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Effect of Resistive Coupled Microwave Sintering on the Microhardness of $Y_3Al_5O_{12}$

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Abstract

Phase pure $Y_3Al_5O_{12}$ was synthesized using an auto-ignited combustion technique. A novel resistive coupled microwave sintering technique was used to sinter the samples to >99% of the theoretical density at 1470ºC for a soaking duration of 20 minutes. In resistive coupled microwave sintering there was a substantial reduction in sintering temperature and soaking duration compared to the conventional sintering and susceptor assisted microwave sintering. The pellets sintered using the novel method showed better hardness of 13.9 GPa compared to the pellets sintered via the other two sintering techniques. The results clearly indicate that the $Y_3Al_5O_{12}$ samples sintered via resistive coupled microwave technique can effectively be used as infrared domes and windows in advanced homing missiles for strategic defence applications.

Keywords: Combustion synthesis; resistive coupled microwave sintering; microhardness.

INTRODUCTION

Infrared transparent ceramics found to have applications in infrared windows and domes in homing missiles and spacecrafts employed for strategic defense and space missions [1]. The purpose of an infrared window at the nose cone of the homing missile is to protect the highly delicate infrared sensor from the harsh environments of the missile flight. $Y_3Al_5O_{12}$ (YAG) is widely used as a laser host material. Its low thermal expansion coefficient, high optical transparency, high thermal shock resistance and better stability at relatively high temperature make it an ideal candidate for infrared transparent windows [2]. But high temperature sintering for long soaking duration deteriorates the transmittance and hardness properties of YAG [3]. Enhancing the hardness without sacrificing the optical properties is a major challenge in the fabrication of infrared transparent ceramics [1].

This work is an effort to improve the hardness of existing infrared transparent YAG windows by densifying the sample using a novel sintering strategy called resistive coupled microwave sintering, without surrendering the transmittance properties, by rectifying the flaws in the presently available processing techniques.

EXPERIMENTAL

Nanostructured $Y_3Al_5O_{12}$ was synthesized using a single step auto-igniting combustion technique [4]. Stoichiometric amount of high purity Y $(NO_3)_3.6H_2O$ (99.99%, Alfa Aesar, USA) and Al $(NO_3)_3.9H_2O$ (99.99%, Alfa Aesar, USA) were dissolved in double distilled water to make a clear solution. Citric acid was added to the precursor solution which act both as fuel and the complexing agent. The pH of the precursor mixture was adjusted to ~7 by adding nitric acid and ammonium hydroxide [5]. Here the ammonium nitrate formed during the reaction between the nitric acid and ammonium hydroxide acts as an extra oxidant which can control the particulate properties without changing the proportions of the other reactants of the chemical reaction. The solution containing the precursor mixture was heated using a hot plate at 250 ºC in a ventilated fume hood. The solution boils on heating and undergoes dehydration accompanied by foam. The foam then ignites by itself on persistent heating giving voluminous and fluffy product of combustion.

The phase purity of the nanopowder plays a vital role in the fabrication of the infrared transparent window. The as-prepared samples were characterized by X-ray diffractometer (X'pert pro, PANalytical, the Netherlands) with Cu Kα radiation in the range of 20–60º in steps of 0.0840 for the determination of crystalline structure and phase of the nanomaterials. The average crystallite size was estimated for all the samples from Scherrer's equation. The phase purity of the as prepared sample was confirmed using FTIR spectroscopy (Spectrum 2, Perkin-Elmer, Singapore) in the range 400-4000 cm^{-1} using the ATR method. The phase pure YAG powder was uniaxially compacted in to pellets in a 14mm diameter steel die at 20MPa using a hydraulic press. The sintering of the disc shaped pellets were carried out in a high temperature furnace with molybdenum disilicide heating elements (TE-4050, Therelek, India) which employs the resistive heating. Sintering of the pellets was also carried out using susceptor assisted microwave furnace (VBCC/MF/86, VB Ceramics Consultants, India). The microwave heating was realized using a pair of 2.45 GHz magnetrons with power 1.1KW each. The temperature controller is able to maintain a temperature within the chamber with a maximum error limit of $\pm 1^{o}C$. The maximum possible error in estimating the temperature by the pyrometer is given as $\pm 10^{o}C$.

A resistive coupled microwave furnace with a pair of molybdenum disilicide heating elements (VBCC/HMF/71, VB Ceramics Consultants, India) was used for sintering the samples by effectively coupling the resistive and microwave heating. In resistive coupled microwave sintering method the green body gets microwave energy directly from a pair of 2.5GHz magnetrons with power 1.1 kW each and the heating

power rate can be controlled effectively. In addition to this the pellet is getting heat from a pair of molybdenum disilicide heating elements as in conventional furnace which is also controlled according to the processing requirements. Uniformly distributed fast heating of the entire green body by effectively coupling the microwave and resistive power results in high quality infrared transparent ceramics with reduced grain size and minimum porosity which can be tailored to fabricate high quality infrared transparent windows cost effectively for demanding missions. In a resistive coupled microwave furnace one can effectively couple the resistive and microwave heating powers. A series of sintering trials were conducted by coupling different percentage of microwave power and resistive power to optimize the sintering procedure. In the present work the resistive and microwave heating were effectively coupled in the ratio 60:40 below 1100 ^{o}C and there after it was fixed at 40:60. The experimental density of the sintered pellets were calculated using Archimedes principle. The hardness of the sintered samples were tested using Vickers indenter method (HMV 2TAW, Shimadzu, Japan).

RESULTS AND DISCUSSION

The phase purity of the crystallites of the as prepared powder was investigated in detail using the X-ray diffraction technique. The X-ray diffraction pattern of the as prepared $Y_3Al_5O_{12}$ powder is shown in Fig.1. All the diffraction peaks were indexed for their respective *hkl* planes and found that they were in good agreement with the peak positions in JCPDS file 330040 for body centred cubic structure of $Y_3Al_5O_{12}$. The crystallites size were calculated using Scherrer formula [6]. The crystallites were found to be in the size range of 10-24 nm and the average size of the crystallites was 16.0 nm. The crystallite size calculated from the high intensity peak corresponds to the (420) plane of $Y_3Al_5O_{12}$ was 17.3 nm and d-spacing was 0.2662 nm and the corresponding value in the JCPDS file is 0.2687 nm. The XRD results confirm the formation of phase pure cubic $Y_3Al_5O_{12}$ nanoparticles by the auto ignited single modified combustion synthesis without carrying out post annealing or calcination process.

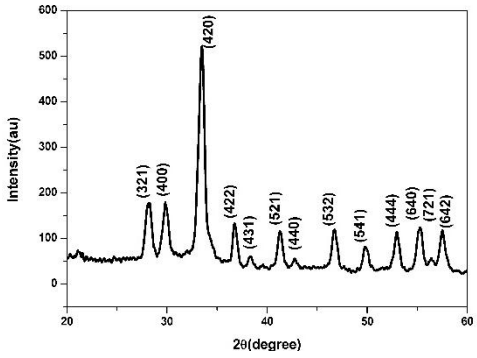

Figure 1: XRD pattern of as synthesized $Y_3Al_5O_{12}$

FTIR transmittance spectrum of as prepared $Y_3Al_5O_{12}$ is shown in Fig.2. The peaks at 566 cm^{-1} and 507 cm^{-1} are asymmetric vibrations of Al-O bond in octahedral arrangement of the garnet structure where as the peaks at 786 cm^{-1}, 718 cm^{-1} and 688 cm^{-1} correspond to the aymmetric stretching vibrations Al-O bond in the tetrahedral arrangement and matches very well with the single crystal FTIR data[7,8]. No other absorption peaks were observed in this range, which shows that no residual nitrate or any other impurities are present in the as prepared powder.

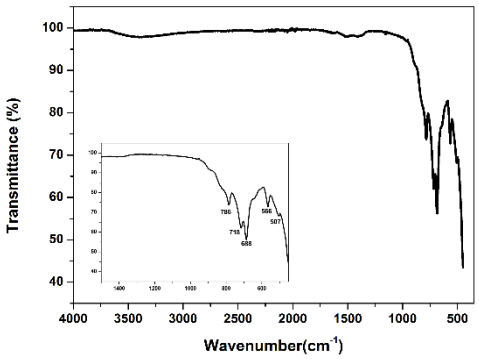

Figure 2: FTIR transmittance spectrum of as prepared $Y_3Al_5O_{12}$

The phase pure yttrium aluminium powder was uniaxially compacted into pellets in a 14 mm diameter steel die at 20 MPa using a hydraulic press. To study the sintering behaviour of the sample different sintering techniques are used and an effective comparison among the sintering processes which employ resistive, susceptor assisted microwave heating and resistive coupled microwave heating are carried out, for the ease of discussion they are coded as YG_R, YG_{SM} and YG_{RM} respectively.

For effective comparison of the sintering techniques and to optimize the sintering strategy a number of green pellets with same compacting conditions are used in the sintering process. Sintering behaviour of the sample was studied on disc shaped $Y_3Al_5O_{12}$ pellets using resistive coupled microwave heating and the results are compared with that using conventional resistive heating and susceptor assisted microwave heating. The relative densities of pellets sintered using different sintering techniques are shown in the Fig.3.

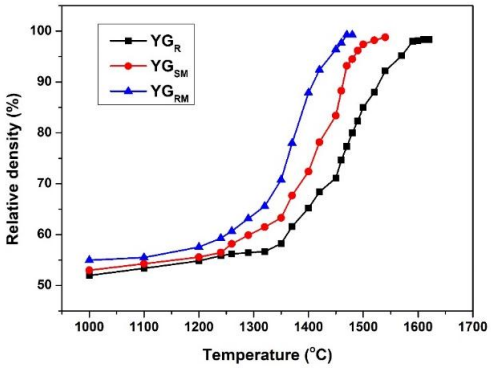

Figure 3: Variation in relative density of $Y_3Al_5O_{12}$ pellets with sintering temperature

In resistive heating the pellets attained only 98.3 ± 0.03 % of the theoretical density at 1610^{o}C for a soaking time of 2h at

a heating rate of 10 ^{o}C min^{-1}. In susceptor assisted microwave heating the pellets achieved 98.8 ± 0.05 % of the theoretical density at 1540 ± 10 ^{o}C for a soaking duration of 20 minutes at a heating rate of 40 ^{o}Cmin^{-1}. But in the resistive coupled microwave heating, pellets were heated at a constant rate of 40 ^{o}Cmin^{-1} and are sintered to 99.3 ± 0.03 % of theoretical density by holding for only twenty minutes at 1470 ± 10 ^{o}C without any additives or application of pressure. The advantage of resistive coupled microwave heating over conventional furnace heating lies in the heating mechanism. In resistive coupled microwave heating the sample pellet simultaneously attains heat from the microwave generated by the magnetrons and molybdenum heating elements, which enhances the densification to a great extent.

In the present work to study the effect of load and grain size on the sintered pellets different loads 0.98, 1.96, 2.94 and 4.9 N are applied on the pellets sintered using resistive heating, susceptor assisted microwave heating and resistive coupled microwave heating. For every load five indentations were made on the surface at different positions from which the average apparent hardness for a particular load is measured. The hardness values obtained for different loads on the pellets sintered via different techniques are shown in Fig. 4.

The maximum hardness of 14.3 GPa is shown by the YG_{RM} pellet for a load of 0.98N. The percentage decrease of hardness with load is minimum in the case of YG_{RM}, whereas the minimum hardness is shown by the pellet YG_R and the percentage decrease in hardness with load is greater for it. The details are tabulated in Table 1. It is found that the apparent hardness of the sample decreases with indentation load ie a positive ISE behaviour.

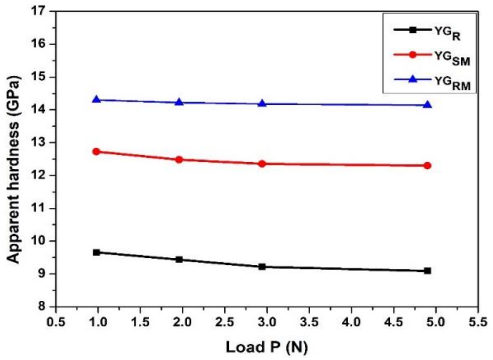

Figure 4 : Variation in apparent hardness with load in YG_R, YG_{SM} and YG_{RM} pellets

Table 1: Variation in apparent hardness of YG_R, YG_{SM} and YG_{RM} pellets with load

Load P (N)	Apparent Hardness (GPa)		
	YG_R	**YG_{SM}**	**YG_{RM}**
0.98	9.66	12.73	14.29
1.96	9.43	12.48	14.22
2.94	9.29	12.36	14.18
4.9	9.09	12.29	14.14

A modified PSR (MPSR) model was used to analyze the variation in hardness with load [9]. It is a semi empirical relation connecting the load P and the indentation size d and is given by

$$P = a_0 + a_1 d + a_2 d^2 \qquad (1)$$

Where P is the applied load, d is the indentation size, a_0, a_1 and a_2 are parameters obtained from curve fitting of the experimental results. Here *'a_0'* is the term related to the residual stresses generated in the specimen surface, a_1 is a constant related to the proportional resistance of the specimen which is directly proportional to the Young's modulus and *'a_2'* is a constant related to load independent micohardness. The load independent hardness called true hardness H_T can be obtained from a_2 by the relation

$$H_T = k a_2 \qquad (2)$$

Where k is a constant equal to 1.8544 for Vickers indenter and 14.229 for Knoop indenter [10]. A P versus d graph is plotted and the parameters obtained are tabulated in Table 2. The P versus d graph is shown in Fig.5.

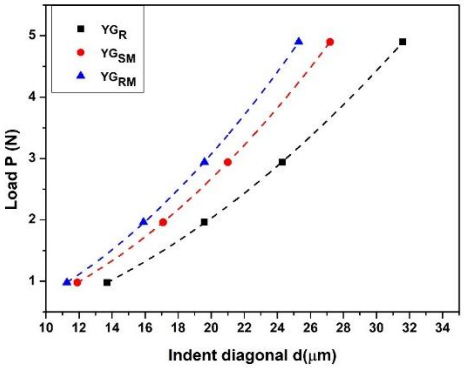

Figure 5: Variation in indentation size of YG_R, YG_{SM} and YG_{RM} pellets with load

Table 2: True hardness of YG_R, YG_{SM} and YG_{RM} pellets based on MPSR model

Samples	a_0 **(N)**	a_1 **(N/μm)**	$a_2 = \frac{P_c}{d_0^2}$ **(N/μm^2)**	H_T **(GPa)**
YG_R	0.0406	0.01226	0.00456	8.45
YG_{SM}	0.0778	0.00326	0.00664	12.31
YG_{RM}	0.0192	0.00432	0.00751	13.93

The true hardness of sample is relatively high in the case of YG_{RM} compared to the hardness of the pellets sintered by the other two sintering mechanisms. This may be due to the substantial reduction in sintering temperature and soaking duration in resistive coupled microwave sintering which hinders the grain growth [4]. Most of the materials with grain sizes in the nanometer range exhibit significantly higher values of micro hardness compared to their coarse grained

counterparts [11]. A material with larger grain size will have more dislocation pile up, leading to a bigger driving force for dislocations to move from one grain to another. So a comparatively less load is required to move from one grain to another. But if the grain size is less the increased fraction of grain boundaries act as pinning points which impedes further dislocation propagation [12].

CONCLUSION

Nanostructured $Y_3Al_5O_{12}$ is synthesized using an auto ignited combustion technique. The detailed analysis of XRD revealed that yttrium aluminium garnet ($Y_3Al_5O_{12}$) powders synthesized by the single step auto-igniting combustion technique is phase pure and crystallized in face centred cubic lattice with an average crystallite size of ~15 nm. FTIR spectroscopic data also supports the XRD result that the sample is phase pure as no major impurity peaks are observed in the spectrum. A novel sintering strategy called resistive coupled microwave sintering is developed and optimised during the course of work by effectively coupling resistive heating and microwave heating in definite proportions. By this method the sintering temperature is reduced by ~70^{o}C compared to that in susceptor assisted microwave sintering and by ~140^{o}C compared to that in conventional sintering. In the resistive coupled microwave sintering the ponderomotive force triggered at comparatively low temperature which enhance the mass transport may be the reason behind substantial reduction in sintering temperature and soaking duration. The pellet sintered using resistive coupled microwave heating shows high load independent hardness of 13.93 GPa and is a remarkable result that it is achieved without compromising the transmittance properties. The hardness corresponding to the pellets YG_{SM} and YG_R are 12.31 and 8.45GPa respectively. The results clearly indicate that the yttrium aluminium garnet ($Y_3Al_5O_{12}$) nanophase powder synthesized using single step combustion method followed by resistive coupled microwave sintering can be used very effectively for the fabrication infrared transparent windows and domes with improved properties.

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