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Semi-Quantitative Estimation of Ce³⁺/Ce⁴⁺ Ratio in YAG:Ce³⁺ Phosphor under Different Sintering Atmosphere

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Abstract

In order to confirm the relationship between the luminescence and the ratio of Ce³⁺/Ce⁴⁺ more clearly, a series of YAG:Ce³⁺ (Yttrium Aluminum Garnet, $Y_{2.94}Al_5O_{12}:0.06Ce^{3+}$) phosphors were prepared under different sintering atmosphere. A semi-quantitative analysis based on X-ray photoelectron spectroscopy (XPS) was introduced to study the mole ratio of Ce³⁺/Ce⁴⁺ in the as-synthesized YAG:Ce³⁺ phosphors. The results indicated that the percentage of Ce³⁺/(Ce³⁺ + Ce⁴⁺) reached 88.46% under the reduction atmosphere. The emission intensity of YAG:Ce³⁺ phosphors was increased significantly with the increasing of Ce³⁺ concentration.

Keywords

1. Introduction

As a classic yellow emission phosphor, YAG:Ce³⁺ is one kind of widely used phosphor due to its high quantum efficiency, good thermal conductivity and wide wave band properties. It has been extensively studied in both the preparation methods and luminescence properties. However, the prepared material always contains Ce⁴⁺ which does not contribute to luminescence theoretically. In order to strengthen the emission intensity, sintering under reduction atmosphere and charge compensation are usually adopted method to increase the Ce³⁺ content in YAG:Ce³⁺ materials.

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Generally, cerium compounds exhibit complex features due to hybridization with ligand orbitals and fractional occupancy of the valence 4f orbitals. Although some theory and researches have been elaborated, absolute assignment of the features has not been made. In the study of Edmond Abi-aad *et al.* [1], the Ce 3d XPS spectra of the CeO_2 prepared with different alkali solutions (KOH, NH_4OH) have the same shape with six peaks at Bes (Binding Energies) 882.5, 888.7, 898.2, 900.7, 907.6 and 916.5 (±0.2) eV, respectively. In the case of M. Cabala *et al.* [2], they observed splitting of cerium 3d core level in two doublets corresponding to configuration $3d^9 4f^1$ components at binding energies of 904.5 eV, 886.0 eV and $3d^9 4f^2$ at 900.3 eV, 881.9 eV, respectively. CHAI Chunlin *et al.* [3] carried out the XPS analysis of sample CeO_2/Si, they believed the peak of 881.34 eV was attributed to Ce3d signal of non stoichiometric CeO_2 and the characteristic peak of Ce^{3+}—884.9 eV and 903.4 eV were obtained. In order to determine the oxidation state of Ce in $Ce_{0.9}Fe_{0.1}O_{1.97}$, Ying Zuo *et al.* [4] evaluated the XPS spectra of Ce (3d) region and three doublets from CeO_2 and two doublets from Ce_2O_3 could be identified. The assignment of Ce^{4+} 3d component ($3d_{5/2}$: 882.6 eV, 888.6 eV, 898.3 eV; $3d_{3/2}$: 901.1 eV, 907.3 eV, 916.8 eV) and Ce^{3+} 3d component ($3d_{5/2}$: 885.4 eV; $3d_{3/2}$: 903.7 eV) from XPS spectra were collected. A number of related works have been done [5]-[9].

In this paper, the proportion of Ce^{3+}/Ce^{4+} was measured using the XPS method. In a word, there will be displacement of the BEs and the analysis should be carried out on the basis of different cerium compounds. In order to confirm the relationship between the luminescence and the ratio of Ce^{3+}/Ce^{4+} more clearly, a series of YAG:Ce^{3+} phosphors were prepared under different sintering atmospheres. The relationship between the ratio of Ce^{3+}/Ce^{4+} and the luminescence was studied by XPS as a semi-quantitative method.

2. Experimental

YAG:Ce^{3+} phosphors were synthesized via the conventional high temperature solid-state reaction method. The stoichiometric amount of Y_2O_3 (99.999%), Al_2O_3 and Ce_2O_3 (99.999%) were weighted accurately ($Y_{2.94}Al_5O_{12}$: 0.06Ce) and then well mixed and grinded using planetary ball mill. The samples were placed in a ceramic heater at 1550°C for 2 h. The only difference is the sintering atmosphere: with both carbon powder and flowing nitrogen atmosphere, with carbon powder but no nitrogen, with nitrogen atmosphere but no carbon powder, the last with neither of them.

Both emission spectrum and excitation spectrum of the phosphor were measured by a ZOLIX Omni-λ luminescence photoluminescence (PL) spectrophotometer (Xe lamp). We also measured the surface states of cerium electrodes by using a AXIS Ultra DLD X-ray photoelectron spectroscopy (XPS). The Al Kα line was used as an X-ray source. The minimum resolution was 0.48 eV (Ag $3d_{5/2}$). Microscopy of the phosphor was measured on a Hitachi S4800 scanning electron microscope (SEM).

3. Results and Discussion

The binding energies were generally using the C 1s peak (284.7 eV) as a standard (**Figure 1**). According to the standard XPS spectra, the characteristic peak of Ce^{3+} $3d_{5/2}$ and Ce^{3+} $3d_{3/2}$ is 884 eV and 902 eV, respectively. Then for Ce^{4+} is eV and respectively. When the chemical environment of atomic changed, there will be displacement of the BEs of inner electrons.

In our case, the instrument automatically identified the Ce3d$_{5/2}$ at 899.9eV. Although the displacement of BEs happens, according to related reports [10], the maximum value would be 17.9 eV. So combined with measured data we inferred the peak of 899.9 eV was consist of Ce^{3+} $3d_{5/2}$ and Ce^{4+} $3d_{3/2}$. In consideration of these factors and the obtained data, we identify the 882 eV, 888 eV, 899 eV and 903 eV as the fitting peaks.

Figures 2-5 show the XPS spectra of Ce 3d of four YAG:Ce^{3+} samples, by a binding energy scan from 880 to 910 eV at a rate of 100 meV per step and a 40 eV pass energy. The dwell time was 120 ms. All the spectra were fitted and the areas of each fitting peak were measured. It is well known that the fraction of Ce^{3+} ions can be obtained by calculating the ratio of peak areas: f (Ce^{3+}) = area (Ce^{3+})/area (Ce^{3+} + Ce^{4+}). The linear background was subtracted before curve fitting.

Figure 2 showed the XPS patterns of Ce3d sintered in air. Four peaks of binding energy were observed to be located at 888.131 eV for Ce^{4+} $3d_{5/2}$, 890.301 eV for Ce^{3+} $3d_{5/2}$, 900.611 eV for Ce^{4+} $3d_{3/2}$ and 904.47 eV for Ce^{3+} $3d_{3/2}$, respectively. **Table 1** showed the calculated result. The ratio of Ce^{3+} is about 68.14% while Ce^{4+} is about 31.86%. As we know, O_2 will oxidize some Ce^{3+} to Ce^{4+} at high temperature in air. So the ratio of Ce^{3+} is low sintered in air.
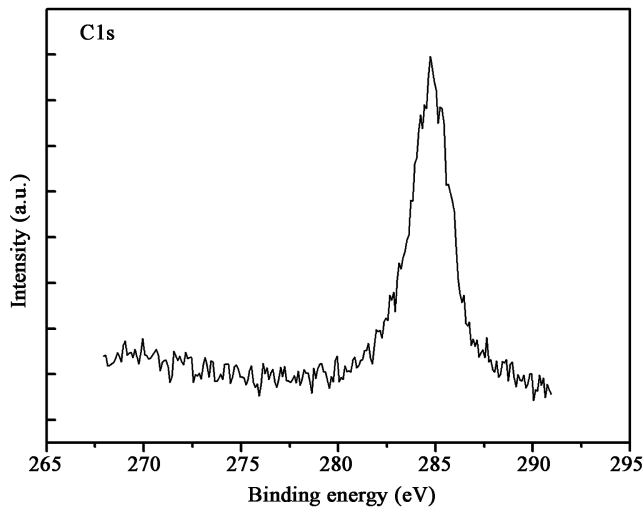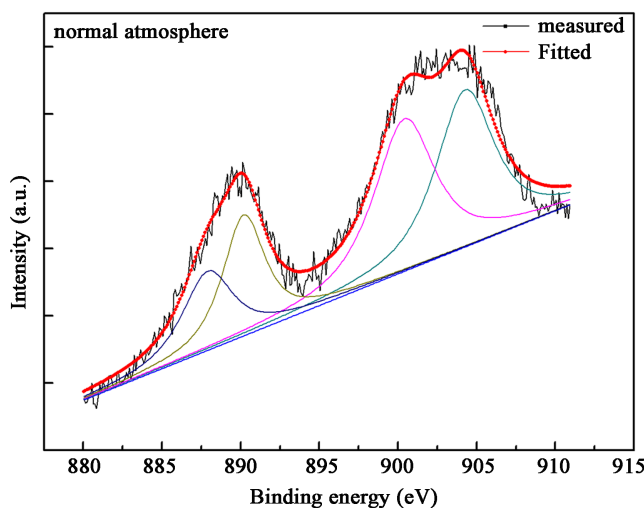
Figure 1. XPS patterns of C1s.

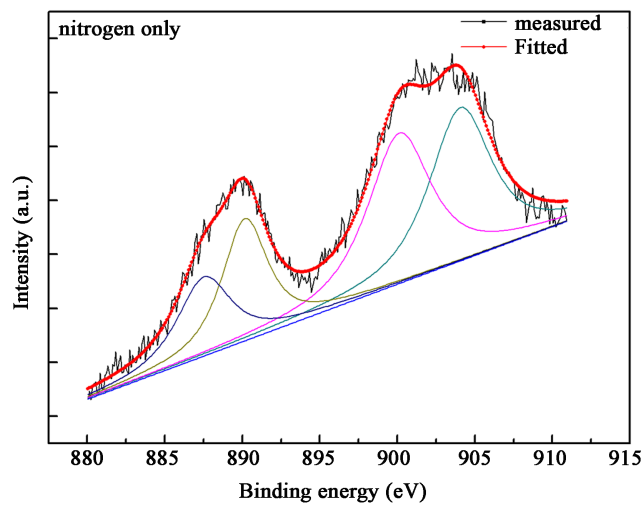**Figure 2.** XPS patterns of Ce3d in air atmosphere sample.

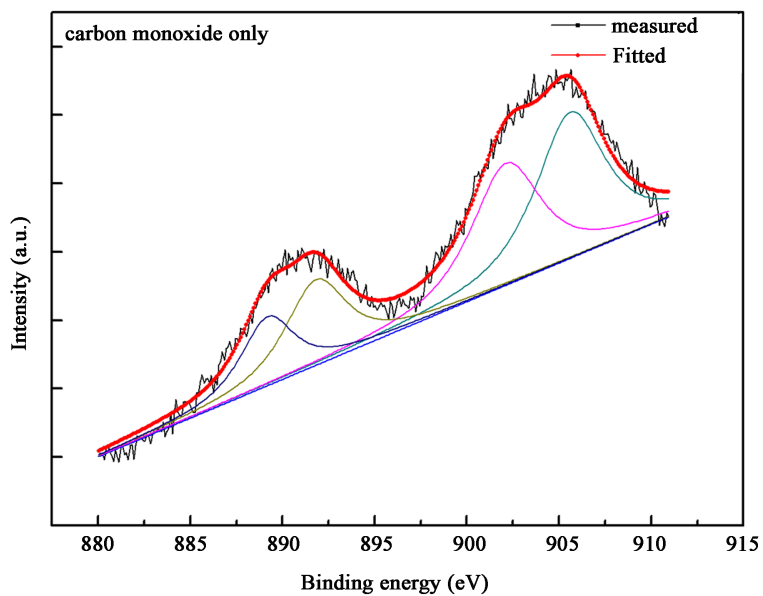**Figure 3.** XPS patterns of Ce3d in nitrogen only atmosphere sample.

Figure 4. XPS patterns of Ce3d in carbon monoxide only atmosphere sample.
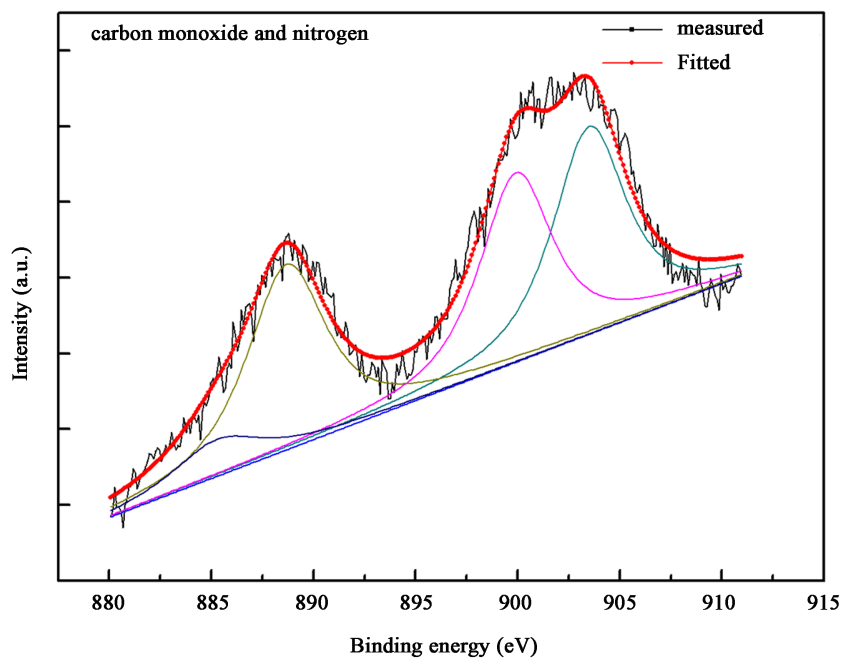

Figure 5. XPS patterns of Ce3d in carbon monoxide and nitrogen atmosphere sample.

Table 1. Calculation of the ratio of $Ce^{3+}/(Ce^{3+} + Ce^{4+})$ sintered in air.

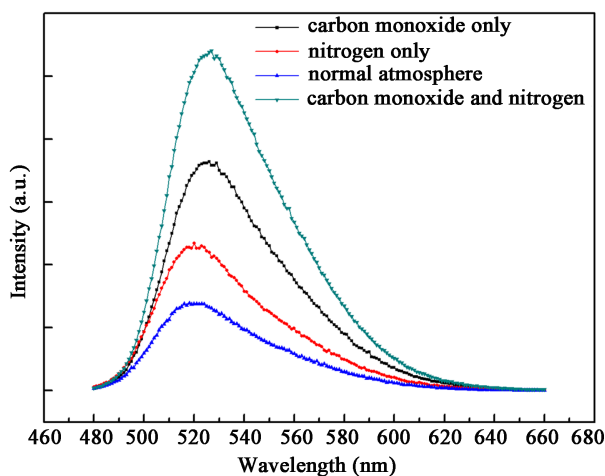|	$Ce^{3+} 3d_{5/2}$	$Ce^{3+} 3d_{3/2}$	$Ce^{4+} 3d_{5/2}$	$Ce^{4+} 3d_{3/2}$
Peak eV	890.301	904.47	888.131	900.611
Half-widths	3.09	4.07	4.01	4.83
Area	9007.23	6529.135	3961.859	3301.55
Sum	15536.365		7263.409	
Ratio %	68.14		31.86	

The XPS patterns of Ce3d sintered in nitrogen atmosphere was showed in **Figure 3**. Peaks at 887.5111 eV was for Ce^{4+} $3d_{5/2}$, 890.151eV for Ce^{3+} $3d_{5/2}$, 900.131 eV for Ce^{4+} $3d_{3/2}$ and 904.061 eV for Ce^{3+} $3d_{3/2}$, respectively. **Table 2** showed the calculated result. The ratio of Ce^{3+} is about 75.33% while Ce^{4+} is about 24.67%. The concentration of O_2 was low in nitrogen atmosphere. This reason will prevent some Ce^{3+} oxidized to Ce^{4+}. So the ratio of Ce^{3+} sintered in nitrogen is bigger than sintered in air.

Figure 4 indicated the XPS patterns of Ce3d sintered in carbon monoxide atmosphere. Peaks at 889.181eV was for Ce^{4+} $3d_{5/2}$, 891.811 eV for Ce^{3+} $3d_{5/2}$, 902.131 eV for Ce^{4+} $3d_{3/2}$ and 905.601 eV for Ce^{3+} $3d_{3/2}$, respectively. **Table 3** showed the calculated result. The ratio of Ce^{3+} is about 77.55% while Ce^{4+} is about 22.45%. Some Ce^{4+} was reduced to Ce^{3+} by carbon monoxide in carbon monoxide atmosphere under high temperature. So the ratio of Ce^{3+} sintered in carbon monoxide atmosphere is bigger than sintered in the two kinds of atmosphere referred above.

Figure 5 showed the XPS patterns of Ce3d sintered in carbon monoxide and nitrogen mixed atmosphere. The peaks at 885.262 eV and 899.923 eV were for Ce^{4+} $3d_{5/2}$, and 888.669 eV, 903.507 eV were for Ce^{3+} $3d_{5/2}$, respectively. The calculated result was showed in **Table 4**. The ratio of Ce^{3+} is about 88.46% while Ce^{4+} is about 11.54%. In the mixed atmosphere, oxidation of some Ce^{3+} to Ce^{4+} were prevented due to the lack of O_2, while some Ce^{4+} were reduced to Ce^{3+} by carbon monoxide. So the ratio of Ce^{3+} was the largest sintered in mixed atmosphere.

Figure 6 showed the emission spectra of samples prepared under different sintered atmosphere. The YAG: Ce^{3+} phosphor sintered under carbon monoxide and nitrogen atmosphere showed the strongest luminescence. The sample has the biggest ratio of $Ce^{3+}/(Ce^{3+}+Ce^{4+})$ (88.46%) in the four conditions. The lowest luminescent was sintered in air, which possess the ratio of $Ce^{3+}/(Ce^{3+} + Ce^{4+})$ 68.14%. It can be preliminary confirmed that with the increasing of the ratio of Ce^{3+}, the emission intensity increases gradually.
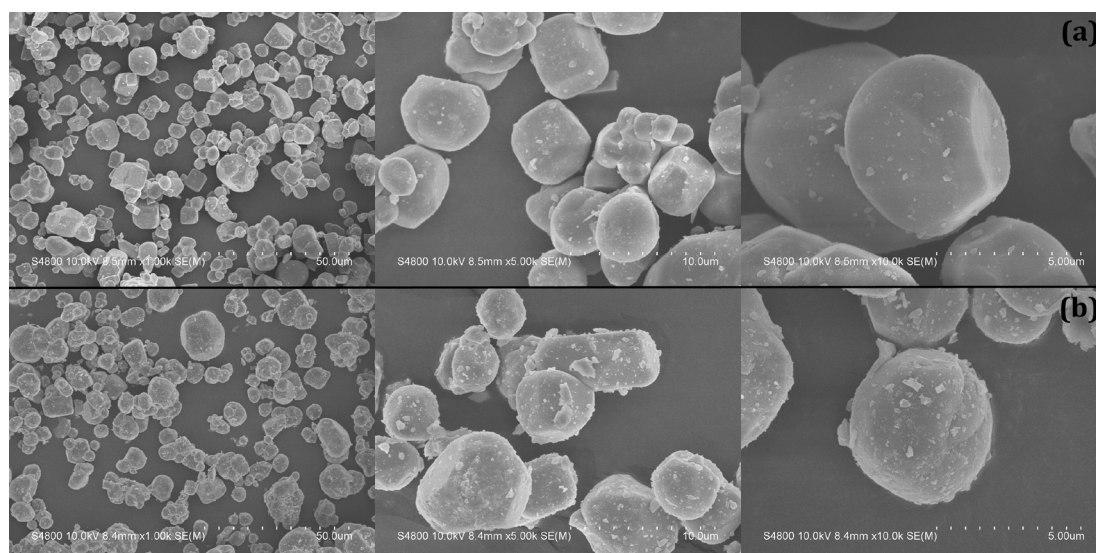
Figure 7 gives the SEM images of YAG:Ce^{3+} phosphors prepared with: a) normal atmosphere and b) carbon monoxide and nitrogen, respectively. We can see that the different sintering atmosphere has no influence on the SEM pictures. Both of them have some conglomeration phenomenon which is common in high temperature solid state reaction method and the crystallites were irregular spheres.

Figure 6. The emission spectra of YAG:Ce^{3+} phosphors under different sintering atmosphere.

Table 2. Calculation of the ratio of $Ce^{3+}/(Ce^{3+} + Ce^{4+})$ sintered in nitrogen atmosphere.

	Ce^{3+} $3d_{5/2}$	Ce^{3+} $3d_{3/2}$	Ce^{4+} $3d_{5/2}$	Ce^{4+} $3d_{3/2}$
Peak eV	890.151	904.061	887.511	900.131
Half-widths	3.53	4.75	4.15	4.88
Area	12864.954	9900.169	4474.192	2982.79
Sum	22765.123		7456.982	
Ratio %	75.33		24.67	

Figure 7. SEM images of YAG:Ce^{3+} phosphors prepared with: (a) Air atmosphere; (b) Carbon monoxide and nitrogen atmosphere.

Table 3. Calculation of the ratio of Ce^{3+}/(Ce^{3+} + Ce^{4+}) sintered in carbon monoxide atmosphere.

	Ce^{3+} 3d$_{5/2}$	Ce^{3+} 3d$_{3/2}$	Ce^{4+} 3d$_{5/2}$	Ce^{4+} 3d$_{3/2}$
Peak eV	891.811	905.601	889.181	902.131
Half-widths	3.97	4.48	3.48	4.5
Area	15664.42	14062.6	5163.849	3442.57
Sum	29727.02		8606.419	
Ratio %	77.55		22.45	

Table 4. Calculation of the ratio of Ce^{3+}/(Ce^{3+} + Ce^{4+}) sintered in carbon monoxide and nitrogen mixed atmosphere.

	Ce^{3+} 3d$_{5/2}$	Ce^{3+} 3d$_{3/2}$	Ce^{4+} 3d$_{5/2}$	Ce^{4+} 3d$_{3/2}$
Peak eV	888.669	903.507	885.262	899.923
Half-widths	4.622	4.259	5.125	4.247
Area	14898.14	8591.221	1838.019	1225
Sum	23489.361		3063.019	
Ratio %	88.46		11.54	

4. Conclusion

In conclusion, XPS was used as a semi-quantitative method to determined the mole ratio of Ce^{3+}/(Ce^{3+} + Ce^{4+}) in phosphor. The percentage of Ce^{3+} was 88.46%, 77.55%, 75.33% and 68.14% under four different sintering atmosphere. It confirmed that under the same preparation conditions and within the quenching concentration, the high ratio of Ce^{3+}/(Ce^{3+} + Ce^{4+}) could enhance the emission intensity in phosphor.

Acknowledgements

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