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ARTICLE

Effect of PEG Addition on the Properties of YAG:Ce Phosphor Synthesized via a Homogeneous Precipitation Method

Ren Yixuan, Gou Li, Ran Junguo

Sichuan University, Chengdu 610065, China

Abstract: YAG:Ce precursors were synthesized via a homogeneous precipitation method with the addition of different molecular mass of PEG (PEG 6000 and PEG 10000) used as dispersant. The FT-IR spectra show that no significant difference is found between the precursors. SEM images indicate that the size of the primary particles with PEG is much smaller than that of the sample without PEG. Confirmed by the DSC traces and X-ray diffraction (XRD), the crystallization of YAG is a one-step process without any intermediate phase. The crystallization of YAG is significantly promoted and the oxidation of Ce^{3+} is inhibited by addition of PEG, which enhances the luminescent properties of YAG:Ce phosphor.

Key words: YAG:Ce phosphor; homogeneous precipitation; phase evolution; PEG

YAG:Ce, i.e. cerium doped yttrium aluminum garnet ($Y_3Al_5O_{12}$:Ce^{3+}) is a well-known phosphor material that has been widely used in the field of white-light-emitting dioxide (WLED)[1].

The traditional solid-state reaction[2] method requires a high reaction temperature near 1600 °C. So various soft- chemical methods, such as co-precipitation method[3,4], sol-gel method[5,6], hydrothermal method[7,8], combustion method[9,10], have been employed to synthesize YAG:Ce phosphor. During the calcination process, the precursors synthesized via different methods will experience different phase evolution processes. As a result, the crystallization temperature of YAG is changed.

The homogeneous precipitation method [11-13] is one of the co-precipitation methods, in which hydrolysis of urea will produce CO_3^{2-} and OH^-. This is the main chemical reaction that leads to precipitate. The slow release of CO_3^{2-} and OH^- can provide a mild chemical condition, by which precipitation takes place in the solution uniformly. It is different from the precursors synthesized by other precipitation methods in which ammonia or hydrogen carbonate is used as precipitant directly.

In order to control the morphology of the YAG:Ce phosphor, some kinds of dispersant such as polyethylene glycol (PEG)[5,14], cetyltrimethyl ammonium bromide (CTAB)[15,16], $(NH_4)_2SO_4$[17,18] were employed. When dispersant is added, the morphology of particles is greatly affected. In previous researches[5,14], only the dispersion effect which could modify the surface and the morphology of particles was discussed. Few research focused on the change of reaction during calcination, especially the effect on the crystallization of YAG. The formation of YAG may be influenced by the addition of PEG, which can cause a significant impact on the luminescence properties of YAG:Ce phosphor. In a traditional calcination process, either inert atmosphere or reducing atmosphere was employed to prevent the oxidation of Ce^{3+}. Calcinating directly under air atmosphere was considered as the way that initiated the oxidation reaction.

In the present study, the precursor of YAG:Ce phosphor was synthesized via the homogeneous method owing to its ease of scale-up production. PEG with different molecular mass was added. The as-prepared precursor was calcined at the same

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Corresponding author: Gou Li, Ph. D., Professor, Department of Inorganic Materials, Sichuan University, Chengdu 610065, P. R. China, Tel: 0086-28-85401280, E-mail: gouli@scu.edu.cn

temperature under the air atmosphere. With the addition of PEG, even calcinating under air atmosphere, the oxidation process was still inhibited. A term named “micro-atmosphere” was proposed to explain the mechanism of prevention of the oxidation of Ce^{3+}.

1 Experiment

Based on the stoichiometric ratio of $Y_{2.94}Ce_{0.06}Al_5O_{12}$, a certain amount of Y_2O_3, $Ce(NO_3)_3{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ were weighed precisely. The Y_2O_3 were dissolved in HNO_3 and the surplus HNO_3 was heated to evaporate. The $Al(NO_3)_3{\cdot}9H_2O$ and $Ce(NO_3)_3{\cdot}6H_2O$ were dissolved in deionized water. And all of the nitrate solutions were mixed together. The amount ratio of urea to metal ion was 50:1. The concentration of the urea solution was set to 2 mol/L. After mixing the cation solution and the urea solution together, the solution was divided equally into three parts. A certain amount (5wt%) of PEG with a molecular mass of 10000 was added into one part of solution. The same amount of PEG with a molecular mass of 6000 was added into another part of the solution. The last part of the solution without any other reagent was set as the negative control. All of the mixed solution were heated to 90 °C for 5 h. The final precipitate, after aging for 12 h, was filtered, washed and dried. The as-prepared precursors were calcined at the same temperature (900 or 1200 °C) for 2 h under the air atmosphere.

The thermal analysis of the precursors was carried out on DSC (Differential Scanning Calorimetry) analyzer (STA449-F3 NETZSCH Germany) with a heating rate of 20 °C/min up to 1200 °C. Fourier transmission infrared spectroscopy (FT-IR Nexus 670 Thermo Nicolet USA) was used with KBr pellet method. X-ray diffraction (XRD Philips X’ Pert Pro MPD DY1291) was employed to identify the phase of each final product by the Kα radiation of Cu with a wavelength of 0.15418 nm. The morphology was observed by the field emission scanning electron microscope (FESEM JEOL JSM-7500F Japan). The luminescent properties of YAG:Ce phosphor was measured by a fluorescence spectrophotometer (F4600 Hitachi Japan).

2 Results and Discussion

2.1 FT-IR spectra of precursors

The FT-IR spectra of the precursors with PEG 10000, PEG 6000 and without PEG are demonstrated in Fig.1. As shown in Fig.1, the bands around 3500 cm^{-1} are caused by the stretching vibration of OH^- which comes from the absorbed water at the surface of the particles. The peaks around 850, 1400 and 1500 cm^{-1} are due to the vibration of CO_3^{2-}.

It is confirmed by the results of FT-IR spectra that the precursor synthesized by the homogeneous precipitation method is carbonate and the existence of PEG with different molecular mass could hardly change the composition of the as-prepared precursors.

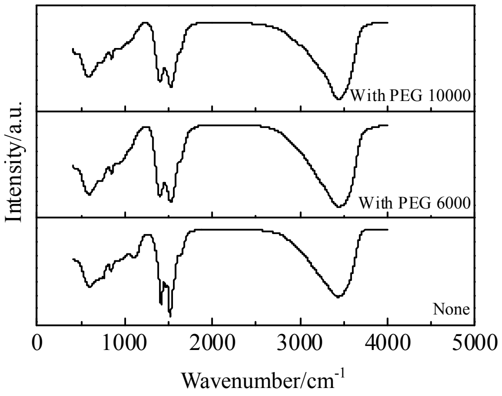

Fig.1 FT-IR spectra of precursors

2.2 Thermal analysis

The DSC curves are demonstrated in Fig.2. As shown in Fig.2a, a board endothermic band found near 300 °C is caused by the removal of the absorbed water. The sharp exothermal peaks at 904, 998 and 1034 °C confirmed that the formation of YAG lattice was a multi-step process[19].

As shown in Fig.2b, a broad endothermic band near 300 °C corresponds to the evaporation of absorbed water. There is a sharp endothermic peak at 926 °C. And confirmed by the TG curve, the continuous mass loss process is completed at that temperature. It means that the decomposition of carbonate and residual PEG has not completed until 926 °C. The exothermal peak at 933 °C is due to the crystallization of intermediate phase. The exothermal peak at 1037 °C is related to the crystallization of YAG. As shown in Fig.2c, compared with Fig2.b, no significant difference has been found until 927 °C. The only exothermic peak located at 934 °C is attributed to the crystallization of YAG. The absence of any other exothermic peak indicates that the crystallization of YAG is a one-step process without forming any intermediate phase, which gives a clue that the formation of YAG lattice is promoted by addition of PEG.

2.3 Phase identification of the calcining powder

As confirmed by the DSC curves, the phase evolution process is changed by the addition of PEG. In order to identify the intermediate phase during calcination process, the precursors were calcined at 900 °C. The XRD patterns of the precursors calcined at 900 °C are shown in Fig.3. The XRD pattern of the sample without any PEG added is significantly different. When calcined at 900 °C, both the samples with PEG 10000 added and the sample with PEG 6000 added are still amorphous. However, the phase Y_2O_3 (JCPDS No.43-1036) is found in the sample without PEG added. According to the DSC curves (Fig.2a), the exothermic peak at 904 °C is confirmed by the evidence of crystallization of Y_2O_3.

As shown in Fig.3, when calcined at 1200 °C, pure YAG (JCPDS No.33-0040) is obtained. But the CeO_2 phase (JCPDS No.34-0394) is found in the sample without PEG added.

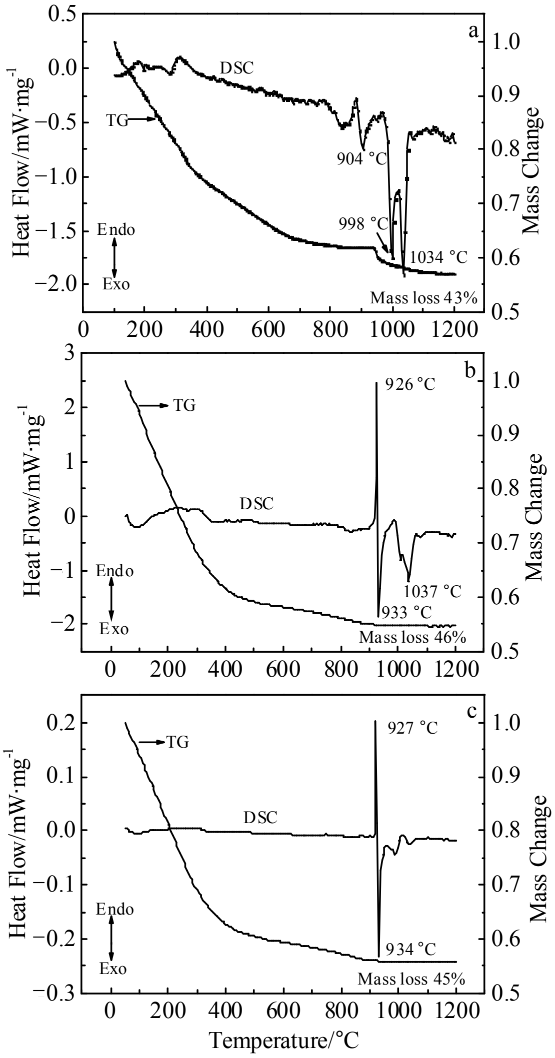

Fig.2 DSC and TG curves of the sample without PEG (a), with PEG 6000 (b), and PEG 10000 (c)

The possible reason is that the Ce^{3+} was oxidized to Ce^{4+} when calcined at a high temperature under air atmosphere. And CeO_2 appears as separated phase in the YAG matrix. As a result, the amount of trivalent cerium ion decreases and the luminescent properties of the YAG:Ce phosphor becomes poor. No CeO_2 phase is found in the samples with either PEG 6000 or PEG 10000 added. The XRD patterns confirm that the oxidation of Ce^{3+} has been inhibited by addition of PEG.

2.4 Morphology

Fig.4 shows the SEM morphologies of the phosphor with different molecular mass of PEG added and without any PEG added. All primary particles are approximately spherical. The primary particles smaller than 200 nm are observed clearly in Fig.4c. When PEG is added, the size of the primary particles becomes smaller compared with the sample without any PEG added, which leads to much agglomerated particles. Sintering necks are formed between the particles. By sintering the primary particles together, the bigger aggregates are formed.

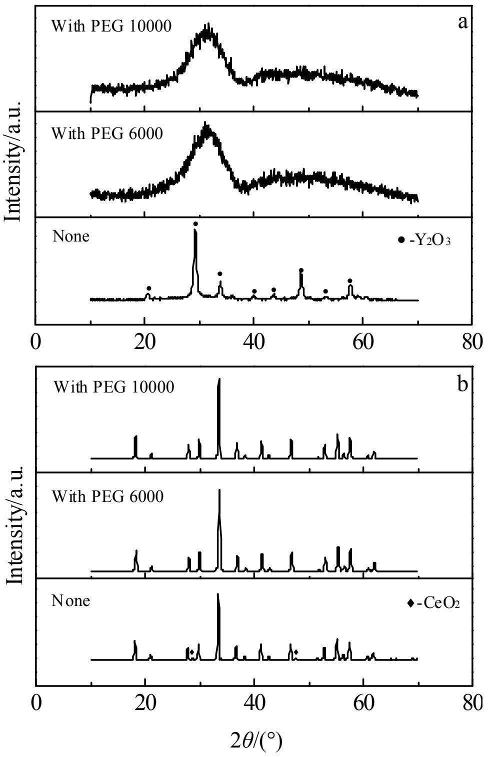

Fig.3 XRD patterns of samples calcined at 900 °C (a) and 1200 °C (b)

There are at least two aspects to infer the effect of PEG. During the process of homogeneous precipitation, the PEG molecules are covered on the surfaces of the particles which are just precipitated from the solution. With the forming of the layer of PEG molecules, the growth of the particles is inhibited. On the other hand, the molecular structure of PEG is chain-like. When the particles with PEG molecules attached come together, these chain-like molecules are easy to entangle with each other. Then a network is developed to link the particles together. From Fig.4a and Fig.4b, it is confirmed that the entanglement between the particles is strengthened with the increase of the length of PEG molecular chain. This leads to a strong network which connects the particles together. As a result, the sinterability is improved and the agglomeration becomes more uniform.

As shown in Fig.4, the pores among the particles are smaller than those of the sample without PEG added. The pores among the particles are the main passages for the movement of the gas generated by the decomposition of precursors during calcination process. However, it is difficult for the gas to escape through the small pores. It accounts for that the diffusion mass transfer is dominative when the size of pores decreases. When the size of pores is large, the convective mass transfer is dominative for the movement of the gas, which is highly effective and consumes low energy. The diffusion mass transfer activated by the diffusion activation energy could be obvious when the temperature is

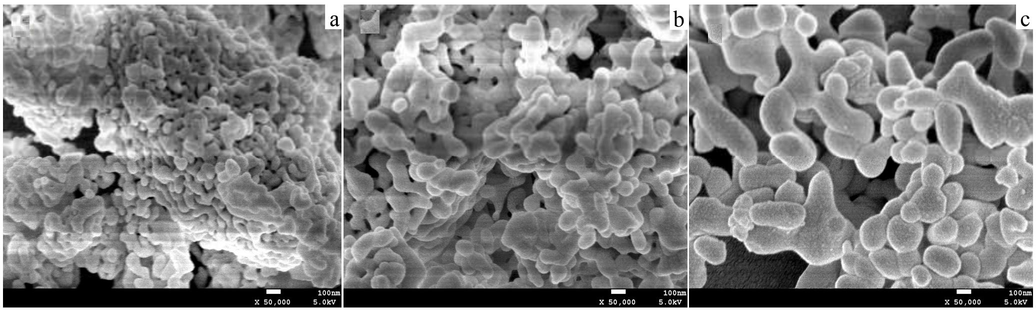

Fig.4 SEM images of YAG:Ce phosphor with PEG 6000 (a), with PEG 10000 (b), and without PEG (c)

high enough. The sharp endothermic peak in DSC curves (Fig.2b and Fig.2c) can be explained in this way.

XRD patterns also confirm that different morphologies affect the phase evolution during calcination process. The particles become smaller and the reaction activity is improved because of the dispersion of PEG. From the XRD patterns of the precursors calcined at 900 °C (Fig.3) and the DSC curves (Fig.2b and Fig.2c), when the PEG is added, the phase evolution changes in comparison to the sample without PEG. Pure YAG can be prepared in the sample with PEG 10000 in a one-step process without forming any intermediate phase. As shown in Fig.2c, there is only a sharp exothermic peak located at 934 °C. From the XRD patterns, after being calcined at 1200 °C under air atmosphere, the CeO_2 phase is found in the sample without PEG added, while no CeO_2 phase is found in the samples with PEG added. It seems that during calcination process carbon dioxide or carbon monoxide produced by the decomposition of precursors is difficult to remove because of the small pores between the particles and occupied pores. In this way a local inert or reducing atmosphere named micro-atmosphere is created around particles. As a result, the oxidation of Ce^{3+} is inhibited. Under reducing atmosphere, diffusion is accumulated by producing oxygen ion vacancies.[20,21] So YAG is synthesized at a lower temperature of 934°C. With the calcination temperature increasing, oxygen ions from heated air will occupy vacancies of host lattice to build up YAG structure. In lower temperature ranges, oxidation of Ce^{3+} is inhibited due to the reducing atmosphere produced by addition of PEG. The reason is that Ce^{3+} as a separated ion does not occupy the lattice site of YAG structure. As the temperature increase, YAG crystal structure forms and the Y^{3+} is replaced by Ce^{3+}. Substitutional Ce^{3+} in YAG structure would not be oxidized even if there is no sufficient reducing atmosphere at a higher temperature where carbonate and PEG decompose thoroughly.

2.5 Luminescent properties

The excitation spectra and emission spectra are demonstrated in Fig.5. There are two broad excitation bands located at 343 and 452 nm, in the excitation spectra. The emission spectra show a broad band located at 536 nm. And the location of the peaks can hardly be changed with the addition of PEG. However, when PEG is added, the intensities of both excitation and emission spectra are enhanced. And the sample with PEG 10000 added gains the strongest intensity followed by the sample with PEG 6000 added.

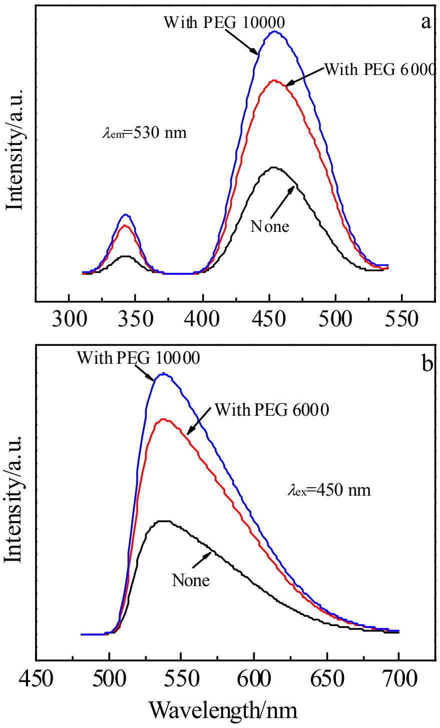

Fig.5 Excitation spectra (a) and emission spectra (b) of the YAG:Ce phosphor with PEG 6000, PEG 10000 and without PEG

Compared with the sample without PEG added, the luminescent properties are improved by the inhibition of oxidation of Ce^{3+} with the addition of PEG. According to the discussion above, regular aggregates with large size can also improve the luminescent properties.

3 Conclusions

1) The compositions of the precursors synthesized via the homogeneous precipitation process hardly change when the PEG is added. They are all carbonates. Morphology of

YAG:Ce phosphor is different after calcination.

2) PEG is not only a kind of dispersant during precipitation process, but also creates a local reducing atmosphere around particles during calcination process.

3) The formation temperature of crystalline YAG is decreased to 934 °C without any intermediate phase formation. The crystallization of YAG is significantly promoted and the oxidation of Ce^{3+} is inhibited by addition of PEG.

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聚乙二醇对均相法制备的 YAG:Ce 荧光粉性能的影响

任羿烜，苟　立，冉均国

(四川大学, 四川 成都 610065)

摘　要：在均相沉淀法制备 YAG:Ce 荧光粉前驱体的过程中，分别将分子量为 6000 和 10000 的聚乙二醇（PEG）作为分散剂添加到反应体系中。傅里叶变换红外光谱结果未发现不同分子量聚乙二醇的加入会对所制得的 YAG:Ce 前驱体产物的化学组成产生明显影响。相比于未添加聚乙二醇的样品，扫描电子显微镜（SEM）图像显示随着聚乙二醇的加入荧光粉的颗粒尺寸明显减小。在添加聚乙二醇的样品中，差示扫描量热分析（DSC）和 X 射线衍射（XRD）的结果证实了在钇铝石榴石（YAG）的结晶过程中没有任何中间相的形成，表明聚乙二醇的加入能够显著地促进 YAG 晶相的形成并且同时抑制 Ce^{3+}的氧化反应，最终大幅提高 YAG:Ce 荧光粉的荧光性能。

关键词：YAG:Ce 前驱体；均相沉淀法；物相演化；聚乙二醇（PEG）

作者简介：任羿烜，男，1988 年生，硕士，四川大学材料学院无机材料系，四川 成都 610065，电话：028-85401280，E-mail: athlon1919@163.com