

Engineering Oxygen Vacancies towards Self-Activated BaLuAl_xZn_{4-x}O_{7-(1-x)/2} Photoluminescent Materials: An Experimental and Theoretical Analysis

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Supporting Information

Details of DFT calculation and level of theory:

The full potential linearized augmented plane wave (FPLAPW) method [1] is a procedure for solving the Kohn-Sham equations for the ground state density, total energy, and (Kohn-Sham) eigenvalues of a many-electron system by using a basis set. In FPLAPW method we divide the unit cell into (I) non-overlapping atomic spheres (centered at the atomic sites) and (II)

an interstitial region. In the interstitial region a plane wave expansion is used $\Phi_{k_n} = \frac{1}{\sqrt{\Omega}} e^{ik_n \cdot r}$

$$; \quad \text{with } k_n = \kappa + K_n \quad (1)$$

where κ is the wave vector in the Brillouin zone (BZ), K_n is a reciprocal lattice vectors and Ω is the volume of the unit cell. Each plane wave is augmented by an atomic-like function in every atomic sphere. Inside each atomic sphere, the solutions for a spherically symmetric potential are the atomic basis functions which consist of radial functions, $u_l(r, E)$, multiplied by spherical harmonics.

For typical valence states with azimuthal quantum number l , the radial function is regular at the origin and varies with energy. This energy dependence is linearized by selecting an expansion energy E_l , near the center of the band and writing the atomic function as:

$$\Phi_{k_n} = \sum_{lm} [A_{lm, k_n} u_l(r, E_l) + B_{lm, k_n} u_l'(r, E_l)] Y_{lm}(\hat{r}) \quad (2)$$

where u_l is solution of the radial Schrödinger equation and u_l' is its energy derivative. For each atom and lm there are two free coefficients, A_{lm} and B_{lm} , which are chosen such that (at the sphere boundary) the plane wave with wave vector, k_n , joins continuously on to the atomic function value and slope.

These linearized augmented plane waves (LAPW's) form the basis for expanding the crystalline orbitals (Bloch states) and provide a rapidly converging series.

$$\Psi_{\kappa} = \sum_n C_n \Phi_{k_n} \quad (3)$$

All low lying core states are included as frozen core states (k independent but but calculated self-consistently by solving an atomic Dirac equation.

Sometimes it is necessary to extend the LAPW basis set with so called local orbitals (LO's)[2]. With such an extension, higher-level semi-core states can be treated, together with the valence states, in one LAPW calculation instead of two (valence and semi-core states) energy windows. This LO scheme avoids the problem of non-orthogonality that can occur in calculations in which the semi-core states are either frozen or treated in separate energy window. A LO is chosen such that it vanishes in value and slope at the muffin-tin radius and includes an additional radial function, corresponding to a different principle quantum number:

$$\Phi_{lm}^{LO} = [A_{lm} u_l(r, E_{1,l}) + B_{lm} u_l(r, E_{1,l}) + C_{lm} u_l(r, E_{2,l})] Y_{lm}(\hat{r}). \quad (4)$$

The LO is then added to usual LAPW basis set in equation (3). The inclusion of LO's makes the computation of matrix elements somewhat more difficult but one has a better model and saves computational time, since no semi-core states need to be calculated in separate LAPW run.

In FP-LAPW method the potential and charge density are expanded (a) into lattice harmonics (inside each atomic sphere) and (b) as a Fourier series (in interstitial region) and thus they are completely general, so that the scheme is termed as full-potential calculation

$$\sum_{LM} V_{LM}(\hat{r}) Y_{LM}(\hat{r}) \quad \text{Inside sphere}$$

$$V(\hat{r}) =$$

$$\sum_K V_K \exp(i\mathbf{K} \cdot \mathbf{r}) \quad \text{Outside sphere} \quad (5)$$

In order to have few LM values in the lattice harmonics equation (5), a local coordinate system for each atom sphere is defined, according to the point symmetry of the corresponding atom. This specifies a rotation matrix that relates the local to the global coordinate system of the unit cell.

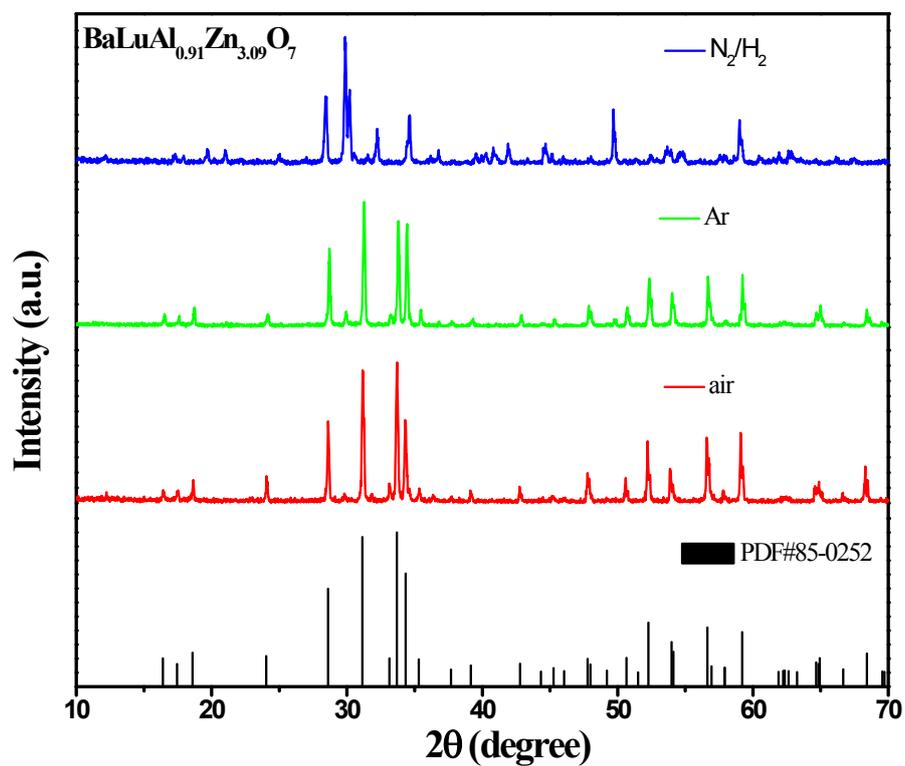


Fig. S1. XRD patterns of nominal $\text{BaLuAl}_{0.91}\text{Zn}_{3.09}\text{O}_7$ phase prepared at different atmosphere, and the standard pattern (PDF# 85-0252) of $\text{BaLuAl}_{0.91}\text{Zn}_{3.09}\text{O}_7$ is also given as a comparison.

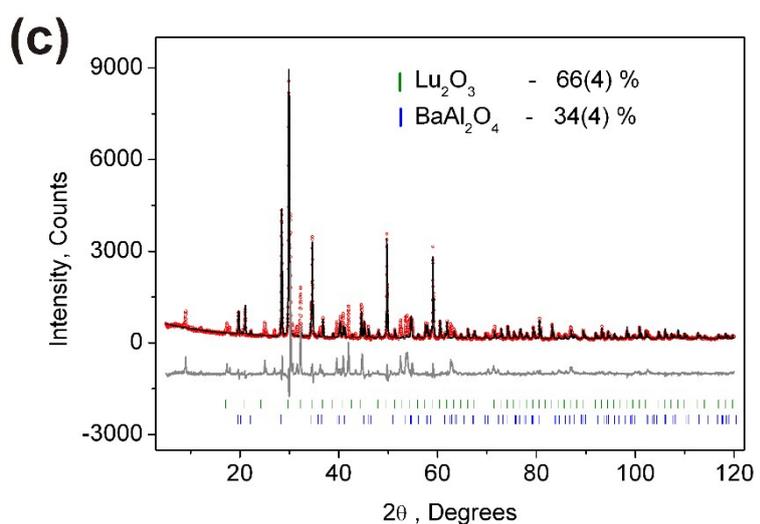
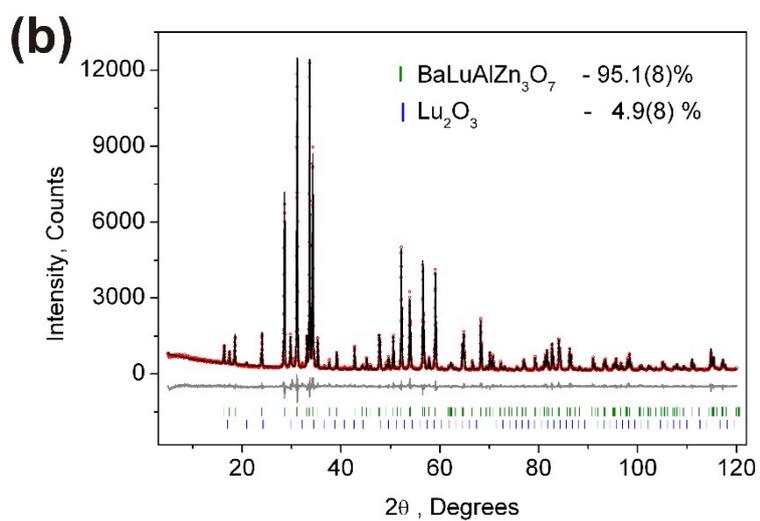
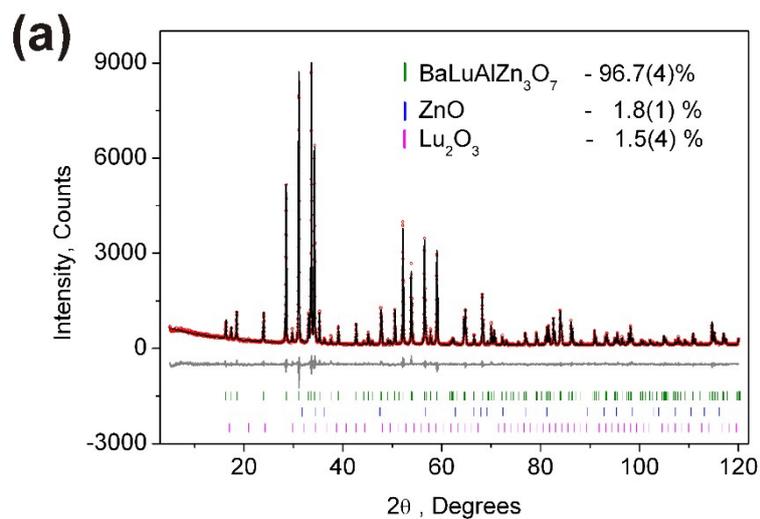


Fig. S2. Difference Rietveld plot BaLuAl_{0.91}Zn_{3.09}O₇ prepared in air (a), Ar (b), and N₂-H₂ (c) atmosphere.

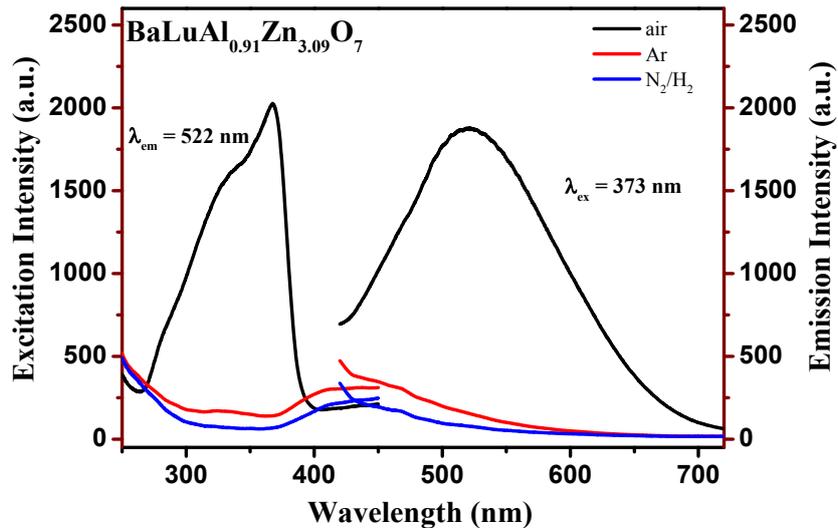


Fig. S3. Photoluminescence excitation (left) and emission (right) spectra of nominal $\text{BaLuAl}_{0.91}\text{Zn}_{3.09}\text{O}_7$ phase prepared at different atmosphere.

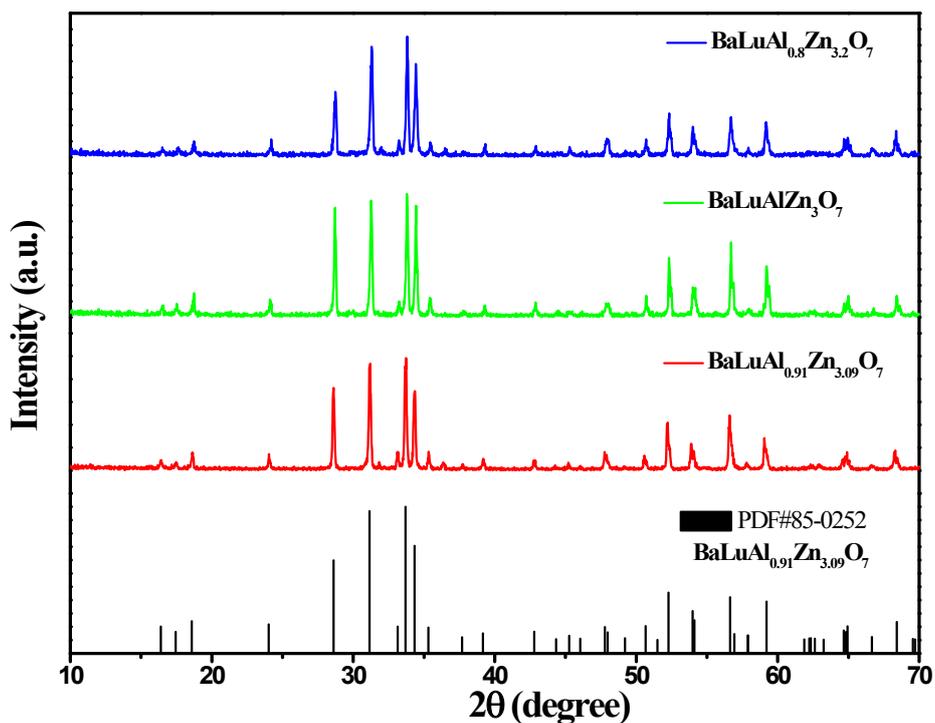


Fig. S4. XRD patterns of the $\text{BaLuAlZn}_3\text{O}_7$, $\text{BaLuAl}_{0.91}\text{Zn}_{3.09}\text{O}_7$ and $\text{BaLuAl}_{0.8}\text{Zn}_{3.2}\text{O}_7$ samples depending on different Al/Zn ratio.

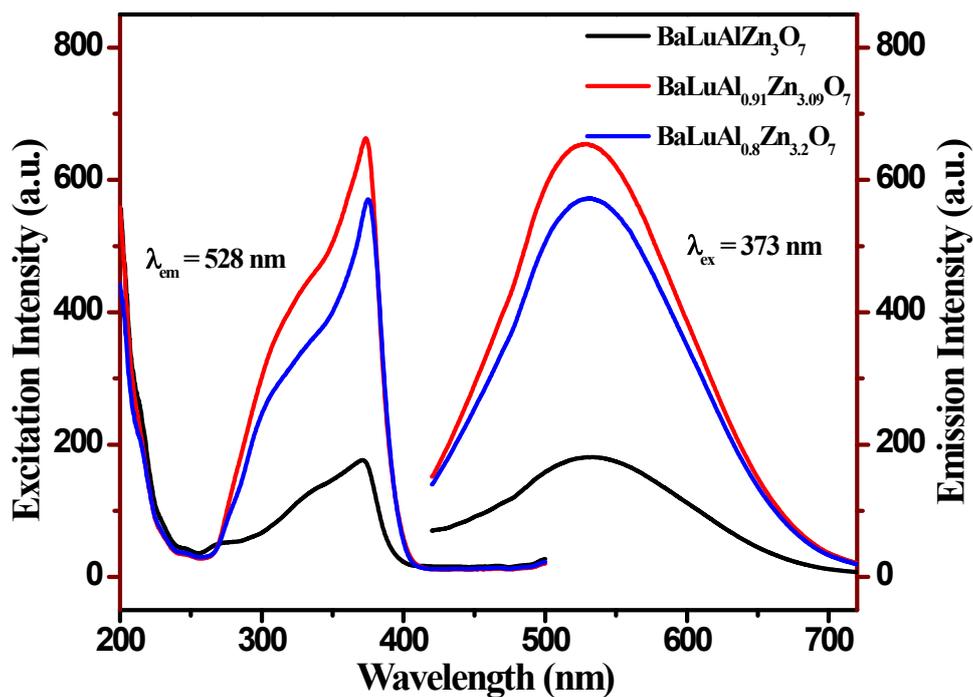


Fig. S5. Photoluminescence excitation (left) and emission (right) spectra of BaLu(Al,Zn)O₇ depending on different Al/Zn ratio, (a) Al/Zn = 1:3, (b) Al/Zn = 0.91/3.09, (c) Al/Zn = 0.8/3.2.

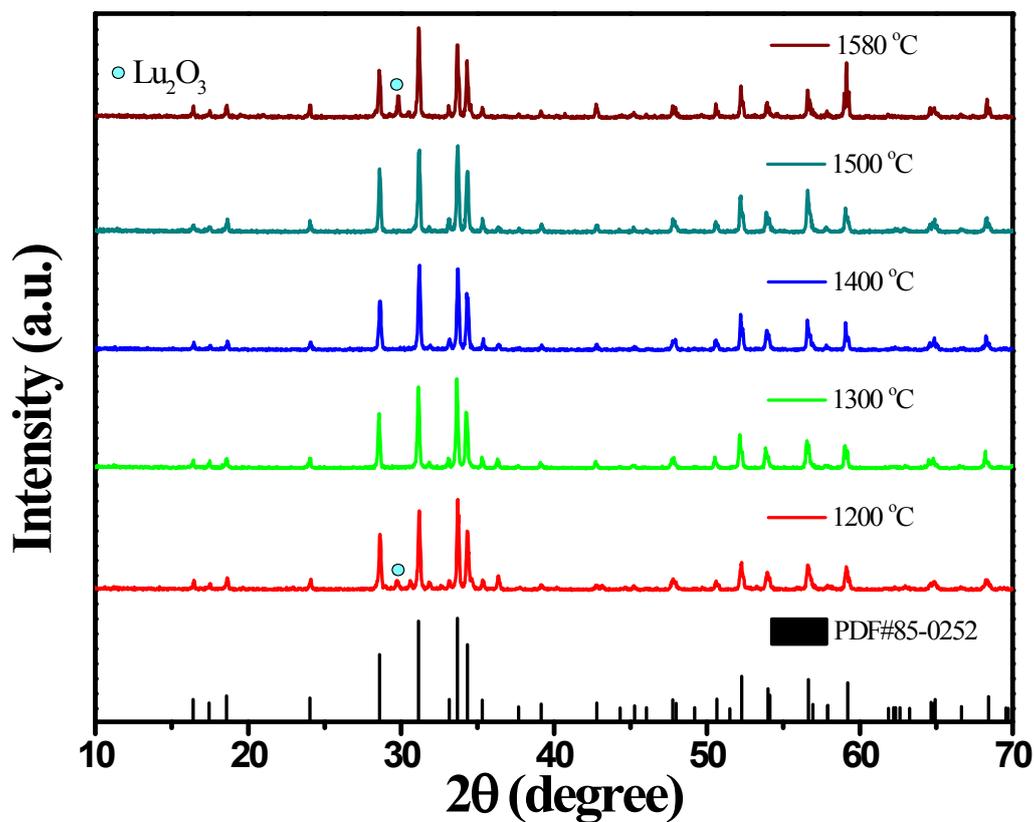


Fig. S6. XRD patterns of BaLuAl_{0.91}Zn_{3.09}O₇ phosphors prepared at different annealing temperatures.

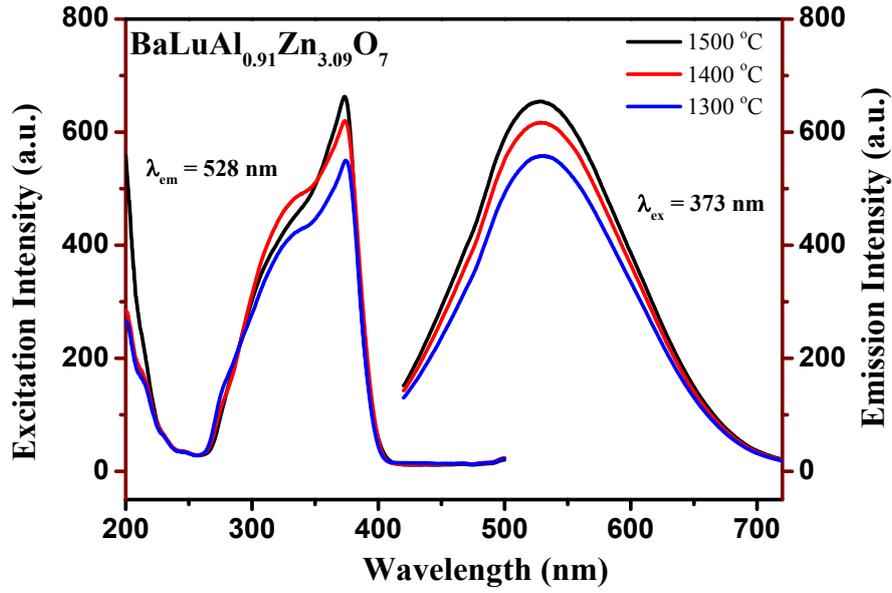


Fig. S7. Photoluminescence excitation (left) and emission (right) spectra of $\text{BaLuAl}_{0.91}\text{Zn}_{3.09}\text{O}_7$ phosphors prepared at different annealing temperatures.

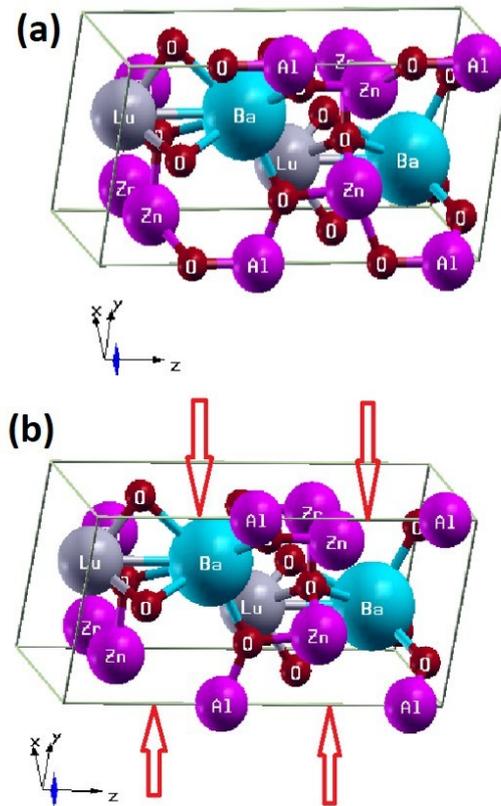


Fig. S8. Relaxed unit cells of (a) $\text{BaLuAl}_{0.91}\text{Zn}_{3.09}\text{O}_7$ and (b) that with two oxygen vacancies introduced at Q1 and O3 sites.

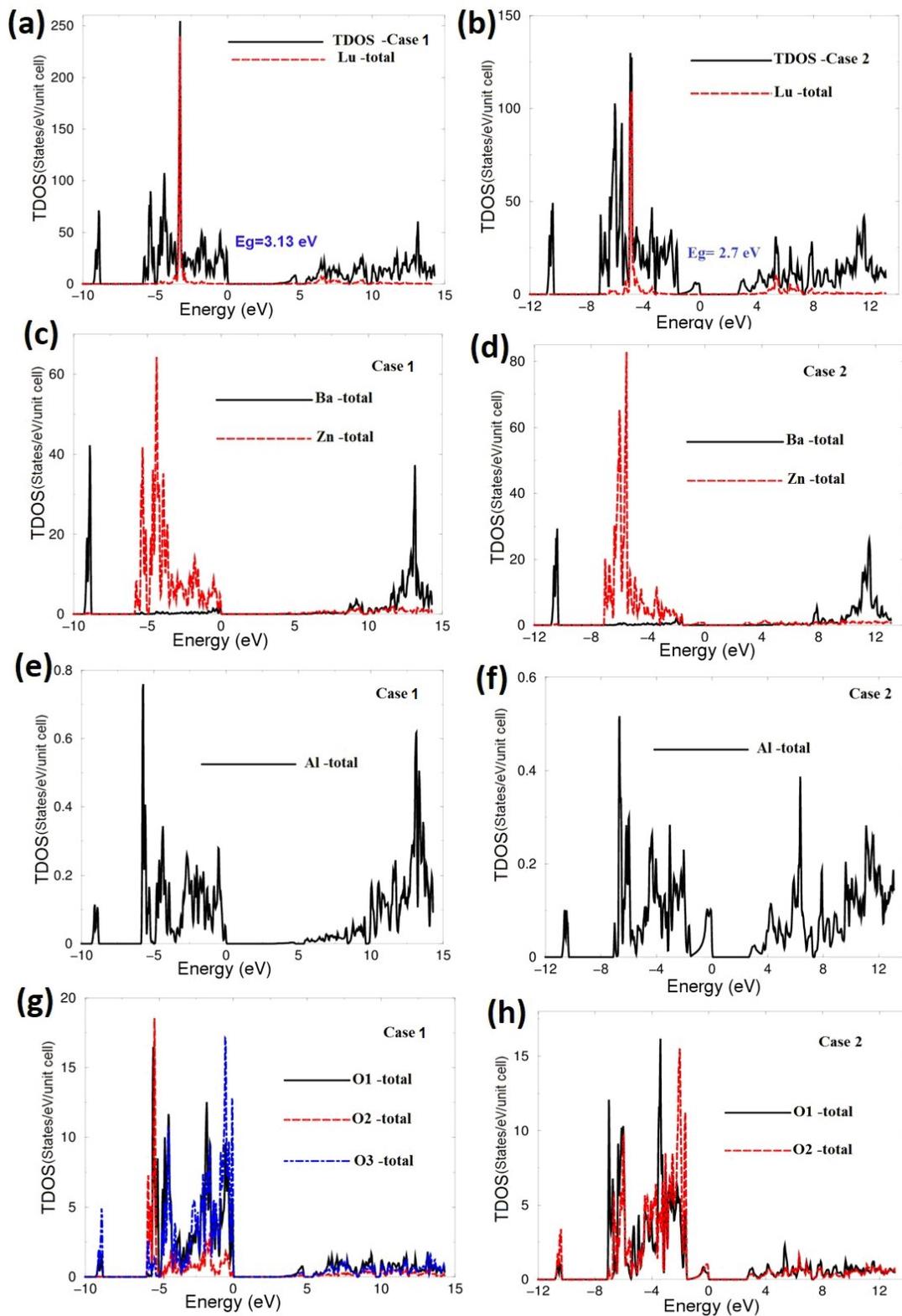


Fig. S9. Total DOS and partial DOS of constituted atoms for stoichiometric and defected $\text{BaLuAl}_{0.91}\text{Zn}_{3.09}\text{O}_7$ phosphor for different cases.

References

- [1] Blaha, P.; Schwarz, K.; Madsen, G. K. H.; Kvasnicka, D.; Luitz, J. WIEN2k, An augmented plane wave plus local orbitals program for calculating crystal properties, Vienna University of Technology, Austria (2001)
- [2] Sing D. J., Phys. Rev. B 43, 6388 (1991).