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. The commercial competitiveness of next-generation devices depends on new ceramics with improved properties and/or reduced processing costs. Phase equilibria determination integrated with systematic experimental/theoretical chemistry–structure–property studies contributes toward the fundamental understanding and rational design of these technologically important materials.

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Next-generation ceramic packaging requires fabrication of multilayered structures that include embedded functional dielectric ceramics. Technical challenges include understanding and control of deleterious reactions at interfaces during firing. A detailed study of the system Ag-Bi_2O_3-Nb_2O_5-O_2 is in progress to develop a model of interfacial interactions applicable to other co-fired metal–ceramic systems. A partial phase diagram of the system has been determined, and includes a new compound, $Bi_5AgNb_4O_{18}$, which is also observed as a product in Ag/$BiNb_5O_{15}$ reaction couples. Surface diffusion was found to dominate mass transport of Ag at the reaction interface — this phenomenon could be important for co-firing metals with porous ceramics. Further modelling will incorporate kinetic aspects of interfacial reactions using equilibrium thermodynamics as a basis.

Important transducer/actuator materials include Pb-containing perovskite-type relaxor ferroelectrics. First-principles (FP) methods were successfully used to calculate the phonon frequencies for the prototype relaxor $PbMg_{1/3}Nb_{2/3}O_3$. In FP studies of $PbTiO_3$, the dipole moment generated by a nearest-neighbor Pb-O vacancy pair was calculated; the results demonstrate that local electric fields generated by defects strongly affect physical properties. Calculations were also performed for a Pb-free relaxor, $K_{1-x}Li_xTaO_3$. For small x, Li ions are displaced from centrosymmetric positions. The dominant mechanisms for Li hopping between off-centered positions and the resulting effects on the dielectric response were determined.

First-principles methods were also applied to the microwave dielectric system (1–x)$CaAl_{1/2}Nb_{1/2}O_3$–x$CaTiO_3$. The resulting model yields a dielectric constant that increases with increasing disorder, and increases nonlinearly with increasing x, in agreement with experiment.

Experimental studies of microwave ceramics include structural analyses (by x-ray and neutron powder diffraction) combined with dielectric property correlations of the technically important $Ba_3M^{2+}M^{5+}{}_2O_9$ (M^{2+} = Mg, Zn, Ni; M^{5+} = Nb, Ta) systems. In these systems, the M^{5+} cations tend to undergo a second-order Jahn–Teller distortion and hence shift from the centers of the [MO_6] octahedra — this effect occurs simultaneously with 2:1 B-site cation ordering. Both phenomena influence dielectric response. Modeling of the crystal structures using bond valence methods is in progress to understand the interplay between the distortion and dielectric behavior.

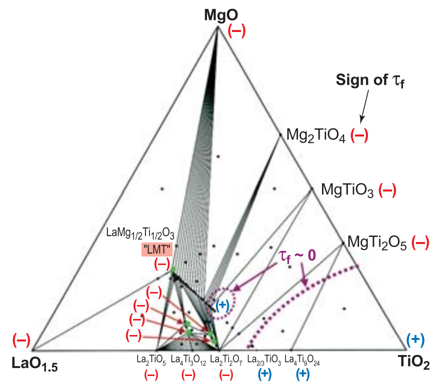

Figure 1: *Subsolidus phase relations in the La_2O_3–MgO–TiO_2 system (air, ≈1450 °C), sign of the temperature coefficient of resonant frequency (τ_f; in parentheses), and approximate locations of two regions of temperature-stable (τ_f = 0) equilibrium mixtures (dotted lines).*

Subsolidus phase equilibria, crystal chemistry, and dielectric behavior were studied for the La_2O_3–MgO–TiO_2 system and for the ternary sections $LaMg_{1/2}Ti_{1/2}O_3$–$CaTiO_3$–La_2O_3 and $LaMg_{1/2}Ti_{1/2}O_3$–$CaTiO_3$–$La_{2/3}TiO_3$. Six phases form in the La_2O_3–MgO–TiO_2 system, and extensive perovskite-type solid solutions form in both ternary sections (see Figure 1). By mapping dielectric properties (relative permittivity and temperature coefficient of resonant frequency, τ_f; 5–10 GHz) onto the phase diagrams, the compositions of temperature-stable (τ_f = 0) compounds and mixtures were predicted. From these studies, it was determined that the quaternary La_2O_3–CaO–MgO–TiO_2 system contains an extensive single-phase, perovskite-type volume through which passes a surface of temperature-stable compositions with relative permittivities in the range of 40 to 50.

Contributors and Collaborators

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