

## Green Approach to Green-Conversion Material and Green-Agriculture:

### Alkaline-Earth Metal Sulfide Phosphors

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#### S1 Absorption Spectra of Chlorophylls and Sunlight Spectrum

As shown in Fig. S1, the absorption spectra of chlorophylls concentrate in near UV-blue (400-470 nm) and red (620-700 nm) regions. However, compared with sunlight spectrum, the majority of the sunlight located at the range from 480 to 620 nm is wasted and unusable for photosynthesis.

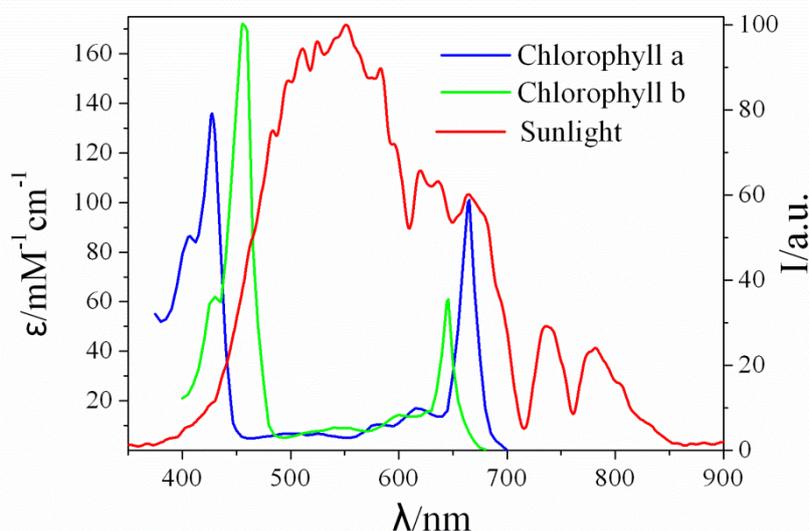


Figure S1 Comparison of absorption spectra of chlorophylls and sunlight spectrum

#### S2 Phase and composition identification of reaction between AEO (AE = Mg or Ba) and ZnS

The ionic radius of Mg<sup>2+</sup> (0.72 Å) is much smaller than that of Ca<sup>2+</sup> (0.99 Å) but

similar to that of  $\text{Zn}^{2+}$  (0.74 Å). The reference <sup>1</sup> suggested  $\text{Mg}^{2+}$  ions should replace  $\text{Zn}^{2+}$  rather than  $\text{Ca}^{2+}$  sites. On a hypothesis that  $\text{Mg}^{2+}$  was introduced into  $\text{Ca}^{2+}$  site, the shrunken AE-O bond could not maintain the intermediate state  $\text{Ca}_{1-m}\text{Mg}_m\text{ZnOS}:\text{Eu}^{2+}$  solid solution integrated so as to make it collapsed. As shown in Fig. S2a, the compositions of the samples are consistent with the above opinion. With low concentration,  $\text{Mg}^{2+}$  ions are introduced into  $\text{Zn}^{2+}$  sites, which is helpful to keep the oxysulfide stabilized. As a result, a CaZnOS phase is detective except for CaS ( $m \leq 0.2$ ). However, when the addition of  $\text{Mg}^{2+}$  is over 0.3, a residual amount of ZnS as well as MgO gradually increases because the decrease of calcium content leads to less oxysulfide in the initial stage in resulting of more unreacted reactants. Meanwhile, the yield of target product CaS shrinks for the same reason. Then, it can be speculated that it is nearly impossible to prepare (Ca,Mg)S-based solid solution materials by this IPTM method since  $\text{Mg}^{2+}$  ion is repulsive to  $\text{Ca}^{2+}$  site in the intermediate state.

With respect to Ba-contained solid solution, on one hand,  $\text{Ba}^{2+}$  (1.35 Å) is too big compared with  $\text{Ca}^{2+}$ . Only a slight amount of  $\text{Ba}^{2+}$  ions can be accommodated to an expansive structure of  $\text{Ca}_{1-k}\text{Ba}_k\text{ZnOS}$ . On the other hand, BaZnOS develops an orthorhombic crystal <sup>2</sup> on its own totally far from the hexagonal space group of CaZnOS <sup>3</sup>. Thermal expansion and decomposition of BaZnOS have not been studied, and obviously it is not easy to make it decomposed. By contrast, the introduction of  $\text{Ba}^{2+}$  improves the stability of CaZnOS. As displayed in Fig. S2c, except for CaS, a residual undecomposed CaZnOS phase is recorded when the addition content of Ba ( $k$ ) is only 0.02. Moreover, if  $k$  is over 0.2, the as-obtained samples appear gray and glassy. As a result, there is little prospect of synthesizing (Ca,Ba)S solid solutions through IPTM approach.

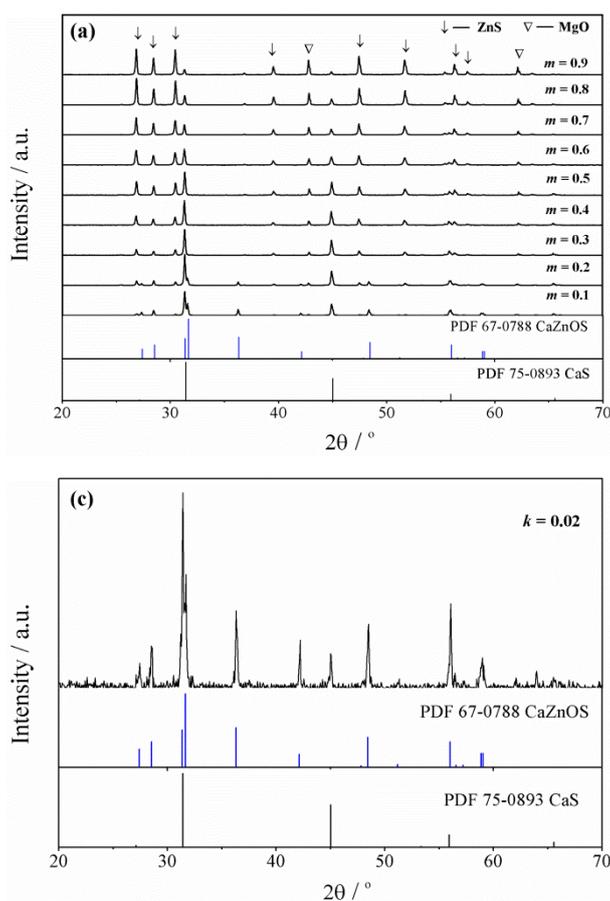


Figure S2 XRD patterns of  $\text{Ca}_{1-m}\text{Mg}_m\text{S}: 0.1\%\text{Eu}^{2+}$  (a) and  $\text{Ca}_{1-k}\text{Ba}_k\text{S}: 0.1\%\text{Eu}^{2+}$  (c) phosphors

### S3 Phase and composition identification of reaction between SrO and ZnS

To confirm the intermediate state in the course of solid solutions  $(\text{Ca,Sr})\text{S}$  via the IPTM method, we carried out a reaction between SrO and ZnS under 1000 °C. As a result, except for SrS, ZnO and a  $\text{SrSO}_4$  impurity, an unknown phase is observed belonging to nothing in the present inorganic crystal structure database. Meanwhile, the unknown phase is also detective in the solid solution sample with  $n = 0.9$ , just overall blue-shifted to higher  $2\theta$  values due to a smaller ionic radius of  $\text{Ca}^{2+}$  introduced in  $\text{Sr}^{2+}$  site in this situation. The XRD patterns of this unknown phase approximate but differ from the mixture of Sr- and Zn-contained oxides and sulfides, which coincides with the phenomenon of CaZnOS and BaZnOS in comparison with their respective cations-involved oxides and sulfides. Therefore, we believe that the recombination of  $\text{Sr}^{2+}$  and  $\text{S}^{2-}$  should also undergo a similar intermediate state of oxysulfide like CaZnOS.

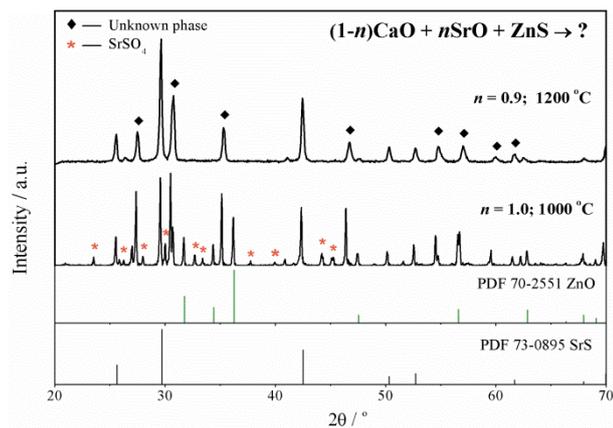


Figure S3 XRD patterns of Sr-rich samples

### Supplementary reference:

1. C. J. Duan; T. H. Hintzen; S. Rosler, *US Patent App.* 2011.
2. Z. A. G. Sarah Broadley, Furio Corà, Catherine F. Smura, and Simon J. Clarke, *Inorg. Chem.* 2005, **44** (24), 9092-9096.
3. C. F. S. Timothy Sambrook, and Simon J. Clarke, *Inorg. Chem.* 2007, **46** (7), 2571-2574.