

Quantitative Site Occupancy Determination of Multi-Rare-Earth Elements Doped in Ca_2SnO_4 Phosphor by Electron Channeling Microanalysis

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Various types of phosphors have been synthesized by doping rare-earth activators to the host materials. To obtain efficient luminescence from the synthesized phosphor it is important to control on which atomic site and how much the doped rare-earth elements occupy. At the same time it is also crucial to make sure whether the doped impurities substitute the correct site as designed. Diffraction techniques (X-ray and/or neutron) with Rietveld analysis have been usually applied for those purposes, though they do not sometimes work well when the scattering powers of the host elements and impurities are not different from each other.

X-ray fluorescence analysis based on electron channeling effects in transmission electron microscopy (TEM) has been called ALCHEMI (Atom Location by Channeling Electron Microanalysis) [1], that provides direct information on which host element site an impurity element occupies. We extended the ALCHEMI method in twofold: (i) electron energy-loss spectroscopy (EELS) associated with TEM was employed to obtain site-selective chemical state analysis, by combining the many-beam dynamical electron scattering theory with the first principles electronic state calculations [2]; (ii) the statistical analysis technique of the original ALCHEMI [3,4] applied to the case containing two kinds of impurities.

The newly developed method above applied to a Ca_2SnO_4 phosphor material (Fig. 1) with $\text{Eu}^{3+}/\text{Y}^{3+}$ doped by various contents ($\text{Ca}_{2-x}\text{Eu}_x\text{Sn}_{1-y}\text{Y}_y\text{O}_4$ ((x, y) = (0.2, 0.0), (0.2, 0.2), (0.5, 0.5)), which shows photoluminescence (PL) at 616 nm ($\text{Eu}^{3+} \ ^5\text{D}_0 \rightarrow \ ^7\text{F}_2$ electric dipole transition). PL intensity plotted as a function of dopant concentration exhibits a maximum at a composition of $\text{Ca}_{1.8}\text{Eu}_{0.2}\text{Sn}_{0.8}\text{Y}_{0.2}\text{O}_4$, as shown in Fig. 2. It was found by XRD-Rietveld analysis [5] that in the Eu^{3+} single doped sample the dopant equally occupied the Ca^{2+} and Sn^{4+} sites, while in the co-doped samples Eu^{3+} occupied the Ca^{2+} site and Y^{3+} the Sn^{4+} site. Since the Ca^{2+} site is coordinated by seven oxygen atoms, the asymmetric configuration around which may be an origin of the stronger PL intensities.

The present statistical ALCHEMI revealed that in the co-doped samples Eu^{3+} and Y^{3+} occupied the Ca^{2+} and Sn^{4+} sites approximately by the fractions of 7:3 and 3:7, respectively, which still kept the charge neutrality condition, irrespective of the dopant concentration, as shown in Table 1. EELS of the dopant elements revealed no change in the nominal valency or fine structures for any samples, while the K-shell absorption edge of oxygen showed a distinct broadening of the fine structure at the composition of $\text{Ca}_{1.5}\text{Eu}_{0.5}\text{Sn}_{0.5}\text{Y}_{0.5}\text{O}_4$, as shown in Fig. 3. This suggests local lattice distortions around oxygen, which may reduce the PL intensity.

References

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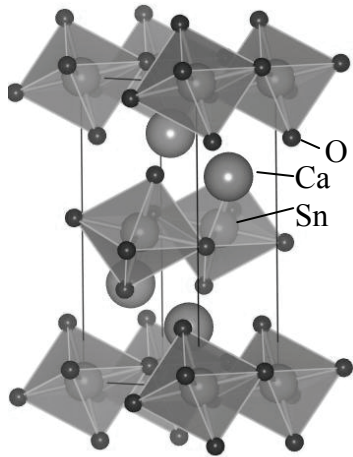


FIG. 1. Structure of Ca₂SnO₄.

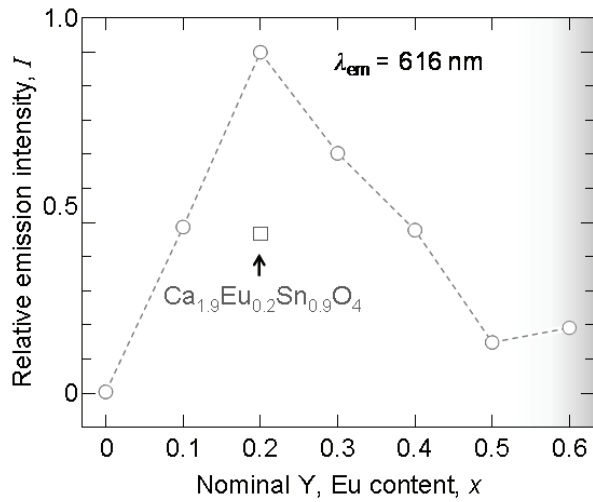


FIG. 2 PL intensity as a function of dopant conc.

TABLE 1 Evaluated compositions of the samples, in which Ca_{2-x}Eu_xSn_{1-y}Y_yO₄ with (x, y) = (0.2, 0.0), (0.2, 0.2), (0.5, 0.5) are respectively referred to as Eu20, Eu20Y20 and Eu50Y50.

Site	Element	Ca ₂ SnO ₄	Eu20	Eu20Y20	Eu50Y50
Ca site	Ca	2.00	1.89±0.01	1.77±0.04	1.46±0.04
	Eu	0.00	0.11±0.01	0.15±0.02	0.36±0.02
	Y	0.00	0.00±0.00	0.08±0.02	0.18±0.02
Sn site	Sn	1.00	0.91±0.01	0.83±0.04	0.54±0.04
	Eu	0.00	0.09±0.01	0.05±0.02	0.14±0.02
	Y	0.00	0.00±0.00	0.12±0.02	0.32±0.02

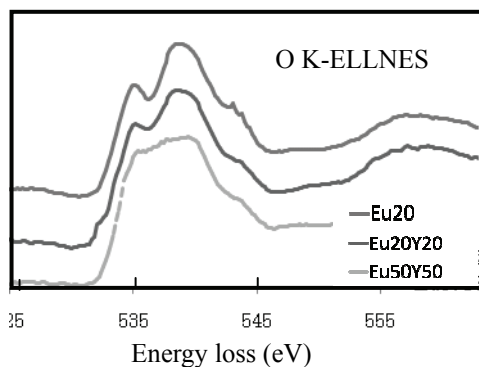


FIG. 3 Oxygen K-ELNES of the samples. Each spectrum is shifted vertically for better visibility.