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Tm,Ho:YAG 透明陶瓷的制备及性能

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摘 要：采用溶胶凝胶法制备 Tm,Ho:YAG 纳米粉体以及透明陶瓷，并对纳米粉体和透明陶瓷进行了分析。结果表明：在经过了 900 ℃煅烧后,纳米粉体已经形成了 YAG 晶相,在 785～398 cm^{-1} 这一范围的特征振动峰是 YAG 特有的晶格所引起的振动。**Tm,Ho:YAG** 透明陶瓷结构致密。在 1.97～2.03μm 的测试波长范围内，透过率大于 84%。经过 780 nm 的泵浦光源激发后,能够稳定的发出波长为 2.03 μm 的激光。

关键词：激光材料；纳米粉体；稀土离子；透明陶瓷
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Preparation and Properties of a Tm, Ho: YAG Transparent Ceramic

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Abstract: $Tm^{-}$and Ho^{-}codoped yttrium aluminum garnet (YAG) nanopowders were prepared by the sol–gel method, and a transparent ceramic was prepared from the obtained powders. X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, and fluorescence spectroscopy were used to analyze the synthesized nanopowders and transparent ceramic. The results show that after calcination at 900 ℃, the nanopowders formed the crystal phase of YAG, and the characteristic peaks in the range of 785 to 398 cm^{-1} correspond to vibrations of the unique lattice of YAG. After preparing the transparent ceramic, a compact structure was achieved. In the range of 1.97–2.03 μm, the transmittance was greater than 84%. After excitation by a 780 nm pumped light source, stable laser emission at a wavelength of 2.03 μm was produced.

Keywords: laser materials; nanopowders; rare-earth ions; transparent ceramics

With the advancement of society and the needs of human life, laser materials have received increasing attention and have been regarded as the main research topic in the fields of medical technology and the military. The preparation methods for laser materials are constantly being updated with the latest developments in science and technology. The most powerful example is the emergence of ruby lasers[1–2]. Since 1 960, researchers have increasingly focused on the preparation of polycrystalline ceramics for the following reasons: 1. In the preparation process, the growth cycle of the YAG crystal is long, and the size control is relatively complex; in contrast, the process to prepare polycrystalline YAG ceramics is simple, the cycle is short, and the cost is low. 2. During crystal growth, each group is arranged in an orderly manner, which will have a certain impact on the uniformity of the concentration of doped ions, while the polycrystalline ceramic has a disordered structure, which can make the doped ions uniform. 3. In terms of fluorescence properties, both types of material have similar properties and can be used to produce stable laser output, so polycrystalline ceramics have gradually become the best material to replace crystals. Therefore, current research focuses on the synthesis of high-purity nanopowders, the preparation of transparent polycrystalline ceramics with low scattering loss *via* advanced sintering of the obtained powders, and finally, the use of polycrystalline ceramics to replace single crystals as an

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essential component of solid-state lasers[3].

At present, there are many materials that can be used as a matrix, such as yttrium gallium garnet (YGG), gadolinium gallium garnet (GGG), and yttrium aluminum garnet (YAG). YAG possesses a stable cubic structure. Therefore, rare-earth-doped YAG is an excellent upconversion luminescent material because of its superb physical and chemical properties. Most of the rare earth ions that are doped into YAG are lanthanides because these elements have typical ladder-like energy level diagrams [4-7]. The 4f energy levels of lanthanides are not completely filled. Thus, these elements can absorb visible photons, transfer the energy through upconversion to cause an electron transition, and emit laser light at a specific wavelength. However, the single doping of Ho into Y_2O_3 as the active ion decreases the luminescence efficiency of the material. Therefore, the codoping of two rare earth ions (Ho and Tm) is favored. Tm acts as a sensitizer and transfers energy to Ho, which acts as the luminescent center and lases at a wavelength of 2 μm. The codoping greatly improves the luminescence efficiency and stability of the material. This topic has become a research focus [8–11].

In this study, two rare earth elements, Ho and Tm, were codoped into the YAG matrix by the sol–gel method. A transparent ceramic was prepared by using the obtained target powders. The properties of the transparent ceramic were characterized by thermogravimetry-differential thermal analysis (TG–TA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and other test methods.

1 Experimental

1.1 Preparation of Tm, Ho: YAG powder

Analytically pure Ho_2O_3, Tm_2O_3, and Y_2O_3 were used as the main raw materials. First, 1% of Y^{3+} ions were replaced by Ho^{3+} ions, and 2% of Y^{3+} ions were replaced by Tm^{3+} ions[12]. The appropriate amounts of raw materials were weighed according to the stoichiometry of $(Y_{0.97}Ho_{0.01}Tm_{0.02})_3Al_5O_{12}$. Ho_2O_3 and Tm_2O_3 were mixed and dissolved in excess of 6 mol/L concentrated nitric acid. The resultant solution was magnetically stirred at 60 ℃ to evaporate the excess nitric acid, and the stirring was stopped when the raw materials were dissolved. Then, $Al(NO_3)_3·9H_2O$ was dissolved in an appropriate amount of deionized water, and the two solutions were uniformly mixed and placed on a magnetic stirrer for thorough stirring. After the salt solution became clear, it was cooled to room temperature. Next, citric acid was added to the solution, and the resulting mixture was continually stirred until the citric acid was completely dissolved. After the solution became clear again, ammonia hydroxide ($NH_3·H_2O$) was added dropwise to the solution to adjust the pH to 1–2. The solution was then heated to 60 ℃, and the stirring continued for 1.5 h. When the solution became viscous, the angle of the container was adjusted, and the viscous solution was stirred with a glass rod so that the stirring bar could continue to rotate. The speed of the stirring bar was carefully controlled at this time. Finally, the gel became transparent when the stirring bar could no longer rotate. The container was removed from the magnetic stirrer and placed into a preheated oven. The gel was dried at 200 ℃ for 2–4 h. At this time, the sample became fluffy because of citric acid, and the color became reddish brown or even black. After the fluffy sample was removed from the oven, anhydrous ethanol was added. The resulting mixture was transferred to a mortar and ground to obtain the nanopowder precursor. The powdered precursor samples were placed in crucibles and sintered in a furnace at 700, 800, 900, and 1 000 ℃ for 4 h to obtain the target powders.

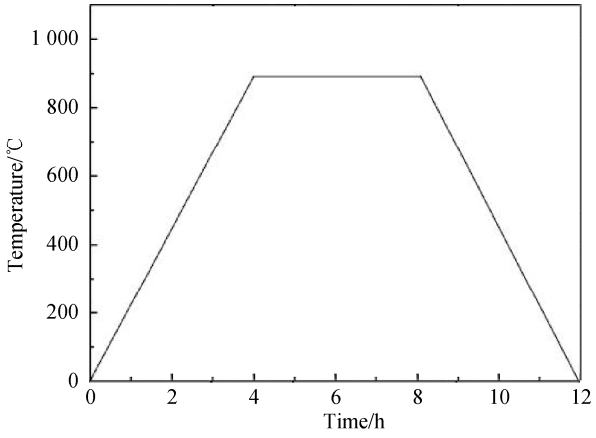


Fig. 1 Sintering temperature curve for Tm, Ho: YAG precursors

1.2 Preparation of the ceramic

An appropriate amount of sintered Tm, Ho: YAG nanopowder was weighed and placed in an agate mortar. Anhydrous ethanol and tetraethyl orthosilicate (TEOS) were added to the powder. The resulting mixture was fully ground and mixed. After all the ethanol was evaporated, the sample was screened by a 170 mesh sieve. The sieved sample was placed in a mold and pressed into a pellet at 20 MPa for approximately 15 min. Then, the pellet was pressed in an isostatic press at 200 MPa for 5 min or more to obtain the round green body of the ceramic. Next, the obtained green body was placed in a

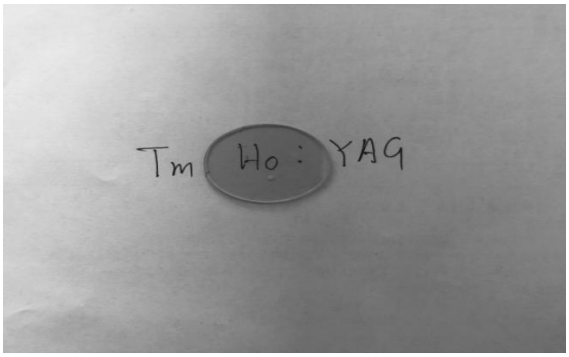


Fig. 2 Tm, Ho: YAG transparent ceramic sample

vacuum sintering furnace with an ultimate vacuum condition of 1×10^{-3} MPa. The sample was sintered at 1 750 ℃ for 22 h, slowly cooled to room temperature, and then removed to obtain the Tm, Ho: YAG transparent ceramic sample with a size of ϕ 20 mm×2 mm and a density of 2.77 g/cm^3.

1.3 Characterization

The Tm, Ho: YAG nanopowder samples were characterized by an Ultima IV X-ray diffractometer (Rigaku, Japan) with Cu Kα radiation. The X-ray tube voltage was 40 kV, the tube current was 20 mA, and the scan rate was 4°/min. The thermal stability of the samples was analyzed by a Q50 type thermogravimetry-differential thermal analyzer (TA Instruments, USA) in flowing air and at a heating rate of 10 ℃/min. The morphology of the Tm, Ho: YAG transparent ceramic and the compactness of its surface were characterized by a Quanta 450 FEG scanning electron microscope (FEI, USA). The infrared spectrum of the sample was obtained on an FTS-135 Fourier transform infrared (FT-IR) spectrometer (BIO–RAD). The fluorescence spectrum of the ceramic was obtained on a PL9 000 photoluminescence fluorescence spectrometer (PFS) with an excitation wavelength of 780 nm from an Ar ion laser. The transmittance of the ceramic sample in the wavelength range of 1.97-2.03 μm was measured by a UH4150 (factory No. 285018-001) spectrophotometer.

2 Results and discussion

2.1 XRD analysis

Fig. 3 shows the XRD patterns of the precursors after sintering at 700, 800, 900, and 1 000 ℃. Compared with the standard spectrum of YAG, the crystal phase of YAG appears after 700 ℃ calcination. However, crystallization is not fully completed at this temperature, and many impurity peaks are detected. After calcination at 800 ℃, the sample exhibits a good morphology and has fewer impurity peaks. After calcination at 900 ℃, there are almost no impurity peaks, and the crystallization is almost complete. Nanopowders that are obtained under this condition can be used to prepare the transparent ceramic for subsequent tests. After calcination at 1 000 ℃, the crystal phase of YAG was pure. Therefore, 900 ℃ is the optimal sintering temperature for Tm, Ho: YAG. The nanopowder calcined at 900 ℃ was selected for the following study.

2.2 FT-IR analysis

Fig. 4 shows the FT-IR vibrational spectrum of the Tm, Ho: YAG sample calcined at 900 ℃. The broad peak at 3 457 cm^{-1} is attributed to the stretching vibration of O–H in water. The vibration peak at 1 621 cm^{-1} corresponds to the bending vibration of O–H in the sample, which indicates that the surface of the sample adsorbed a small amount of water from the air. Therefore, the small vibration peak at 1 510 cm^{-1} is assigned to the CO_3^{2-} that formed by dissolving a small amount of CO_2 into the adsorbed water. The characteristic vibration peaks at 785, 731, and 690 cm^{-1} in the fingerprint region are attributed to the vibrations of the Y–O and Al–O bonds. The sharp vibration peaks in the range of 570–398 cm^{-1} are ascribed to the Ho–O and Tm–O bonds formed by the doping of Ho and Tm rare earth ions into the YAG crystal. In conclusion, the sample calcined at 900 ℃ exhibits the YAG phase, and the doped rare earth ions are stably incorporated into the lattice of YAG[13–14].

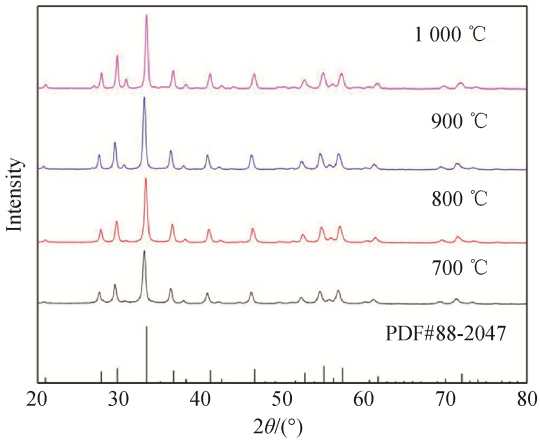


Fig. 3　XRD patterns of Tm,Ho:YAG nanopowders

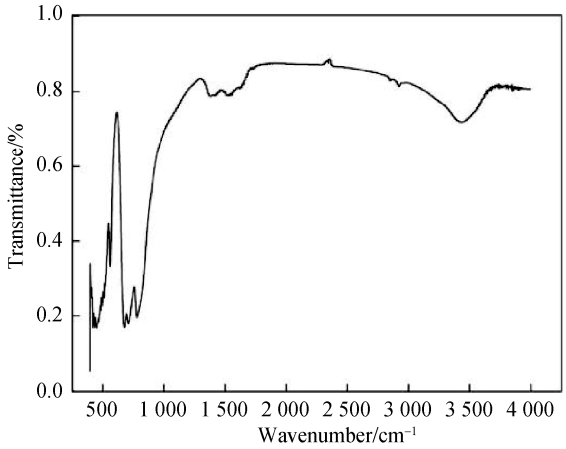


Fig. 4　FT-IR spectrum of Tm, Ho: YAG powder sample

2.3 TG–DTA

The TG-DTA curves of the Tm, Ho: YAG powder precursor are shown in Fig. 5. The mass loss of the sample is a continuous process, and the total loss is approximately 43%. There is a significant mass loss at 116.67 ℃ in the TG curve, and a slight fluctuation exists in the corresponding DTA curve, which indicates the evaporation of free water from the precursor. At this time, the mass loss is approximately 6.2%, and the free water in the precursor has evaporated completely. The sharp and clearly exothermic peak at 447.63 ℃ is associated with the decomposition of nitrate in the nanopowder sample. The TG curve shows a significant downward trend. This result suggests that NO_3^- in the sample has been completely decomposed at this temperature, and the corresponding mass loss is approximately 18.7%. The

strong exothermic peak at approximately 660.31 ℃ is associated with the formation of the YAG crystal phase. As evidenced by the TG curve, the sample has an apparent mass loss (approximately 17.9%) at this temperature. After 907.27 ℃, the TG curve levels off, and there are no evident endothermic or exothermic peaks in the DTA curve. Since the DTA curve presents a certain temperature hysteresis, the temperature required for the complete formation of the YAG crystal phase obtained by TG-DTA analysis is slightly higher than the temperature determined by XRD. In summary, the YAG crystal phase can be formed after sintering the Tm, Ho: YAG powder precursor at 900 ℃. There is no interference from other impurity phases, and the quality of the sample is excellent.

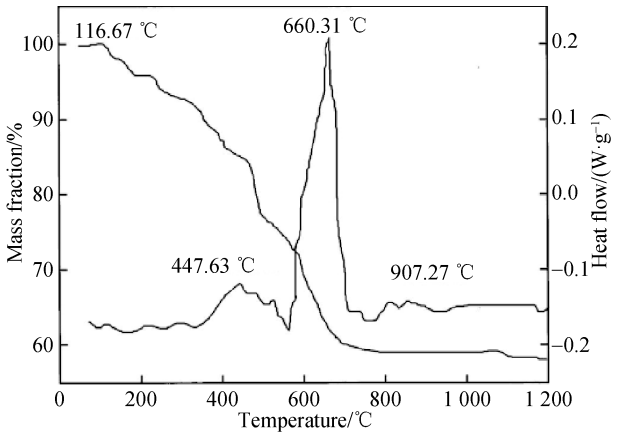


Fig. 5 TG-DTA curves for the precursors Tm, Ho: YAG powder

2.4 Fluorescence of the ceramic

Fig. 6 shows the fluorescence spectrum in the range of 1 600–2 200 nm for the Tm, Ho: YAG transparent ceramic excited by a 780 nm pumped light source at room temperature. A series of emission peaks are observed in this range. According to the energy level analysis, when the sample is subjected to 780 nm light, the emission peaks in the range of 1 650 to 1 950 nm are mainly caused by the $^3H_6 \rightarrow {}^3H_4$ transition of Tm^{3+}. The strongest emission peak in this range is located at 1 941 nm. The electrons that are excited to the $^3H_4$ level eventually undergo relaxation so that the photons are distributed at the $^3F_4$ level. Because the $^3F_4$ level of Tm^{3+} is close to the $^5I_7$ level of Ho^{3+}, energy can be transferred from the $^3F_4$ level of Tm^{3+} to the $^5I_7$ level of Ho^{3+}. Finally, Ho^{3+} transitions from $^5I_7$ to the ground state $^5I_8$ and emits laser light with a wavelength of 2.03 μm[15].

The energy level conversion mechanism of Tm and Ho is shown in Fig. 7 and is described below:

$$780\ \text{nm} + {}^3H_6(Tm^{3+}) \rightarrow {}^3H_4 \quad (1)$$

$${}^3H_4(Tm^{3+}) \rightarrow {}^3F_4(Tm^{3+}) + 6\,000\ \text{cm}^{-1} \quad (2)$$

$${}^3F_4(Tm^{3+}) + 6\,000\ \text{cm}^{-1} \rightarrow {}^5I_7(Ho^{3+}) \quad (3)$$

$${}^5I_7(Ho^{3+}) \rightarrow {}^5I_8(Ho^{3+}) + 2\ \mu\text{m} \quad (4)$$

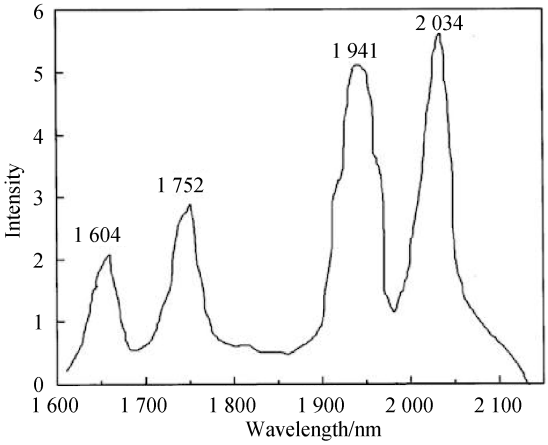


Fig. 6 Fluorescence spectrum of Tm, Ho: YAG transparent ceramic

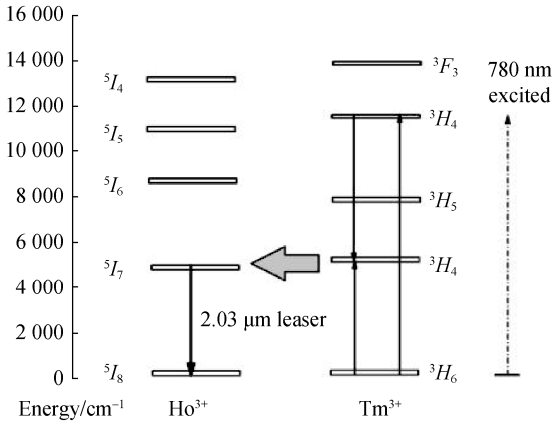


Fig. 7 Energy level conversion mechanism for Tm and Ho after 780 nm light excitation

2.5 Cross-sectional morphology of ceramics

Fig. 8 shows the cross-sectional SEM image of the transparent ceramic. Fig. 9 reveals the connections between the particles in this region. The cross-section of the ceramic exhibits a good morphology. The structure is compact, and the porosity is low. The quality of the ceramic is excellent.

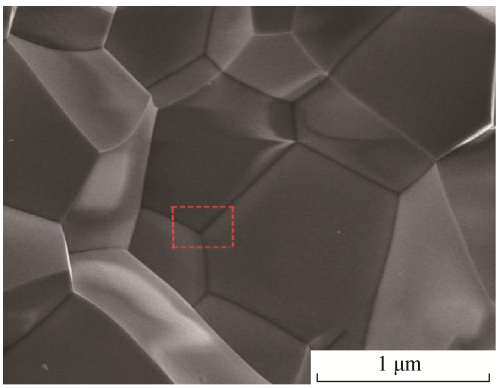


Fig. 8 SEM image of the ceramic section

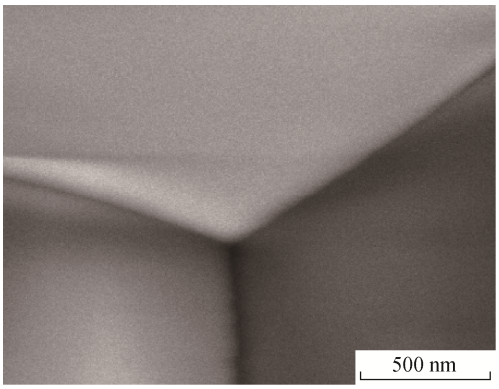


Fig. 9　SEM image of the ceramic section

2.6　Transmittance of the ceramic

Fig. 10 shows the transmittance of the Tm, Ho:YAG transparent ceramic. The transmittance is 84.48% in the wavelength range of 1.97–2.03 μm. The transparency is good, which indicates that the transparent ceramic can be used as a stable laser material.

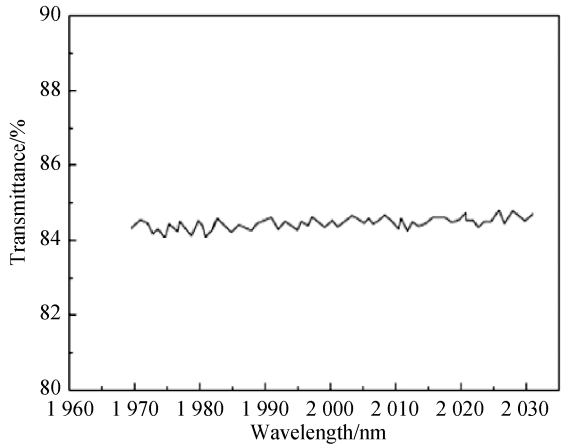


Fig. 10　Tm, Ho: YAG transparent ceramic transmittance

3　Conclusion

In this study, a Tm, Ho: YAG nanopowder was synthesized by the sol–gel method and was used to prepare a transparent ceramic. The mass loss of the nanopowder after sintering was approximately 43%. The XRD and IR analyses indicate that a stable YAG crystal phase was formed. The obtained transparent ceramic presented a good cross-sectional morphology, uniform particle distribution, low porosity, and uniform particle size. The transmittance of the transparent ceramic in the wavelength range of 1.97–2.03 μm was more than 84%, which satisfies the requirement for transparent ceramics. Upon 780 nm light excitation, a laser beam with a wavelength of 2.03 μm was stably emitted.

References:

[1] MAIMAN T H. Stimulated optical radiation in Ruby Masers[J]. Nature. 1960, 187(4736): 493–494.

[2] MAIMAN T H. Optical and microwave-optical experiments in Ruby[J]. Phys Rev Letters. 1960, 4(11): 564–566.

[3] WANG Bo. Characteristics and key technologies of Nd: YAG laser ceramics(in Chinese, dissertation). Xi'an: Xidian University. 2015.

[4] LIU Dongyang, WANG Desheng, LI Han, et al. Preparation and characterization of YAG:Ce^{3+} phosphor[J]. Bull Chin Ceram Soc. 2013, 31(4): 988–991.

[5] LUO Junming, LI Yongxiu, Deng Liping, et al. Fabrication of Er^{3+}:Y_2O_3 nanocrystalline powder for upconversion luminescence by coprecipitation[J]. Rare Met Mater Eng. 2007, 36(8): 1 436–1 439.

[6] LUO Junming, JIAO Yamei, Deng Liping, et al. Preparation and luminescent properties of Y_2O_3:Yb^{3+}, Tm^{3+} nanopowder[J]. J Synth Cryst. 2017, 46(3): 410–415.

[7] LI Zhonghua, LI Changmin,ZHANG Yingying, et al. Upconversion fluorescence of Ho^{3+}/Yb^{3+}codoped bismuth gallate glass[J]. J Chin Ceram Soc. 2008, 36(1): 123–127.

[8] XIE Huicai. Preparation and properties of rare-earth ions doped into YAG for transparent laser ceramics (in Chinese,dissertation). Beijing: BeijingUniversity of Chemical Technology. 2013: 1–85.

[9] WANG Yong. Preparation and characterization of Ce:YAG nanopowder and transparent ceramics(in Chinese,dissertation). Shenzhen: Shenzhen University, 2015: 1–74.

[10] HUANG Qingming, YU Jianshi. Upconversion luminescence characteristic of Sc^{3+}/Tm^{3+}/Yb^{3+}-tridoped nano hexagonal $NaYF_4$[J]. J Chin Ceram Soc. 2011, 39(7): 1170–1174.

[11] DAI Shixun, LI Xujie, NIE Qiuhua. et al. Upconversion luminescence in Yb^{3+}-sensitized Er^{3+}/Yb^{3+}-codoped tellurite glasses[J]. Acta Phys Sin. 2007, 56(9): 5518–5525.

[12] ZHU Zhongli, LIN Hai. Preparation and luminescence property of Ho,Tm:$Yb_3Al_5O_{12}$ nanopowder[J]. J Chin Ceram Soc. 2015, 43(1): 87–92.

[13] LU Bing. Preparation and characterization of rare-earth-doped YAG phosphors and transparent films (in Chinese, dissertation). Shenzhen: Shenzhen University, 2016: 1–83.

[14] MA Xuetao. Preparation and characterization of rare-earth-doped YAG transparent ceramic powders (in Chinese, dissertation). Changchun: Changchun University of Science and Technology, 2013: 1–47.

[15] ZENG Fanming, LI Chun, LIN Hai, et al. Spectral properties of Tm- and Ho-codoped BYF laser crystal.[J]. J Synth Crystls. 2012, 41(S1): 250–253.