



PREPARATION AND CHARACTERIZATION OF LANTHANUM AND SAMARIUM ZIRCONATE POWDERS FOR TBC APPLICATION

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ABSTRACT

In this present research work, Sm_2O_3 and La_2O_3 have been used as the dopant or stabilizer to Zirconia powder as a candidate for TBC. Various characterization tests have been conducted such as XRD, EDAX, and Particle Sizes etc. to optimize and determine the dopant concentration for partial or full stabilization of Zirconia. And to study the effect of stabilization of Zirconia, two methods have been followed: 1. Powder preparation by Agate jar mixing. 2. Powder preparation by planetary high-energy wet ball mill method. In the first and second methods, we have studied stabilization of Zirconate by phase transformation at various sintering temperatures using XRD and chemical compositions of lanthanum and samarium zirconate powders using EDAX analysis, after calcinated for various temperatures. From the first method, stabilization of Zirconia is very less due to higher particle size and higher calcination temperature of 1625°C . From the second method stabilized zirconate formed due to smaller particles size and optimum calcinations temperature of 1435°C .

Keywords: *Thermal Barrier Coating, Zirconate Phase, Powder Preparation by Agate Method, Wet Ball Milling Method, XRD and EDAX.*

1. Introduction

Thermal barrier coating (TBC) systems are increasingly utilized in heat exposed components of energy conversion systems to achieve a gradient between high surface temperature and the lower temperature of internal cooling [1,2]. The set of used materials can resist to extreme thermal and mechanical loads during durability from 100.000h. Maximum high constructive elements are the rotating blades of turbines of the first step. Nowadays they work at service temperature above 1200°C (stationary gas turbine) (plane turbine). The ability to increase the high gas temperatures has resulted from a combination of material improvements and the development of more complicated arrangements for internal and external cooling. Some of this increase will be made possible by the further adoption of thermal barrier coatings.

Thermal barrier coatings have been used for some years on static parts, initially using magnesium zirconate, but more recently yttria-stabilised Zirconia has become the material choice [3,4]. A typical TBC system consists of a substrate, the metallic bond coat and the yttrium stabilized zirconium (YSZ) TBC [5,6]. Coating system with temperature gradient thickness of top and bottom coat is approximately $300\mu\text{m}$. To improves the service life of such components and to

operate the turbine more efficiently at higher temperature various material approaches have been proposed and exploited. In the wake of this development made continuous efforts are to improve the processing technology and the characteristics of the coating properties.

Zirconates have drawn the attention of several research groups as a promising alternative to YSZ. These materials with a pyrochlore structure [9] have a fair TEC (in the range of $9-10 \times 10^{-6} \text{ K}^{-1}$) which is comparable with PSZ. The main advantages of zirconates are their low sintering activity, low thermal conductivity (20% lower than PSZ), and good thermal cycling resistance [7,8]. The disadvantage is the high TEC in some of the Zirconates which results in residual stress in the coating, and can cause coating delamination. Some materials in this category; e.g. $\text{BaO} \cdot \text{ZrO}_2$, $\text{SrO} \cdot \text{ZrO}_2$, and $\text{La}_2\text{O}_3 \cdot 2\text{ZrO}_2$, undergo phase transformation or become non-stoichiometric during heating due to improper selection of doping agent. The total porosity in plasma sprayed zirconates is less than 10% [9] which is lower than the porosity in plasma sprayed PSZ. The porosity has a vital role in thermal insulation, process modification is required to increase the level. (17)

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1.1 Phase transformation cycle

The forward (monoclinic to tetragonal) transition occurs at 1200°C and there will be a tetragonal to cubic phase between 2370°C, the reverse (tetragonal to monoclinic) between 850°C and 1000°C depending upon the surface and strain energies created during (monoclinic to tetragonal) transformation.

Transformation in the present work we focused to study the various phase formation characteristic of the Zirconate powders, calcinated at various temperature conditions. The Phase transformations cycles are given below. [10, 11]

(800-1200°C) (2370°C) (2380°C)
 Monoclinic ↔ Tetragonal ↔ Cubic ↔ Liquid

Phase transformations cycle

1.2 Zirconite powder preparation

The preparation of plasma sprayable grade powders consisted of the following steps as specified in the below given chart.

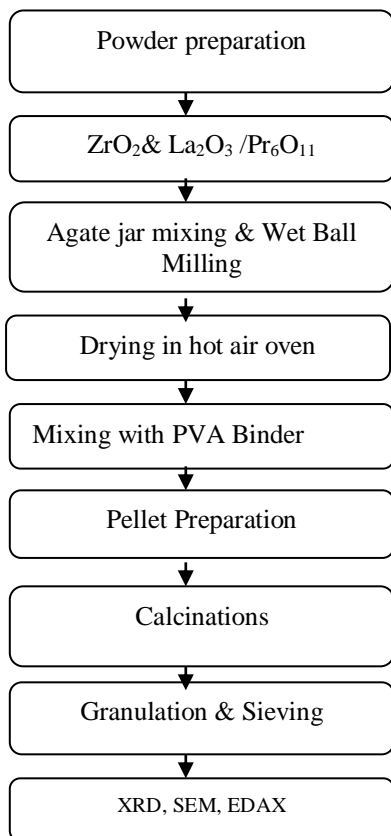
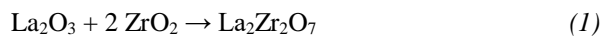


Fig.1 Powder Preparation Flow Chart

2. Experimental Work

The powders of 1.33kg La₂O₃ and Sm₂O₃ (1kg of ZrO₂, 1.3221kg of La₂O₃ and Sm₂O₃) powder were synthesized using agate jar method and planetary high-energy wet ball mill method. Reagent-grade oxide powders of ZrO₂ were used as raw materials. In this agate jar method, the raw materials were weighed both La₂O₃ and ZrO₂ in an accuracy of 0.01 grams and mixed in an agate jar for about 1 hour by human hand and finally we get a Lanthanum doped zirconate and samarium doped zirconate powders.

The powder composition obtained from the following equation. (1).

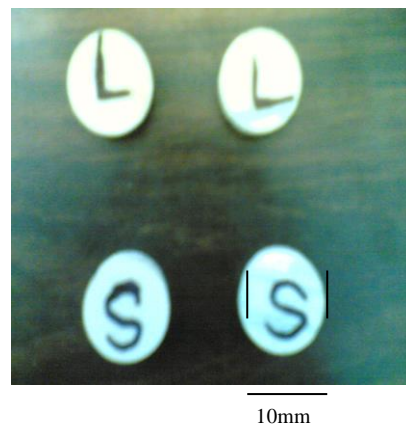


Proportions: 325.82 / 246.44 = 1.3221

For 1kg of ZrO₂, 1.3221kg of La₂O₃ is required.

2.1 Pellet preparation

Adequate amount of PVA is mixed with the ceramic powders. PVA binder solution is used as a binder because the natural ceramic material does not have the binding property, also the addition of PVA binder does not affect the composition of the ceramic mixture. It evaporates on heating to a temperature up to 600°C. Care should be taken to add optimum amount of PVA binder as, excess addition, leads to voids in the pellets and lower addition leads to inadequate binding. For the present work we selected 7.5% Poly Vinyl alcohol (PVA) solution and compacted into 10mm diameter and 5mm thickness of circular pellets. By the application of force 25N using a fly press. The number of circular pellets formed was exposed to sunlight for drying. The prepared Lanthanum and Samarium Zirconate pellets of are shown in Fig.2.



L-lanthanum contained pellets
 S-Samarium contained pellets
 Scale: 1: 1

Fig. 2 Circular Pellets of 10mm Diameter and 5mm Thickness

The prepared Lanthanum and Samarium Zirconate pellets were taken for calcinations in lantern high temperature furnace. Calcinations were done for 1625°C for 6 hours, the calcinations details are explained below section 2.2.

2.2 Calcinations cycle

The metal powder, after being compacted into a briquette is then taken through calcination operation. This operation is carried out at a temperature below the highest melting constituent of that metal powder mixture. [12] Calcination could be done using lantern furnace up to 1625°C and pallet were sintering in the following ways [a].0 to 1000°C for 7 hours, [b].1000 to 1400°C for 6 hours, [c]. Soaking at 1400°C for 2 hours, [d].1400°C to 1625°C for 2 hours, [e]. Soaking at 1625°C for 4 hours, [f]. Steady state cooling and it is shown in Fig.3 [11, 12, 13].

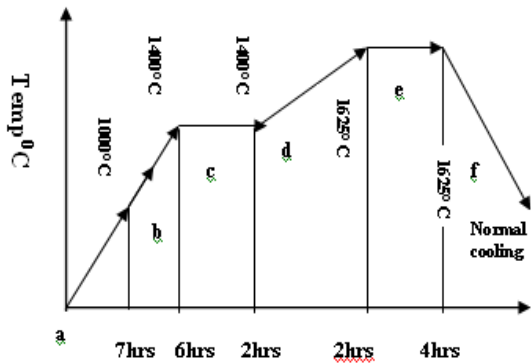


Fig.3 Calcinations Cycle

2.3 X-ray analysis

The calcined pellets are powdered particle sizes of less than 53 microns and analyzed in X-Ray Diffractometer in order to identify the different phases present in the plasma sprayable powder.

In the first agate jar method; there is no formation of zirconate because stabilization of Zirconia is very less due to higher particle size of $d_{90}=10.67\mu\text{m}$, $d_{50}=6.881\mu\text{m}$, $d_{10}=5.68\mu\text{m}$ and higher calcination temperature of 1625°C. This can be evident from the peak intensities of XRD results shown in Fig.4.

3. Zirconate Powder Preparation using Planetary High-Energy Wet Ball Mill Method

The preparation of plasma sprayable grade powders consisted of the following steps as specified in the Fig.1 Raw materials are commercially available at a 99.5% purity chemicals of La_2O_3 , and Sm_2O_3 , ZrO_2

were weighed to an accuracy of 0.01g and wet ball milled in an agate media for 24 hours and the slurry was oven dried at about 150°C for 6 hours. [14, 15] The dried powder was mixed with 7.5% Poly Vinyl alcohol (PVA) and compacted into circular pellets. By fly press at the force of 25N, we get a number of 10mm diameters and 5mm thickness of circular pellets. The prepared Lanthanum and samarium Zirconate pellets of are shown in Fig.2.

The prepared Lanthanum and Samarium Zirconate pellets taken for calcinations in lantern high temperature furnace. The calcinations was done for 1435°C for 6 hours, the calcinations details are shown in Fig.3. The calcinations temperature is optimized to 1435°C for 6, since particle sizes are reduced up to 5µm. After calcinations the pellets are then crushed into a powder and sieved and the prepared powders are taken into XRD analysis. From the analysis it has been found that 98% of stabilized Zirconate is obtained [16].

4. Results and Discussions

The results and discussions of characterization of lanthanum and samarium zirconate powders prepared from two methods such as:

4.1 Agate jar method/XRD analysis

The sintered pellets were powdered for the particle sizes of less than 53 microns. And placed in a X-ray diffractometer to find out the various phases present in the powders.

The XRD pattern of lanthanum based zirconia prepared by agate jar mixing is as shown in Fig.4

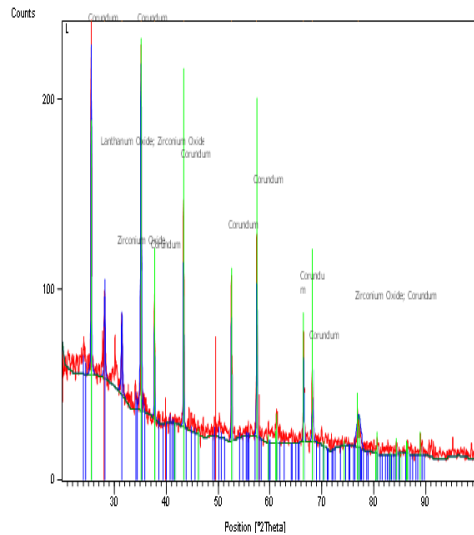


Fig.4 XRD Pattern of Lanthanum Oxide based Zirconia by Agate Jar Method

Stick Pattern

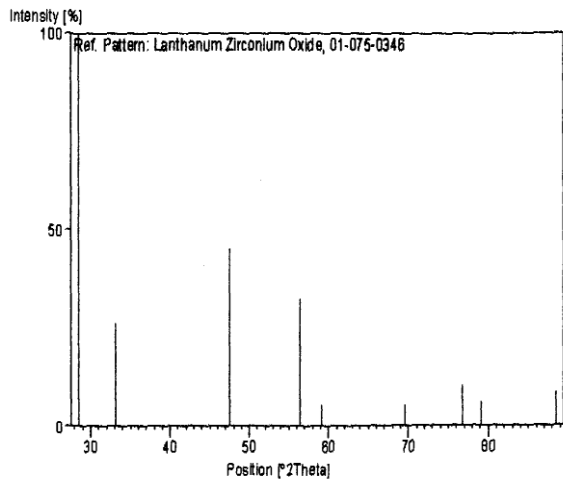


Fig. 5 Pattern Obtained from Standard ICDD for Lanthanum Zirconate

The above Figs.4 and 5 shows that the sintered sample XRD pattern of lanthanum oxide based zirconia. Compared with the peak list obtained from XRD with the peaks Intensities of the standard ICDD values, majority of the XRD peak intensities are not matching with standard ICDD values of peak intensities. From above results we observed that there was no formation of zirconates because instead of zirconate, corundum was obtained due to higher calcinations temperature of 1625^oC and higher particle size. So Lanthanum Zirconate was not found and at the time of calcinations temperature at 1625^oC samarium was evaporated and lanthanum doped zirconium withstood for the temperature of 1625^oC but no phases are observed and hence powder prepared by agate jar mixing method stabilized zirconate will not be obtained. So there is no scope for future work in both lanthanum and samarium.

4.2 Wet ball mill method/XRD analysis

The X-ray diffraction measurements were carried out on powdered samples using a high-resolution SIEMENS D 500 diffractometer. Filtered CuK_α λ =1.54056 Å (40kV, 25mA) was used. The diffraction diagram was measured using a step size of 0.02, scan rate of 10° per minute and a scan range between 30^o to 80^o in 2θ range in flat plate geometry radiation. XRD patterns were recorded using X-ray Diffractometer.

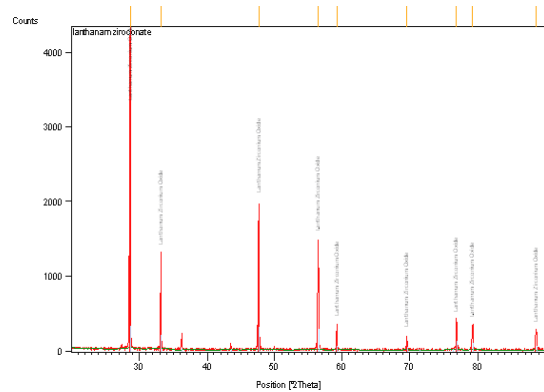


Fig. 6 Xrd Pattern of Lanthanum Oxide based Zirconia

Stick Pattern

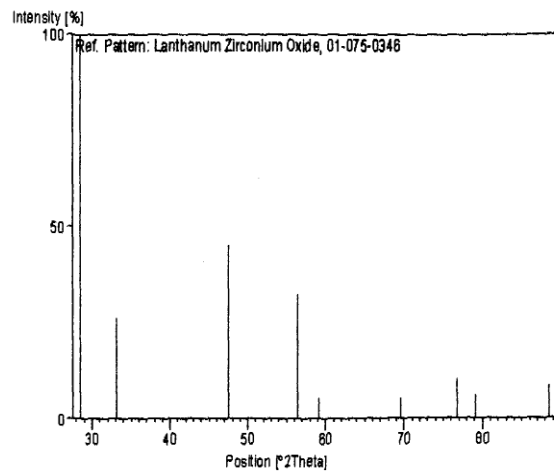


Fig.7 Pattern obtained from Standard ICDD for Lanthanum Zirconate

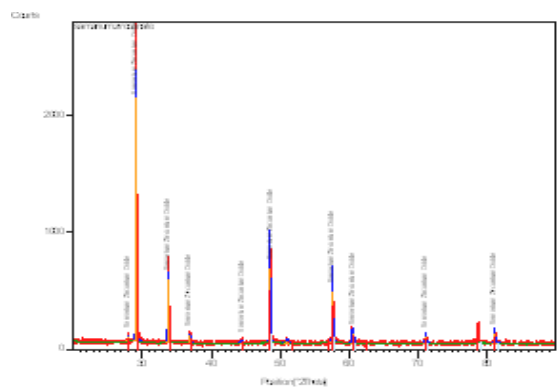


Fig. 8 XRD Pattern of Samarium Oxide based Zirconia

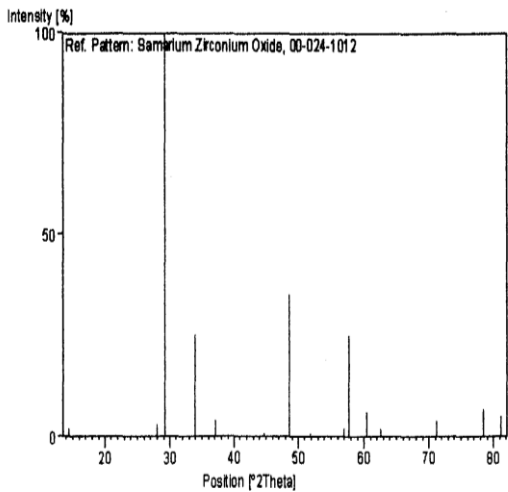


Fig. 9 Pattern Obtained from Standard ICDD of Samarium Zirconate

Fig. 6 and 7 shows the XRD pattern obtained for Lanthanum oxide based Zirconia powders comparing the high intensity peak list of cubic phase obtained from XRD with the peaks of the standard ICDD values, majority of the peaks with their respective intensities which could be matched with ICDD results (file number 075-0346). To a first approximation, this phase has a cubic perovskite type structure. And we observed stable phase transformation no phase change during heating and cooling cycle. This observation agrees well with those derived from the ICDD results and confirms the formation of lanthanum zirconate. Most of the peaks are cubic phases and are homogeneous phases remaining are mixed phases because uniform distribution temperature due to steady state heating and the calcinations temperature has a strong influence on the crystal structure, homogeneity and the unit cell volume of the calcinated powders of La_2O_3 and ZrO_2 . The resulting $\text{La}_2\text{Zr}_2\text{O}_7$ powders presented more agglomerated as the calcinations temperature increased [15].

The XRD pattern obtained for samarium oxide based zirconia is as shown in the above Fig. 8 and 9, Comparing the peak list obtained from XRD with the peaks of the standard ICDD values, majority of the peaks with their respective intensities which could be matched with ICDD results (file number 024-1012). This phase has a cubic perovskite type structure. Most of the peaks with their respective intensities match. And we observed stable phase transformation, no phase change during heating and cooling cycle. This confirms the formation of Samarium zirconate. Most of the peaks are cubic phases and are homogeneous phases remaining are mixed phases because homogeneous

steady state heating and the calcinations temperature has a strong influence on the crystal structure, homogeneity and the unit cell volume of the calcinated powders of Sm_2O_3 and ZrO_2 . The resulting $\text{Sm}_2\text{Zr}_2\text{O}_7$ powders presented more agglomerated as the calcinations temperature increased.

From the above XRD results both the materials are undergo stable phase transformation and no phase changes occur during heating and cooling cycle but compare to Samarium Lanthanum Zirconate withstands high temperature and majority of peaks are cubic and very less minor peaks of mixed phase. Whereas in Samarium Zirconate majority of peaks are cubic and minor peak are of unknown phase after calcinated at 1435°C [13].

4.3 Energy dispersive X-ray analysis

The energy dispersive X-ray analysis was done in the scanning electron microscope (SEM) for composition analysis of the powder. EDAX has been conducted for the raw powders before calcination or for the mixtures after calcination. The electron beam in a SEM has energy typically between 5,000 and 20,000 electron volts (eV). The energy holding electrons in an atom (binding energy) ranges from a few electron volts to many kilovolts. By collecting and analyzing the energy of these X-rays, the constituent elements of the specimen can be determined. [15]

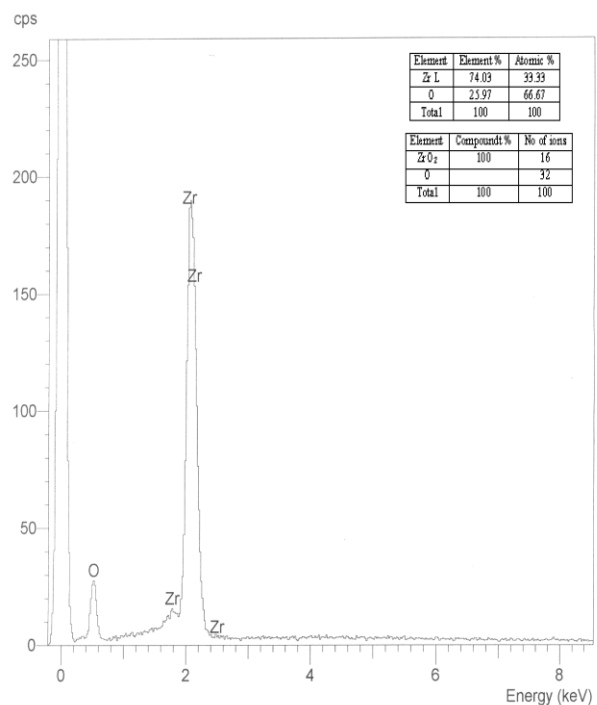


Fig. 10 EDAX of ZrO₂

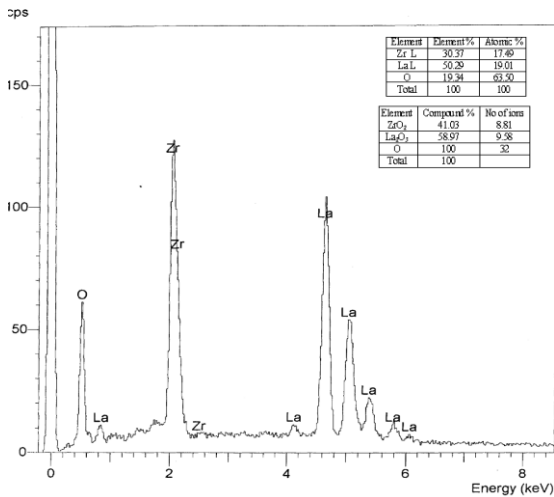


Fig. 11 EDAX of La₂Zr₂O₇

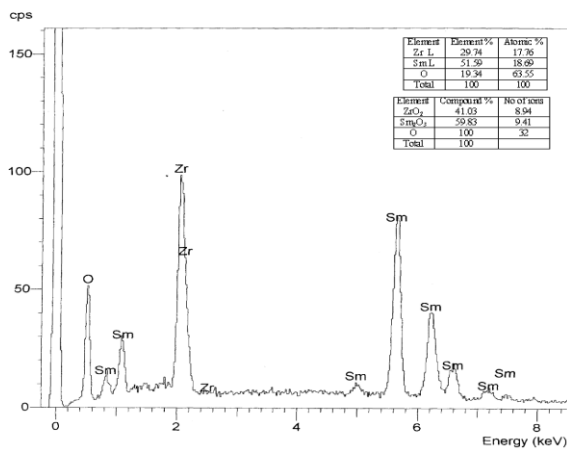


Fig. 12 EDAX of Sm₂Zr₂O₇

The above Fig.10 shows the chemical analysis of unsintered ZrO₂. Here we used EDAX analyses to find out the element%, atomic %, compounds and number of ions present in the powder. After analysis we observed that Zr having the element % of 74.03 and atomic % of 33.33 and Oxide contained element % of 25.97 and atomic % of 66.67 and the number of ions present in the ZrO₂ are 16 and for the Oxide the number of ions are 32.

Fig.11.Shows the mixture containing 41.03% of ZrO₂ and 58.97% of La₂O₃. From the chemical analysis we found Zr element % is 30.37, La element % is 50.29 and Oxide element % of 19.34 and here the ions presents for 41.03%ZrO₂ and 58.97% La₂Zr₂O₇ are 8.81 and 9.58 respectively. For the oxide number of ions are 32. After sintering no other oxides

are found to this compound but number of ions are dispersed during calcinations. Fig.12. Shows the mixture containing 40.17% of ZrO₂ and 59.83% of Sm₂O₃. From chemical analysis we found Zr element % is 29.74, Sm element % is 51.59, and oxide element % of 19.34 and here the ions present for 40.17% of ZrO₂ and 59.83% of Sm₂O₃ are 8.94 and 9.41, respectively. For the oxide number of ions are 32 after sintering, no other oxides found to this compound but number of ions are dispersed during calcinations

From the evidence of the above Figs.10, 11 and 12, the chemical analysis of calcinated lanthanum and samarium zirconate powders. From the EDAX analysis we observed pure lanthanum and samarium zirconate has been found and no other oxides and no chemical composition changes found from the calcinated powder. Here there is a more number of La₂O₃ and Sm₂O₃, ZrO₂ peaks and less number of oxide peaks, because the mixture contains 41.03% of ZrO₂ and 58.97% of La₂O₃ and 40.17% of ZrO₂ and 59.83% of Sm₂O₃ and also pure Zirconia oxide is shown in fig.10.

5. Conclusions

Some of the structural properties of La₂Zr₂O₇ and Sm₂Zr₂O₇ were studied and the powder was prepared by Agate jar mixing and Wet ball milling. Based on the experimental investigation, the following conclusions are drawn.

- i. In the first agate jar method; there is no formation of Lanthanum and Samarium Zirconate because stabilization of Zirconia is very less due to large particle size and high calcination temperature of 1635°C.
- ii. In the second method planetary high-energy wet ball mill method Lanthanum and Samarium Zirconate was formed at calcination temperature of 1435°C. Hence wet ball mill method is most suitable to get 98% of stabilized Zirconate where smaller powder particles sizes are essential.

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Nomenclature

Symbol	Meaning	Units
F	Force	N
d	diameter	mm
V	Voltage	KV
I	Current	mA
E	Binding Energy	eV