EFFECT OF SINTERING MECHANISM ON THE THERMAL PROPERTIES OF $MgAl_2O_4$

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Abstract : ***$MgAl_2O_4$ is a promising infrared transparent ceramics used as infrared window in strategic defence and space missions. The present work reports the effect of different sintering mechanisms on the thermal properties of $MgAl_2O_4$. A modified combustion technique was used to synthesize nanostructured $MgAl_2O_4$. The average crystallite size estimated using Scherrer formula was ~20 nm. A novel resistive coupled microwave sintering technique which couples the resistive heating and microwave heating was effectively employed to sinter infrared transparent $MgAl_2O_4$ to 99.3% of the theoretical density. To study the influence of sintering mechanisms on the thermal properties of the sample two other variants of sintering strategies namely resistive sintering and susceptor assisted microwave sintering were also employed. The thermal conductivity, thermal diffusivity and the specific heat capacity of the sintered pellets were analyzed in detail.***

IndexTerms - Combustion synthesis, Resistive coupled microwave sintering, thermal conductivity, thermal diffusivity, infrared transparent window.

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1. INTRODUCTION

Magnesium aluminate spinel is one of the focal choices of the researchers working in the field of infrared transparent ceramics, due to its exceptional properties which include high mechanical strength at room temperature as well as at elevated temperatures, high resistance against chemical attack, thermal shock resistance, thermal stability, high melting point, moderate thermal conductivity, isotropic cubic structure, absence of birefringence, low thermal expansion coefficient, high corrosion resistance and moderate infrared cut-off [1-4].

The ceramics which are used for fabricating infrared transparent ceramics should process high thermal stability at elevated temperatures. If any decomposition or phase changes occur at elevated temperatures during missile flight it will adversely affect the transmittance properties and the mechanical strength. Ceramics whose anions are oxides, are generally stable at elevated temperatures can effectively be used as infrared transparent windows. Heat energy can be transmitted through solids via electrical carriers (electrons or holes), lattice waves (phonons), electromagnetic waves, spin waves, or other excitations. In solid oxides heat is mainly carried by lattice vibrations. The thermal conductivities of solids vary dramatically both in magnitude and temperature dependence from one material to another. This is caused by differences in sample sizes for single crystals or grain sizes for polycrystalline samples, lattice defects or imperfections, dislocations, anharmonicity of the lattice forces, carrier concentrations, interactions between the carriers and the lattice waves, interactions between magnetic ions and the lattice waves etc. [5].

Thermal conductivity of the sample play a vital role in designing high quality infrared transparent windows. During the missile flight there is a possibility to have a considerable temperature difference between the outer and inner surfaces of the window. If the window material is unable to tolerate this thermal stress it will shatter. Resistance to thermal failure by thermal shock is a critical requirement for some applications. Thermal shock figure of merit can be used for a comparison of the thermal shock resistance of different materials. The larger the figure of merit, the greater the heat flux that can be withstood by the material without catastrophic failure. If a dome is made thinner, less temperature difference builds up between the inner and outer surfaces during rapid heating and there is less thermal stress [1]. The parameter that governs the rate of thermal diffusion is called the Biot number β,

$$\beta = \frac{th}{k} \qquad (1)$$

Where 't' is the thickness of the window, 'h' is the heat transfer coefficient which gives the power that enters the material per unit area per unit temperature difference between the atmosphere and the surface and 'k' is the thermal conductivity of the material. The Biot number is low when the heat moves rapidly through the material. In mild thermal shock regime it is ideal to have $\beta << 1$.

Ideally domes and windows should be made as thin as necessary to withstand aerodynamic pressures to obtain the maximum thermal shock resistance [6]. For a minimum thickness window Klein mild thermal shock figure of merit K' is given by the relation,

$$K' = \frac{S^{3/2}(1-\upsilon)k}{\alpha E} \qquad (2)$$

In the above relation 'S' is the strength, 'υ' is the poisson's ratio, 'k' is the thermal conductivity, 'α' is the thermal expansion coefficient and 'E' is the Young's modulus.

From the above equations it is clear that the thermal shock resistance of a window is highly dependent on the thermal conductivity. To obtain a low Biot number and high thermal shock resistance figure of merit the window material should possess high thermal conductivity. Ideally the thermal conductivity values should be in the range 7-50 $Wm^{-1}K^{-1}$ [7].

In solids, the main heat carriers are electrons, photons, magnetic excitations and phonons. In a non-magnetic dielectric crystalline solids such as the transparent materials of the present interest, only phonons participate in thermal conduction at ambient temperature. At elevated temperatures, photons also contribute via radiation. The thermal conductivity k can be expressed as,

$$k = \frac{1}{3} C \, \mathrm{v} \, l \qquad (3)$$

Where 'C' is the specific heat capacity per unit volume, 'v' is the velocity of the carrier and 'l' is the mean free path of the carrier. The phonon velocity is not a significant function of temperature. The specific heat capacity of a solid is zero at absolute zero and initially

increases until approaching the limiting value at a characteristic Debye temperature which is near or below the room temperature for the material and increases after that. Mean free path decreases with increase in temperature. Thus the thermal conductivity of solids has a characteristic temperature dependence. At low temperatures ie below Debye temperature '*k*' is influenced by '*C*' and rises rapidly from 0K. At high temperatures '*k*' is influenced by 'l' and decreases with temperature. This high temperature regime is the region of interest for aero dynamic heating during missile flight. So anything that contribute to the phonon scattering will affect the thermal conductivity of the sample and consequently the thermal shock resistance. ie vacancies, interstitials, foreign atoms and different atoms in a compound all affect the thermal conductivity. At very high temperatures '*k*' increases again in transparent solids due to photon contributions [7]. Phonon mean free paths remain small even at low temperatures if the material is polycrystalline and 'l' is restricted to the dimensions of the crystallites [8].

In the present work a novel resistive coupled microwave sintering is used to densify magnesium aluminate spinel samples to a high density. The thermal and hardness properties of the samples are studied in detail. To study the influence of the resistive coupled microwave sintering on the properties two other variants of sintering methods resistive heating and susceptor assisted microwave sintering were also employed. The studies on thermal properties are limited the variation in the thermal conductivity, thermal diffusivity and the specific heat capacity variations of the sintered pellets with temperature as these are the decisive factors in thermal shock resistance.

2. EXPERIMENTAL PROCEDURE

A single step auto-igniting combustion synthesis was used to prepare nano structured $MgAl_2O_4$.Stoichiometric amount of high purity $Mg(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$ (99.99%, Alfa Aesar, USA) dissolved in double distilled water to make a clear solution. Citric acid was then added to it as a complexing agent [9]. Amount of citric acid was calculated based on total valence of the oxidizing and the reducing agents for maximum release of energy during combustion [10] . Nitric acid was used as oxidising agent and ammonia as fuel and the pH of the solution is monitored till it became 7. The precursor mixture made from high purity chemicals was stirred well for an hour using magnetic stirrer to get a uniform solution. The solution containing the precursor mixture was heated using a hot plate at 250 ^oC in a ventilated fume hood. The solution boiled on heating and had undergone dehydration accompanied by foam. The foam then auto ignited 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 pure spinel 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 heating elements (TE-4050,Therelek, India) which employs the resistive heating. Sintering was also carried out using susceptor assisted microwave furnace (VBCC/MF/86,VB Ceramics Consultants, India) with silicon carbide susceptors and a resistive coupled microwave furnace (VBCC/HMF/71,VB Ceramics Consultants, India). The microwave heating was realized using a pair of 2.45GHz magnetrons with 1.1KW each and for Resistive coupled microwave heating, a pair of molybdenum disilicide heating elements were used in addition to the pair of magnetrons. The experimental density of the sintered pellets was calculated using Archimedes principle. Thermal conductivity and diffusivity of the samples were measured and compared using nano flash thermal conductivity meter (LFA 447, NETZSCH, Germany).

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of as-synthesised $MgAl_2O_4$. All the peaks agree well with the XRD data reported in JCPDS file no.73-1959 and are indexed for a face centred cubic structure. This result confirms the formation of single-phase $MgAl_2O_4$ nanoparticles without carrying out post annealing or calcination process. The d-spacings and the 2θ values of as prepared sample are compared with the JCPDS reference data and found to be in good agreement. The average crystallite size is calculated using the Scherrer formula [11] $D=0.9\lambda/(\beta \cos\theta)$ where λ is the wavelength of CuKα radiation, β is the full width at half maximum, and θ is the Bragg's diffraction angle. The particles are found to be in the size limit of 20 nm. These results show that the single step combustion method offers an excellent and economic way for the preparation of phase pure $MgAl_2O_4$ nano powder.

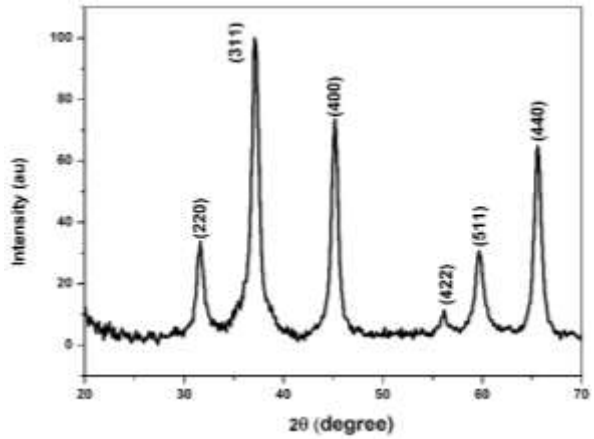

Figure. 1: XRD pattern of as prepared nano $MgAl_2O_4$.

To study the sintering behaviour of the sample different sintering techniques were used which employ resistive, susceptor assisted microwave and resistive coupled microwave heating. For effective comparison of the sintering techniques and to optimise the sintering strategy a number of green pellets with same pressing conditions are used in the sintering process. The pellets sintered via resistive heating, susceptor assisted microwave heating and resistive coupled microwave heating are coded as S_R,S_{SM} and S_{RM} respectively. The first derivative

of the variation in relative density versus temperature plot is termed as densification which is equal to $\frac{1}{\rho_0}\left(\frac{d\rho}{dT}\right)\times 100$, where $\left(\frac{d\rho}{dT}\right)$ is the increase in sintered density with temperature and ρ_0 is the theoretical density of the sample.

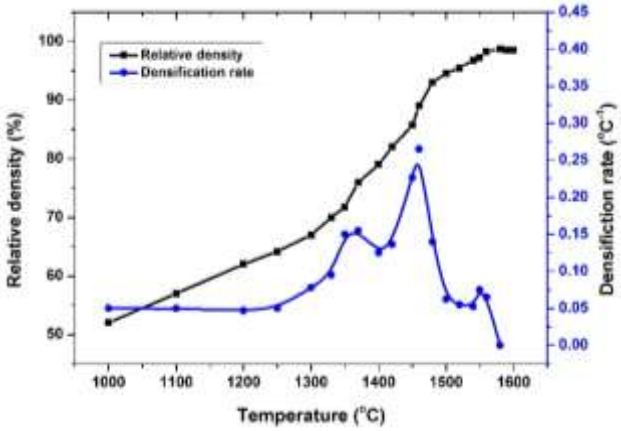

Figure 2: Variation in relative density and densification rate of the sample with sintering temperature during conventional sintering.

Initially the compacted pellet is placed in a conventional furnace which employs resistive heating. A uniform heating rate of $10^{o}Cmin^{-1}$ is used for the process. During the trial and error approach it is observed that a heating rate below this the grain size become large and a rate above this produce some cracks in the pellet. Figure 2 shows the variation in relative density and the densification rate with temperature. In conventional sintering it is found that the variation in relative density with temperature is very small up to $1250^{o}C$ after which the densification rate gradually increases and peaks around $1460^{o}C$. The pellet is sintered to 98.7% of theoretical density by holding for two hours at $1580^{o}C$.

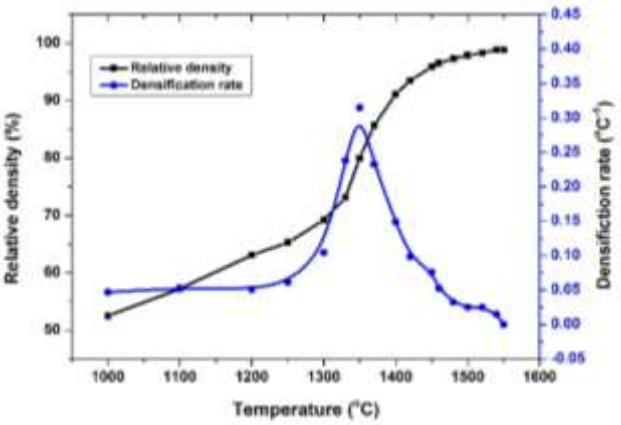

Figure 3: Variation in relative density and densification rate of the sample with sintering temperature during microwave sintering.

In microwave sintering the pellet is placed in the microwave chamber in a silicon carbide susceptor and a heating rate of $40^{o}Cmin^{-1}$ is used for sintering the sample. The result is amazing that the pellet achieved a density of 98.9% of the theoretical density at $1540^{o}C$ for a soaking duration of just 20 minutes. In addition to the microwave energy the pellet is absorbing heat from the silicon carbide susceptor in which the pellet is placed which helps to couple the microwave energy effectively in a low loss material like spinel. The densification rate analysis shown in figure 3 reveals that in microwave sintering the densification rate triggers around $1250^{o}C$ and peaks around $1350^{o}C$ which is $110^{o}C$ lower than that observed in conventional sintering.

A novel sintering strategy by coupling different proportions of microwave heating and resistive heating is also utilised to sinter infrared transparent spinel. In a microwave hybrid furnace, the pellets kept in the silicon carbide susceptor are heated at a constant rate of $40^{o}Cmin^{-1}$. The maximum sintered density is obtained for the pellet sintered by coupling the resistive and microwave heating in the ratio 60:40 respectively up to $1100^{o}C$ and in the ratio 40:60 thereafter. The pellet is sintered to 99.2% of the theoretical density at a much lower temperature of $1450^{o}C$ at a soaking duration of 20 minutes. It is found that the sintering temperature is reduced considerably in microwave hybrid heating. From the figure 4 it is clear that the densification rate triggers around $1200^{o}C$ and peaks around $1350^{o}C$. The substantial reduction in sintering temperature and fast densification at a comparatively low temperature yield highly sintered pellets with reduced grain size. In this technique the sample pellet is simultaneously attaining heat from the microwave generated by the magnetrons and molybdenum heating elements, which enhances the densification to a great extent. Microwave hybrid sintering is thus found to be a promising sintering method, effectively promoting the densification of spinel at lower temperature.

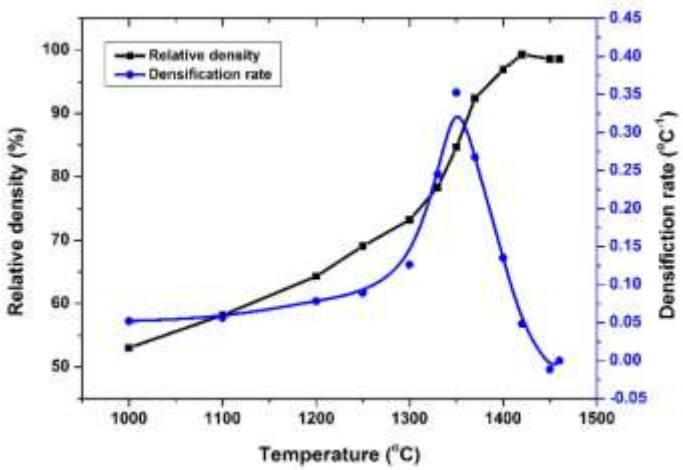

Figure 4: Variation in relative density and densification rate of the sample with sintering temperature during microwave hybrid sintering.

Thermal conductivity and diffusivity play crucial role in the performance of window materials. The greater the thermal conductivity the more rapidly heat is transferred across the window and the thermal shock resistance of the window will be high [1]. During the missile flight there is a possibility to have a considerable temperature difference between the outer and inner surfaces of the window. If the window material is unable to tolerate this thermal stress it will shatter. To obtain high thermal shock resistance figure of merit the window material should possess high thermal conductivity. Ideally the thermal conductivity values should be in the range 7-50 $Wm^{-1}K^{-1}$ [7].

The thermal diffusivity of the sample pellets sintered via resistive heating, susceptor assisted microwave heating and resistive coupled microwave heating are measured using laser flash thermal conductivity method. Figure 5 shows the thermal diffusivity of the samples S_R, S_{SM} and S_{RM} at different temperatures. It is observed that diffusivity is decreasing with increase in temperature. The diffusivity is maximum for the pellets sintered via resistive heating. For the S_{SM} and the S_{RM} pellets the diffusivity is found to be low. The deterioration of diffusivity attributes to the reduced grain size which accelerate phonon scattering at the grain boundaries.

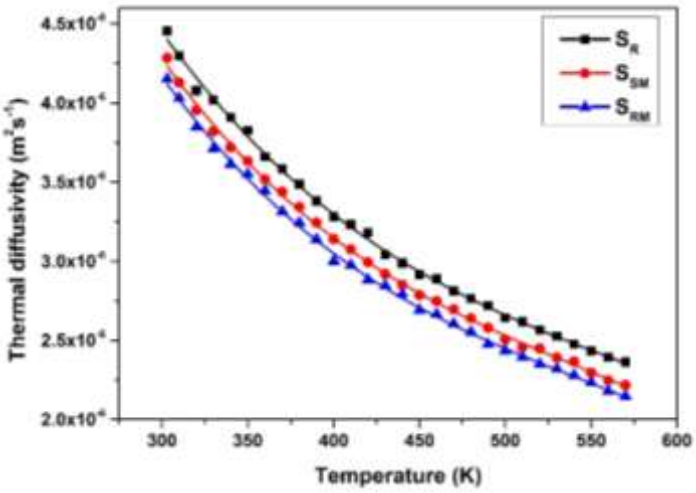

Figure 5: Thermal diffusivity of S_R, S_{SM} and S_{RM} pellets at different temperatures

The thermal conductivity of the sample pellets sintered via resistive heating , susceptor assisted microwave heating and resistive coupled microwave heating at different temperatures and their least squares fit to the data are as shown in the figure 6. The thermal conductivities of the samples at 303K are 14.04, 13.59 and 13.24 $Wm^{-1}K^{-1}$ respectively. We have observed a systematic decrease in the values of thermal conductivity as it is expected in increasing temperatures. As reported in literatures the thermal conductivity of poly crystalline oxides decreases as temperature increases [12]. It is observed that in the case of S_{RM} pellet the thermal conductivity is slightly less than that in microwave processed and normal heat processed pellets. This is attributed to the reduced grain size, ie as grain size decreases phonon scattering increases and consequently conductivity decreases [13]. The reduction in thermal diffusivity and thermal conductivity will deteriorate the performance of the infrared transparent window. But it is important to note that there is no substantial reduction in thermal diffusivity and conductivity compared to the theoretical values and the values are in the range ideally suggested for infrared transparent windows [7]. The increase in phonon scattering by small grains attributes to the reduction in thermal diffusivity in the sample S_{RM}. Thermal resistivity which is the reciprocal of thermal conductivity is calculated for different pellets and its variation with temperature is plotted in figure 7.

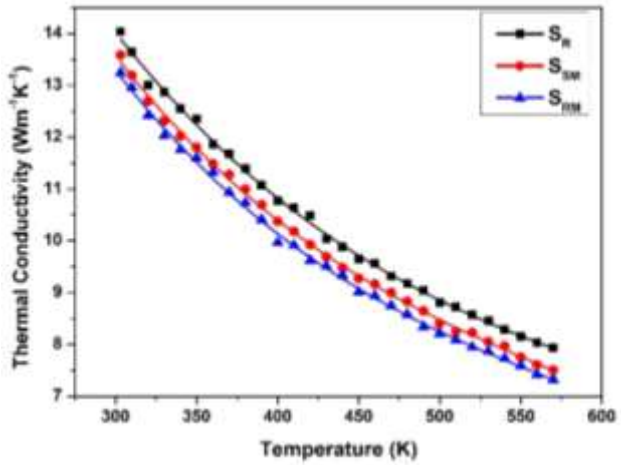

Figure 6: Thermal conductivity of S_R, S_{SM} and S_{RM} pellets at different temperatures

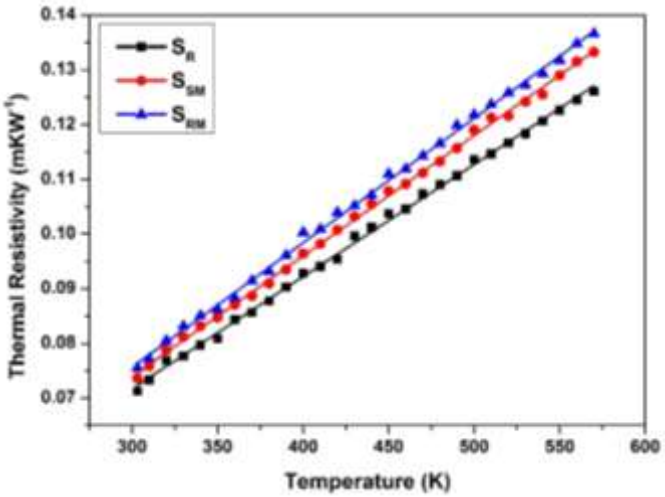

Figure 7: Thermal resistivity of S_R, S_{SM} and S_{RM} pellets at different temperatures

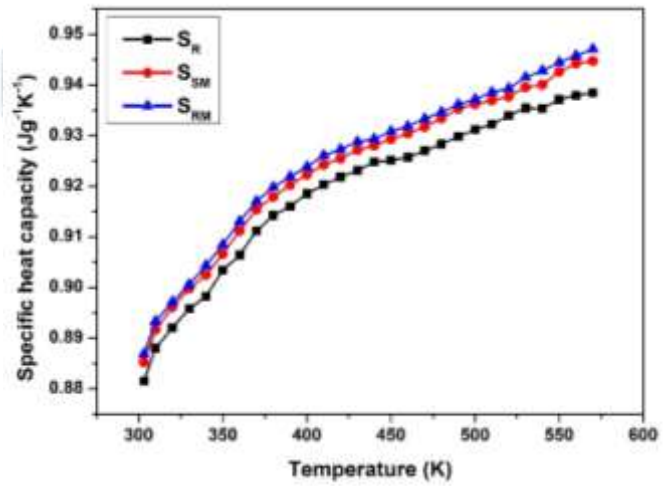

Figure 8: Specific heat capacity of S_R, S_{SM} and S_{RM} pellets at different temperatures

The specific heat capacity of the samples are calculated from the thermal conductivity k and thermal diffusivity D and density ρ using the relation $C = \frac{k}{D\rho}$. The variation in specific heat capacity with temperature is shown in Figure 8. The results reveal that resistive coupled microwave sintering is an effective technique to sinter magnesium aluminate spinel at a relatively low temperature. The enhanced sinterability and substantial reduction in sintering temperature and soaking duration, may be due to the ponderomotive mechanism common in field assisted sintering technique [14, 15].

Conclusions

The detailed analysis of XRD revealed that magnesium aluminate spinel powder synthesized by the single step auto-igniting combustion technique is phase pure and crystallised in face centred cubic lattice with an average crystallite size of ~20 nm. 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 ~120°C compared to that in susceptor assisted microwave sintering and by ~160°C compared to that in conventional sintering. There is a nominal reduction in the thermal conductivity and diffusivity of the pellet sintered using resistive coupled microwave heating compared to the other two pellets fabricated using susceptor assisted microwave heating and resistive heating, but the values are in the ideal range suitable for infrared transparent windows.

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