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The workhorse dielectric for multilayer ceramic capacitors is barium titanate, which was originally considered for capacitors nearly 50 years ago.

Technically creative people must ask "Isn't there another, better material"? KEMET has been active in the search for non-barium titanate capacitor dielectrics with enhanced properties. One, a lead niobate Z5U dielectric, has been in commercial use by KEMET for several years. Another, using a different crystal structure, is currently under development.

The following article by Dr. Koripella, who is active in KEMET dielectric research, provides a summary of these innovative technologies.

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Dielectrics Beyond Barium Titanate

by Dr. C. R. Koripella

Barium titanate ($BaTiO_3$) is currently the most widely used dielectric material in ceramic capacitors. However, to improve the performance and cost-effectiveness of multilayer ceramic capacitors, alternatives to barium titanate are being sought. This paper describes KEMET's research into new dielectric materials, first by reviewing the function of dielectrics and then by discussing two structures suitable for dielectric materials.

The Function of Dielectrics

In its simplest form, a parallel-plate capacitor consists of two metal electrodes separated by a dielectric material. The dielectric is the insulator that prevents electrons from jumping across the plates. To be useful as a dielectric, the material must be an insulator, and should have a high dielectric constant and low dielectric loss.

Some materials, because their unique crystal structure creates permanent dipoles, are easily polarizable. Polarization causes an increase in the charge density on a capacitor. The materials in which the direction of polarization can be changed by applied voltage are called ferroelectric. The ratio of the charge density in a capacitor with a dielectric material between the two metal electrodes to that with vacuum between them is called the "relative dielectric constant.' Ferroelectric materials usually possess a high dielectric constant and are used as dielectric materials for ceramic capacitors.

Dielectric Materials of Ceramic Capacitors Perovkites

Most useful ferroelectric materials for ceramic capacitor applications have the perovskite structure. This is usually represented as ABO_3, where A and B are cations occupying specific sites in the structure. Barium titanate ($BaTiO_3$), the most widely used dielectric material for ceramic capacitors, belongs to this classification. Let's look at why $BaTiO_3$ such an effective dielectric.

$BaTiO_3$

Unmodified $BaTiO_3$ has a cubic perovskite structure and a Curie point of 1200C. As Figure 1 illustrates, above 1200°C $BaTiO_3$ has Ba^{2+} ions at the corners, O^{2-} at the center of the faces, and Ti^{4+} at the center of the cell. The smaller cations (Ti^{4+}) fill the octahedral holes (the B-sites), and the larger cations (Ba^{2+}) fill the dodecahedral holes (the A-sites).

But below 120°C, there is a slight but important shift in the ions. The central Ti^{4+} ions shift in one direction with respect to the corner Ba^{2+} ions, and the O^{2-} shift in the opposite direction. This movement separates the centers of positive and negative charges, creating a permanent electric dipole. As curve A of Figure 2 demonstrates, the temperature dependence of the dielectric constant of pure $BaTiO_3$ peaks at 20 and 120°C. With the application of chemical additives which shift and modify the dielectric properties, useful dielectrics are developed (see Figure 2, curve B).

$BaTiO_3$ dielectrics have many advantages. Their dielectric constant is relatively high, and their long history in processing has yielded a reasonably good understanding of the chemistry necessary to produce the desired electrical characteristics. The dielectric constant for $BaTiO_3$-based materials has been improved over time to produce K-10,000 Z5U, K-5,000 X7R for high-fire dielectrics, and K-7000 Z5U and K-3000 X7R for low-fire dielectrics.

Complex Perovskites

Complex perovskites were originally studied by Russian workers in the early 1960s. The primary advantages of these structures are higher dielectric constants and lower sintering temperatures, (which permits the use of lower-cost electrodes).

A complex perovskite is formed by replacing the Ba portion of $BaTiO_3$ crystal structure with Pb, and the Ti with a mixture of cations such as Mg, Fe, Nb, Zn to yield an average charge of four. Some complex perovskites are ferroelectrics with peak dielectric constants as high as 20,000 and sinter at temperatures below 1000°C. Thus, complex perovskites can be used in multilayer ceramic capacitors with silver palladium or even pure silver electrodes, reducing the cost of manufacture while increasing the dielectric constant.

Some complex perovskites based on lead magnesium niobate and lead iron niobate have been developed by KEMET for multilayer capacitor application (see References 1,2). One structure with a dielectric constant of 12,000 at a sintering temperature of 1000°C has been in large-scale production for more than five years. A second dielectric with an even lower sintering temperature is used successfully with pure silver electrodes.

Lead-based structures present some attractive alternatives to traditional dielectrics, but their control process is still a challenge because of the relative volatility of lead oxide.

Tungsten Bronze Structure Compounds

One alternative to the perovskite structure in ferroelectric applications is the use of the potassium tungsten bronze structure. Like perovskites, this structure contains oxygen octahedra, but they are linked in such a way that they create three types of openings, two of which contain an A^-ion. The B^-ions (typically niobium or tantalum) are inside the oxygen octahedra. One example of this class is lead metanibate ($PbNb_2O_6$) which has A-sites only 5/6 filled and presumably a random distribution among the six A- sites. Figure 3 depicts a two-dimensional view of the tungsten bronze structure seen from the top.

The dielectric compositions of interest in this class are based on modified lead metaniobate. In 1978 Corning developed a dielectric composition for ceramic capacitors with a dielectric constant of about 4000 with X7R characteristics and a sintering temperature range of 1200-1340°C (References, 3). A French group developed a composition based on a mixture of a tungsten bronze material and a complex perovskite; this material has a dielectric constant of 2000 with X7R characteristics and can be sintered at 1050°C (References, 4). KEMET has produced some experimental products with dielectric constants of 5000 and X7R characteristics at a sintering temperature of 1100°C.

Conclusions

To continuously improve the dielectrics used in ceramic capacitors, KEMET is actively researching the application of new dielectric materials to reach higher dielectric constants with lower sintering temperatures.

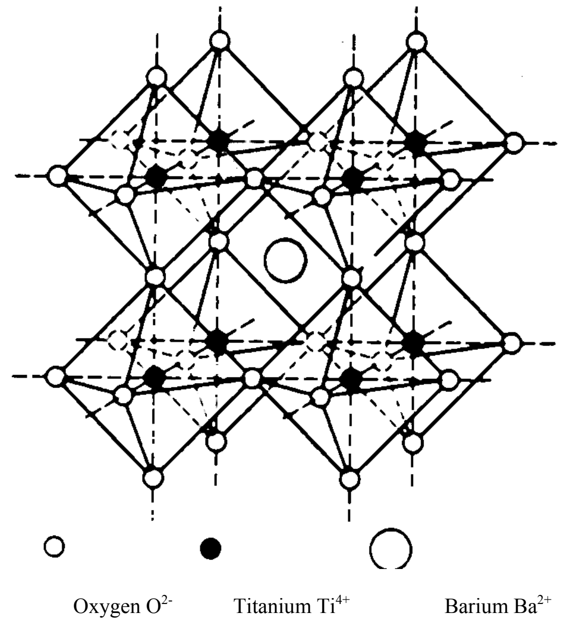

Figure 1. Cubic $BaTiO_3$. Ba on A-site. Ti on B-site.

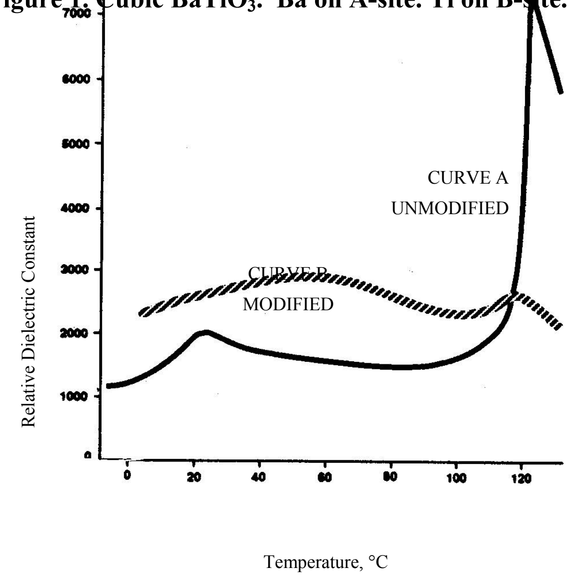

Figure 2. Relative dielectric constant of unmodified (Curve A) and modified (Curve B) $BaTiO_3$.

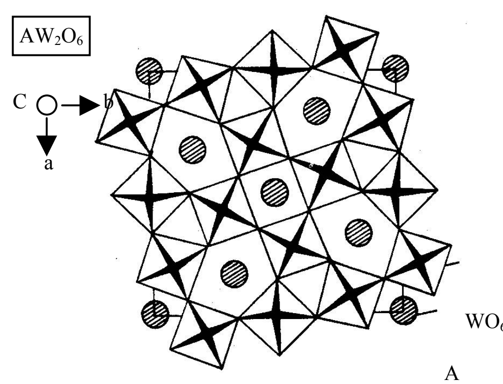

Figure 3. Tungsten Bronze Structure

References

1. KEMET U.S. Patent #4,550,088 (1985)
2. KEMET U.S. Patent #5,011,803 (1991)
3. Corning U.S. Patent #4,283,752 (1981)
4. A. Harve, J. M. Haussonne, G. Desgardin, *"American Ceramic Society,"* Annual Meeting 1990.