Phase Equilibria and Properties of Dielectric Ceramics

Ceramic compounds with exploitable dielectric properties are widely used in technical applications such as actuators, transducers, capacitors, and resonators or filters for microwave communications. Phase equilibria determination integrated with systematic chemistry–structure-property studies contribute toward the fundamental understanding and rational design of these technologically important materials with improved properties and/or reduced processing costs.

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Cost and performance are the primary and secondary drivers, respectively, for today's commercial needs in the area of dielectric ceramics. For example, component suppliers and builders of 2 GHz cellular infrastructure are critically impacted by the high cost of tantalum-containing ceramics needed for dielectric resonators: only a single ceramic material, perovskite-like $Ba_3ZnTa_2O_9$ (BZT), is available with the needed properties. Interest is keen to reduce its processing costs or to find an alternative, less-expensive substitute. The results of an experimental phase equilibria study of the system (Figure 1) revealed that BZT ceramics must be processed so that ZnO volatilization occurs along the two-phase join between BZT and $Ba_8ZnTa_6O_{24}$ (8L) to prevent the formation of deleterious air-sensitive compounds high in BaO content, or dielectrically poor "TTB" type phases.

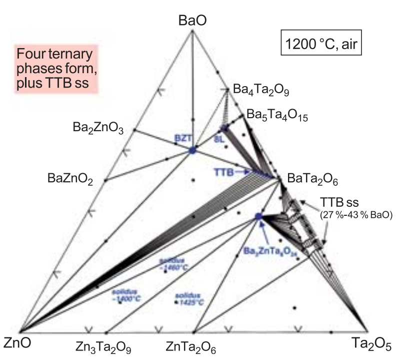

Figure 1: Phase equilibria diagram determined for the system containing the important commercial ceramic $Ba_3ZnTa_2O_9$ (BZT).

A potential replacement for BZT is the analogous compound with less costly niobium, $Ba_3ZnNb_2O_9$. The phase equilibrium diagram determined for this system (Figure 2) provides processing information for this ceramic and clearly indicates that its dielectric loss cannot be improved by liquid-phase sintering in the presence of low-melting, electrically acceptable $ZnNb_2O_6$, because the two compounds do not occur in equilibrium with each other. Such mixtures, instead, will form dielectrically poor impurity phases.

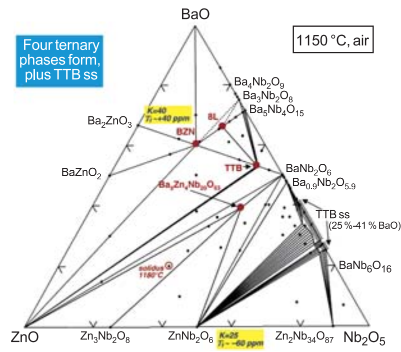

Figure 2: Phase equilibria diagram determined for the system containing $Ba_3ZnNb_2O_9$ (BZN), a possible BZT alternative.

Systematic studies of the $Ba_3MNb_{2-x}Sb_xO_9$ (M = Mg, Ni, Zn), system were carried out to manipulate the crystal chemistry and high-frequency (> 2 GHz) dielectric properties by progressive substitution of Sb^{5+} (d^{10}) for Nb^{5+} (d^0). The results showed that control of permittivity and tuning of the temperature coefficient to zero was possible with appropriate substitution. Optimal dielectric losses were obtained for specimens with low x-values and 2:1-type ordered perovskite structures.

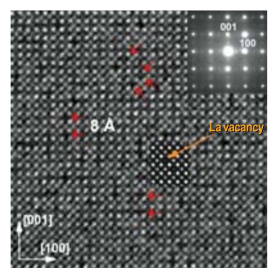

Figure 3: HRTEM image of 50:50 $LaMg_{1/2}Ti_{1/2}O_6$-$La_{2/3}TiO_3$. Dark crosses denote La vacancies, deduced from image simulations (insert). Short-range order of La vacancies is revealed as pairs of dark crosses in both the [001] and [100] directions and causes diffuse superlattice reflections in the diffraction pattern.

Detailed structural studies of the $LaMg_{1/2}Ti_{1/2}O_6$-$La_{2/3}TiO_3$ solid solution were carried out to elucidate the origin of the anomalous changes in permittivity and temperature coefficient near 50:50. The results showed that the abrupt changes in properties were accompanied by the disappearance of one octahedral tilting mode and the onset of short-range ordering of La vacancies.

Contributors and Collaborators

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