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# Effect of different calcination techniques on the morphology and powder flowability characteristics of Rare-earth Zirconates ( $Re_2Zr_2O_7$ ; Re = La, Gd, Nd, Y) synthesized by solid-state high-energy milling process

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Rare-earth zirconate ( $Re_2Zr_2O_7$ , Re = La, Gd, Nd, Y) ceramic materials was synthesized by solid-state reaction method through high-energy ball-milling process (HEBM) and subsequently followed by two different calcination techniques. The impacts of the two different calcination techniques on the phase structure, morphology, powder flowability (i.e. particle size and distribution, specific surface area, pore size and pore volume) were studied. The effectiveness of the calcination techniques of the resulting  $Re_2Zr_2O_7$  powders were investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Scanning electron microscopy (SEM) techniques. The outcomes demonstrated that both calcination techniques could produce  $Re_2Zr_2O_7$  powders with an excellent pyrochlore structure. The calcination (CVC) technique. The rare-earth zirconate powders exhibited different particle size distribution. The resulting particle median diameter was about 2.5-45 µm for CVC and 1.36-2.27 µm for MWC. The powder flowability of  $Re_2Zr_2O_7$  powders was strongly dependent on the particle size and distribution. Thus MWC technique for the preparation of  $Re_2Zr_2O_7$  powders is the best choice of powder processing to achieve desired properties.

Key words: Convectional calcination, Microwave calcination, rare-earth zirconates, Powders flowability, Morphology, High-energy ball-milling.

# Introduction

In recent years, much more attention has been focused on rare-earth zirconate based materials due to their commercial applications in the field of thermal spray coatings in gas turbines and diesel engines, and as host for the immobilization of high level radioactive waste and surplus actinides, as solid electrolytes, oxidation catalysts and oxygen monitoring sensors, high temperature fuel cell applications and proton solubility due to their important properties which include high melting point (2300 °C), low thermal conductivity (1.56 W.m<sup>-1</sup>.K<sup>-</sup> <sup>1</sup>, 1000 °C), high thermal expansion coefficient, excellent thermal stability, high ionic conductivity, high radiation stability, high tolerance to defects, low elastic modulus and good corrosion resistant performance [1-8]. The rareearth zirconates exhibits two structures namely: pyrochlore structure (space group Fd3m) and fluorite structure (space group Fm3m) [1, 9-10]. The pyrochlore structured materials is usually expressed by the general formula  $A_2B_2O_7$ , where A is rare-earth (trivalent metal ion) and B is either a transition metal or a p block metal ion (tetravalent metal ion) [6, 11-12]. The structure of the

rare-earth zirconates (A2B2O7) present in one of the two forms are closely related to the ionic radius of A<sup>3+</sup> and  $B^{4+}$  [6, 11-12]. If this ratio is in the interval range of  $1.46 \leq r~(A^{3+})$  / r  $(B^{4+}) \leq 1.78,$  the ordered pyrochlore structure can become stable at atmospheric pressure [1]. The phase transition of the rare-earth zirconates from the Fd3m pyrochlore structure (after a heat treatment >1300 °C) to the Fm3m defect fluorite structure (after heat treatment in the temperature range from 700 to 1200 °C) is an order disorder transition, which involves the disordering of the anions, as well as the disordering of the cations [1]. The phase structure of pyrochlore A<sub>2</sub>B<sub>2</sub>O<sub>7</sub> ceramic materials mainly depends on the final annealing temperature. The change in the degree of structure order has a significant impact on the properties such as thermal expansion coefficient, ionic conductivity, radiation resistance and photo catalytic activity [1].

Thermal spray coatings are thus used for the thermal and chemical protection of metallic components of turbine engines such as blades, vanes and transition pieces. Currently, thermal spray coatings can be deposited directly on the substrate using various techniques, such as (1) Atmospheric plasma spraying (APS) (2) Electron beam-physical vapor deposition (EB-PVD) (3) High velocity oxygen-fuel (HVOF) spraying (4) Vacuum plasma spraying (5) Low-pressure plasma spraying [13-15]. The structure and properties of the coatings by thermal spraying depends strongly upon the feedstock

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powder morphologies, injection of feedstock into the energetic flow, and spray coating operating conditions [16]. Indeed, the feedstock powder particle size distribution (in the 20-45 µm range) and morphology are related to its manufacturing route and it varies from spherical to irregular or blocky [16-17]. Irregular shapes range from cubic like structures to needles with high elongation ratio close to unity [18]. Moreover, blocky particles are always dense, spherical where as the irregular ones can be dense or porous [16]. Powder morphology is also a key parameter for particle behavior upon penetration within the thermal spray coating equipment [16]. The flowability of the powders is extremely important in all thermal spray coating processes [17-18]. Poor flowability results due to fluctuations in powder feed rate and thus produces an inhomogeneous coating structure [16, 19]. The powder mass flow rate depends directly upon its specific mass, which is the highest for dense spherical particles [19]. Flowability remains a crucial factor which affects the design and processing of the thermal spray feedstock powder in handling equipment such as hoppers, bins, filling and packing operations, etc [16]. During the past decades, a lot of techniques have been carried out on the measurement and characterization of powder flowability which includes; Hausner ratio (HR), Carr's compressibility index (CI), angle of repose (AOR) test, shear test, measuring the time required to discharge a given amount of powder from a flowmeter and flow function [18-20].

Traditionally, Re<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> powders are synthesized through different wet substance strategies like hydrothermal method [6], salt-assistant combustion [21], solgel processing [7, 22], co-precipitation route [23-24] and molten salt techniques [25]. The Re<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> powders integrated by these strategies are littler than 1µm however they contain residual hydroxide particles, which brings about the arrangement of between granular pores [6-7, 21-25]. For huge scale creation of Re<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> powders, mechanochemical handling route is thought to be the most solid strategy. The mechanochemical route has a few favorable circumstances over both traditional solidstate reaction and liquid forms, which incorporates the utilization of minimal effort raw materials, a rearranged procedure and the capacity to acquire micrometer-sized particles (in the 30-90 µm range) [26]. Mechanochemical technique, for example, high-energy milling is portrayed by the continued welding, distortion and crack of the constituent powder materials. The mechanical enactment energy amid handling prompts an expansion in the reactivity of the powders, as a result of devastation of agglomerates and particles of the beginning powders. This procedure not just includes the physical diminishment of particle size, yet in addition utilizes milling energy to start different phase transitions among the powders. Phase transitions happen at low temperatures amid the highenergy ball-mill activity with no outside heat source [27]. Additionally, high-energy ball-milling can extraordinarily

enhance the reactivity of rare-earth zirconate powders, in this way lessening the phase formation temperature of the rare-earth zirconates. Powder flowability of the rare-earth zirconate powders are greatly influenced by their powder morphology and particle size. Morphology and particle size relies on the starting powder attributes and the kind of heating route followed [16]. In any case, if densification increments with calcination temperature, particle grain size becomes correlatively finished a specific temperature. As per the learning of the author(s), there is no appropriate writing which corresponds the impact of processing and the sort of calcination process utilized on the powder flowability attributes of rare-earth zirconates. In this present work, Re<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> powders were synthesized by solid-state reaction through high-energy ball-milling process utilizing  $Re_2O_3$ , Re = La, Gd, Nd, Y and ZrO<sub>2</sub> materials and subsequently followed by the conventional and microwave calcination. Properties of the Re<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> powders integrated by high-energy ballmilling process finished by consequent calcination two distinctive source of heating techniques were investigated and revealed.

# **Experimental**

# Synthesis of Re<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> powder

In the present work,  $Re_2Zr_2O_7$  [Re = La, Gd, Nd, Y] powders with the desired compositions as shown in Table 1 was synthesized by solid-state reaction followed by two different calcination techniques [28-30]. One is Conventional Calcination (CVC) technique where conventional heating was performed in an electric furnace in air at 1400 °C (5 °C/min) for 12 h. The other is Microwave Calcination (MWC) technique where microwave heating was performed in an indigenously outlined microwave furnace with silicon carbide susceptor at 1050 °C (25 °C/min) for 18 min with  $Re_2O_3$  [Re = La, Gd, Nd, Y] (99.99% purity, Central Drug House Pvt. Ltd, New Delhi, India and Sisco Research Laboratories Pvt. Ltd, Taloja, India) and ZrO<sub>2</sub> (98.50% purity, Central Drug House Pvt. Ltd, New Delhi, India) as the starting materials. Heating patterns in conventional and microwave furnaces are shown in Fig. 1 [30]. After heat treatment, a deionized water based suspension of Re<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> powders were ball milled using high-energy ball-mill for 8 h with zirconia balls. The powders in the suspension was completely

Table 1. Composition (wt %) of the new rare-earth zirconates  $(Re_2Zr_2O_7)$ .

Materials	Composition (Wt %)						
	La <sub>2</sub> O <sub>3</sub> wt%	Gd <sub>2</sub> O <sub>3</sub> wt%	Nd <sub>2</sub> O <sub>3</sub> wt%	Y <sub>2</sub> O <sub>3</sub> wt%	ZrO <sub>2</sub> wt%		
$La_2Zr_2O_7$	57	_	_	_	43		
$Gd_2Zr_2O_7$	_	60	_	-	40		
$Nd_2Zr_2O_7$	_	_	58	_	42		
$Y_2Zr_2O_7$	_	_	_	48	52		



Fig. 1 Heating patterns in conventional and microwave furnaces [30].

separated by precipitation from water with a centrifuge and dried in hot air oven at 110 °C for 24 h. After drying, the powders were calcined in a conventional furnace at 1550 °C for 2 h and microwave at 1200 °C for 3 min, separately. The schematic diagram of the  $Re_2Zr_2O_7$  powders processing in the solid-state reaction is shown in Fig. 2.

#### Characterization of Re<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> powder

The rare-earth zirconate ( $Re_2Zr_2O_7$ ) pyrochlore powders were characterized for powder X-ray diffraction (XRD), FTIR, particle size, Scanning electron microscopy (SEM), BET specific surface area, density and powder flowability. The XRD patterns were obtained with a diffractometer (Bruker D8 advance) using Cu K $\alpha$ radiation. The morphology of the calcined rare-earth zirconate powders was investigated by HR-SEM (F E I Quanta FEG 200-High Resolution Scanning Electron Microscope). Horiba laser particle size distribution analyzer (LA-950V2) was used to determine the particle size and distribution of the calcined rare-earth zirconate powders. The specific surface area, pore volume and pore size values of the calcined rare-earth zirconate powders were recorded using nitrogen adsorption technique at liquid nitrogen temperature (Micromeritics ASAP 2020 porosimeter). The bulk density, tap density values of the calcined pyrochlore powders were determined by the graduated cylinder method. Fourier transform infrared spectra of pyrochlore rare-earth zirconates was measured using a Perkin-Elmer Spectrum1 FT-IR spectrometer which consists of globar and mercury vapor lamp as sources, an interferometer chamber comprising of KBr and mylar beam splitters followed by a sample chamber and detector and the entire region of 450-4000 cm<sup>-1</sup> is covered.. The flowability of the calcined rare-earth zirconate powders were determined using Hausner Ratio (HR) and Compressibility Index (CI). The Compressibility Index and the Hausner Ratio are calculated according to the following equation [18]:

Hausner Ratio (HR) =  $\rho_t / \rho_b$ Compressibility Index (CI) =  $[(\rho_t - \rho_b) / \rho_t)]$  X 100 Where  $\rho_b$  is the powder bulk density (g/cc)

 $\rho_t$  is the powder tapped density (g/cc)



Fig. 2. The schematic diagram of the  $Re_2Zr_2O_7$  powders processing in the solid-state reaction.



Fig. 3. XRD pattern of  $La_2Zr_2O_7$  (a) CVC (b) MWC at different stages.



Fig. 4 XRD pattern of  $Gd_2Zr_2O_7$  (a) CVC (b) MWC at different stages.

### **Results and Discussion**

Fig. 3, 4, 5 and 6 shows the XRD patterns of the  $Re_2Zr_2O_7$  [Re = La, Gd, Nd, Y] ceramic powders synthesized by the solid-state reaction technique using high-energy ball-milling process [HEBM] followed by two different calcination techniques.

XRD patterns of the La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> at different two calcination techniques are recorded in Fig. 3. XRD pattern (A&B) shows that the major peaks are close to mono phase ZrO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> and also two strong main peaks of 2 $\theta$  between 27° [311] and 29° [222] are indications of the pyrochlore structure of La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> in both calcination techniques. In microwave calcination process additional La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> peaks were observed. Pattern (C) shows that as the calcination temperature was increased, the peaks corresponding to La<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> disappeared, and a single La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> phase was formed and no additional peaks were observed, which indicated that pure La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> with pyrochlore structure could be synthesized at lower temperature and soaking time through microwave calcination technique compared

to the conventional technique. The diffraction peaks corresponds to the pyrochlore crystal system  $La_2Zr_2O_7$  (JCPDS: 73-0444). Moreover, with increase in the microwave calcination temperature from 1050 °C to 1200 °C, the peak intensity of the  $La_2Zr_2O_7$  in the XRD patterns become stronger, which corresponds to the growth of the crystal at lower temperature and soaking time when compared to the conventional calcination technique. When compared with the CVC XRD pattern (C), the peaks  $2\theta \approx 77$  ° [662] and 79 ° [840] corresponding to  $La_2Zr_2O_7$  with pyrochlore structure also appeared in the MWC.

Fig. 4 shows the XRD patterns of the Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> prepared by solid-reaction process calcined by CVC and MWC method respectively. In Fig. 4(a) and 4(b) the XRD pattern (A) shows that the crystallinity is very high with major peaks of different phases of ZrO<sub>2</sub> and Gd<sub>2</sub>O<sub>3</sub>. The superstructure peaks of the pyrochlore phase  $(2\theta \approx 72^{\circ}, 79^{\circ})$  does not appear in the XRD patterns. This result shows that the Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> powders prepared through both the CVC and MWC method exhibited a disorder defective fluorite structure, belonging to the Fm3m space group. The peaks at  $2\theta \approx 30^{\circ}$  [311], 34° [222], 58° [440] appeared after the ball-milling process in both calcination techniques as shown in pattern (B). As shown in Fig. 4(b) pattern (C) an excellent Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> phase was formed in microwave calcined powder with no impurities peaks. However, the pyrochlore superstructure peaks at  $2\theta \approx 30^{\circ}$  [311], 34 ° [222], 49 ° [511], 58 ° [440] appeared in the XRD patterns. The Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (JCPDS: 16-0799) powders were indexed according to the ordered pyrochlore structure of the Fd3m space group. This result indicates that the calcination temperature was lowered (from 1550 °C to 1200 °C) and soaking time was shortened (from 2 h to 3 min) by MWC, when compared with conventional calcination technique (CVC) as shown in Fig. 4(a) pattern (C).

The XRD patterns of the Nd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> at different stages and at two different calcination techniques are shown in Fig. 5. The Nd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> single crystals were obtained by calcining the as burnt powders. A clear phase transition from precalcination to calcination could be noticed in Fig. 5(a) & 5(b). It is shown that the Nd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> phase formation starts during heat treatment, but the crystallinity was quite low. As the calcination temperatures were increased to 1550 °C (CVC) and 1200 °C (MWC), a single phase of Nd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (JCPDS:17-0458) was formed and no impure peaks were observed, which indicates that pure Nd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> with pyrochlore structure could be synthesized at lower temperature by MWC, when compared with convectional calcination technique (CVC).

Fig. 6 shows the XRD patterns of the  $Y_2Zr_2O_7$  powders calcined by the two different calcination techniques. It is well known that four major peaks namely  $2\theta \approx 30^{\circ}$  [222], 34.7° [400], 49.7° [440], 59.2° [622] are



Fig. 5 XRD pattern of  $Nd_2Zr_2O_7$  (a) CVC (b) MWC at different stages.



Fig. 6 XRD pattern of  $Y_2Zr_2O_7$  (a) CVC (b) MWC at different stages.

characteristic of a defect fluorite structure. These characteristic peaks can also be indexed on the basis of the pyrochlore structure. In general there are two additional peaks corresponding to  $2\theta = 36.3^{\circ}$  [331] and  $2\theta = 43.6^{\circ}$  [511] in the pyrochlore structure [2]. The existence of [331] and [511] peaks is the key to distinguish the pyrochlore structure from the fluorite structure. In Fig. 6(a) pattern (C) the two peak reflections did not appear. But in Fig. 6(b) pattern (C) a minor peak at  $2\theta = 43.6^{\circ}$  [511] reflection was detected. Therefore, the present microwave calcined  $Y_2Zr_2O_7$ powder of the pyrochlore structure could be synthesized at lower temperature by MWC when compared with the conventional calcined Y2Zr2O7 powder. However, the JCPDS date files corresponding to the pyrochlore oxides are not available. Therefore these pyrochlore phases were compared with the literature.

The FTIR spectra of the rare-earth zirconate calcined powders by two different calcination techniques are shown in Fig. 7. The FTIR spectrum curves of the as prepared  $La_2Zr_2O_7$  powder at two different calcination techniques are shown in Fig. 7(a). Several characteristic absorption bands can be observed at about 534, 737, 1052, 1383, 1640, 2921, 3443, 3608 cm<sup>-1</sup> by MWC. The detection of absorption bands centered at about 3608 cm<sup>-1</sup> is an evidence of the residual water molecules contained in the particles, and the absorption band at 1640 cm<sup>-1</sup> represents another vibration of bonds that existed in La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> or ZrO<sub>2</sub>. Simultaneously, a strong band occurred below 800 cm<sup>-1</sup> due to the formation of Zr-O- Zr, La-O- La or La-O-Zr chemical bonds via solid-state reaction at the two different calcination techniques.

Fig. 7(b) shows the FTIR spectra of the  $Gd_2Zr_2O_7$ powder which shows the characteristic absorption peaks at 3350, 2912, 1049, 723, 575 cm<sup>-1</sup> by MWC. The broad peak at about 723 scm<sup>-1</sup> is attributed to the M  $(Zr^{4+}, Gd^{3+})$ -O bond stretching vibration, demonstrating that a strong chemical reaction between the metal and the oxygen ions and the metal ions had occurred, resulting in a molecular level dispersion. The characteristic absorption band at 3434 cm<sup>-1</sup> can be seen in Fig. 7(b) CVC which are ascribed to the Gd-O vibration, and the band at 1051 cm<sup>-1</sup> are attributed to the absorption of ZrO<sub>2</sub>. In addition, the large absorption band between 600 and 500 cm<sup>-1</sup> is usually ascribed to the stretching vibration between the high value metals and oxygen. The positions of the absorption peaks are consistent with the peaks in Fig. 7(b), indicating that the Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> powders prepared by the solid-state with two different calcination techniques exhibited the similar structure.

The FTIR spectra of  $Nd_2Zr_2O_7$  calcined powders at two different calcination techniques are shown in Fig. 7(c). As shown in Fig. 7(c) a strong absorption peaks was observed at about 536, 1494, 1635, 3406, 3605 cm<sup>-1</sup>. To confirm these peak positions, FTIR spectra of ZrO<sub>2</sub>,  $Nd_2O_3$  were also recorded. The FTIR spectrum of ZrO<sub>2</sub> gave strong absorptions at 1648, 1386, 1066 cm<sup>-1</sup>. Therefore, the strong bands observed at 3406, 1635 cm<sup>-1</sup> in  $Nd_2Zr_2O_7$  could be due to Zr-O, Nd-O vibrations.

The FTIR spectra of  $Y_2Zr_2O_7$  powders are shown in Fig. 7(d). The broad peak observed in the range 3300-3500 cm<sup>-1</sup> corresponds to the stretching vibration of the physically absorbed M (Zr<sup>4+</sup>, Y<sup>3+</sup>)-O group on the surface. It shows that the peak observed at 514 cm<sup>-1</sup> corresponds to the pyrochlore phase, which is in good agreement with the literature data.

Fig. 8 shows the particle size distribution (PSD) of the rare-earth zirconate powders (Re<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>) [Re = La, Gd, Nd, Y] at two different calcination techniques. It can be seen from Fig. 8(a) that conventional calcined La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> powders posses a median diameter of  $3.7 \pm$ 2.7 µm with a mean size of D<sub>10</sub>, D<sub>50</sub> and D<sub>90</sub> at 0.4, 3.7 and 10.7 µm respectively. In the case of microwave calcined La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> powders, the particle size distribution (PSD) is found to be lower than CVC with a median diameter of  $1.7 \pm 1.1$  µm and the mean size of D<sub>10</sub>, D<sub>50</sub>



Fig. 7. FTIR spectrum of the (a) La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (b) Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (c) Nd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (d) Y<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> at two different solid-state calcination techniques.



Fig. 8. Particle size distribution of the (a) La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (b) Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (c) Nd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (d) Y<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> at two different calcination techniques.

and  $D_{90}$  are 0.9. 1.7 and 3.7 µm respectively. Therefore, it is evident that the particle diameter in both calcined powders (CVC and MWC) is almost similar (less than 10 µm). The particle size distribution (PSD) of La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> curves shows that both the calcined powders had >20 µm size particles only about 4.5-5% but about 3-4% of the particles size were in the range of 20-45 µm. In Fig. 8(b) shows that the particle size distribution of the  $Gd_2Zr_2O_7$  powders had a median diameter of  $2.5 \pm 33 \,\mu\text{m}$  with a cumulative mean diameter of  $D_{10}$ ,  $D_{50}$ , and  $D_{90}$  at about 0.4, 2.5 and 42.7  $\mu\text{m}$  respectively, obtained by the conventional solid-state calcination method. In the case of microwave calcined  $Gd_2Zr_2O_7$  powders the particle diameters were almost similar to the conventional

powders. From the PSD curve of Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>, it was found that both the calcined powder had a particle size of  $> 20 \,\mu\text{m}$  at about 14%. The PSD of the parent  $Nd_2Zr_2O_7$  is shown in Fig. 8(c). The measured median particle diameter of the conventional calcined  $Nd_2Zr_2O_7$  powder are about  $43 \pm 35 \mu m$ , corresponding to an microwave calcined powder particle diameter of approximately  $1.7 \pm 0.9 \,\mu\text{m}$ . Therefore, it is evident that the particle diameter of microwave calcined powder is lower than the conventional powders. The particle size distribution of  $Y_2Zr_2O_7$  is shown in Fig. 8(d). The particle size distribution curve of the conventional calcined Y<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> powder shows a broad size distribution with an average agglomerated particle size of  $263 \pm 83.7 \,\mu\text{m}$  which is lower than that of the microwave calcined  $Y_2Zr_2O_7$  powder (1.4 µm). The CVC particle size distribution is very suitable for the thermal spray coating feedstock powders. It is evident that 77% of the particles in the bulk are above 20 µm in size.

The effectiveness of the two different calcination techniques on the particle size distribution of rare-earth zirconate powders clearly shows that the obtained particle size is few microns in both the solid-state calcination techniques. It is suitable for the thermal spray coating feedstock systems.

Table 2 shows the specific surface area, pore volume and pore diameter of the rare-earth zirconates by two different calcination techniques. As shown in Table 2, the specific surface area of the calcined microwave rare-earth zirconate powders (Re<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>) is found to be around  $0.5-1.9 \text{ m}^2/\text{g}$ , which is higher than that of the calcined conventional powders  $(0.37-0.98 \text{ m}^2/\text{g})$ . In addition, hysteresis loops were observed at a relative pressure below 0.2, indicating that all the rare-earth zirconate powders have a very low pore volume (no porosity) as the pore diameter varies between 200-220 nm. Nitrogen adsorption isotherm linear plot against relative pressure (P/Po) of rare-earth zirconates in both calcination techniques are shown in Fig. 9. This isotherm (Fig. 9) may be classified as type II isotherm according to the BET surface area. This type of isotherm represents unrestricted monolayer-multilayer adsorption. It has a hysteresis loop, which could be classified as type A, characteristic of a cylindrical shaped capillaries open at both ends [31].

Table 2. Structural properties of rare-earth Zirconate powders.

The SEM images of the as prepared  $La_2Zr_2O_7$ particles are shown in Fig. 10. The LZ-CVC (Fig. 10a) was prepared by solid-state conventional calcination at 1550 °C for 2 h. In comparison, LZ-MWC (Fig. 10b) was prepared by solid-state microwave low temperature calcination at 1200 °C for 3 min. Both powders exhibit a sphere like morphology, dispersed uniformly and the particle size was in the micro scale. Compared to MWC, powders calcined at CVC appears to have a more compact microstructure, and the particle size increases. It is due to calcination of  $La_2Zr_2O_7$  particles with increase in the calcination temperature.

Fig. 11(a) and (b) shows the representative SEM micro-graphs of the  $Gd_2Zr_2O_7$  powders prepared by the two different calcination techniques. The particle size of the powders were different for different sample. Fig. 11(a) reveals that  $Gd_2Zr_2O_7$  powders prepared by the



**Fig. 9.**  $N_2$  adsorption isotherm linear plot against relative pressure of rare earth zirconates at different calcination techniques (a) CVC (b) MWC.



Fig. 10. Morphology of the  $La_2Zr_2O_7$  powders at different magnifications (a) CVC (b) MWC.

Materials	Conventional calcination process (CVC)			Microwave calcination process (MWC)			
	BET Specific surface area (m <sup>2</sup> /g)	Pore volume X $10^{-3}$ (cm <sup>3</sup> /g)	Pore diameter (nm)	BET Specific surface area (m <sup>2</sup> /g)	Pore volume X $10^{-3}$ (cm <sup>3</sup> /g)	Pore diameter (nm)	
$La_2Zr_2O_7$	0.6929	1.745	203	0.9928	2.102	190	
$Gd_2Zr_2O_7$	0.6492	1.623	211	0.5354	1.565	138	
$Nd_2Zr_2O_7$	0.9808	2.015	185	1.9017	4.021	102	
$Y_2Zr_2O_7$	0.3751	1.258	395	0.7952	1.879	170	



**Fig. 11.** Morphology of the  $Gd_2Zr_2O_7$  powders at different magnifications (a) CVC (b) MWC.



Fig. 12. Morphology of the  $Nd_2Zr_2O_7$  powders at different magnifications (a) CVC (b) MWC.

CVC technique consist of nearly spherical particles with a diameter of about 2.5  $\mu$ m and crystalline shape is irregular and agglomeration is obvious. The morphologies of the Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> powders synthesized by the MWC technique are shown in Fig. 11(b). The particles are almost spherical in shape but the diameter is only 2.2  $\mu$ m, less agglomeration is evident due to larger grain size and lower surface energy.

The SEM images of the two different calcination techniques of  $Nd_2Zr_2O_7$  particles are shown in Fig. 12. The grain size of the as prepared NZ-CVC (Fig. 12a) particles is about 3.23 µm, crystalline structure is



Fig. 13. Morphology of the  $Y_2Zr_2O_7$  powders at different magnifications (a) CVC (b) MWC.

irregular, and agglomeration is obvious. However the grain size of the as prepared NZ-MWC particles (Fig. 12b) is about 1.42  $\mu$ m which is smaller than that of NZ-CVC particles. The NZ-CVC particles exhibits remarkable agglomeration and the surface shows interfaces, but the NZ-MWC particles grew uniformly and has less agglomeration (Fig. 12b).

The SEM images of the  $Y_2Z_2O_7$  powders prepared by the two different calcination techniques are shown in Fig. 13. The morphology and particle size of the  $Y_2Z_2O_7$  prepared by the CVC technique are quite different when compared with the  $Y_2Z_2O_7$  prepared by the MWC technique. As shown in Fig. 13(a), the grain size of the sample seems to be in the range of few microns. The surface morphology is uniform and few particles are agglomerated. The average grain size is about 4.31 µm with a nonuniform grain size distribution. However, when analyzing the samples prepared by MWC (Fig. 13b), it is found that the average grain size is only about 2.63 µm, with a uniform grain size distribution.

The physical properties and flow characteristics of the rare-earth zirconate powders are tabulated in Table 3. HR and CI are two important qualitative parameters commonly used to show the powder flowability for they are relatively easy to measure. Table 3 shows the relationship between the bulk density, tap density, HR and CI of the samples prepared by two different

**Table 3.** Physical properties and Flow characteristics of the  $Re_2Zr_2O_7$ , Re = La, Gd, Nd, Y powders at two different calcination techniques.

	Conventional calcination process (CVC)			Microwave calcination process (MWC)				
Materials	Bulk density (g/cc)	Tap density (g/cc)	HR	CI (%)	Bulk density (g/cc)	Tap Density (g/cc)	HR	CI (%)
$La_2Zr_2O_7$	1.67	2.30	1.38	27.40	1.29	1.94	1.50	33.51
$Gd_2Zr_2O_7$	1.51	1.64	1.09	7.93	1.60	1.76	1.10	9.10
$Nd_2Zr_2O_7$	1.07	1.24	1.19	13.71	1.12	1.27	1.13	11.81
$Y_2Zr_2O_7$	1.52	1.78	1.17	14.61	1.3	1.52	1.17	14.47

calcination techniques. A decrease in the value of HR and CI indicates a decrease of the powder cohesiveness, which means that the flowability becomes very free flow. It can be seen (Fig. 8) that as powder particle size decreases, both HR and CI increases gradually, which indicates poor flowability due to cohesive flow. Lu et al. [32] also obtained similar results. Furthermore, it can also be seen from Table 3 that the values of HR and CI for microwave calcined La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> powders are larger than those of the conventional calcined La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> powders, which means that the flowability of LZ-MWC is worse than that of LZ-CVC. Chi- Ying Wong [33] and Guiling Xu et al. [18] both found that the results of the powder flowability characteristics were greatly affected by particle size, and there is a critical particle size range above which the powder flowability did not show significant improvement.

# Conclusions

Rare-earth zirconate  $[Re_2Zr_2O_7, Re = La, Gd, Nd, Y]$ ceramic powders were synthesized by solid-stare reaction through high-energy ball-milling using rareearth oxide and zirconia materials, followed by conventional and microwave calcination techniques. The impacts of calcination techniques on the crystal structure, functional groups, particle size, specific surface area, morphology, density and powder flowability have been investigated and reported in detail. It was found that the high-energy ball-milling process using zirconia balls followed by conventional and the microwave heating processes could produce micro-sized and impurity free pyrochlore  $\text{Re}_2\text{Zr}_2\text{O}_7$  [ $\text{Re}_2\text{Zr}_2\text{O}_7$ , Re = La, Gd, Nd, Y] powders. The average particle size of the microwave calcined powders varied between 1.36 to 2.27 µm which is found to be lesser than that of the conventionally calcined Re<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> powders. Phase purity of the Re<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and the extent of pyrochlore present were clearly evident from the XRD patterns and the highly intense peak at a wavenumber of 535 cm<sup>-1</sup> in the FTIR spectrum. Microwave calcined Re<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> powders showed the highest value of pyrochlore structure crystallinity, lowest particle size and highest specific surface area. The microwave kinetics seems to have made an impact in the reduction the particle size and distribution at the same time maintaining the pyrochlore crystal structure. Powder flow characteristic value of the calcined powders by both techniques were superior due to the micro-sized particles, specific surface area (less than  $1.0 \text{ m}^2/\text{g}$ ) and superior pyrochlore crystal structure of the grains. Also microwave heating consumed 47 times less energy and 7 h less than that consumed by the conventional heating process. Thus, the high-energy ball-milling followed by subsequent conventional calcination method is most suitable but microwave calcination method can with reduced heating rate is also suitable, an energy conserving

method for the synthesis of the rare-earth zirconate suitable for the thermal spray coating applications

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