

CaTiO₃:Eu powders: synthesis and morphology approaches

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Abstract - CT:Eu-HTMW powders with 0.5, 1.0 and 2.0% molar ratio of Eu³⁺ ions were synthesized by Microwave-Hydrothermal system and heated at 140°C for 10 min and characterized by powder X-ray diffraction (XRD), FE-SEM images and room temperature photoluminescence spectroscopy. These materials present the cubes-like morphology, so the spherical particles of the Eu₂O₃ are not observed, indicating that Ca²⁺ are substituted by Eu³⁺ in the CaTiO₃ lattice and no change is observed in the typical morphology of pure CT-HTMW compounds. The decay time of the Eu³⁺ ⁵D₀₋₇F₂ transition ($\lambda_{exc.}=394$, $\lambda_{em.}=614$ nm) fit one exponential curve and is similar for all samples, indicating that only one type of Eu³⁺ site is present in the CT framework.

Microwave assisted hydrothermal method is a potential technique for synthesize crystalline CaTiO₃:Eu powders being a genuine low temperature method, which allows high heating rates and short annealing times by reason of direct interaction from microwave radiation with the matter¹. The fast reaction is attributed to the microwave coupling of water bond for hydroxide complex cluster in an aqueous sheath, allowing like this an uniform heating of the whole solution². Rare-earth ions are used to dope perovskite-type oxides not only as a probe to investigate local centers and energy but also to provoke changes in the optical behavior or improve the capacitance response making possible to use these ceramics as high frequency ultrasonic transducers². Europium doped calcium titanate (CaTiO₃:Eu) micro-cubes-like powders were synthesized by hydrothermal microwave (HTMW) method with 0.5, 1.0 and 2.0% molar ratio of Eu³⁺ ions. These materials were characterized by powder X-ray diffraction (XRD), FE-SEM images and room temperature photoluminescence spectroscopy.

CT:Eu-HTMW powders were synthesized mixing TiCl₄, CaCl₂.2H₂O and Eu₂O₃ in H₂O, and mineralized by KOH solution (6.0M). This mixture was loaded in a Teflon autoclave, which was sealed and placed in the Microwave-Hydrothermal system and heated at 140°C for 10 min. Ca²⁺, Ti⁴⁺ and Eu³⁺ hydroxides lose their OH groups enabling them to interact between Ti (network former) and Ca (network modifier) leading to CT:Eu precipitation. Thus, this can be described as the reason for qualifying the HTMW method as a typical bottom-up process for perovskite ceramics. Even under milder conditions the water viscosity is still low, it is plausible to assume that the mobility of dissolved ions are higher under hydrothermal conditions than normal ones, taking into account the increase of effective collision crash rate, producing irreversible oriented attachments during the hydrothermal microwave path. CT-Eu³⁺ doped present the cubes-like morphology (Figure 1), so the spherical particles of the Eu₂O₃ are not observed, indicating that Ca²⁺ are substituted by Eu³⁺ in the CaTiO₃ lattice and no change is observed in the typical morphology of pure CT-HTMW compounds. The decay time of the Eu³⁺ ⁵D₀₋₇F₂ transition ($\lambda_{exc.}=394$, $\lambda_{em.}=614$ nm) fit one exponential curve (Figure 2) and is similar for all samples, indicating that only one type of Eu³⁺ site is present in the CT framework.

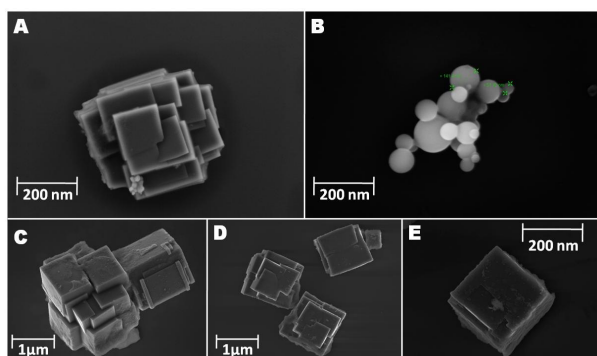


Figure1. FE-SEM micrograph of Ca_{1-x}Eu_xTiO₃ (x= 0.5, 1 and 2% molar ratio of Eu³⁺ ions) powders (A) CT-pure, (B) Eu₂O₃-pure, (C) CT:Eu (0.5%), (D) CT:Eu (1.0%) and (E) CT:Eu (2.0%).

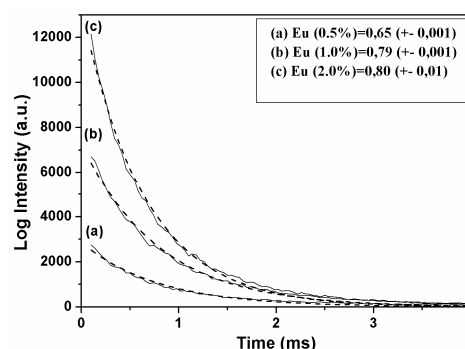


Figure2. Decay curve of the Eu³⁺ emission for the Ca_{1-x}Eu_xTiO₃-HTMW samples (x= 0.5, 1.0 and 2.0% molar ratio of Eu³⁺ ions) (a) CT:Eu (0.5%), (b) CT:Eu (1.0%) and (c) CT:Eu (2.0%). Dotted line show the fit to first exponential function.

References

- [1] Komaeni, S.; Roy, R.; Li, Q. H., Mater. Res. Bull. 1992, 27, 1303.
- [2] Suna, W.; Li, C.; Li, J.; Liu, W. Mater. Chem. Phys. 2006, 97, 481.
- [3] Dunbar, T. D.; Warren, W. L.; Tuttle, B. A.; Randall, C. A.; Tsur, Y. J. Phys. Chem. B. 2004, 108, 908.