

Abstract Submitted
for the MAR15 Meeting of
The American Physical Society

Investigation of Interactions between the Doped Rare Earth Ions and Encaged Radicals in C12A7:RE³⁺ Using Optical and EPR Spectroscopy CARTER LAYFIELD, LI MA, XIAO-JUN WANG, Georgia Southern Univ — Doped calcium aluminates (C12A7) (C12A7:Eu³⁺ and C12A7:Mn²⁺) have been prepared using solid state reaction methods. The Eu³⁺ and Mn²⁺ dopants can both occupy the Ca²⁺ positions in C12A7. The unique cage-like structure of C12A7 allows different anions, such as oxygen, hydrogen to be trapped in cage by modifying the sample preparation or treatment conditions. The effects of these encaged anions/radicals on the local symmetries of Ca²⁺ have been studied using photoluminescence from C12A7 doped with Eu³⁺, which is a sensitive environmental probe. The effects can also be independently observed from the hyperfine structure of electron paramagnetic resonance spectra in C12A7 doped with Mn²⁺. Our results showed: 1) the presence of 5D₀ to 7F₀ transition implies that Eu³⁺ is at a non-centrosymmetric site in all caged radical centers; 2) this singlet transition is doubled when superoxides are encaged in C12A7, indicating that the sites of calcium (or Eu²⁺) ions are not identical due to the distortion of the encaged anions; 3) a blue shift of the transition occurred due to nephelauxetic effects in asymmetry sites. We have also observed double sets of EPR signals of sextet hyperfine splitting for Mn²⁺ in C12A7-O but single sets in C12A7-H. We conclude that the local symmetry around Ca²⁺ positions are distorted more when superoxide is encaged in C12A7. Finally, RE³⁺ doped C12A7 samples have been systematically prepared and the interactions between the encaged ions and RE³⁺ emission centers studied using EPR spectroscopy.

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Date submitted: 14 Nov 2014

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