

Effect of heat treatment on the crystallization of Nd:YAG ceramics

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Abstract: The $(Y_{0.99}Nd_{0.01})_3Al_5O_{12}$ nano-sized powders were synthesized by low temperature combustion (LCS), using Nd_2O_3 , Y_2O_3 , Al $(NO_3)_3 \cdot 9H_2O$, ammonia water and citric acid as starting materials. This method effectively solves the problems caused by solid-state reaction at high temperature and hard agglomerates brought by chemical precipitation method. The powders were characterized by TG-DTA, XRD, FT-IR and TEM, respectively. The crystallite sizes were calculated by Scherrer's formula using the full width at half maximum of YAG(420) diffraction lines. The study focused on the crystallization of ceramics with different heat treatment temperatures. The experiments show that the forming temperature of YAG crystal phase is 850 °C and YAP crystal phase appearing during the calcinations transforms to pure YAG at 1050 °C. The particle size of the powders synthesized by LCS is in the range of 20~50 nm depending on the thermal treatment temperature. With the temperature increasing, the mean grain sizes ascend, the stand deviations keep at about 2.0 and the crystal lattices decrease. The grains grow mainly by the grain boundary diffusion. The lattice parameter expansion is caused by an increase of the repulsive dipolar interactions at the surfaces of particles.

Key words: Laser ceramics; Neodymium-doped yttrium aluminum garnet (Nd:YAG); Nano-sized powders; Low temperature combustion synthesis (LCS)

CLC number: TN21 **Article ID:** A **Document code:** 1007-2276(2005)03-0373-05

热处理温度对掺钕钇铝石榴石陶瓷析晶的影响

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摘要: 采用氧化钕、氧化钇、硝酸铝、氨水以及柠檬酸作为原材料, 以低温燃烧法(LCS)制备出纳米粉末材料。该方法解决了固相反应的高温合成及化学沉淀法的粉体团聚问题。通过热重-差热(TG-DTA)、X-射线粉末衍射(XRD)、傅里叶红外透射(FT-IR)和透射电镜(TEM)测试手段研究粉末的特性, 采用谢莱方程(Scherrer)根据 YAG(420)晶面的衍射曲线半峰宽数据计算出晶粒尺寸, 详细研究陶

收稿日期: 2004-08-02; 修订日期: 2004-08-20

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瓷材料在不同热处理条件下的析晶情况。研究表明:YAG 相的形成温度为 850 ℃,在热处理过程中出现 YAP 中间相,于 1050 ℃转变成纯 YAG 相,颗粒在不同的热处理条件下呈现不同的尺寸,在 20~50 nm 范围变化。随着热处理温度的升高,平均晶粒尺寸增加,晶粒尺寸的标准偏差保持在 2.0 左右,晶格参数逐渐减小。晶粒主要以晶界扩散形式进行生长,晶格参数膨胀是由晶粒表面的排斥偶极距所造成的。

关键词: 激光陶瓷; 掺钕钇铝石榴石(Nd:YAG); 纳米粉末; 低温燃烧法(LCS)

0 Introduction

Transparent polycrystalline neodymium-doped yttrium aluminum garnet ($\text{Nd}:\text{Y}_3\text{Al}_5\text{O}_{12}$, Nd:YAG) ceramics, laser ceramic matrix materials, with predominantly chemical stability, highly doped ion concentration, excellent optical performance and high temperature stability, is gradually becoming a substitute for single crystals^[1,2]. It is evidently that homogeneously dispersed, less agglomerated and nano-sized precursor powders are extraordinarily favorable to form ceramic green bodies. Presently, the conventionally used methods to produce Nd:YAG powders are solid-state processes^[3], chemical precipitation methods^[4] and sol-gel techniques^[5].

The LCS, firstly used by Pechini in 1967 to synthesize capacitor ceramics, is one of the simplest methods for synthesizing ceramic nano-sized powders^[6]. A very porous sponge-like compound is formed due to release of a large amount of gaseous products formed in low temperature combustion reaction between metal nitrates used as oxidizer and citric acid used as chelating agent, reducer and fuel in the reactant system. The crystallized mixed oxides produced above are perfectly homogeneous at temperature lower than 1100 ℃, and the cross-linked polymer structures can effectively prevent the powders from agglomerating. Study and control of crystallization during the heat treatment can guide the ceramic sintering and effectively prevent the abnormal crystallization. The homogenous microscopy of ceramic can be obtained with good crystallization, so the transparency can be increased.

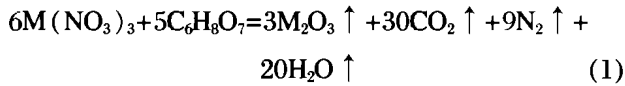
In this article, the $(\text{Y}_{0.99}\text{Nd}_{0.01})_3\text{Al}_5\text{O}_{12}$ nano-sized

powders were produced by LCS. The pure cubic YAG crystal phase could be obtained at the temperature as low as 1100 ℃. The study focused on the crystallization of Nd:YAG at different heat treatment temperatures.

1 Experimental

1.1 Synthesis

At the beginning of LCS process, the neodymium, yttrium stock solution were prepared by dissolving the neodymia (Nd_2O_3 , 99.99%) and yttria (Y_2O_3 , 99.99%) in slightly excess nitric acid under heating and stirring by hot magnetic stirrer and were dissolved in deionized water. The aluminum stock solution was prepared by dissolving aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, AR) in deionized water. According to the stoichiometry of $(\text{Y}_{0.99}\text{Nd}_{0.01})_3\text{Al}_5\text{O}_{12}$, the Nd^{3+} , Y^{3+} and Al^{3+} were 0.0003, 0.0297 and 0.05 mol in the solution, respectively. Next, the stock solutions of Nd^{3+} , Y^{3+} and Al^{3+} were mixed with 0.067 mol citric acid aqueous solution according to stoichiometry of fuel-oxidizer^[7]. After being stirred for 0.5 h, the pH value detected by an electrode (Delta 320, Mettler Toledo) was adjusted to 1.5~2.0 using ammonia water ($\text{NH}_3 \cdot \text{H}_2\text{O}$, AR) and the mixed solution was added with 0.5 wt% ethyl silicate (TEOS, AR) as sintering aid. Then the solution was violently stirred for 1~2 h. At last, a light yellow transparent gel was obtained after evaporation of water. The dried gel was then heated on a resistor oven and the combustion occurred together with a red flame lasting for 3~5 min. Eventually the porous black powders were obtained. The combustion reaction could be represented as equation (1)^[8]:



Where the products were CO_2 , N_2 , H_2O and the oxides, M was Nd^{3+} , Y^{3+} and Al^{3+} in ratio 0.03:2.97:5. Here, the ammonia water reacting with nitric acid formed ammonium nitrate which was used as the catalyst to lower the ignition temperature of the gel and produce more gases to reduce the agglomeration of particles. After being milled with zirconia balls in a planetary miller for 0.5 h, the black powders were calcined at different temperatures from 600~1300 °C for 2 h according to TG-DTA analysis results.

2.2 Characterizations

Differential-thermal and thermal-gravimetric analysis (Pyris-Diamond DTA-TG, Perkin-Elmer, USA) were conducted simultaneously on the black powders heating at 10 °C/min up to 1200 °C in an oxygen atmosphere. X-ray diffractions (D/max 2500 V, Rigaku, Japan) were used to determine the crystal phase evolution during calcinations using nickel-filtered CuK_α radiation in the range of $2\theta=20\text{--}60^\circ$ (15.406 nm, 40 kV×200 mA). The crystallite sizes were calculated by the Scherrer's formula using full width at half maximum of YAG (420) diffraction line. The lattice parameter values were calculated by the XRD results. The powders calcined at 1100 °C after being ultrasonically dispersed in ethanol were observed by TEM (JEM-2010EX, JEOL, Japan).

2 Results and discussion

2.1 TG-DTA analysis

TG-DTA results of the black powder are given in Fig.1. The 6.7% weight loss at 96 °C is caused by dehydration of physically absorbed water accompanied by a small endothermic peak. The apparently decrease in weight and sharp exothermic peak focus in the temperature range of 250~550 °C corresponding to decompositions and oxidation reactions of organic matters in the black powders with 33.6% weight loss. The third weight

loss occurs during 850~1050 °C relevant to exclusion of

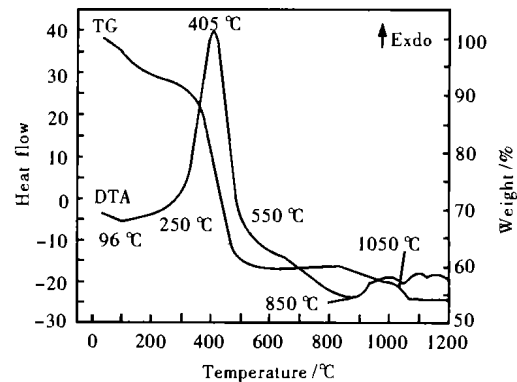


Fig.1 TG-DTA analysis of the as-synthesized powders

carbon dioxide strongly absorbed on the surface of nano-sized particles with weight loss of 5.5%. The total weight losses are around 46%. The DTA traces indicate a broad band endothermic peak at 850 °C and a narrow band endothermic peak at 1050 °C. The peak at 850 °C is related to crystallization of YAG phase and the peak at 1050 °C is the transformation of YAP to YAG, which can be confirmed by XRD shown in Fig.2.

2.2 XRD analysis

Fig.2 shows the X-ray diffraction patterns of the powders calcined at different temperatures decided by TG-DTA results. The powders remain amorphous up to 800 °C with only a broad band centering at corresponding to (420) plane of YAG indicating the start of YAG crystallization. At 900 and 1000 °C, the characteristic peaks of YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$) together with two small peaks of intermediate phase YAP (YAlO_3) appear, which is indicative of microcrystalline YAG and YAP materials. Above 1100 °C, there is no other crystal phase in the material except YAG, as is confirmed by the #ICPDs 33~40 card. This temperature is lower than the solid-state methods, in which YAP and YAM ($\text{Y}_4\text{Al}_2\text{O}_9$) persist above 1300 °C. The peak intensities strengthen and shapes become narrow with the temperature increasing indicating crystallite growth of powders. Using the Scherrer's formula on the full width at half maximum of YAG (420) diffraction lines, the grain

sizes at different temperature are calculated. The statistic histogram and mean grain size are shown in Fig.3.

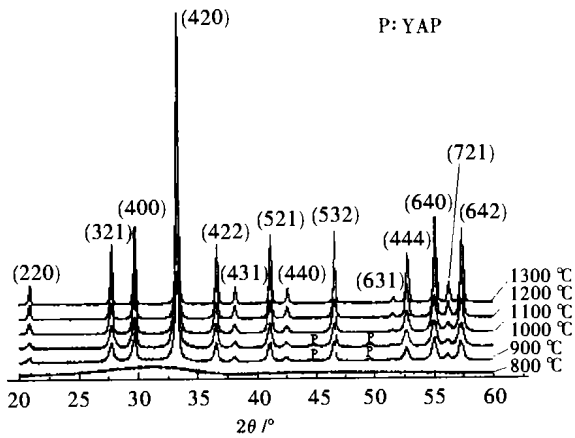


Fig.2 XRD diffraction patterns of powders calcined at different temperatures

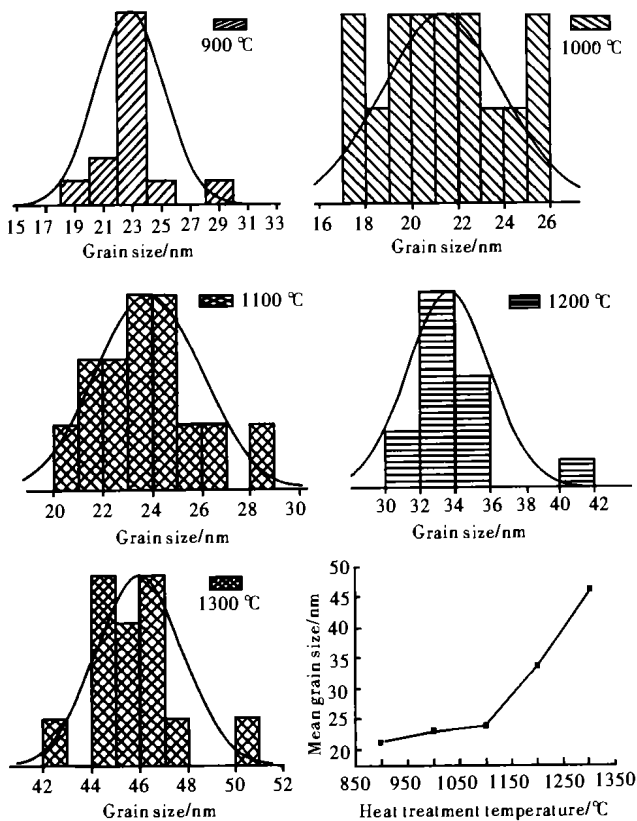


Fig.3 Statistic histogram of grain sizes and mean grain sizes at different temperatures

From Fig.3, the grain size distribution shapes keep almost the same and the mean grain size grows slowly below 1100 °C and rapidly above this temperature, indicating the ceramic green body will densify quickly above this temperature. The stand deviations of mean

grain sizes keep at about the same value 2.0. According to the grain growth mechanism, where is the mean grain size, is the mean grain size at and is a constant. The exponent is often found to be between 2 and 4 [9]. According to the line shape, the grain linearly grow mainly by the grain boundary diffusion. Table 1 is the comparison of crystal lattice parameter values between YAG ceramic calculated from XED results and single crystal from #JCPDs 33~40 card.

Tab.1 Comparison of crystal lattice parameter values between YAG ceramic and single crystal

Crystal plane	Single crystal/nm	Ceramic/nm				
		900 °C	1000 °C	1100 °C	1200 °C	1300 °C
(220)	1.201	1.205	1.203	1.205	1.202	1.202
(321)	1.201	1.204	1.204	1.204	1.203	1.201
(400)	1.201	1.204	1.204	1.204	1.203	1.201
(420)	1.201	1.204	1.204	1.204	1.203	1.201
(422)	1.201	1.203	1.204	1.204	1.203	1.202
(431)	1.201	1.204	1.203	1.204	1.203	1.202
(521)	1.201	1.204	1.204	1.203	1.202	1.201
(440)	1.200	1.204	1.204	1.204	1.202	1.202
(532)	1.201	1.203	1.203	1.203	1.202	1.201
(631)	1.201	none	none	1.203	1.202	1.201
(444)	1.201	1.203	1.203	1.203	1.202	1.201
(640)	1.201	1.204	1.204	1.203	1.202	1.201
(721)	1.200	1.203	1.204	1.204	1.202	1.201
(642)	1.201	1.203	1.204	1.203	1.202	1.201

From Table 1, the lattice parameter values of Nd:YAG ceramics are larger than those of single crystal. This phenomenon is defined as lattice expansion caused by nano-sized crystallite. The lattice parameter is gradually decreasing and close to those of single crystal as the calcined temperature increases. In oxide particles, the bonds have a directional character. At the outer surface of each particle, there will be unpaired electronic orbitals, which will repel with each other. This contribution from the surface layer increases with the decreasing particle

size and leads to large values of the lattice parameter than those of the single crystal^[10].

2.3 TEM analysis

TEM micrographs of the powders calcined at 1100 °C for 2 h are shown in Fig.4. The powders are lightly crushed in a mortar and pestle before TEM observation. It can be seen that all particles show the irregular shapes and are linked together because of high calcined temperature indicating that the crystallites grow at the high temperature. The particles measured from different areas are less than 50 nm. The obtained values are in good agreement with those of XRD diffraction patterns, which indicates that the powders are in nano-size. The produced powders are efficiently favorable for the ceramic green body forming and pores exclusion. The abnormal grain growth during sintering can be restrained and the homogeneous microscopy of Nd:YAG ceramics can be obtained.

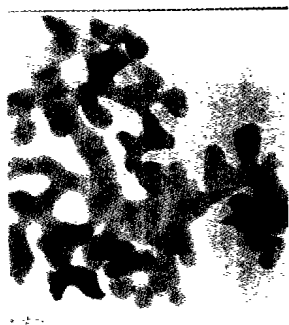


Fig.4 TEM micrograph of precursor powders

3 Conclusions

The homogeneously dispersed, less agglomerated $(Y_{0.99}Nd_{0.01})_3Al_5O_{12}$ nano-sized powders with size less than 50 nm, were successfully synthesized by the low temperature combustion. The crystallization temperature of YAG phase is at 850 °C. The intermediate crystal phase YAP appears during calcinations and transforms to YAG at 1050 °C. The crystallites grow with the calci-

ned temperature increasing. The emission line intensity enhances with the sintered temperature increasing due to higher crystallization. The effectively induced cross section σ_m with the value $4.03 \times 10^{-19} \text{ cm}^2$ at 1065 nm is about 44% higher than that of single crystal indicating that ceramics have the potential to become the laser matrix.

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好消息: 据检索统计,《红外与激光工程》2004年第1~6期全部被EI核心数据库(compendex)收录。这与多年来广大读者、作者对我们的支持是分不开的,在此表示感谢! 欢迎继续投稿。