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JOURNAL OF RARE EARTHS
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JOURNAL OF RARE EARTHS, Vol. 31, No. 11, Nov. 2013, P. 1102

Optical property of $SmAlO_3$ applied as 1.06 μm laser absorbing material

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Received 21 May 2013; revised 28 August 2013

Abstract: $SmAlO_3$ powders were successfully synthesized through the citrate sol-gel combustion method. The phase evolution of the prepared powders were characterized using thermal gravimetric (TG) analysis, differential scanning calorimetry (DSC) analysis and Fourier transform infrared spectroscopy (FTIR). X-ray diffraction (XRD) was applied to examine the purity of the powders. The reflective properties of $SmAlO_3$ with changing temperatures were investigated by ultraviolet-visible near-infrared spectrophotometer (UVPC) specular reflection spectrum. The results displayed that pure $SmAlO_3$ phase with preferable reflectivity at 1.06 μm could be obtained at 900 ºC for 2 h. Furthermore, the reflectivity of $SmAlO_3$ at various temperatures from –40 to 500 ºC transformed within ±0.1%, and all maintained below 1% at 1.06 μm. The absorbance of $SmAlO_3$ in the resin solution was 2.134 and the moral absorption coefficient was about 384.8 in the work. The study indicated that $SmAlO_3$ powders may be a promising kind of heat resistant absorbing material for 1.06 μm laser defense, which could be further applied to laser absorbing coatings with a wide range of temperatures.

Keywords: $SmAlO_3$; laser absorption; heat resistant; sol-gel combustion method; rare earths

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Since 1999, when Cho et al.[1] proposed $LnAlO_3$ (Ln= Pr, Nd, Sm, Dy, Gd, Er, La and Y) as dielectric resonators and HTSC microwave devices materials, $SmAlO_3$ has aroused attention from diversified aspects due to its dielectric[2–4], magnetic[5,6], and electrical[7,8] properties. However, the optical property of $SmAlO_3$ has not been studied yet. So far, $SmAlO_3$ powders have been prepared by conventional solid-state method[1,2,4] applying Sm_2O_3 and Al_2O_3 as raw materials and flux technique using PbO_2, PbF_2 as flux[9], while these processes require high calcination temperatures and cost much more time, hence, sol-gel combustion method turns out to be a preference[3,5,10].

As the development of laser probing and laser guidance, laser defense becomes more and more important in modern military. Using laser absorbing materials is one of the most effective methods to achieve laser defense, it is a concernful issue to research and prepare 1.06 μm laser absorbing materials. For Sm^{3+}, there is an expanded absorption peak around the wavelength at 1.06 μm, which is ascribed to the electron transitions of Sm^{3+}. $SmBO_3$ powders display low reflectivity at values of 0.4%–1% at 1.06 μm[11]. Al/Cr_2O_3 composite particles and $NaDyF_4$ have been reported to exhibit preferable absorption properties for 1.06 μm laser[12,13]. In the present work, $SmAlO_3$ powders were successfully prepared by the nitrate-citrate sol-gel combustion method, and for the first time, the optical property of $SmAlO_3$, with the emphasis on 1.06 μm laser absorption performance was reported, meanwhile, the heat resistant property of $SmAlO_3$ was also covered in the paper.

1 Experimental

$SmAlO_3$ powders in the present work were prepared by nitrate-citrate sol-gel combustion technique[10,11]. The starting materials were Sm_2O_3 (purity 99.99%), aluminum nitrate ($Al(NO_3)_3\cdot 9H_2O$, analytical grade), nitric acid (HNO_3, analytical grade) functioning as acid and oxidant, hydrated citric acid ($C_6H_8O_7\cdot H_2O$, analytical grade) applied as chelating agent and fuel. To make it clear, the specific process is revealed in Fig. 1. Stoichiometric amounts of Sm_2O_3 and $Al(NO_3)_3\cdot 9H_2O$ required for $SmAlO_3$ compositions were dissolved in dilute nitric acid, to obtain aqueous $Sm(NO_3)_3$ and $Al(NO_3)_3$ solutions, respectively. With appropriate dosage of citric acid added in, the mixed solution was stirred continuously by a magnetic agitator at 60–70 ºC to obtain transparent solution. It turned out to be totally yellow transparent sol with the eliminating of excess water. The sol transformed into transparent sticky gel about 4 h later by continuous stirring. After being heated at 180 ºC for 3 h in the oven, a yellow, fluffy, expanded precursor was yielded, which was due to the self-combustion process. It was accompanied by the evolution of brown fume and also the eliminating of the remaining water. During this process, vigorous oxidation-reduction reaction took place

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Foundation item: Project supported by Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD)

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DOI: 10.1016/S1002-0721(12)60411-6

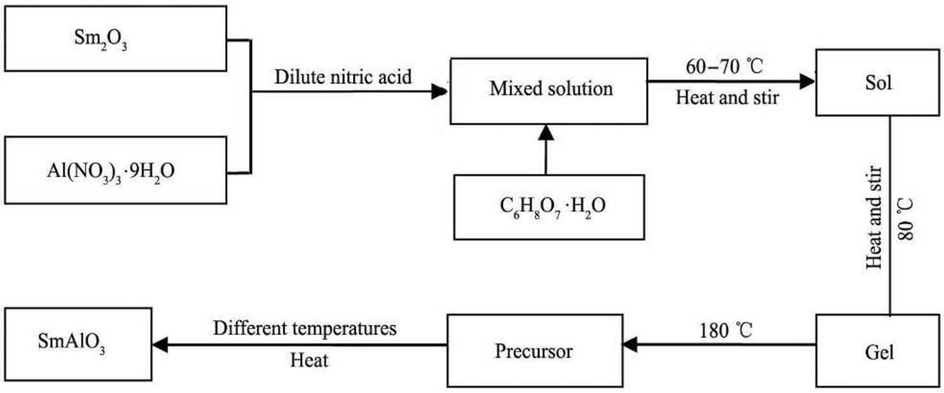

Fig. 1 Flow chart for the preparation of $SmAlO_3$ powder by sol-gel combustion method

among the remained citric acid, nitrates and the formed transparent gel. Meanwhile, the reaction gave out a great amount of heat, thus promoted and accelerated the whole process. In order to achieve the desired product, the precursor was treated at different temperatures from 800 to 1100 ºC for 2 h in a muffle furnace in air. The prepared $SmAlO_3$ powders were then processed at different temperatures shifting from –40 to 500 ºC for 5 h to test the temperature performance. To test the absorbance, a certain amount of $SmAlO_3$ was added into the ethanal (analytical grade), curing agent and polyvinylbutyral (PVB) with the quality ratio of 1:1:3:3 to obtain the resin coating.

Differential scanning calorimetry and thermo gravimetric (TG-DSC) analysis (Model NETZSCH STA449C) was carried out to analyze the original precursors and reaction processes in air atmosphere at a heating rate of 20 ºC/min. The crystal phases at different temperatures were identified by X-ray diffraction pattern analysis (XRD, D/max 2500) using nickel filtered Cu Kα radiation (λ=0.15406 nm) in the range of 2θ=20°–80°. Fourier transform infrared spectroscopy (FTIR, NICOLET-5700) was performed to characterize the chemical binding evolution. To obtain the reflective spectrum and the transmittance of $SmAlO_3$ in the resin coating, Shimadzu UV-3101PC spectrophotometer with an integrating sphere was applied from 900–1200 nm. The heat performance tests of $SmAlO_3$ powders were operated in the environmental test chamber (WGD/SJ702).

2 Results and discussion

The TG/DSC curves of the precursor are provided in Fig. 2. There were four main stages in the TG curve during the heating process. The first stage, a mass loss of 13.3% is observed from room temperature to 350 ºC, which is due to the removal of molecular water and the volatilization and decomposition of excess dilute nitric acid. It was accompanied by a small endothermic peak on DSC curve. Secondly, the main mass loss of 37.3% ranging from 350 to 480 ºC, along with a sharp exothermic peak around 425 ºC in the DSC curve, may be caused by the decomposition and combustion of citric acid, elimination of COO^-, CO_3^{2-}, NO_3^{2-}. The third stage, a mass loss of 5.1% between 700 to 850 ºC corresponding to a flat endothermic peak around 800 ºC in the DSC curve can be attributed to the decomposition of amorphous carbonate. Last but not least, a small and flat exothermic peak appears around 900 ºC with no significant mass loss, it may be the evidence of crystallization of $SmAlO_3$, while this temperature is about 100 ºC higher than that in Fig. 3, which is relevant to the hysteresis effect of the instrument[14].

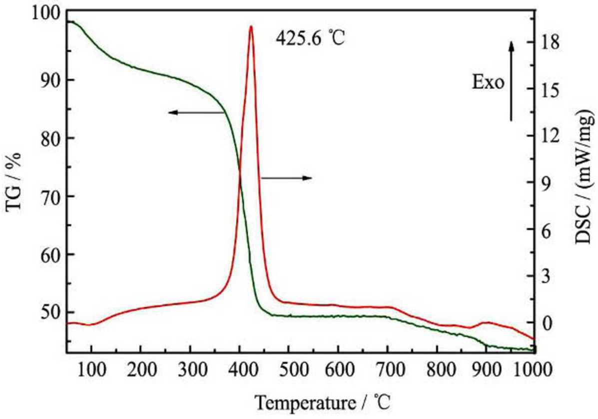

Fig. 2 TG/DSC curves of the precursor

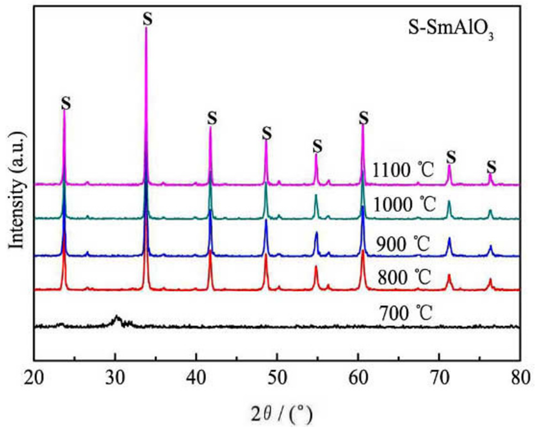

Fig. 3 XRD patterns of $SmAlO_3$ powders calcined at different temperatures for 2 h

XRD patterns of heat-treated $SmAlO_3$ powders under