Synthesis and Characterization of $La_2Zr_2O_7$ Nanoparticles

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This paper focuses on advanced thermal barrier coatings (TBC) for extreme temperature protection of metallic components, particularly in gas turbine engines. The study highlights the significance of developing CBT materials with exceptional sintering resistance and low thermal conductivity. Pyrochlore-type rare earth zirconium oxides, such as Lanthanum Zirconate (La2Zr2O7), are identified as promising candidates due to their superior properties compared to alternatives like Yttria-stabilized zirconia. The research employs sol-gel method to synthesize La2Zr2O7 CBT powder. The process involved in obtaining a clear and homogeneous sol (colloidal suspension of solid particles in a liquid medium) using a metal inorganic salt precursor, Citric Acid as a chelating agent, Polyethylene Glycol as a dispersive agent, and Formamide as a gelation inducer. The resulting gel displayed a homogeneous La-O-Zr composition. The amorphous xerogel was transformed into the pyrochlore phase of spherical shape with grain sizes ranging from 80 to 200 nm through series of heat treatments up to 1200 °C. As the temperature increased, the grain size expanded to 500 nm to 1μm at 1400°C, while maintaining a uniform dispersion and spherical morphology. Phase identification of La2Zr2O7 and its microstructural analyses were carried out through XRD, SEM, and EDAX.

Keywords: thermal barrier coatings (TBC), gas turbine engines.

1. Introduction

One of the main characteristics of nanoparticles is their high surface-to-volume ratio. This refers to the proportion of atoms located at the surface of the particles compared to the total number of atoms in the particle. Because nanoparticles are so small, the ratio of atoms at the surface to atoms in the bulk of the particle is much higher when compared to bulk materials. This high surface-to-volume ratio gives nanoparticles unique properties, such as increased reactivity and surface energy. Nanoparticles can be made from a wide range of materials, including metals, ceramics, and polymers. They can be synthesized through a variety of methods, such as chemical synthesis, physical vapor deposition, and ball milling. The method used to synthesize nanoparticles can affect their size, shape, and properties[1].

In recent years, there has been a remarkable surge of interest in the development and investigation of nanostructured coatings. This growing fascination stems primarily from the remarkable properties exhibited by such coatings when compared to their micrometer-sized counterparts.By scaling down the structural dimensions to the nanometer level, a multitude of advantages can be achieved.

One of the foremost benefits lies in the remarkable increase in strength, accompanied by a marked improvement in toughness. Simultaneously, reducing the structural scale leads to a higher coefficient of thermal expansion while effectively decreasing the apparent density and elastic modulus. Furthermore, the apparent thermal conductivity experiences a notable reduction, among a plethora of other potential enhancements.

Some notable examples of these applications include thermal barrier coatings (TBCs), which offer exceptional insulation in high-temperature environments. Similarly, abradable coatings in aero-engines exhibit impressive wear resistance. Nanostructured coatings also find their utility in Solid Oxide Fuel Cells (SOFCs), where they serve as electrolytes and porous electrodes, thereby enhancing the performance and efficiency of these energy conversion devices. Additionally, they are employed in the production of wear-resistant coatings, bio-medical coatings, as well as coatings designed to manipulate and enhance photocatalytic and emission properties[2,3].

In essence, the development and exploration of nanostructured coatings have captivated researchers and industry professionals alike due to their ability to unlock a wide range of unparalleled benefits. These advancements pave the way for transformative applications across various domains, enabling significant progress and innovation in fields as diverse as energy, transportation, healthcare, and environmental sustainability.

TBCs typically consist of a ceramic material, which is applied to the surface of the component usingtechniques such as plasma spraying, or electron beam physical vapor deposition[4]. The ceramic material used in TBCs has alow thermal conductivity, which means it can act as an effective insulator against heat. This helps to reduce the temperature of the component and protect it from thermal damage, such as cracking or melting. TBCs can also help to increase engine efficiency by reducing the amount of heat lost to the surrounding environment, which can be a significant source of energy loss in high-temperature applications.

Among the promising candidates for TBCs, Pyrochlore-type rare earth zirconium oxides, such as Lanthanum Zirconate, have garnered attention. Compared to other TBC options like Yttria-stabilized zirconia, Lanthanum Zirconate TBCs offer several advantageous properties. They exhibit higher phase stability, lower thermal conductivity, reducedsintering rate, absence of phase transformation, and lower coefficient of thermal expansion at elevated temperatures[5]. These characteristics make pyrochlore oxides like Lanthanum Zirconate ideal for overcoming challenges related to high-temperature operations in gas turbine engines, resulting in improved efficiency, reduced emissions, and decreased fuel consumption.

In the present work, Lanthanum Zirconate nanoparticles have been synthesized by sol-gel method and characterized the processed particles through XRD, SEM, and EDAX.

2. Experimental

2.1 Materials

Lanthanum Zirconate nanoparticles have been synthesized using following materials.

Lanthanum Nitrate [La $(NO_3)3\cdot6H_2O$]

Zirconium Oxychloride [$ZrOCl_2\cdot8H_2O$]

Distilled Water and Ethanol [H_2O/C_2H_5OH]

Citric Acid [$C_6H_8O_7$]

Formamide [CH_3NO]

Polyethylene Glycol [C_2H_4O]

Lanthanum Nitrate is commonly used as a precursor material in the synthesis of lanthanum zirconate nanoparticles through the sol-gel process. Zirconium Oxychloride is used as a precursor material in the synthesis of zirconia (ZrO_2) nanoparticles through the sol-gel process. Citric Acid is used as a chelating agent in the synthesis of lanthanum zirconate and other metal oxides. Chelating agents are organic compounds that bind to metal ions and help to control their reactivity and distribution during the synthesis process. Formamide is a solvent that is used in the synthesis of lanthanum zirconate and other metal oxides. It is a polar organic solvent with a high boiling point, which makes it useful for dissolving and stabilizing metal salts during the synthesis process. Polyethylene Glycol is a commonly used additive used in the synthesis of lanthanum zirconate and other metal oxides. It is a water-soluble polymer with a wide range of molecular weights and functional groups, which makes it useful for controlling the properties of the synthesized nanoparticles. Ethanol is commonly used as a solvent in the solgel process for the synthesis of lanthanum zirconate nanoparticles. Double distilled water is commonly used in the sol-gel process for the synthesis of lanthanum zirconate nanoparticles because it is highly purified and free from impurities that can interfere with the reaction or affect the properties of the final product[6].

2.2 Material Synthesis

The synthesis of lanthanum zirconate typically involves several methods, including solid-state reaction, sol-gel process, and chemical vapor deposition (CVD).

Out of these methods, sol–gel method can confirm mixing precursors at the molecular level, thus producing powders with high compositional homogeneity and stoichiometry control. Also, this method requires low temperature, is of low cost, and can generally be done under room conditions with general lab equipment, all of which make its processing convenient. Conventionally, precursors employed in this method are usually metal alkoxide, expensive and sensitive to moisture, heat and light, and mechanism of fabrication of $La_2Zr_2O_7$ using alkoxide has been extensively investigated. Studies on $La_2Zr_2O_7$ nanoparticles using other precursors beside metal alkoxide have been popular in recent years. Vladimir et al.,[5] synthesized nanocrystalline $La_2Zr_2O_7$ with pyrochlore structure using metal inorganic salt as precursor, but the particles were of low crystalline degree, and obviously sintering from 1000°Cto 1200°C. Linggen Kong synthesized pyrochlore type $La_2Zr_2O_7$ powders using zirconium(IV) bis(diethyl citrate) dipropoxide and lanthanum nitrate hexahydrate as a new precursor via combining the sol–gel technology and complex precipitation processing, and the particle size was about 200

- 600 nm when calcined at 1200 °C. Nanoparticles with single-pyrochlore phase, higher crystalline degree, and lower particle size require to be synthesized and the mechanismof structure evolution from wet sol to powders is worth to be studied. Ten trials have been carried out.

2.3 Steps involved in Synthesis

Step 1

Take 5.00 g $ZrOCl_2{\cdot}8H_2O$ and 6.66 g La $(NO_3)3{\cdot}6H_2O$ and separately dissolve them in distilled - ethanol solution in a test tube with proper molar amounts till a homogeneous transparent solution is obtained.

$ZrOCl_2{\cdot}8H_2O + 4H_2O + 2C_2H_5OH \rightarrow Zr^{4+} + 2Cl^- + 12H_2O + 2C_2H_5OH$ La $(NO_3)_3{\cdot}6H_2O + 6H_2O + 3C_2H_5OH \rightarrow La^{3+} + 3NO^{3-} + 6H_2O + 3C_2H_5OH$

The reactions involve the dissociation of the metal salts into their respective ions in solution, which are then coordinated with water molecules and ethanol molecules to form stable complexes. The resulting solutions should be homogeneous and transparent due to the formation of these complexes.

Step 2

After stirring for 1 hour respectively, the solutions were mixed in appropriate proportions with 0.65 g Citric Acid and 0.70 g. Formamide added to the resultant solution with a molar ratio ofZr^{4+}: La^{3+}: CA: FA = 1:1:0.2:1.5 while stirring.

$2Zr^{4+} + 3La^{3+} + 10H_2O + 3C_6H_8O_7 + 4HCONH_2 \rightarrow 2ZrO_2{\cdot}3H_2O + 3La2(C_6H_6O_7)_3{\cdot}xH_2O +$

$4CO(NH_2)_2 + 9H^+$

Furthermore, lanthanum zirconate exhibits a relatively low thermal conductivity. This property is highly desirable for TBCs as it helps to reduce heat transfer through the coating, thereby creating a thermal gradient between the coating surface and the substrate surface. This thermal gradient acts as a thermal barrier, minimizing the heat flow into the underlying substrate and allowing for higher operating temperatures. Consequently, the use of lanthanum zirconate TBCs can enhance the overall efficiency and performance of gas turbines by extending their temperature operating range. This can lead to a more uniform and homogeneous distribution of nanoparticles, which can be beneficial for their stability, size, and optical properties.

This can lead to a more uniform and homogeneous distribution of nanoparticles, which can be beneficial for their stability, size, and optical properties. Formamide is often used to initiate gelation in sol-gel synthesis due to its ability to form hydrogen bonds and participate in self-assembling processes. When added to a precursor solution, formamide can induce the formation of a gel-like network, which can serve as a template for the growth of nanoparticles. The gelation process can be triggered by temperature, pH, or the addition of other agents, and can be used to control the size, shape, and distribution of nanoparticles. Water-Ethanol mixture is prepared to dissolve the precursor materials La $(NO_3)_3{\cdot}6H_2O$ and $ZrOCl_2{\cdot}8H_2O$ at the ratio 1:2.5 and 1:1 respectively (Water: Ethanol). The following amount of water-ethanol mixture was added to the starting precursor materials to dissolve them.

After dissolving the precursors separately using water-ethanol mixture the solutions are stirred for 1 hour to obtain homogenous solution, both the solutions are mixed in a single beaker and 0.625 ml of Formamide and 0.65 g of Citric acid is added to the mixed solution dropwise while stirring.

Step 3

Then, 0.28 g Polyethylene Glycol is added to produce a homogeneous transparent solution. Polyethylene glycol (PEG) is a polymer that can act as a stabilizer and help to form a homogeneous transparent solution. The addition of PEG to the Zr^{4+} and La^{3+} ion solution can be represented by the following equation:

$$2Zr^{4+} + 3La^{3+} + 10H_2O + n\ PEG \rightarrow 2ZrO_2 \cdot 3H_2O + 3La\ (PEG)n \cdot xH_2O + 9H^+$$

In this equation, PEG acts as a stabilizer and forms a complex with the La3+ ions, helping to maintain a homogeneous transparent solution. The value of "n" depends on the molecular weight of the PEG used.

Step 4

After stirring for 2 hours at room temperature, the mixture was poured into a crucible and kept at 80 °C for around 20 hours to form a wet gel and then dried at 110 °C for 5 hours.

$$2ZrO_2 \cdot 3H_2O + 3La\ (PEG)n \cdot xH_2O \rightarrow La_2Zr_2O_7 + nH_2O + 3nPEG$$

In this equation, the drying process removes the water molecules and causes the formation of a crystalline $La_2Zr_2O_7$ phase. The PEG molecules are also removed during the drying process, leaving behind a porous ceramic material. The formation of a wet gel occurs when the sol, a colloidal suspension of solid particles in a liquid medium, is transformed into a three dimensional network of solid particles. The formation of this gel structure is influenced by many factors, including the temperature at which the process is carried out. The Crucible is kept in the open air a Heater can be used for the heating process. The heating must be continued until a wet gel is formed; it might require around 20 hours if heating. After the wet gel is formed, the temperature is risen to 110 °C to dry the wet gel and form the xerogel.

Step 5

Finally, the xerogel was calcined in air at different temperatures ranging from 200 °C to 1400°C using 5 °C/min ramps and 2 hours dwell times.

$$La_2Zr_2O_7 + heat \rightarrow 2La_2Zr_2O_7 + O_2$$

Oxygen gas (O_2) is expected to be released during calcination, as seen in the chemical equation for the process. The release of other gases such as water vapor and carbon dioxide may also occur due to the decomposition of any residual organic matter or other impurities present in the xerogel.

The calcination of nano particles involves the process of heating the particles at high temperatures to remove any residual solvents or organic compounds that may have been used in the manufacturing process.

2.4 Material Characterization

Phase identification of Lanthanum Zirconate and its microstructural analyses were carried out through XRD, SEM, and EDAX.

XRD is a valuable technique for analyzing nanoparticles as it can provide information about crystal structure, size, and composition of the test sample. Nanoparticles can exhibit different phases or polymorphs, and XRD can help in identifying and distinguishing between them. By comparing the XRD pattern of nanoparticles with known reference patterns, researchers can determine the specific phases present in the sample[7].

SEM analysis provides high- resolution imaging capabilities, allowing researchers to visualize individual nanoparticles andobtain detailed information about their surface features. It is also a relatively fast and versatiletechnique that can be applied to a wide range of nanoparticle materials[8].

EDAX analysis can help determine the elemental composition of the nanoparticles, identify impurities or contaminants, and assess the stoichiometry of the material. The analysis relies on the interaction between the sample and a focused electron beam. It is a useful technique for identifying impurities, determining the homogeneity of a material, and characterizing the composition of thin films and coatings.

3. Results and Discussion

3.1 XRD Analysis

XRD can detect structural changes in nanoparticles due to various factors, such as temperature, pressure, or chemical reactions. By monitoring the evolution of the XRD pattern under different conditions, researchers can gain insights into phase transformations, lattice expansion or contraction, and other structural changes.

XRD was carried out for the obtained samples before calcination, i.e., in the xerogel phase and after calcination. The expected results show the presence of a lot of disturbances in the xerogel formed after heat treating it with higher peaks appearing at a 2-theta around 32° as shown in Fig. 1.

There are peaks available between the 30-35° range indicating that Lanthanum Zirconate is present in the sample and calcination can be carried out to remove these impurities. Hence post calcination the samples' XRD results were taken and analyzed. After complete calcination to 1400 °C and carrying out XRD test, the sample result presented in Fig. 2 is similar to the result obtained by Kaijin Huang [9]. The result shows the formation of major peaks at 29°, 33°, 48° and 57° indicating the formation of pyrochlore structured LanthanumZirconate by sol-gel process.

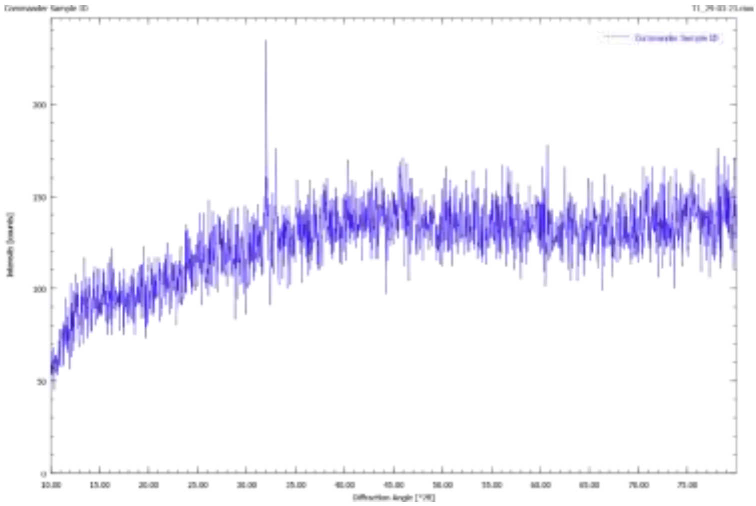


Fig. 1: XRD Results obtained before calcination

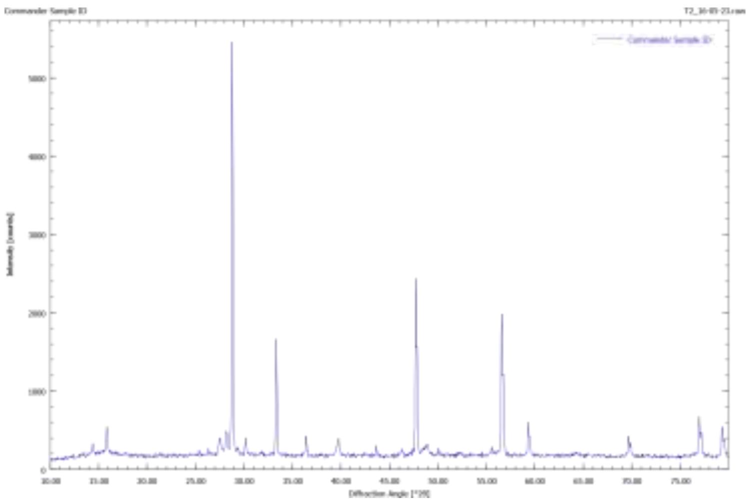
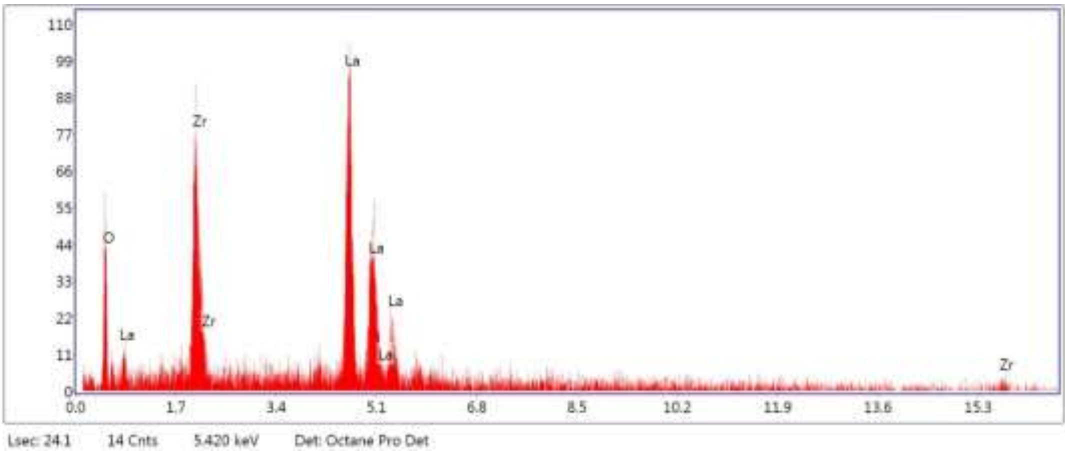


Fig. 2: XRD Results obtained after 1400˚C calcination

3.2 EDAX Analysis

EDAX analysis provides valuable information about the elemental composition of nanoparticles, aiding in their characterization and understanding of their properties. The intensity of the X-ray peaks in the spectrum are used to estimate the relative abundance of the elements. This information helps to determine the stoichiometry or elemental ratio within the nanoparticles. The results obtained in the in the present study (Fig. 3) are identical to the results obtained by Hongyang Zhao et al.[10].



Element	Weight %	Atomic %
O	21.30	67.04
Zr	23.39	12.91
La	55.31	20.05

Fig.3: EDAX Results obtained after Calcination

3.3 SEM Analysis

SEM analysis was employed to obtain direct information about the size and morphologies of the $La_2Zr_2O_7$ powders. The SEM images of the $La_2Zr_2O_7$ powders calcined at different magnifications are shown in Fig 24. The powders exhibit a sphere-like morphology, disperses uniformly and the particle size is in nanoscale.

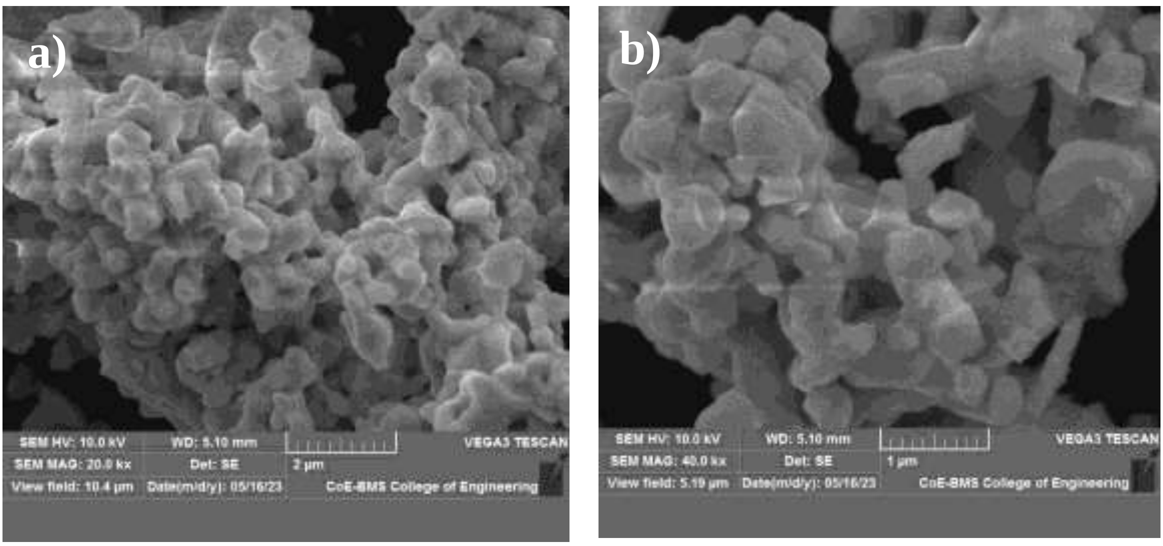


Fig. 24 SEM images at differentmagnifications: a) Lower magnification and b) Higher magnification

4. Conclusion

A single pyrochlore phase of nanocrystalline Lanthanum zirconate powder was successfully synthesized via a non-alkoxide sol-gel technique. The process involved obtaining a clear and homogeneous sol using a metal inorganic salt precursor, Citric Acid as a chelating agent, Polyethylene Glycol as a dispersive agent, and Formamide as a gelation inducer. The resulting gel displayed a homogeneous La-O-Zr composition. Through heat treatment, the amorphous xerogel transformed into a ceramic structure. At 1200 °C, the powders transitioned into the pyrochlore phase with grain sizes ranging from 80 to 200 nm. As the temperature increased, the grain size expanded to 500 nm to 1μm at 1400 °C, while maintaining a uniform dispersion and spherical morphology. Synthesized Lanthanum zirconate can be as a thermal barrier coating material for applications in gas turbines, jet engines, power generation systems, automotive engines, aerospace components, and industrial furnaces.

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