

Lead-Free Oxides for Electrical Energy Storage

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Abstract: This work is part of ongoing international research into electrical energy storage, often referred to as the “missing link” of the energy transition. Indeed, as global electricity production is mainly based on fossil fuels that generate CO₂, which causes climate change, the energy transition currently underway around the world aims to promote “green growth” dominated by renewable energies such as wind and solar energy. However, although this new system is carbon-free, it remains at the mercy of the weather, as its energy production varies according to seasons, months, and days, with irregular and unstable efficiency. For these renewable energies to be considered completely reliable primary energy sources, it is necessary to have efficient systems for storing the electrical energy produced, enabling it to be transformed from instantaneous flow energy into available stored energy.

Dielectric capacitors are storage systems that have established themselves as one of the solutions to energy problems due to their advantages, such as environmental friendliness and very fast energy charging and discharging. The capacitor has an infinite lifespan: A Li-Ion battery lasts for 1000 to 3000 cycles, while a dielectric capacitor can undergo millions of charge/discharge cycles without losing its capacity. Finally, capacitors are much more resistant to high voltages and high temperatures than batteries or even supercapacitors, allowing them to operate in extreme temperature environments, such as vehicle engines.

The aim of this work is to contribute to the development of new lead-free oxides for the production of capacitors with high electrical energy storage capacity. Currently, capacitors based on the material PbZrTiO₃ (PZT) can store high energy densities, but this oxide contains lead. However, the European RoHS directive, in force since July 1, 2006, bans lead, which is a hazardous substance that must be replaced by other materials that are harmless to health and the environment. Accordingly, it is necessary to implement materials without these prohibited substances, and presenting low losses, high and stable dielectric permittivity in frequency and temperature. Among lead-free oxides, the perovskite material SrTiO₃ exhibits low dielectric losses, and its dielectric properties can be improved by substituting Sr²⁺ ions at the A sites with ions of the same valence. In particular, Sr_{1-x}Ca_xTiO₃ material with (0.30 ≤ x ≤ 0.40) presents a rich orthorhombic structural symmetry (Pbcm) evolution, responsible for antiferroelectric (AFE) behavior at room temperature. In this work, we present the dielectric and ferroelectric study of this material in the form of ceramics and thick films in this range of compositions in order to remain close to the possible antiferroelectric (AFE) phase, with the aim of maximizing the stored electrical energy densities and the energy efficiency of the material.

Keywords: Strontium calcium titanate, ceramics, thick films, dielectrics, energy storage capacitors