Supplementary Information

 $Sr_{2.975-x}Ba_xCe_{0.025}AIO_4F$: A highly efficient green-emitting oxyfluoride phosphor for solid state white lighting

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Photoluminescence quantum efficiency (PLQE) in solid samples was determined using a setup described in Ref. S1 and experimental procedures adjusted for opaque and scattering samples. The samples were deposited on transparent quartz substrates (Chemglass) with dimensions of $\sim 12 \times 12$ mm. Powders were encapsulated into silicone resin (GE Silicones, RTV615). Both substrates and encapsulant do not exhibit a noticeable absorption at emission and excitation wavelengths used in the experiments. The samples were placed into a spectralon-coated integrating sphere (6 inch diameter, Labsphere) at the angle slightly different from normal incidence to avoid back reflection of the laser beam. The sphere's output port was screened from the sample by a baffle. The luminescence was collected by a large numerical aperture lens and directed onto a calibrated silicon photodiode (Newport UV818). The output of the detector was fed into a transimpedance input of a lock-in amplifier (SRS SR810). Bandpass and long-wavelength pass filters were introduced in front of the detector in order to separate excitation



Figure S1. Schematic diagram of quantum efficiency measurement in the study.

light and photoluminescence. Use of interference filters allowed to completely avoid problems

related to the filter's autofluorescence typical for Schott glass filters. Excitation laser beam was modulated by a chopper (SRS SR540), which also provided a reference signal for the lock-in amplifier. Use of the lock-in detection technique made the setup insensitive to the ambient light. Ar⁺-laser (Spectraphysics Beamlock 2065) was used for generation of light with wavelength of 457 nm and 407 nm light was produced by a compact solid state laser (Crystalaser). The laser power used in experiments was about 1-2 mW.

Determination of PLQE relies on the measurements of number of photons absorbed and emitted by the sample. First, a response of the empty sphere (X_{las}) is measured without any filters in the detection channel. In this measurement, an empty sample holder is inserted into the sphere to account for the losses induced by contaminants. Blank substrates with a drop of the pristine encapsulant proved not to affect the reading (i.e., they do not absorb the laser light). Then a bandpass filter ($\Delta\lambda \sim 10$ nm) is installed in front of the detector and response of the system is measured again (X_f). This enables us to find an exact value of the filter transmission at the laser wavelength ($T_{las} = X_f / X_{las}$). Then a sample is mounted into the sphere with the laser beam hitting the material studied. The corresponding lock-in amplifier reading is recorded (X_s^{las}). These measurements enable one to determine the number of photons absorbed by the sample (absorption of light by other components inside the sphere is considered to be negligible):

$$N_{abs} = A(X_{las} - X_S^{las} / T_{las}) \tag{1}$$

where *A* is the components-dependent calibration coefficient (see the discussion below). Then the bandpass filter was replaced with a long wavelength-pass filter with cut-on wavelength about 20 nm longer than the laser emission line. Interference filters by Omega Optical (3rd Gen and ALP series interference filters) provide OD5 suppression of the laser light and high transmission at the photoluminescence wavelengths, and are autofluorescence-free. The corresponding lock-in amplifier reading is then recorded (X_s^{PL}). The number of PL photons emitted is given by the expression

$$N_{em} = B X_S^{PL} \tag{2}$$

Here, B is another instrument-dependent parameter. Thus, PLQE can be determined as:

$$PLQE = \frac{X_{S}^{PL}}{(X_{las} - X_{S}^{las} / T_{las})} \frac{B}{A} = \frac{X_{S}^{PL}}{(X_{las} - X_{S}^{las} / T_{las})} \frac{1}{K}$$
(3)

Correction factor K which incorporates parameters A and B is identical to that introduced in the Ref. S1 and accounts for the variation of detector's sensitivity, sphere's and optics response, as well as the long wavelength-pass filter transmission as a function of wavelength. It's trivial to demonstrate that

$$K = \frac{\int I(\lambda)Q(\lambda)S(\lambda)T(\lambda)d\lambda}{Q(\lambda_{las})S(\lambda_{las})\int I(\lambda)d\lambda}$$
(4)

where $Q(\lambda)$ is the detector quantum efficiency, $S(\lambda)$ – sphere and optics response function, $T(\lambda)$ – long wavelength-pass filter transmission as a function of wavelength. $I(\lambda)$ – is the photoluminescence spectrum of the material studied which can be acquired on a fluorimeter. λ_{las} is the excitation laser wavelength. Detector's quantum efficiency was taken from the calibration certificate provided by the vendor. Filter's transmission was measured on a UV-Vis spectrophotometer (Shimadzu UV-2401PC). Integrating sphere's and optics response function was determined using a home-built tunable light source comprised of 300W Xe lamp (Oriel), monochromator (Newport Cornerstone), and optical fiber light delivery system (Oriel). First, the power output of the tunable light source was measured directly using the calibrated detector. Then the power spectrum was measured again by injecting the light from the fiber into the sphere and placing the photodiode in the position used for PLQE determination. An IgorPro applet was developed to calculate *K* rapidly in the daily work.

Calibration of the setup was verified using liquid reference samples placed into a 1mm thick quartz cell emulating a film. Fluorescein and Rhodamine B were used as reference materials. PLQE values in reference samples matched the literature values [S2] with high accuracy (less than $\pm 2\%$ error). Since the liquid samples are non-scattering we used both original protocol from Ref. S1 and the one described above. Both methods produced nearly identical results. We have measured commercial YAG:Ce³⁺ phosphors encapsulated into the silicone resin in order to evaluate the system performance with opaque and scattering samples. The data obtained are similar to those reported by the manufacturer (less than $\pm 5\%$ error). However, in order to achieve high accuracy, the sample's absorption coefficient at the laser wavelength must be at least 10 % and PLQE should be at least 10% as well. For poorly absorbing and dim samples the error of PLQE determination can be significant. In the samples studied in this work, absorption coefficient was greater than 10% and PLQE was quite high as well, so the anticipated error is about $\pm 5\%$. Samples degradation may be an additional source of error.

Reference

[S1] Greenham, N. C.; Samuel, I. D. W.; Hayes, G. R.; Phillips, R. T.; Kessener, Y. A. R. R.; Moratti, S. C.; Holmes, A. B.; Friend, R. H. *Chem. Phys. Lett.* **1995**, *241*, 89.
[S2] Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 2nd edition; Kluwer Academic: New York, 1999.