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ARTICLE

Preparation and Properties of Yb:YAG and Nd:YAG Nanocrystals

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Abstract: Yb:YAG and Nd:YAG nanocrystals were synthesized by a ultrasound-microwave-assisted alkoxide hydrolysis precipitation method. The effect of reaction parameters including the microwave radiation power, microwave radiation time and calcination temperature on the composition of the products was investigated. The Yb:YAG and Nd:YAG nanocrystals were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) and photoluminescence (PL) spectrum. The results show that the pure phase Yb:YAG and Nd:YAG nanocrystals can be obtained at microwave radiation power of 385 W, microwave radiation time of 30 min and calcination temperature of 1100 ℃. The cooperative luminescent intensities of the Yb:YAG and Nd:YAG nanocrystals reach the maximum at the calcination temperature of 1100 ℃.

Key words: Yb:YAG; Nd:YAG; nanocrystals; luminescence; microwave

The host $Y_3Al_5O_{12}$ (YAG) is optically isotropic and mechanically robust with high thermal conductivity[1-3]. An Yb-doped material is one of the most promising laser materials for the next generation of efficient, high power lasers, due to superior availability of diode-pump, and high storage-energy capability. Among various kinds of Yb-doped materials, Yb:YAG has been focused on due to its high thermal strengths in thermal shock parameter and thermal conductivity[4-6].

Recently, wet chemical methods are widely used such as sol-gel[7,8], co-precipitation[9], spray pyrolysis[10], combustion[11] and their improvement methods[12,13] to synthesize YAG nanocrystals. In the new method, a microwave technique can reduce time and energy consumption of the reaction, enhance the velocity, yield and selectivity of all kinds of reaction[14-17]. Ultrasonic cavitation could hugely enhance the velocity of heterogeneous reaction, promote the formation of new solid phase, and control the dimension and distributing of grain[18,19].

In this study, Yb:YAG and Nd:YAG nanocrystals have been synthesized by a ultrasound-microwave-assisted alkoxide hydrolysis precipitation method. The effect of reaction parameters including the microwave radiation power, microwave radiation time and calcination temperature on the composition of the products has been investigated. The morphology and PL properties of Yb:YAG and Nd:YAG nanocrystals have been reported.

1 Experiment

Yb:YAG and Nd:YAG nanocrystals were synthesized by a ultrasound-microwave-assisted alkoxide hydrolysis precipitation method. The metal aluminum particles and proper amount of anhydrous aluminum chloride were added to isopropanol. The mixed solution was refluxed around 85 ℃ until the aluminum isopropoxide was successfully prepared. The yttrium isopropoxide was also synthesized using the above mentioned method. The aluminum isopropoxide, yttrium isopropoxide and $M(NO_3)_3$ (M = Yb, Nd, molar ratio is Al:Y:M = 5:2.97:0.03) were added dropwise into the 1 L and 0.4 mol/L ammonium bicarbonate solution by an ultrasound radiation time of 5 h.

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Afterwards, the products were centrifuged, washed several times with deionized water and anhydrous ethanol and then dried in a microwave oven. The precursors were calcined at 1000, 1100 and 1200 ℃ for 2 h to obtain products. The XRD of the synthesized powder was measured on an Empyrean X-ray diffractometer with Cu Kα radiation to reveal the phase composition. The SEM microscopy (JSM-6360LV) and HRTEM microscopy (JEM-2100F) were used to study the morphology and grains size of the products. Emission and excitation spectra were recorded on a F-7000 FL spectrophotometer with xenon lamp as radiation source.

2 Results and Discussion

2.1 XRD analysis

Fig.1 shows the XRD patterns of Yb:YAG and Nd:YAG prepared at different microwave radiation power. The diffraction peaks of the sample prepared at 385 W are indexed as $Y_3Al_5O_{12}$ phase (JCPDS card number 73-1370) and no impurity peaks are detected. The characteristic peaks are higher in intensity and narrower in spectral width, indicating the products are of good crystalline.

In addition to the radius of Yb^{3+} ion (r=0.0985 nm) similar to the Y^{3+} ion (r = 0.102 nm), their crystalline chemical properties are similar. Therefore when the Y^{3+} ion is replaced by Yb^{3+} ion, the powders keep the crystalline structures of YAG. The radius of Nd^{3+} ion (r=0.102 nm) is larger than that of Y^{3+} ion, but when the Y^{3+} ion is replaced by Nd^{3+} ion, the Nd:YAG nanocrystals also keep the crystalline structures of YAG. The two phases, YAG and YAM (JCPDS card number 14-0475) are obtained when using microwave radiation power of 231 W and 539 W. As it is seen, pure phase Yb:YAG and Nd:YAG can be grown completely at microwave radiation power of 385 W.

Fig.2 shows the XRD patterns of Yb:YAG and Nd:YAG prepared with different microwave radiation time. The powders have characteristic diffraction peaks of YAG phase without intermediate phases like YAM when using microwave radiation time of 30 and 40 min.

Fig.3 shows the XRD patterns of Yb:YAG and Nd:YAG prepared at different calcination temperatures. It can be seen that the broadening diffraction peaks have better crystalline, when using calcination temperature of 1100 ℃.

This is because some reactions occur in the precursor. A large number of nuclei of samples are produced like an explosion in the microwave radiation process, and Y^{3+}, Al^{3+}, Yb^{3+} or Nd^{3+} ions and related anions are nucleated at the same time [17]; it avoided nucleate of crystals step by step in conventional method. Those advantages can improve the crystalline of Yb:YAG and Nd:YAG nanocrystals, after microwave radiation of 30 min and calcination of 1100 ℃ for precursor. However, too high calcination temperature against pure phase YAG will affect the homogeneous distributing of composition, so it will decrease crystalline of products.

2.2 EDS analysis

As can be see, the optimum conditions to synthesize Yb:YAG and Nd:YAG pure phase are: microwave radiation

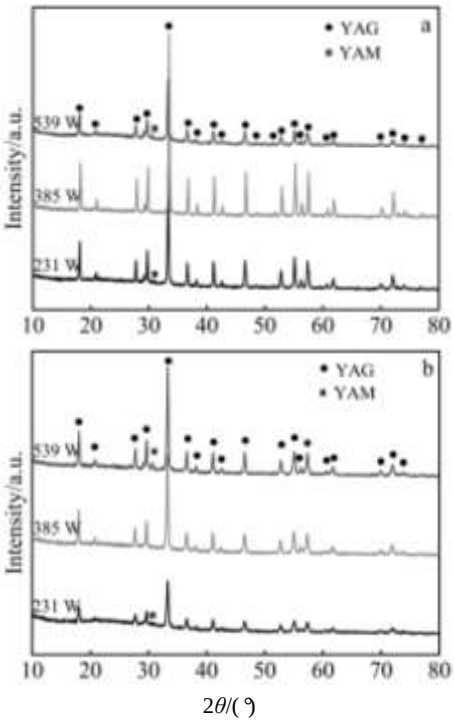

Fig.1 XRD patterns of Yb:YAG (a) and Nd:YAG (b) prepared at different microwave radiation power

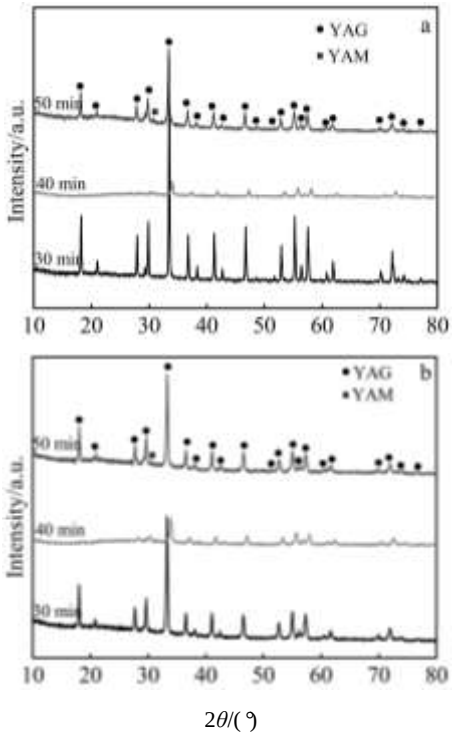

Fig.2 XRD patterns of Yb:YAG (a) and Nd:YAG (b) prepared with different radiation time

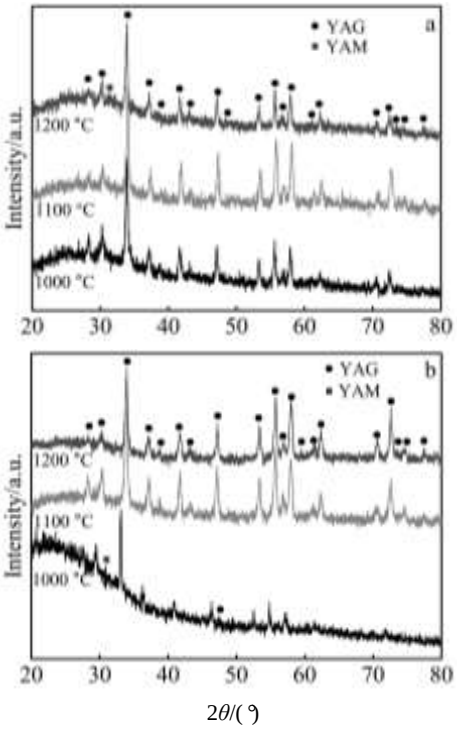

Fig.3 XRD patterns of Yb:YAG (a) and Nd:YAG (b) prepared at different calcination temperatures

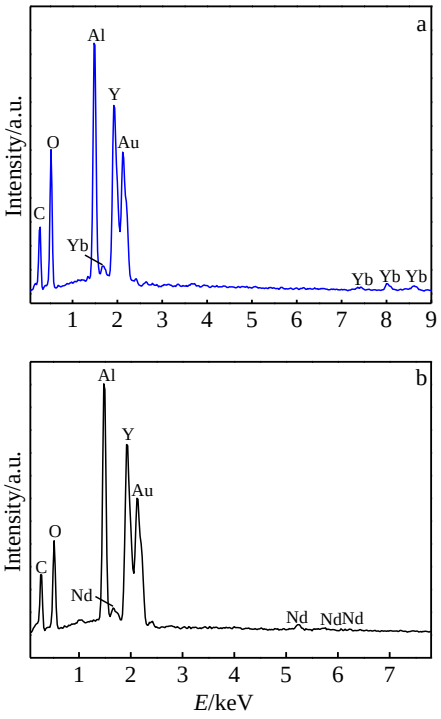

Fig.4 EDS spectra of Yb:YAG (a) and Nd:YAG (b) nanocrystals

power 385 W, microwave radiation time 30 min and calcination temperature 1100 ℃. Fig.4 shows the energy dispersive spectrum (EDS) of as-prepared Yb:YAG and Nd:YAG nanocrystals under above condition. No peaks of other elements except Y, Al, *M* (*M*=Yb or Nd), O, C, and Au are observed. The carbon and gold peaks in the spectrum come from the carbon film of conductive adhesive and gold plating process.

2.3 Morphology analysis

The morphology of the as-prepared samples was characterized with SEM, TEM and HRTEM. Fig.5a and 5b show that the Yb:YAG has uniform sphere and the average size is about 100 nm. Fig.5c and 5d show that the Nd:YAG has uniform sphere and the average size is about 70 nm. Insets of Fig.5b and 5d show the HRTEM image of Yb:YAG and Nd:YAG, respectively. In the insets, the crystal grains almost grow without defects.

2.4 Photoluminescence property

The PL emission spectra of the Yb:YAG nanocrystals prepared at different calcination temperatures using an excited wavelength of 367 nm are shown in Fig.6a. The relatively strong blue emission peak at 454, 469, 484, 493 nm can be seen, which is may be attributed to the recombination of an electron and a photogenerated hole caused by surface defects and oxygen vacancies.

The PL excitation spectra of the Yb:YAG nanocrystals prepared at different calcination temperatures using an excited

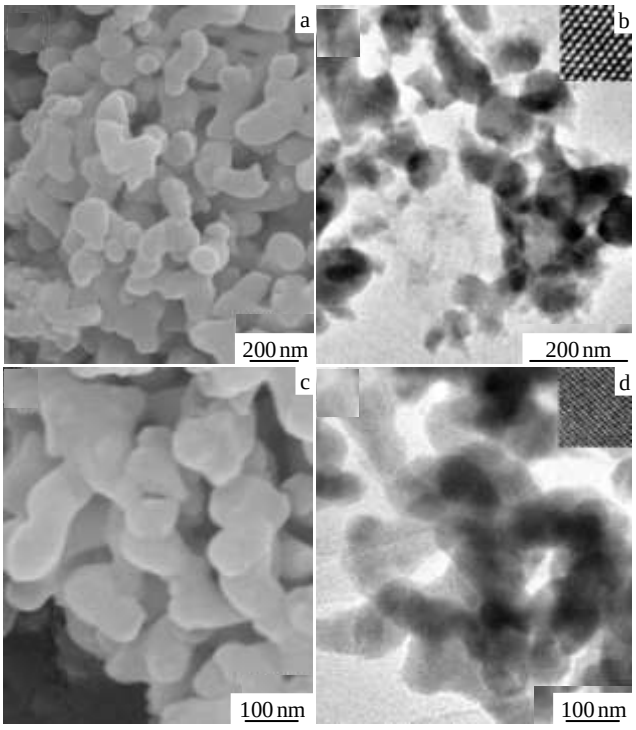

Fig.5 SEM (a, c), TEM (b, d) and HRTEM (inset in 5b and 5d) images of Yb:YAG (a, b) and Nd:YAG (c, d) nanocrystals

wavelength of 646 nm are shown in Fig.6b. It can be seen that the excitation spectra for Yb^{3+} two excitation bands are located at 307 and 365 nm.

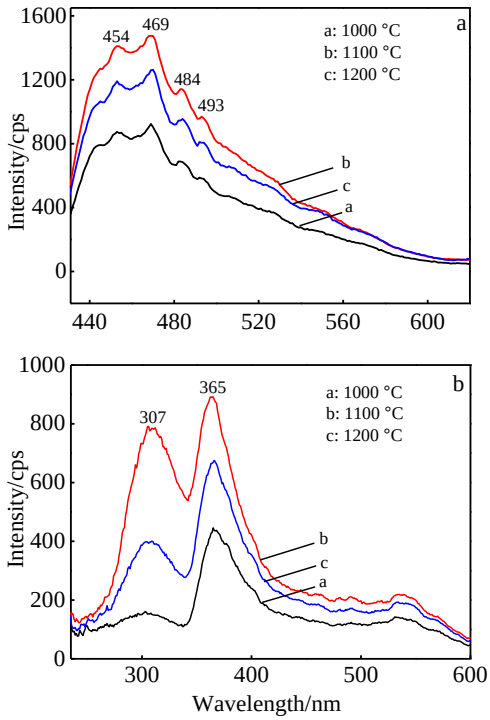

Fig. 6 PL emission (a) and excitation (b) spectra of the Yb:YAG nanocrystals at different calcination temperatures

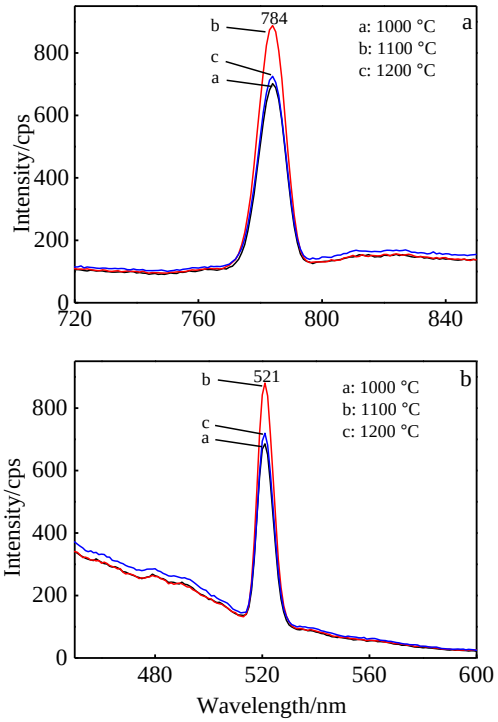

Fig. 7 PL emission (a) and excitation (b) spectra of the Nd:YAG nanocrystals at different calcination temperatures

The advantages of the Yb^{3+} ion derive from its simple electronic structure. There are only two energy level manifolds, a ground $^2F_{7/2}$ state and an excited $^2F_{5/2}$ state. Because of fewer electronic shield outside Yb^{3+}, the interaction between Yb^{3+} ions can be easily produced. In Yb:YAG nanocrystals, energy transfer occurs between Yb^{3+} through the Coulomb interaction, and the activation energy transfer from one to another ion. Both excited states Yb^{3+} are annihilation simultaneously, leading to cooperative luminescence.

The PL emission spectra of the Nd:YAG nanocrystals prepared at different calcination temperatures using an excited wavelength of 520 nm are shown in Fig.7a. The strong emission peak at 784 nm can be seen, which is may be attributed to the energy level transition of $^4I_{9/2} \rightarrow {}^4F_{5/2}$ of Nd^{3+}. The PL excitation spectra of the Nd:YAG nanocrystals prepared at different calcination temperature using an excited wavelength of 784 nm are shown in Fig.7b. It can be seen that the excitation spectra are located at 521 nm, which is may be attributed to the energy level transition of $^4I_{9/2} \rightarrow {}^4G_{7/2}$ of Nd^{3+}.

As shown in Fig. 6 and Fig. 7, the luminescent intensity increases with the increasing calcination temperature. After the temperature exceeds 1100 ℃, the luminescent intensity decreases with the increasing calcination temperature. The luminescence efficiency increases with the increasing crystallization[20], which agrees well with XRD measurements (see Fig.3). Fig.6 and Fig.7 show the optimum temperature of the best luminescent intensity is 1100 ℃.

3 Conclusions

1) Yb:YAG and Nd:YAG nanocrystals are successfully synthesized by the ultrasound-microwave-assisted alkoxide hydrolysis precipitation method. The pure phase Yb:YAG and Nd:YAG nanocrystals with well-crystallized structure are obtained at microwave radiation power of 385 W, microwave radiation time of 30 min and calcination temperature of 1100 ℃.

2) Yb:YAG and Nd:YAG nanocrystals particles are uniform sphere and the average sizes are about 100 and 70 nm, respectively.

3) The cooperative luminescent intensities of the Yb:YAG and Nd:YAG nanocrystals reach the maximum at the calcination temperature of 1100 ℃.

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Yb:YAG 与 Nd:YAG 纳米晶的制备及性能

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摘　要：通过超声-微波辅助醇盐水解沉淀法合成了 Yb:YAG 与 Nd:YAG 纳米晶。研究了微波辐射功率、微波辐射时间及煅烧温度对产物的影响。采用 X 射线粉末衍射(XRD)、扫描电子显微镜(SEM)、高分辨透射电子显微镜(HRTEM)及光致发光谱(PL)等对 Yb:YAG 与 Nd:YAG 纳米晶进行表征。结果表明，在微波辐射功率 385 W、微波辐射时间 30 min、煅烧温度 1100 ℃ 条件下，可以获得纯相 Yb:YAG 与 Nd:YAG 纳米晶。当煅烧温度为 1100 ℃ 时，Yb:YAG 与 Nd:YAG 纳米晶的合作发光强度均达到最大值。

关键词：Yb:YAG；Nd:YAG；纳米晶；发光；微波

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