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XAS/XRD Study on Amphoteric Behavior of Lanthanide Dopants in BaTiO₃

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Barium titanate (BaTiO₃, BT) is the most extensively used perovskite dielectric ceramic material in the electronic industry. Its application includes multilayer ceramic capacitors (MLCs) traditionally made by covering BT with a layer of precious metal and firing. In order to reduce production costs, precious metal electrodes are replaced by base metal electrodes (BME) producing low-cost BME-MLCs and doped with trivalent rare-earth elements such as erbium (Er), holmium (Ho) and dysprosium (Dy) to improve the dielectric properties and lifetime of BME-MLCs. However, fundamental understanding of the role of the dopants is still lacking. Using a combination of XAS spectroscopy and XRD (conventional/high-resolution), we studied site substitution of 1 at.% of Er³⁺, Ho³⁺ and Dy³⁺ in BT ceramics as functions of Ba/Ti stoichiometry and firing conditions (oxidising and reducing), as well as the effect of doping on the structure and microstructure of BT. Our first results suggest that the Ho³⁺ incorporated into the BaTiO₃ lattice at the Ti⁴⁺ sites (Ho³⁺) are compensated by ionized vacancies in the oxygen sublattice (V^o); whereas Dy³⁺ can enter the BaTiO₃ lattice at the Ba²⁺ as well as the Ti⁴⁺ sites. XRD results showed the doped BT exhibit complete solid solubility over all compositions with a tetragonal structure. The findings of this study can help better understand different amphoteric behaviours of the three dopants, which is of great importance for capacitor fabrication.

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