squeezes the unit cell to the point that it reverts back to its cubic symmetry, lowering the dielectric constant once again. Clearly, since the window of optimal particle size is quite small for this material, careful monitoring and control of the fine end of the particle size distribution is required.

Measurement Example

Measurements were made of the two primary constituents that make up a typical dielectric powder using the Horiba LA-950 particle size analyzer. The semi-deagglomerated BaTiO₃ powder is mixed with a dopant formulation to create the final product. An example of the particle size distributions of the two components as well as the final product is shown in Figure 6. The formulation process involves both mixing and deagglomeration. The analyses show that the BaTiO₃ is highly agglomerated prior to mixing but is well dispersed after the formulation is completely mixed.

Conclusion

Knowledge of the particle size of electronic ceramic materials such as BaTiO₃ and associated formulations is critical. The construction and reliable performance of the electronic components made from them depends on accurate information about the particle size distribution.

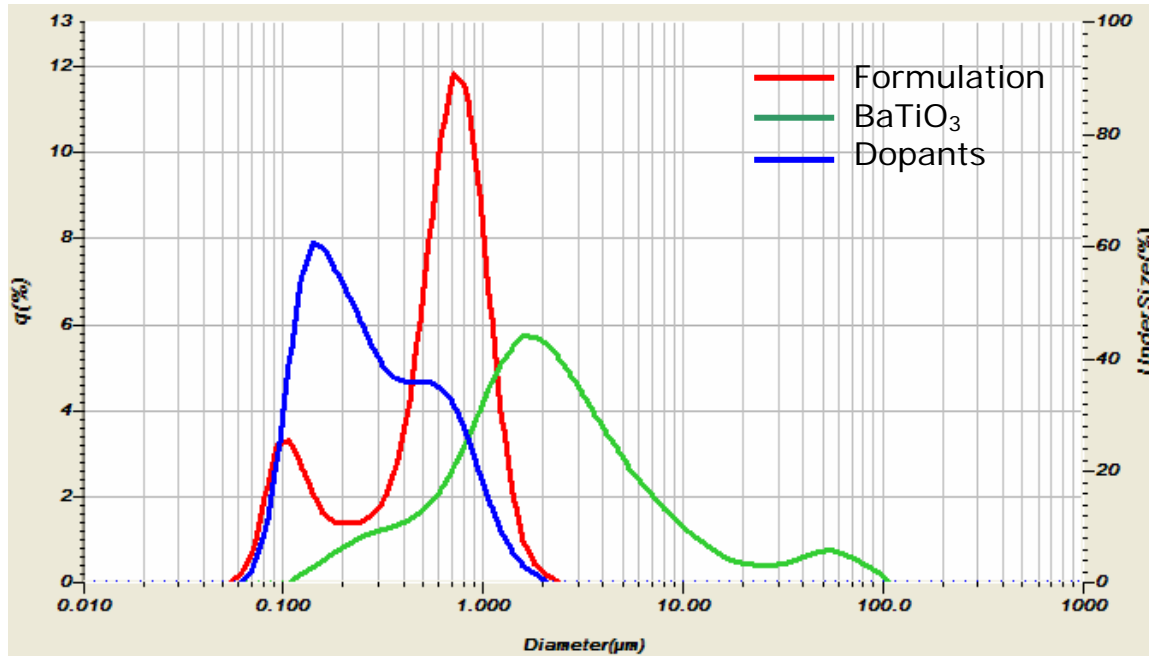


Figure 6

References

- (1) W.D. Kingery et al., *Introduction to Ceramics, 2nd Edition*, 1976, John Wiley & Sons
- (2) M. H. Frey, et al., *Ferroelectrics* (1998), 206-207(1-4/1-2), 337-353.

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