Microwave Sintering of Infrared-Transparent Nanostructured $MgAl_2O_4$ Synthesized by A Modified Combustion Technique

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***Abstract*— Synthesis of nano particles of $MgAl_2O_4$ ceramics (~15 nm) by a single step auto-igniting combustion technique, followed by sintering of the sample by microwave heating to optimum density and their remarkable uv-visible and infrared transmission characteristics are presented in this paper. The combustion synthesized powder was characterized by different powder characterization techniques. The pellets fabricated from ultrafine nano phase $MgAl_2O_4$ powder were sintered to ~99% of the theoretical density by microwave sintering at a comparatively lower temperature of 1520ºC for a soaking time of 20 minutes. The enhanced transmittance of the pellet in the uv-visible (~76%) and mid ir region(~75%) were extensively studied and reported.**

Keywords—Microwave sintering, transmittance

I. INTRODUCTION

Development of high quality polycrystalline infrared transparent ceramics with improved transmittance in the UV-Visible and mid infrared ranges is one of the fields of interest of researchers all over the world. $MgAl_2O_4$ ceramics found to have potential applications in infrared transparent windows and domes due to the moderate infrared cut-off and considerable mechanical, thermal and optical properties[1]. Large size of the grains in the well sintered pellet which is the consequence of the high temperature sintering over 1600ºC for long duration and the deterioration of the mechanical properties is a major challenge in the fabrication of $MgAl_2O_4$ infrared transparent windows. Microwave sintering of the pellets made from nanostructured high quality starting powder synthesized by the modified combustion technique may enhance the mechanical properties without affecting the infrared transmittance in the mid IR range.

A number of fabrication methods [2-7] have been developed successfully so far to synthesize ultrafine nanostructured polycrystalline $MgAl_2O_4$. Among them combustion synthesis is evolved as the economic and efficient method in terms of the cost, time and the complexities in the synthesis of nanomaterials. Especially the modified combustion technique used in the present study is a relatively simple method viz. the omission of high temperature calcinations for prolonged duration, we could obtain phase pure yttria nano particles of extremely small size (5-20 nm) and further compacted to an optimum density at a much lower temperature with high thermal stability and good transparency to infrared radiation using microwave heating technique.

In this paper we report the synthesis of nanostructrured poly-crystalline $MgAl_2O_4$ ceramics by an auto-ignited combustion technique [8]. The structure, vibrational spectra and surface morphology of the combustion synthesized powder are also studied and presented. The sintering behaviour of compacted pellets using microwave sintering and the transmittance of infrared radiations through the sintered pellets in the UV-Visible and mid infrared ranges are also reported.

II. EXPERIMENTAL

A single step auto-igniting combustion synthesis is used to prepare nano structured $MgAl_2O_4$ [9]. As-prepared samples are characterized by X-Ray Diffraction (XRD) by XPERT-PRO X-ray diffractometer for the determination of crystalline structure and phase of the nanomaterial. Particulate properties of the combustion product are examined using transmission electron microscopy (TEM, Model-Hitachi H600 Japan). The as-prepared samples of $MgAl_2O_4$ nanoparticles are recorded using a Shimadzu spectrophotometer (UV-1700). The phase purity of the sample is verified by FT – IR spectroscopy using Perkin elmer spectrum two Fourier Transform Infrared spectrometer (FTIR) in the range 400-4000 cm^{-1} using ATR method.

The pure white $MgAl_2O_4$ powder is uniaxially compacted in to pellets in a 12mm diameter steel die at 20MPa. The pellets are heat treated at 600º C for half an hour to remove the binder and absorbed gases. The pellets are sintered at 1520º C for a soaking time of 20minutes in a microwave furnace with a pair of 2.45GHz magnetrons of 1.1KW and silicon carbide susceptors. The SEM micrographs of the well polished pellets are recorded using JEOL 6390 Scanning Electron Microscope. The transmittance of radiation in the UV-visible and in the IR range is measured using the above mentioned UV-Vis and FTIR spectrometers.

III. RESULTS AND DISCUSSION

The Fig.1, shows the powder XRD patterns of as synthesised $MgAl_2O_4$. X-Ray Diffraction(XRD) analysis of the as prepared powder confirms the formation of phase pure cubic $MgAl_2O_4$ nanoparticles with space group $Fd\bar{3}m$ (227).

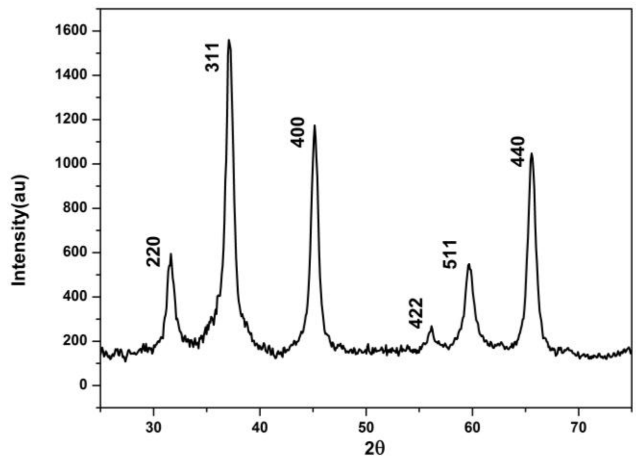

Fig. 1. XRD pattern of as prepared nano $MgAl_2O_4$

All the peaks in the XRD were indexed to a face centred cubic structure with a calculated lattice parameter a=8.03Å agreeing very well with the XRD data reported in Joint Committee on Powder Diffraction Standards (JCPDS) file no. 73-1959. The crystallite size calculated from full-width-half-maximum (FWHM) using Scherrer formula for the major (3 1 1) peak is 15nm and the interfacial spacing corresponding to the plane is 0.242nm. The particles were found to be in the size range of 5-20nm and the average size of the crystallites is 15nm.

The high resolution TEM image shown in the fig. 2. confirms the results obtained from XRD. The different crystallographic planes are in good agreement with the XRD data and corresponding to the clearly visible (311) plane the interfacial spacing is 0.245nm and is found to have a crystallite size of 16nm. Thus single step auto ignited combustion method offers an excellent and economic way for synthesizing phase pure $MgAl_2O_4$ nano powder.

Fig.3. shows the absorption spectra of the as prepared $MgAl_2O_4$. The absorption spectra of the as prepared $MgAl_2O_4$ is measured in the range 200-800nm and it shows that the material absorbs heavily in the shorter wavelength region of the ultraviolet spectrum and transmit long wavelength uv and visible light and hence found applications in the filters and sensors of UV radiations.

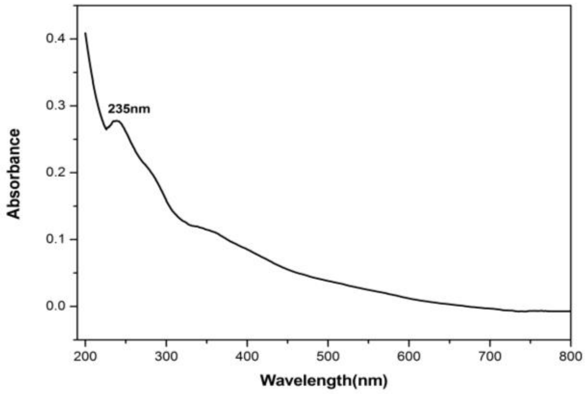

Fig. 3. UV-Vis absorption spectra of as prepared nano $MgAl_2O_4$

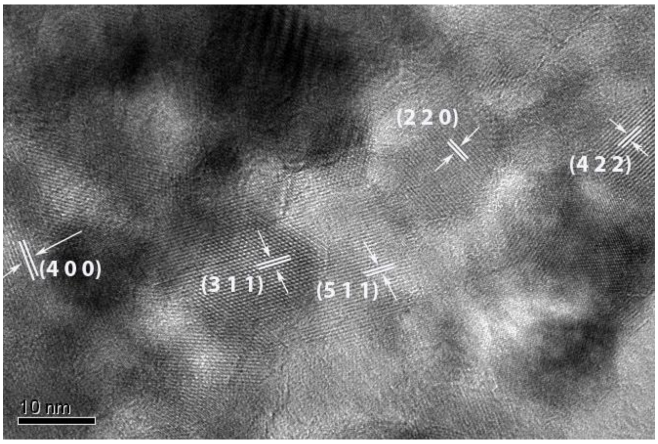

Fig. 2. HRTEM image of as prepared nano $MgAl_2O_4$

The optical absorption in the wavelength region shorter than 400nm is attributed to the transition of electron to the top of the valance band to the bottom of the conduction band. It can be used as an effective UV filter which screen higher energies of the ultraviolet spectrum from 10nm to 120nm which cause biological damage and it also find application as microwave filters.

Fig. 4. shows the FTIR spectrum of as synthesized $MgAl_2O_4$. The metal-oxygen tetrahedron in the spinel structure of $MgAl_2O_4$ can be considered as an isolated unit. The peaks at 481cm^{-1} and 670 cm^{-1} correspond to the metal oxide bending and asymmetric stretching modes of vibration respectively and these values are in good agreement with theoretically calculated zone centre phonon frequencies [10]. A broad absorption peak around 3500 cm^{-1} and around 1650 cm^{-1} are the O-H stretching and H-O-H bending modes respectively of the molecular water adsorbed by the powder. No other absorption peaks are observed in this range which shows that no residual nitrate or organic matter is present in the precursor powder.

The pure white powder is uniaxially compacted in to pellets in a 12mm diameter steel die at 20MPa. Microwave sintering technique is adopted to sinter the pelletized sample to high density.

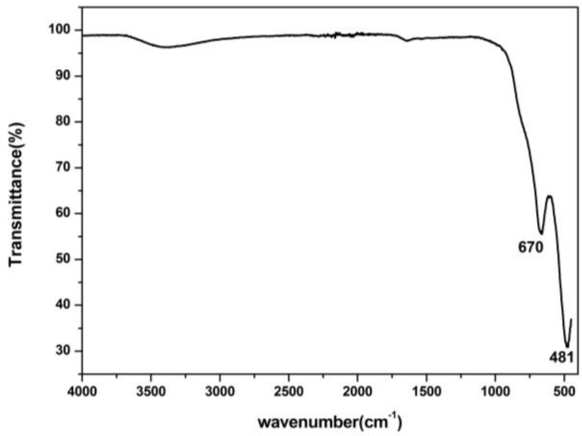

Fig. 4. FTIR spectra of as prepared nano $MgAl_2O_4$

In the microwave furnace a pair of 2.45GHz magnetrons of 1.1KW continuously supply the microwave energy to the sample pellet placed in the silicon carbide susceptors. The heating rate used was 20ºCmin^{-1}. The pellet achieved a density ~99% of the theoretical density at 1520ºC. The soaking time was also very low and is 20min. The significance of the present study in the development of infrared windows and domes is that the sintering is done without adding any sintering aids or by applying pressure at a comparatively low sintering temperature. The well sintered $MgAl_2O_4$ pellet is hand polished and thermal etched at 1400ºC. From the scanning electron micrograph it is clear that the pellet is well sintered. The grains are clearly visible with minimum porosity. The average grain size is ~300nm which is the greatest advantage of the microwave sintering in the fabrication of IR transparent $MgAl_2O_4$. Since microwave sintering allows fast volumetric heating the grain growth is inhibited. The reduction in soaking time is also hindering the grain growth which in turn improve the mechanical properties [11]. Fig.5. shows the SEM micrograph of the microwave sintered pellet.

For transmittance studies the pellet was well polished using diamond paste of different grades in a self-designed polishing machine and after polishing the pellet is found to be translucent. Fig. 6. Shows the photograph of the 0.5mm thick polished pellet placed 2mm above a computer screen.

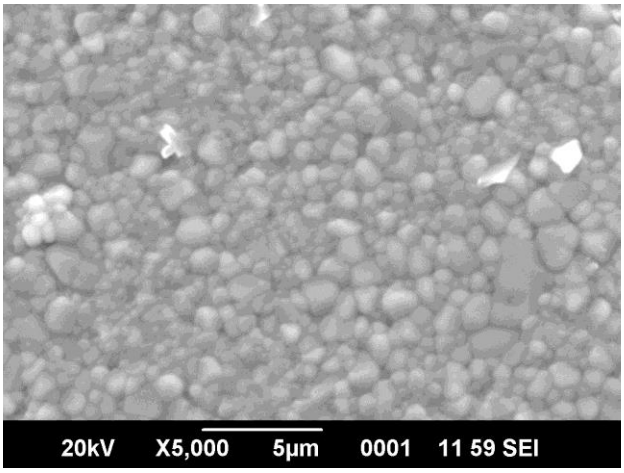

Fig. 5. SEM micrograph of microwae sintered $MgAl_2O_4$

Fig. 6. Photograph of polished $MgAl_2O_4$ pellet placed 2mm above computer screen

Fig.7. shows the transmittance of the well sintered pellet in the Uv-Visible range. It is showing a maximum percentage transmittance of ~76% at 800nm. Which can be further improved by sophisticated polishing mechanisms.

The percentage transmittance of infrared radiations through the sintered sample determines the efficiency of the infrared dome in strategic defense missions. The wavelength region of interest in the designing of homing missiles is 3-5µm ie the mid infrared range. The transmittance studies in the mid infrared range reveals that the well sintered pellets shows a percentage transmittance of ~75% in the mid infrared range. Fig.8 shows the FTIR transmittance spectrum of the well sintered $MgAl_2O_4$ sample.

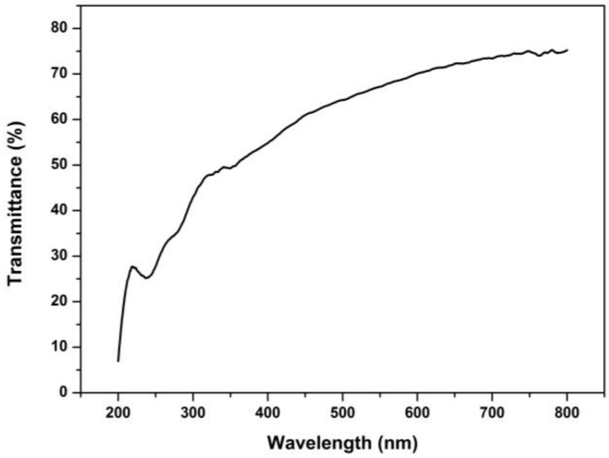

Fig. 7. UV-Vis transmittance spectra of microwave sintered $MgAl_2O_4$

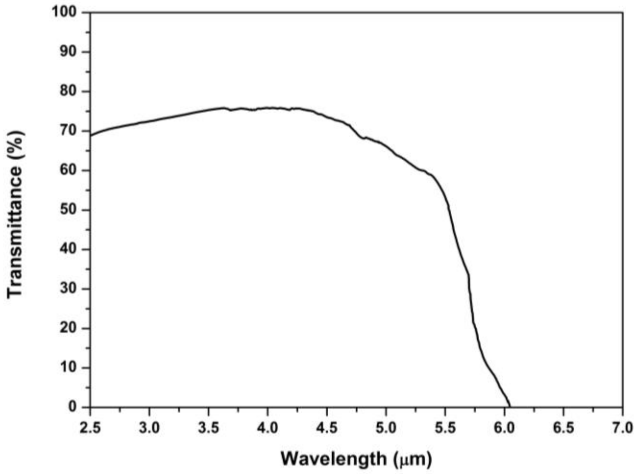

Fig. 8. FTIR transmittance spectra of microwave sintered $MgAl_2O_4$

CONCLUSIONS

In this paper we report the synthesis of $MgAl_2O_4$ by a modified auto-igniting combustion technique and the sintering of the pellets made from the ultrafine nanostructured powder using microwave heating. X-Ray Diffraction (XRD) analysis and the HRTEM analysis reveal that the $MgAl_2O_4$ powder synthesized by the modified combustion technique is phase pure and nanostructured in the size range 5-20nm with an average crystallite size of ~15nm. The UV-Visible absorption spectrum shows that the powder absorbs heavily in the UV region and consequently found applications in the filters and sensors of UV radiations. The FTIR transmittance spectra recorded confirms the phase purity and the transmittance in the range 400-4000cm^{-1}. The pure white $MgAl_2O_4$ powder was uniaxially compacted in to pellets in a 14mm diameter steel die and sintered to 99% theoretical density without any sintering additives or applying pressure at 1520^oC for 20minutes in a microwave furnace. Microwave heating reduces the sintering temperature and the soaking time considerably and there is a substantial reduction in grain size. The SEM micrograph gives the surface morphology of the well sintered pellet and from the SEM it is found that the average grain size is ~300nm. The transmission spectrum of the sintered pellet in the Uv-Vis region reveals that the material is showing a transmittance maximum of 76% in the visible region and the transmittance in the mid infrared region is ~75%. The results evidently indicate that the ultrafine $MgAl_2O_4$ nano powder synthesized using single step combustion method followed by microwave sintering can be used very effectively for the fabrication of improved infrared transparent windows and domes.

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