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Synthesis of magnesium dititanate by citrate gel route and its characterisation

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Abstract

Submicron size powder of magnesium dititanate ($MgTi_2O_5$) has been synthesised by citrate gel route. The process involves complexing Ti^{4+} and Mg^{2+} with citric acid separately. The complexed solutions were mixed in the molar ratio 2:1. Evaporation of excess water resulted in formation of viscous gel. The gel on subsequent drying and calcination at 500°C for 2 h gives single phase $MgTi_2O_5$. The calcined powder shows specific surface area 46 m^2/g. Scanning Electron micrograph of the powder shows agglomerated submicron size powder. The powder when palletised and sintered at 1350°C for 2 h achieved more than 96% of theoretical density.

Keywords: A. Sol–gel processes; C. Dielectric properties; E. Capacitors

1. Introduction

The principal use of the mineral magnesium dititanate ($MgTi_2O_5$) is in ceramics exposed to microwave frequencies [1,2]. A common feature of these ceramics is that they must have a high permittivity, high Q factor (low loss) and good thermal stability of their dielectric characteristics [3,4]. The addition of magnesium dititanate to ceramic materials improves both impact resistance [5] and thermal strain [6]. Magnesium dititanate also makes a ceramic highly compact, thus avoiding dielectric loss [7,8].

Lind and Housley [9] obtained $MgTi_2O_5$ crystals by melting MgO and TiO_2 in the molar ratio 1:2 in air and annealing at 1500°C for 12 h. Wechsler and Navrotsky [10] synthesised $MgTi_2O_5$ powder by calcining the mixture of MgO and TiO_2 in the molar ratio 1:2. However, this process requires high temperature (1400°C), longer time and repeated grinding and calcination. These conventional methods suffer from inherent disadvantage of inhomogeneous mixing of solid constituents giving rise to local compositional variations which can be minimised by repeated calcination and grinding. However, repeated grinding leads to contamination from the grinding media affecting the ultimate properties of interest.

Various solution chemistry routes also have been tried for obtaining $MgTi_2O_5$ at lower calcination temperature and with appropriate stoichiometry and purity. Baura-Pena, Martinez-Lope and Garcia-Clavel [11] synthesised the single phase $MgTi_2O_5$ by coprecipitation of a sulphuric acid solution of Ti^{4+} and Mg^{2+} , in a molar ratio of 2:1, with an aqueous solution of sodium hydroxide at pH$\sim$12 and calcined the precipitate at 540°C for 2 h in dynamic atmosphere (air, oxygen, or an argon stream).

In this paper we give a citrate gel route for the synthesis of submicron size, single phase $MgTi_2O_5$. The process is useful in terms of decreasing the calcination temperature, increasing the level of homogeneity and increasing the purity of the powder.

2. Experimental

2.1. Materials used

2.1.1. $MgCl_2$

Magnesium metal was dissolved in a sufficient quantity of HCl. Magnesium in this solution was analysed by complexometric titration with EDTA using Eriochrome Black-T as an indicator.

2.1.2. $TiCl_4$

Titanium tetrachloride hydrolyses rapidly in water even at room temperature. So addition of $TiCl_4$ to chilled

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water (< 4°C) and storage in a refrigerator for 24 h were preferred for producing a clear solution. Titanium present in the $TiCl_4$ solution was precipitated as $Ti(OH)_4$ by using aqueous solution of ammonia in excess. The precipitate was washed free of chloride ions and dried. Titanium content was analysed gravimetrically as TiO_2 after firing this precipitate at 800°C for 2 h.

2.1.3. *Citric acid*

G.R. grade.

2.2. *Gel and powder preparation*

$MgCl_2$ and $TiCl_4$ solutions were taken separately keeping Mg^{2+} to Ti^{4+} in the molar ratio 1:2. Mg^{2+} and Ti^{4+} in these solutions were bound by using sufficient amount of citric acid to form a stable gel. Mg^{2+} to citric acid in the molar ratio 1:1 and Ti^{4+} to citric acid in the molar ratio 1:2 were used for this purpose. The complexed solutions were mixed and excess water was evaporated until a viscous liquid (gel) was obtained. The gel was vacuum dried in an oven at 100°C for 4 h to get precursor of magnesium dititanate. The thermogravimetric analysis (TGA) of the precursor powder was carried out under air up to 600°C at a heating rate of 5°C/min to know the minimum calcination temperature. The precursor powder was calcined at 500°C for 2 h to form the magnesium dititanate powder.

2.3. *Characterisation methods*

X-ray diffraction (XRD) pattern of the calcined powder was recorded using a Phillips X-ray diffractometer with CuK_α radiation to determine the phases present in the calcined powder and to estimate the crystallite size. The specific surface area of the powder was measured by the conventional BET technique with nitrogen adsorption. The surface morphology of the synthesised powder was studied by scanning electron microscopy (SEM) using a Cambridge, stereoscan-240 model. The calcined powder was deagglomerated by grinding with agate mortar and pestle and by ultrasonic treatment for half an hour using sodium hexa metaphosphate (Calgon) as dispersion medium. The particle size distribution of deagglomerated powder was measured using a Horiba LA-500 analyser employing the laser diffraction technique.

The deagglomerated powder was uniaxially cold pressed in the form of 10 mm dia circular disks at a compaction pressure of 283 MPa using zinc stearate as die lubricant. No binder was used during compaction. The sintering of the green compacts was carried out at 1350°C for 2 h under static air at a heating rate of 10°C/min. The densities of the sintered pellets were determined by the Archimedes Principle. The sintered pellets were well polished and both the faces were coated with conducting silver paste. Dielectric characterisation of the sintered pellets was carried out at a frequency of 10MHz and at room temperature using HP, 419UA, Impedance/Gain-phase Analyser.

3. Results and discussion

Fig. 1 shows TGA and DTG curves of the precursor powder prepared through the citrate gel route. The major weight loss in the temperature range 165°C to 240°C is due to evolution of carbonaceous material and water. There was no weight loss after 500°C which shows that decomposition of the precursor gel has been completed.

The XRD pattern of the powder calcined at 500°C for 2 h is shown in Fig. 2. All the peaks have been indexed to magnesium dititanate. No second phase was detected in the XRD pattern. This confirms synthesis of single phase magnesium dititanate. Crystallite size was calculated by using the Scherrer formula: $D = 0.9\lambda/\beta\mathrm{Cos}\theta$, where D is the crystallite size in nm, λ is the radiation wavelenth (0.15425 nm), θ is the diffraction peak angle and β is the line width at half peak intensity. The crystallite size estimated from X-ray line broadening of the (110) peak was 16 nm.

Specific surface area (S_{BET}) of the calcined powder was $46m^2/g$. The equivalent spherical diameter (D_{BET}) was calculated by using formula: $D_{BET} = 6/\rho S_{BET}$, where ρ is the theoretical density of the powder ($3649\ kgm^{-3}$). Equivalent spherical diameter calculated from specific surface area data was found to be 35 nm.

Fig. 3 shows particle size distribution of the deagglomerated $MgTi_2O_5$ powder revealed median at 0.55 µm and 82% of the particles were below 1 µm. The particles towards higher distribution size are due to presence of agglomerates which did not disperse fully after the ultrasonic treatment. Agglomerates present in the calcined powder were confirmed by scanning electron microscopic studies.

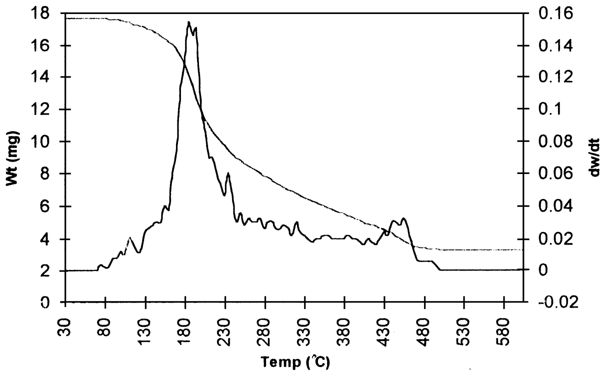

Fig. 1. TGA and DTG curves of precursor powder of magnesium dititanate.

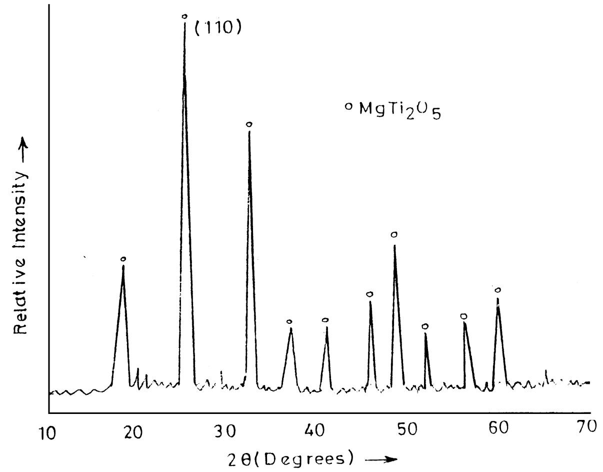

Fig. 2. XRD pattern of the powder calcined at 500°C for 2 h.

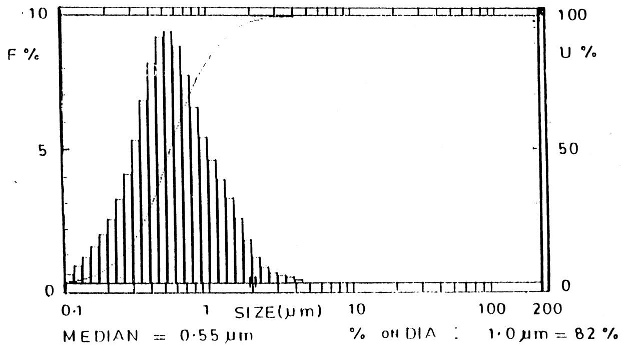

Fig. 3. Particle size distribution of deagglomerated $MgTi_2O_5$ powder.

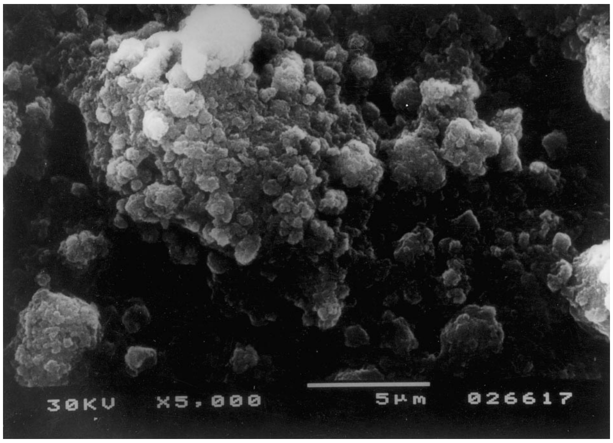

Fig. 4. SEM micrograph of the $MgTi_2O_5$ powder calcined at 500°C for 2 h.

Fig. 4 shows the SEM micrograph (SE image) of calcined powder which reflects the agglomerate nature of the powder and shows irregular morphology. Powder particles are submicron in size. These agglomerates can be broken by grinding with agate mortar and pestle and by ultrasonic treatment. Deagglomerated powder when sintered at 1350°C for 2 h at a heating rate 10°C/min resulted in more than 96% of the theoretical density. Pellets prepared from citrate gel derived powder were adequately dense for microwave applications.

Dielectric properties of sintered $MgTi_2O_5$ were studied at a frequency of 10 MHz and at room temperature. The values obtained for dielectric constant (ε) and dielectric loss ($\tan\delta$) were 17 and 2×10^{-3}, respectively.

4. Conclusions

Single phase, fine particle size $MgTi_2O_5$ powder has been synthesised successfully by a simple chemical route based on low temperature calcination of citrate gel. This powder sinters to a high density (>96%) in 2 h at 1350°C. The process is well suited for the synthesis of magnesium titanate based ceramics.

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