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Hydrolysis Mechanism Analysis of (Ca, Sr)AlSiN₃:Eu²⁺ Red Phosphor Aged Under Pressure Cooker Test and 85°C&85%RH Test: Kinetics Modeling and First-principles Calculation

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Abstract

The (Ca, Sr)AlSiN₃:Eu²⁺ (CSASN:Eu) red phosphor is widely used to improve color rendering of high-power phosphor-converted lighting diode (pc-WLED), but it is always unstable under high temperature and high humidity environments. Therefore, the studies on the temperature and humidity resistance of red phosphors and their aging mechanism have become essential to evaluate its reliability in harsh applications. In this paper, the pressure cooker test (PCT) and 85°C&85%RH aging test were carried out for the CSASN:Eu red phosphors. And, its hydrolysis reaction-driven degradation mechanism was simulated and analyzed based on first-principle calculation, in which the optimized adsorption of simplified CaAlSiN₃(CASN) and H₂O was simulated based on Density Function Theory (DFT) and the specific aging process was analyzed by the charge density difference and ab initio molecular dynamics (AIMD). The experimental results showed that the photoluminescence performance of CSASN:Eu red phosphor dropped gradually and finally disappeared under PCT aging, and its temperature-dependent degradation kinetics followed the Arrhenius model well. Meanwhile, the simulation results indicate that the CASN, reacted with H₂O when the H atoms had a tendency to approach N atoms. Both the temperature and humidity could accelerate the hydrolysis reaction rate.

1. Introduction

At present, the common high-power phosphor-converted lighting diode (pc-WLED) packages are usually composed of blue LED chips coated with phosphors. Phosphors, as one of the key light conversion materials, always are attached importance to the light efficiency, quality, and reliability of high-power pc-WLEDs [1]–[3]. It is mainly used to add red phosphors to improve the color rendering index of white LEDs. The Sulfide-type and Nitride-type red phosphors with Eu²⁺, which are widely used in white LEDs, could contribute to high luminous efficiency but with unstable chemical properties when they are aged under high temperature and high humidity environments [4]. This could cause the reliability issue of pc-WLEDs such as lumen degradation and color shift[5]. Therefore, the influence of environmental factors such as temperature and humidity on red phosphor's degradation becomes an important direction to understand the

degradation mechanism of pc-WLED used in harsh conditions.

The manifestations of phosphor degradation include the reduction of light conversion efficiency and the changes in photometric and chromatic performances. M. Choi *et al.* [6] found that the pH in deionized water with Nitride-type (Sr, Ca)₂Si₃N₈:Eu²⁺ phosphor increased faster, which is because the host material Sr is hydrolyzed by deionized water, resulting in the creation of OH⁻. It is thus assumed that the phosphors underwent the hydrolysis reaction and degradation in high humidity environment. Zhu *et al.* [7] found that the CSASN:Eu phosphor degradation initiated at 150°C and its luminescence was quenched quickly. The degradation mechanism was clarified and proposed to occur via the moisture-enhanced hydrolysis reaction of both the host CSASN and Eu²⁺. Our team also explored the degradation mechanism of CASN:Eu and CSASN:Eu phosphors under high temperature and high humidity aging tests [8] and water immersion tests [9]. It was found that the red phosphors react easily with water in high-temperature and high-humidity environments, accompanied by the thermal quenching effect.

Since the accelerated aging tests are always time-consuming, simulation methods can provide an effective way to evaluate the effect of environmental conditions on the degradation reaction. Some studies have investigated the structure and properties of red phosphors through first-principles calculations. For example, Jang *et al.*[10] calculated formation energies, electronic structures, and optical absorption spectra of various metal dopants in CASN based on DFT, and analyzed the possibility of various dopants. Wang *et al.* [11] investigated the electronic structure, along with the mechanical and optical properties of CASN:Eu, and confirmed the agreement between the used structure and available experimental and theoretical data through DFT.

However, there are relatively few studies using simulations such as molecular dynamics and first-principles calculations to verify the degradation mechanism of phosphors, especially considering the temperature and humidity effects. Our team [12] previously summarized the effect of the hydrolysis reaction of CASN:Eu on the mechanical and interfacial properties of silicone/ CASN:Eu composite, by using both experimental and first-principles calculations. The

experimental and simulation results consistently concluded that the hydrolysis reaction of CASN:Eu could increase the adhesion of CASN:Eu phosphor/silicone interface.

This study investigated the degradation mechanism of the CSASN:Eu red phosphor through both experiments and simulations. PCTs and 85°C&85%RH test were first used to conduct the high temperature and high humidity accelerated aging of selected test samples and the kinetics model was fitted with experimental results. Next, the software Materials Studio (MS) based on first-principle calculation was used to calculate the bind energy, charge density difference, and AIMD of CASN and H₂O, which were used to reveal the hydrolysis mechanism. The remaining parts of this study are organized as follows. Section 2 introduces experiments and methodology. Section 3 discusses the experimental and simulation results. Finally, the concluding remarks are given in Section 4.

2. Experiments and Methodology

In this section, the test samples, experimental setups, and parameter settings in first-principles calculations are presented.

2.1 Test samples and experimental setup

In this paper, a commercial Nitride-type red phosphor CSASN:Eu is selected as the test sample (Code: R6535). The PCTs are performed at 100°C&100%RH, 150°C&100%RH, 200°C&100%RH, 250°C&100%RH, and the 85°C&85%RH test is served as a comparison. The PCT setup is shown in Figure 1.

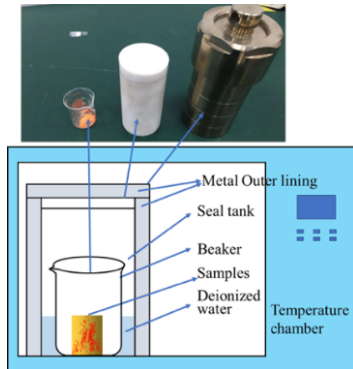


Figure 1. The pressure cooker test setup

The PCT was conducted as follows: First, 5g test samples were placed in a beaker with around 30ml of deionized ion water, which was placed in a poly tetra fluoroethylene (PTFE)-sealed tank; then put the tank into the stainless steel outer lining to form a sealed environment; finally, the whole was put into the chamber at 100°C, 150°C, 200°C, and 250°C for 120 hours. Some samples were taken out every 24 hours and dried for the material property characterization. The setup of 85°C&85%RH test was: 10g samples were put into the 85°C&85%RH test chamber for 1200h. Some samples were taken out every 240h and dried for material property characterization.

The photoluminescence performance, crystal structure, micromorphology and chemical elements of test samples before and after aging were characterized by the thermal

quenching analysis system, XRD and SEM/EDS, respectively.

2.2 First-principles modeling

In this study, simulations were performed based on DFT and AIMD as implemented in the DMol³ package. First, the binding energy of H₂O on different CASN surfaces and different adsorption sites was calculated. The projector-augmented wave function (PAW) method with generalized gradient approximation (GGA) was applied under the Perdew–Burke–Ernzerhof (PBE) of exchange–correlation functional. The all-electron method and double numerical basis set with polarization functions (DNP) were utilized. A Grimme method for DFT-D correction was applied to weaken van der Waals interactions.

For the optimization calculations, a Monkhorst-Pack k-point mesh for the Brillouin zone sampling was used. The convergence criteria of optimized structures were 2×10^{-5} Ha for energy, 0.002 Ha/Å for force, and 0.005 Å for displacement[12]. For electronic structure calculation, the OTFG ultrasoft pseudopotential was used. The energy truncation radius was set as 489.8eV. In the AIMD calculation, the ensemble was set to NVT, and the temperatures were selected as 373K, 423K, 473K, 523K, and 358K corresponding to 100°C, 150°C, 200°C, 250°C, and 85°C, respectively. The temperature control method was set to Massive GGM, the time step was 1 fs, the number of steps was 400, and the trace output was 1 frame/fs. Since the atomic percentage of the Eu element is very small and significantly lower than the other four elements, the simplified CASN model was used in the following simulation[12]. The unit cell of a typical CASN system is an orthorhombic crystal structure (space group Cmc2₁, No. 36) with four atoms----Ca(green), Al(red), and Si(yellow) and N(blue) atoms, as shown in Figure 2.

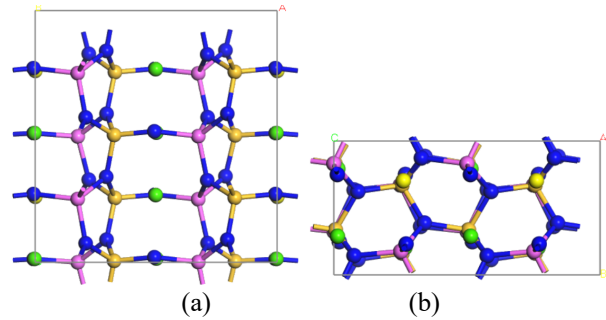


Figure 2. The crystal structure of simplified CASN along the different crystal planes: (a)[0 0 -1]; (b)[0 1 0]

After calculating the binding energy on [0 0 -1] and [0 1 0] crystal planes, the one with lower binding energy was selected for the modeling. A vacuum layer ($\geq 20\text{Å}$) was added in the direction perpendicular to this crystal plane, to avoid the minimum interaction between the periodic structures. To investigate the adsorption of the H₂O molecular on one surface, the binding energy ($\Delta E/\text{eV}$) was calculated by Equation(1):

$$\Delta E = (E_{total} - E_{substrate} - E_{H_2O}) * 27.212 \quad (1)$$

Where E_{total} (/Ha) is the total energy of the CASN and H_2O molecular structure, $E_{substrate}$ (/Ha) is the energy of CASN, and E_{H_2O} (/Ha) is the energy of the H_2O .

3. Results and Discussion

In this section, the results of accelerated aging tests and simulations under different temperature and humidity conditions are described, compared and analyzed accordingly.





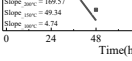
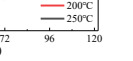










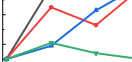
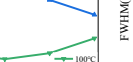




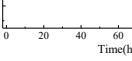
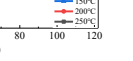
3.1 Experimental results and analysis

The surface appearance changes, photoluminescence performance, XRD and SEM/EDS results in PCTs and 85°C&85%RH test were mainly compared.

(a) Surface appearance

Table 1 shows the apparent color changes in the PCTs. It could be seen that the samples were gradually decolorized, and the higher temperature could accelerate the decolor rate. In the 85°C&85%RH tests, there are minimal color changes as compared.

Table 1. The surface appearance changes of CSASN:Eu phosphor aged under PCTs

	0h	24h	48h	72h	96h	120h
100°C&100%RH						
150°C&100%RH						
200°C&100%RH						
250°C&100%RH						

(b) Photoluminescence and kinetics modeling

The photoluminescence performance evaluation on the test samples before and after aging is mainly determined by the excitation and emission spectrum measurements. Figure 3 shows the emission spectra of the test samples under 475 nm excitation in different PCTs. It could be found that with the emission spectrum intensity decreased sharply or even disappeared under higher temperature. In Figure 4(a), the reaction rate constant k at different temperatures was obtained by linearly fitting the peak intensity of the emission spectrum. As shown in Figure 4(b), the relationship between the reaction rate and the temperature could be modeled by Equation(2-3) [13]:

$$k = A * \exp\left(-\frac{E_a}{R * T}\right) \quad (2)$$

$$\ln k = -\frac{1}{R * T} E_a + \ln A \quad (3)$$

Where A is the Arrhenius constant; R is the molar gas constant 8.314J/(mol·K); T is the thermodynamic temperature K; E_a is the reaction activation energy J/mol or kJ/mol.

In this study, the activation energy E_a of hydrolysis reaction in PCTs was calculated as 45.44 kJ/mol. Some other study reported that the activation energy of these samples is 66.32 kJ/mol [7].

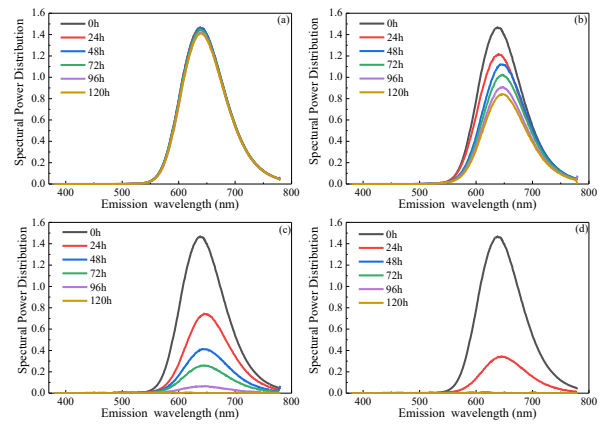


Figure 3. Emission spectrum of CSASN:Eu phosphor aged under PCTs: (a) 100°C&100%RH; (b) 150°C&100%RH; (c) 200°C&100%RH; (d) 250°C&100%RH

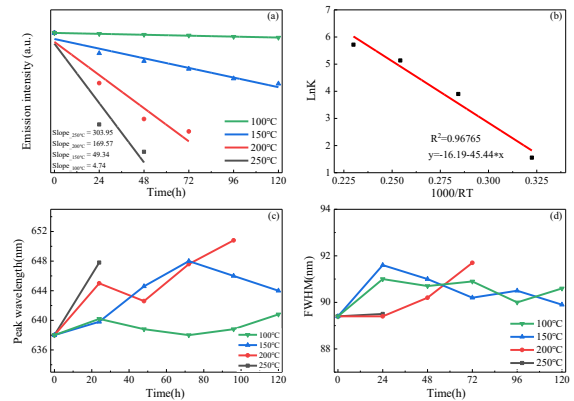


Figure 4. Characteristics of emission spectrum (a) peak intensity (b) Arrhenius fitting equation (c) peak wavelength (d) full width at half maximum(FWHM)

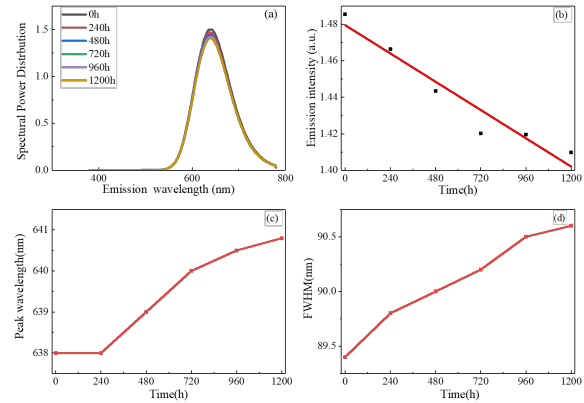


Figure 5. Photoluminescence performance of CSASN:Eu phosphor aged under 85°C&85RH test: (a) emission spectrum; (b) peak intensity; (c) peak wavelength; (d) FWHM

Figure 5 illustrated the photoluminescence performance changes of the test sample aged under 1200h 85°C&85%RH test. It showed that the emission intensity decreased slightly, which indicates the degradation of CSASN:Eu phosphor under this condition was relatively slower than those under PCTs.

(c) XRD analysis

According to the XRD results as shown in Figure 6, it could be found that the crystal phase of test samples mainly consists of $\text{Sr}_{0.2}\text{Ca}_{0.8}(\text{AlSi})\text{N}_3$ and $\text{Sr}_{0.962}((\text{AlSi})\text{N}_3)$ after 120h 100°C&100%RH and 1200h 85°C&85%RH aging tests, and the phase and composition didn't change. After 72h 150°C&100%RH aging, the test samples became with the single composition $\text{Sr}_{0.2}\text{Ca}_{0.8}(\text{AlSi})\text{N}_3$. Under the 200°C&100%RH and 250°C&100%RH, the final resultants were detected as $\text{SrAl}_2\text{Si}_2\text{O}_8$, $\text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_8(\text{OH})_4$ and $\text{Ca}(\text{Al}_2\text{O}_4)_3\text{O}$.

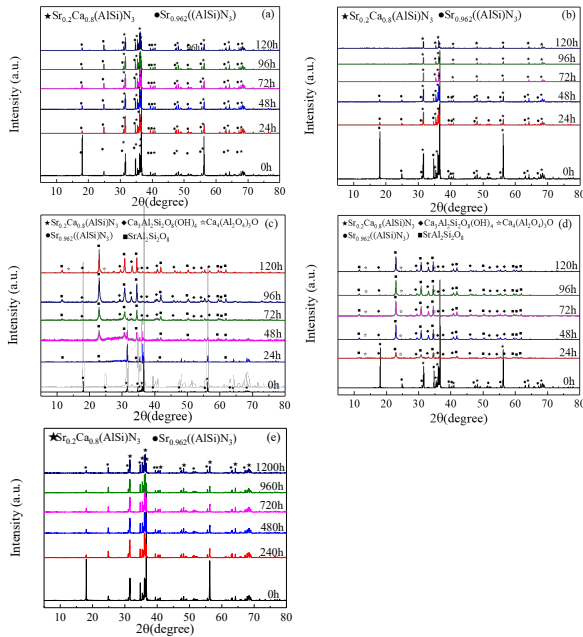


Figure 6. XRDs of CSASN:Eu phosphor aged under: (a) 100°C&100%RH; (b) 150°C&100%RH; (c) 200°C&100%RH; (d) 250°C&100%RH; (e) 85°C&85%RH

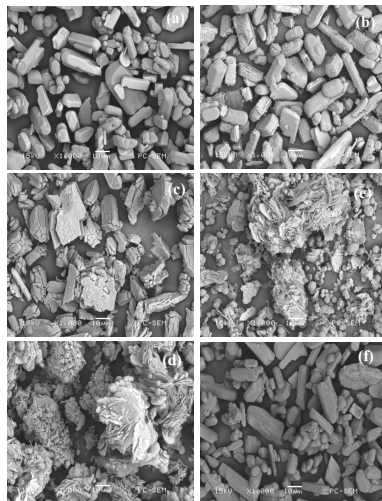


Figure 7. SEMs of CSASN:Eu phosphor aged under: (a) 0h; (b) 100°C&100%RH, 120h; (c) 150°C&100%RH, 120h; (d) 200°C&100%RH, 120h; (e) 250°C&100%RH, 120h; (f) 85°C&85%RH, 1200h

(d) SEM/EDS analysis

As shown in Figure 7, SEM diagrams indicated that after 120h 100°C&100%RH aging, the sample surface began to be rough, and some of the particles appeared to crack. Under 150°C&100%RH, all samples appeared cracks and the crystal structure finally crashed completely under 200°C&100%RH and 250°C&100%RH. The EDS results are shown in Table 2, in which N element reduced to 0, Ca and Sr declined slightly, O increased, and other elements remained basically unchanged. It further proved that the hydrolysis reaction happened more seriously under PCTs than that under 85°C&85%RH, even with 10 times longer aging time.

Table 2. The chemical element content of CSASN:Eu phosphor before and after aging

	N	O	Al	Si	Ca	Sr	Eu
0h	1.46	0	18.2	24.4	21.6	31.2	2.2
100°C&100%RH 120h	0.6	9.62	17.1	22.1	22.0	26.1	2.4
150°C&100%RH 120h	0	14.3	14.7	21.3	16.6	30.7	2.3
200°C&100%RH 120h	0	14.3	15.9	22.8	19.6	25.7	1.8
250°C&100%RH 120h	0	14.9	16.7	22.6	16.3	27.7	1.7
85°C&85%RH 1200h	1.2	5.65	17.7	23.6	20.3	29.7	1.9

Generally, Table 3 provides a brief summary of the experimental results of CSASN:Eu red phosphor aged under 120h PCTs and 1200h 85°C&85%RH test.

3.2 Simulation results and analysis

The static DFT and dynamic AIMD simulations on the simplified CASN and H_2O were performed considering the different temperature and humidity conditions.

(a) Static DFT analysis

Based primarily on the structural stability of CASN, different crystal planes ([0 0 -1] and [0 1 0]) and different adsorption sites (Ca site and N site) were taken into consideration in static DFT simulations. The calculated adsorption reactions between CASN and H_2O were listed in Table 4, where the minimum distances between N atoms from CASN and H from H_2O were determined in the structures before and after adsorption.

First, the binding energy of CASN and H_2O reached to the lowest -1.505 eV at the Ca site of [0 0 -1]. The stable structure model of [0 0 -1] was used in the subsequent simulations. Second, the minimum distances between the N-H atoms were shortened as the H atoms in H_2O tended to move to the N atoms in CASN. According to the experimental outcomes, the reaction produced some gas with a pungent smell, which was assumed as NH_3 . Furthermore, in the difference charge density maps, the yellow region represented electron concentration and the blue region indicated electron loss. The charge may be depleted at the O from H_2O and collected at the Ca from CASN, as well as at the N from CaAlSiN_3 and collected at the H atom from H_2O . However, the total charge transfer

could be negligible under 0K&100%RH, which indicates this mode should be a straightforward physical adsorption.

(b) Dynamic AIMD analysis

In order to consider the humidity effect, it was decided to modify the number of H₂O molecules involved in the reaction, i.e. 10 H₂O molecules and 8 molecules were used to simulate 100%RH and 85%RH respectively. The CASN substrate was set at a total of 84 molecules. The dynamic AIMD simulation results were listed in Table 5. The minimum distances between N atoms from CASN and H from H₂O were measured and normalized in Figure 8.

Accordingly, it appeared that the reaction between CASN and H₂O was accelerated by temperature and humidity rising. The simulated reactions started after 300fs and 200fs under 85°C&85%RH and 100°C&100%RH respectively. The hydrolysis mechanism is assumed that CASN and H₂O reacted chemically with the H atoms from H₂O approaching N atoms from CASN. As for the reaction rate, the reaction started very quickly when the temperature increased.

Table 3. The brief summary of experimental results

Experimental conditions	Ageing duration	Important findings
85°C&85%RH	1200h	1) Photoluminescence performance decreased slightly. 2) No change in the crystal phase composition, but the strength decreased and the particle surface became rough.
100°C&100%RH		1) Photoluminescence performance decreased slightly. 2) The surface color was basically unchanged. 3) No change in the crystal phase composition, but the strength decreased and the particle surface became rough and even small cracks appeared.
150°C&100%RH	120h	1) Photoluminescence performance decreased largely and eventually becomes 0. 2) The surface color became white after 96h. 3) The crystal phase composition started to change. 4) The particle surface cracked.
200°C&100%RH and 250°C&100%RH		1) Photoluminescence performance decreases and becomes after 48h. 2) The surface color became white after 48h. 3) The crystal phase composition completely changed. 4) The particle crashed.

Table 4. The static DFT simulation results

Crystal planes	Adsorption sites	The model before adsorption	The model after adsorption	Binding energy /eV	The N-H distance /Å	Difference charge density maps
[0 0 -1]	N			-1.442	3.206→ 1.647	
	Ca			-1.505	2.748→ 1.628	
[0 1 0]	N			-1.343	3.320→ 1.809	
	Ca			-1.341	2.020→ 1.811	

Table 5. The dynamic AIMD simulation results

Experimental conditions	0fs	100fs	200fs	300fs	400fs
100°C&100%RH					
150°C&100%RH					
200°C&100%RH					
250°C&100%RH					
85°C&85%RH					

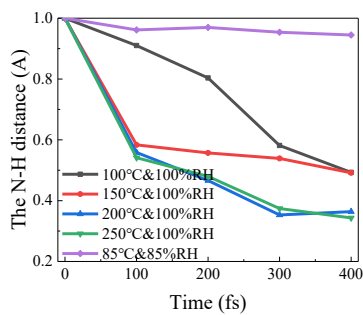
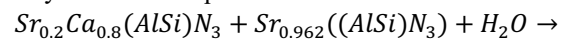
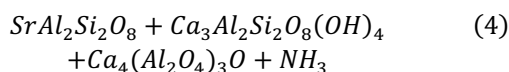


Figure 8. The distance between N atoms from CASN and H atoms from H₂O

Finally, combing the experiments and simulations, it was concluded that the crystal phase composition of CSASN changed and the newly generated phases were assumed as $(Ca_{0.2}Sr_{0.8})Al_2Si_2O_8$, $Ca_3(Al_2O_6)$ and $Ca_{0.92}(Al_{1.8}Si_{2.2}O_8)(H_2O)_{4.3}$. The complete hydrolysis reaction allowed the N atoms to escape as NH_3 by combining with H from H_2O . The primary solid residue was created when O atoms were combined with Al and Si. Intermolecular forces may cause some H_2O molecules to be adsorbed on the solid residue's surface. Thus, the final hydrolysis reaction equation can be assumed as follows:





4. Conclusions

In this paper, the high temperature and high humidity aging tests were performed on CSASN:Eu red phosphors. Its hydrolysis reaction mechanism was simulated and analyzed by using first-principle calculations. The experimental results revealed that the CSASN:Eu red phosphor under more than 100°C PCT 120h aging test appeared a large decrease in emission intensity, and the surface appearance even became entirely white, the particle cracked until completely cracked. By contrast, the samples under 1200h 85°C&85%RH test were relatively more stable. Hence, the temperature and humidity had a significant impact on the hydrolysis reaction rate, which followed the Arrhenius kinetics model well. The simulation results also indicated the hydrolysis mechanism is that CASN and H₂O reacted chemically with some oxides residues, and the H atoms from H₂O had a tendency to approach N atoms from CASN.

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