Dielectric properties of calcium and europium copper titanate ceramics prepared by a sol-gel method

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Calcium copper titanate is an inorganic compound with a chemical formula $CaCu_3Ti_4O_{12}$. It was first synthesized in 1967 by Alfred Deschanv and his colleagues, but it was not until 2000 that Mas Subramanian and his colleagues at DuPont Central discovered a dielectric permittivity in this material that was greater than 10 000 at room temperature. Since then, it has found a widespread use in various fields related to its dielectric properties [1, 2]. $CaCu_3Ti_4O_{12}$perovskite-type phase possesses promising dielectric properties; however, the giant permittivity phenomenon in this material has not been satisfactorily described yet. One of the positive factors could be the presence of secondary phases or substitution of calcium in a dodecahedral position by europium(II). This rare earth cation shows similar ionic radius and electronegativity but differs in valence shell configuration. Such a substitution has not been studied yet more detailed. We prepared a series with a composition of $CaCu_3Ti_4O_{12}$, $Eu_{0,4}Ca_{0,6}Cu_3Ti_4O_{12}$ and $EuCu_3Ti_4O_{12}$. A sol-gel method was used to synthetize precursors, followed by sintering in a temperature range of 1000 °C-1120 °C. Europium was substituted in full stoichiometry of Ca^{II} with the aim to observe whether i) Eu^{II} is stabilized in the perovskite structure and/or ii) possible secondary phases induced by the excess of Eu^{III}positively affect the dielectric characteristics. Samples were characterized by XPS, XRD and SEM. Influence of the microstructure and phase composition on the dielectric properties of the samples (in relation to the sintering temperature) is discussed. Secondary phases and microstructure played an important role in improving the permittivity values. The obtained values of permittivity measured at room temperature are giant up to higher frequencies but differ significantly for some compositions. We found out that the stoichiometric excess of europium in the fully substituted sample produces secondary phases that could be one of the reasons why dielectric characteristics of this sample were much better than those without europium substitution. The sample $EuCu_3Ti_4O_{12}$ pressed by isostatic pressing and sintered at 1120 °C showed a giant permittivity together with very low losses: ε = 20 874 and $tan\ \delta$ = 0.041 (at 10 kHz). These results confirm the published results describing a positive influence of secondary phases on the dielectric behavior.

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[2] Ahmadipour, M., M.F. Ain, and Z.A. Ahmad, A Short Review on Copper Calcium Titanate (CCTO) Electroceramic: Synthesis, Dielectric Properties, Film Deposition, and Sensing Application. Nano- Micro Letters, 2016. 8(4): p. 291-311.