CHAPTER 6
SYNTHESIS AND CHARACTERIZATION OF Ba₂REHfO₅.₅
(RE = La, Pr, Nd and Eu) PEROVSKITE CERAMICS AS
NANOPARTICLES BY A MODIFIED COMBUSTION PROCESS

6.1 Introduction

The details on the synthesis of a new class of complex cubic perovskite ceramic oxides with general formula Ba₂REHfO₅.₅ (RE = La, Pr, Nd, Eu) by the solid state route and their characterisation have been described in the third chapter. The synthesis of these ceramic materials by the solid state reaction method involves the calcination process at high temperatures for prolonged durations. In order to obtain a phase pure Ba₂REHfO₅.₅ material, it was necessary to heat the initial reaction mixture at temperatures between 1350-1375°C for a period of 72 h with two to three intermediate grindings. Moreover, to obtain highly compact sintered products the shaped phase pure powders had to be sintered in the temperature range of 1500-1600°C for at least 10 h. Therefore attempts are made to synthesize the Ba₂REHfO₅.₅ ceramic materials as nanoparticles to obtain better phase purity, homogeneity and sinterability.

6.2 Synthesis of Advanced Ceramics as Nanoparticles

The synthesis of advanced ceramics and specialty materials as nanoparticles initiated in the early 1980’s and today it has turned out to be one of the major challenging fields in material-processing technology (1-5). The importance of these new generation materials, their varied characteristics and their potential applications in industry have been highlighted and discussed in detail in many review articles (6-10). The specific advantages of nanocrystalline materials are superior phase homogeneity, purity, sinterability and microstructure leading to unique mechanical, electrical, dielectric, magnetic, optical, and catalytic properties (11-16). By using the conventional solid state route, it is not possible to obtain
nanosized powders because the initial sizes of the reactants themselves are much higher. Wet chemical methods and vapour phase synthesis are the most widely used methods for the synthesis of nanoparticles of ceramic oxides.

Wet chemical methods or liquid phase synthesis represent a large number of preparation methods, which in general start with an inorganic or metal organic precursor solution (17). The wet-chemical methods can be subdivided into five groups. (i) Dispersion methods: This technique is based on the dispersion of a precursor solution in small droplets or atomisation prior to drying in air or in a non-mixable liquid. In this way, the distance of phase separation during drying and calcining is limited by the dimensions of the submicron droplets. Individual granular particles of the desired ceramic can be obtained by drying these droplets followed by calcinations. Emulsion techniques (18-19), spray pyrolysis (20-21), freeze drying (22-23) etc are the powder preparation techniques based on this method. (ii) Immobilization techniques: In this process, the solution is immobilized by which demixing during the wet chemical preparation is retarded. Immobilization is carried out by the formation of a glassy or gelatinous matrix in which the precursor is dispersed or by making a polymeric network. For example, the precursor can be immobilized by complexation with organic acids or alcohols. Processing from polymeric precursors (24-26), oxalate route (27-29), citrate route (30-32), etc., are techniques employing this principle. (iii) Precipitation: This procedure is in general based on the controlled hydrolysis of an aqueous solution of metal salts or an alcohol solution of metal organic compounds. The precursor solution is strongly diluted, while precipitation takes place in strongly basic or neutral medium. In this way it is possible that the precursor solution precipitates instantaneously with a high nucleation rate. But in the case of multicomponent system it is likely that various components precipitate at different pH values of the solution and this would affect adversely the powder homogeneity. Prior to drying and calcination, the reaction by products such as alcohol, chlorides or
nitrates are washed out by water. Washing may selectively remove a precipitated component, which results in a change in the chemical homogeneity and composition. The filtered precipitate after washing is calcined at high temperatures. Co-precipitation (33-35), hydrothermal synthesis (36-38) etc., are techniques employing the precipitation technique. (iv) Sol-gel processing: Sol-gel process has been proposed to be a very effective method for producing ceramic oxides for various structural and electronic applications (39-41). In sol-gel processing, colloidal particles are in a suspension, a sol is mixed with a liquid, which causes the colloidal particles to join together into a network called a gel. A gel can also be formed by extracting part of the solvent from the sol. Polymerisation during the gelation step greatly restricts chemical diffusion and segregation. The gel is dried and calcined. Sol-gel is a multi step operation involving the processing of high volumes of liquid with relatively low yield and has been pointed out as one of its main drawbacks. (v) Combustion synthesis: Recently, another processing technique termed as self-sustained combustion or combustion synthesis has been used to synthesize fine ceramic powders. The process of combustion synthesis involves rapid decomposition of a saturated aqueous solution containing metal salts, an oxidizer and a fuel. In most of the cases, the powder obtained through the combustion synthesis is phase pure without the need for a calcination process. Therefore the method has energy and cost saving advantages. Combustion synthesis was used by Kingsley et al (42-44) for the synthesis of ceramic oxides. In this method, a mixture of the respective metal nitrates (oxidizers) and urea (fuel) were dissolved in a minimum quantity of water and heated at 500°C. Pramanik et al (45-49) have used the thermolysis of a precursor mass consisting of metal nitrate solutions mixed with polymeric polyvinyl alcohol (PVA) in presence of urea at external temperatures of 300 to 500°C to prepare a variety of ceramic oxides. Hess et al (50) applied the combustion synthesis by using glycine as fuel to prepare yttrium aluminium garnet.
6.3 The Modified Combustion Process*

Our attempts to synthesize the Ba$_2$REHfO$_{5.5}$ ceramic compounds as nanoparticles using any of the above described techniques were not successful. Hence, we have introduced a novel technique to obtain the respective ions in solution and modified the combustion process to obtain nanopowders of the Ba$_2$REHfO$_{5.5}$ (RE = La, Pr, Nd and Eu) ceramic compounds, the details of which are given in this chapter. The basic requirement for the synthesis of an oxide material by the combustion technique is that it should be possible to obtain all the ions involved in a solution. Therefore for the preparation of Ba$_2$REHfO$_{5.5}$ compounds it is necessary that we should have an aqueous solution of the respective rare earth, RE (RE = La, Pr, Nd and Eu), Ba and Hf ions. In the case of Hf based systems it is not possible to obtain an aqueous solution of Hf ions using HfO$_2$, as HfO$_2$ is insoluble even in boiling mineral acids. Hf(NO$_3$)$_3$ and HfOCl$_2$, though soluble, are highly expensive and scarcely available. It was reported that BaHfO$_3$ which is formed by the reaction of BaCO$_3$ and HfO$_2$ at a temperature of 1200°C is soluble in boiling nitric acid (51). Therefore in our present study, we have heated a stoichiometric mixture of BaCO$_3$, the respective rare earth and HfO$_2$ at a temperature of 1200°C for 4 h and succeeded in getting all the required ions for the formation of Ba$_2$REHfO$_{5.5}$ in solution, by dissolving the resultant heated mixture in boiling nitric acid. We have also modified the combustion synthesis used by earlier workers (42-50), by using citric acid as the complexing agent and ammonia as the fuel to obtain nanoparticles of Ba$_2$REHfO$_{5.5}$ ceramic materials. Thus by preparing the solution containing the required ions through a novel route and by changing the complexing agent and oxidant/fuel it was possible to synthesize phase pure nanoparticles of Ba$_2$REHfO$_{5.5}$ compounds in a single step chemical process involving an exothermic reaction.

* US Patent File No.: 09/537252 dated 28 March 2000
Indian patent File No. NF. 58/98 (1999)
6.4 Synthesis of $\text{Ba}_2\text{REHfO}_{5.5}$ Nanoparticles*

Stoichiometric amounts of high purity (99.9\%) $\text{BaCO}_3$, rare earth oxides and $\text{HfO}_2$ were wet mixed with acetone in an agate mortar and the mixed powder was dried in an oven at $\sim$100$^\circ$C. The dried powder was heated at 1200$^\circ$C for 4 h in air. The different phases present in the heated powder was examined by the powder x-ray diffraction technique. Figures 6.1, 6.2 and 6.3 show the XRD patterns of the multiphase systems of the mixtures used to obtain the solutions containing the respective ions for the synthesis of $\text{Ba}_2\text{LaHfO}_{5.5}$, $\text{Ba}_2\text{PrHfO}_{5.5}$ and $\text{Ba}_2\text{EuHfO}_{5.5}$ ceramic compounds as nanoparticles.

![XRD pattern](image)

**Fig. 6.1** XRD pattern of the heat treated (4 h at 1200$^\circ$C) mixture used to obtain a solution containing Ba, La and Hf ions.

It may be noted from the figures that during the heat treatment the $\text{HfO}_2$ present in all the systems have reacted with the other compounds present in the initial mixture. This intermediate multiphase powder was used to obtain aqueous

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solutions of barium, the respective rare earths and hafnium ions. The phases present in the powder used to obtain an aqueous solution of Ba, La and Hf are BaHfO\(_3\), La\(_2\)O\(_3\) and BaCO\(_3\) (fig. 6.1). Ba\(_2\)PrHfO\(_{5.5}\), BaHfO\(_3\), Pr\(_6\)O\(_{11}\) and BaCO\(_3\) are the phases present in the heated mixture used to obtain a solution containing Ba, Pr and Hf ions (fig. 6.2).

![XRD pattern of the heat treated (4 h at 1200°C) powder used to obtain a solution containing Ba, Pr and Hf ions.](image)

The different phases present in the heated powder used to obtain a solution consisting of Ba, Eu and Hf ions are BaHfO\(_3\), Eu\(_2\)O\(_3\) and BaCO\(_3\) (fig. 6.3). The precursor complex for the combustion synthesis was then prepared by adding sufficient quantity of citric acid to the above solution. The oxidant/fuel ratio of the system was adjusted by the addition of ammonium hydroxide and nitric acid. The solution containing the precursor complex at basic pH, having an oxidant/fuel ratio ~ 1, was then heated on a hot plate to about 250°C. The solution boils and undergoes dehydration followed by decomposition producing a foam. The foam gets self ignited giving a highly voluminous and fluffy product.
of combustion. The structure and phase purity of the as prepared solid combustion product was examined using powder XRD technique. The powder was characterised using DTA, TGA, surface area analysis, agglomerate size distribution, FT-IR and high resolution transmission electron microscopy.

Fig. 6.3 XRD pattern of the heat treated (4 h at 1200°C) powder used to obtain a solution containing Ba, Eu and Hf ions.

6.5 Characterisation of the Ba₂REHfO₅.₅ Powders

6.5.1 Structural Characterisation

The structure and phase purity of the as prepared solid combustion product was studied by the powder XRD technique. The x-ray diffraction patterns for the as prepared Ba₂LaHfO₅.₅, Ba₂PrHfO₅.₅, Ba₂NdHfO₅.₅ and Ba₂EuHfO₅.₅ compounds for 2θ values between 20° and 60° are shown in Fig.6.4(A-D) respectively.
Fig. 6.4 XRD pattern of the as prepared (A) Ba$_2$LaHfO$_{5.5}$, (B) Ba$_2$PrHfO$_{5.5}$, (C) Ba$_2$NdHfO$_{5.5}$ and (D) Ba$_2$EuHfO$_{5.5}$ powders synthesised through the modified combustion process.

It may be noted from the XRD pattern that the phase formation of all the compounds is complete during the combustion process itself. There was no need of a calcination step. The broad peaks at $d = 2.950$ Å, $d = 3.020$ Å, $d = 2.989$ Å and $d = 2.984$ Å correspond to the major (220) reflection of Ba$_2$LaHfO$_{5.5}$, Ba$_2$PrHfO$_{5.5}$, Ba$_2$NdHfO$_{5.5}$ and Ba$_2$EuHfO$_{5.5}$ compounds respectively. The crystallite size of the as prepared powders were calculated from the full width half maximum (FWHM) using the Scherrer formula (52)

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where $D$ = crystallite size in nm, $\lambda$ is the wavelength of the x-ray (1.5406 Å), $\beta$ is the corrected half width and $\theta$ is the diffraction peak angle. The calculated crystallite size of the Ba$_2$REHfO$_{5.5}$ compounds synthesized as nanoparticles are given in table 6.1. All the peaks are indexed for a complex cubic perovskite.
structure corresponding to \( \text{Ba}_2\text{REHfO}_{5.5} \) materials. The lattice constant values obtained form the XRD patterns of the \( \text{Ba}_2\text{REHfO}_{5.5} \) powders synthesized through the present modified combustion route are in good agreement with the lattice constant values obtained from their corresponding powders synthesized through the solid state route and are given in table 6.1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Lattice constant (Å)</th>
<th>Full Width at Half Maximum x 10^3 (rad.)</th>
<th>Particle size calculated from XRD (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ba}<em>2\text{LaHfO}</em>{5.5} )</td>
<td>8.311</td>
<td>8.312</td>
<td>7.557</td>
</tr>
<tr>
<td>( \text{Ba}<em>2\text{PrHfO}</em>{5.5} )</td>
<td>8.540</td>
<td>8.541</td>
<td>9.64</td>
</tr>
<tr>
<td>( \text{Ba}<em>2\text{NdHfO}</em>{5.5} )</td>
<td>8.350</td>
<td>8.352</td>
<td>8.126</td>
</tr>
<tr>
<td>( \text{Ba}<em>2\text{EuHfO}</em>{5.5} )</td>
<td>8.347</td>
<td>8.349</td>
<td>10.94</td>
</tr>
</tbody>
</table>

There was no additional phase in the XRD pattern of the as prepared powders. It can be concluded from these observations that the phase formation was complete during the combustion process itself, without the need of a calcination step. The broad nature of the diffraction peaks show the ultrafine nature of the crystallites. It may be noted that a prolonged heating for 72 h at a temperature of 1350°C with three intermediate grindings is necessary to obtain phase pure micron sized \( \text{Ba}_2\text{REHfO}_{5.5} \) powders through the solid state reaction method.

6.5.2 Thermal Characterization

The thermal characterization of the \( \text{Ba}_2\text{REHfO}_{5.5} \) powders obtained directly through the modified combustion process was carried out using a Shimadzu DTA-50H (Japan) differential thermal analyser and a Shimadzu TGA-50H (Japan) thermogravimetric analyser up to a temperature of 1100°C at a heating rate of 10°C/min. in nitrogen atmosphere. The DTA and TGA curves of
the Ba₂LaHfO₅.₅ and Ba₂EuHfO₅.₅ powders synthesized through the present modified combustion method are shown in fig 6.5 and 6.6 respectively. No enthalpy change was observed in the DTA curves up to a temperature of 1100°C which implies that the reaction was complete during the combustion process itself. There was no evidence of any phase transition taking place in the sample up to a temperature of 1100°C. The TGA curves show a weight loss of less than 3%, which may be due to the adsorbed moisture in the sample.

![Fig. 6.5 DTA (a) and TGA (b) curves of the Ba₂LaHfO₅.₅ powder synthesised through the modified combustion process](image)

![Fig. 6.6 DTA (a) and TGA (b) curves of the Ba₂EuHfO₅.₅ powder synthesised through the modified combustion process](image)
6.5.3. **Spectroscopic Studies**

In order to detect the presence of any organic residues in the powder obtained directly after combustion, an IR spectra was recorded on a Nicolet I 400-D FT-IR (USA) spectrometer using the KBr pellet method. Figure 6.7 and 6.8 show the FT-IR spectrums of Ba$_2$LaHfO$_{5.5}$ and Ba$_2$PrHfO$_{5.5}$ powders in the range 400-4000 cm$^{-1}$.

![Fig. 6.7 FT-IR Spectrum of the (a) Ba$_2$LaHfO$_{5.5}$ powder synthesised through solid state reaction method (b) Ba$_2$LaHfO$_{5.5}$ powder synthesised through modified combustion process](image1)

![Fig. 6.8 FT-IR Spectrum of the (a) Ba$_2$PrHfO$_{5.5}$ powder synthesised through solid state reaction method (b) Ba$_2$PrHfO$_{5.5}$ powder synthesised through modified combustion process](image2)
A comparative study between the micron sized solid state powders and the nanosized combustion products shows that the highly exothermic redox reaction in the combustion process is complete and no organic residue is present in the as prepared sample.

### 6.5.4 Physical Characterization

The BET (Brunauer, Emmett and Teller) specific surface area of the powders synthesized through the present modified combustion process were recorded using a Micromeritics unit model Gemini 2360 (USA) using nitrogen as the adsorbent. The powder sample for this study was degassed at 300°C for 2 h. Table 6.2 gives the BET specific surface area and the equivalent particle size of Ba₂REHfO₅₋₅ powders obtained through the present modified combustion process. The particle size was calculated by assuming that all the particles are spherical by using the equation (53):

\[
d = \frac{6}{\rho S}
\]

where \( d \) is the particle size, \( \rho \) is the theoretical density of the material and \( S \) is the specific surface area of the powder.

<table>
<thead>
<tr>
<th>Material</th>
<th>BET surface area (m²/g)</th>
<th>Particle size calculated from surface area (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba₂LaHfO₅₋₅</td>
<td>21</td>
<td>37</td>
</tr>
<tr>
<td>Ba₂PrHfO₅₋₅</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Ba₂NdHfO₅₋₅</td>
<td>27</td>
<td>28</td>
</tr>
<tr>
<td>Ba₂EuHfO₅₋₅</td>
<td>33</td>
<td>23</td>
</tr>
</tbody>
</table>

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6.5.5 Agglomerate Size Analysis

The agglomerate size distribution of the as prepared combustion powders was studied using a Micromeritics sedigraph model 5100. The powder particles were dispersed in water and agitated ultrasonically for 10 minutes. Figure 6.9 and 6.10 show the agglomerate size distribution histogram of the Ba$_2$NdHfO$_{5.5}$ and Ba$_2$EuHfO$_{5.5}$ nanopowders obtained through the present combustion process. It is very clear from the figures that more than 50% of the agglomerates in the as prepared powder lie in a smaller range (< 2 μm). A small fraction of the particles have agglomerate size in between 5-10 μm. The maximum size of the agglomerates as seen from the agglomerate size distribution data is 12 μm.

Fig. 6.9 Agglomerate Size distribution of the as prepared Ba$_2$NdHfO$_{5.5}$ powders synthesised through the modified combustion process
Agglomerate Size

Fig. 6.10 Agglomerate Size distribution of the as prepared Ba₂EuHfO₅.₅ powders synthesised through the modified combustion process

6.5.6 *High Resolution Transmission Electron Microscopic Studies*

High Resolution Transmission electron microscopic (HRTEM) studies were carried out to examine the powder morphology of the as prepared combustion product like particle size, shape, shape distribution, degree of particle agglomeration etc. The high resolution transmission electron microscopic studies were carried out using a JEOL 2000 high resolution transmission electron microscope with a top entry state operating at 200 kV. The samples for the high-resolution transmission electron microscopic studies were prepared by ultrasonically dispersing the powder particles in methanol and allowing a drop of this to dry on a carbon coated copper grid. The carbon films were developed by the vacuum coating technique using an Edward 303 instrument.

The TEM studies of the Ba₂LaHfO₅.₅ powders synthesized through the present modified combustion process showed that the particles are in the nanometer range. Fig. 6.11(a) shows the bright field image of a powder particle
of $\text{Ba}_2\text{LaHfO}_{5.5}$ compound and fig 6.11(b) is the corresponding selected area electron diffraction (SAED) pattern. As seen in the bright field image, the nanocrystalline grains are nearly cuboidal in shape. The average crystallite size as measured from several bright field images is $42 \pm 8$ nm and the agglomerate sizes vary from 0.3 to 0.7 $\mu$m. The ring position and the intensity of the selected area diffraction pattern [fig.6.11(b)] agrees very well with the powder x-ray diffraction data. Table 6.3 gives the electron diffraction data of $\text{Ba}_2\text{LaHfO}_{5.5}$ powder obtained through the present combustion route. The ring pattern in the SAED also indicates the nanocrystalline nature of the $\text{Ba}_2\text{LaHfO}_{5.5}$ powder.

Table 6.3
Electron diffraction data of a powder particle of $\text{Ba}_2\text{LaHfO}_{5.5}$

<table>
<thead>
<tr>
<th>Ring No</th>
<th>Diameter (mm)</th>
<th>d (Å)</th>
<th>Hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.46</td>
<td>4.200</td>
<td>200</td>
</tr>
<tr>
<td>2</td>
<td>21.68</td>
<td>2.950</td>
<td>220</td>
</tr>
<tr>
<td>3</td>
<td>26.26</td>
<td>2.082</td>
<td>400</td>
</tr>
<tr>
<td>4</td>
<td>33.72</td>
<td>1.710</td>
<td>422</td>
</tr>
<tr>
<td>5</td>
<td>40.42</td>
<td>1.330</td>
<td>620</td>
</tr>
<tr>
<td>6</td>
<td>45.02</td>
<td>1.120</td>
<td>642</td>
</tr>
</tbody>
</table>

The HREM lattice imaging was employed to study the intergranular phases present in the combustion product. Fig 6.11(c) shows the lattice image of a grain boundary between two nanocrystallites in an agglomerate. The lattice planes on either side extend up to the grain boundary without any change in the order which indicates the absence of intergranular phases.

The TEM studies of the $\text{Ba}_2\text{EuHfO}_{5.5}$ powder obtained through the present modified combustion process showed that the particles are submicron sized aggregates of nanocrystallites. Fig. 6.12(a) is a typical bright field image of a powder particle and fig. 6.12(b) is the corresponding selected area electron diffraction pattern. Table 6.4 gives the electron diffraction data of $\text{Ba}_2\text{EuHfO}_{5.5}$
Fig. 6.11 (a) Bright field image of a powder particle of $\text{Ba}_2\text{LaHfO}_{5.5}$ compound (b) corresponding selected area electron diffraction (SAED) pattern (c) HREM lattice image of a grain boundary between two nanocrystallites of $\text{Ba}_2\text{LaHfO}_{5.5}$ compound
Fig. 6.12 (a) Bright field image of a powder particle of the $\text{Ba}_2\text{EuHfO}_{3.5}$ compound (b) the corresponding selected area electron diffraction pattern (c) bright field image showing larger crystallites
powder obtained through the present combustion route. The ring pattern in the SAED also indicates the nanocrystalline nature of the Ba$_2$EuHfO$_{5.5}$ powder.

Table 6.4
Electron diffraction data of a powder particle of Ba$_2$EuHfO$_{5.5}$

<table>
<thead>
<tr>
<th>Ring No.</th>
<th>Diameter (mm)</th>
<th>d (Å)</th>
<th>Hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.4</td>
<td>4.189</td>
<td>200</td>
</tr>
<tr>
<td>2</td>
<td>22.5</td>
<td>2.067</td>
<td>400</td>
</tr>
<tr>
<td>3</td>
<td>26.7</td>
<td>1.868</td>
<td>420</td>
</tr>
<tr>
<td>4</td>
<td>30.3</td>
<td>1.453</td>
<td>440</td>
</tr>
<tr>
<td>5</td>
<td>41.2</td>
<td>1.208</td>
<td>444</td>
</tr>
<tr>
<td>6</td>
<td>45.5</td>
<td>1.117</td>
<td>642</td>
</tr>
</tbody>
</table>

The particles are of regular shape with sharp grain boundaries. The individual crystallites appear well bonded with few voids in between. About 85% of the particles in the powder had an average size of 20 nm and the remaining 15% of the particles had a average size of 47 nm [fig. 6.12(c)]. Thus the mean size of the sample is 25 nm with a standard deviation of 13 nm. The ring nature of the electron diffraction pattern is indicative of the polycrystalline nature of the crystallites. The electron diffraction data agrees well with the x-ray diffraction data.

6.6 Sintering of the Ba$_2$REHfO$_{5.5}$ Nanopowders

The sintering behaviour of the Ba$_2$REHfO$_{5.5}$ nanoparticles synthesized through the present modified combustion process was studied in detail. The phase pure Ba$_2$REHfO$_{5.5}$ nanopowders were pressed at a pressure of ~ 450 MPa in the form of circular discs of dimensions 11 mm diameter and ~ 2 mm thickness. These discs were sintered in air in the temperature range 1385-1475°C for a duration ranging from 5 minutes to 4 h. The nanoparticles synthesized through the present method have been sintered to a value >97% of the theoretical density. The relative green densities of the samples were 55 ± 2% for this pressure. The individual
sintering temperature and time required for the $\text{Ba}_2\text{REHfO}_{5.5}$ nanoparticles synthesized through the present combustion method compared with the sintering temperature and time of the respective powders obtained through the solid state reaction method is given in Table 6.5. In all the cases there is a substantial decrease in the sintering temperatures required for the nanocrystalline powders when compared to the micron sized powders obtained through the solid state reaction method. The XRD pattern for $\theta$ between 5 and 90° of sintered $\text{Ba}_2\text{REHfO}_{5.5}$ samples synthesized through the combustion process is shown in figure 6.13 (A-D). The sintered samples were single phase and have the same structure as that of the solid state synthesized powders. The sintering behaviour of the $\text{Ba}_2\text{REHfO}_{5.5}$ nanoparticles are compared with the sintering behavior of their solid state counter parts and they are shown in figures 6.14 and 6.15. It can be clearly seen from the figures that sinterability of nanoparticles is much superior when compared to that of coarse-grained powders synthesized through the solid state route.

![XRD pattern](image)

**Fig. 6.13** XRD pattern of sintered nanopowders of (A) $\text{Ba}_3\text{LaHfO}_{5.5}$, (B) $\text{Ba}_3\text{PrHfO}_{5.5}$, (C) $\text{Ba}_2\text{NdHfO}_{5.5}$ and (D) $\text{Ba}_2\text{EuHfO}_{5.5}$ synthesised through the modified combustion process
Table 6.5
Comparison of sintering parameters of solid state and nanopowders of Ba$_2$REHfO$_{5.5}$ materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Nanoparticles prepared through the modified combustion process</th>
<th>Coarse grained powder synthesized through the solid state route</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sintering Density</td>
<td>Sintering Density</td>
</tr>
<tr>
<td></td>
<td>Temp. (°C)</td>
<td>Time (h)</td>
</tr>
<tr>
<td>Ba$<em>2$LaHfO$</em>{5.5}$</td>
<td>1425</td>
<td>4</td>
</tr>
<tr>
<td>Ba$<em>2$PrHfO$</em>{5.5}$</td>
<td>1435</td>
<td>0.15</td>
</tr>
<tr>
<td>Ba$<em>2$NdHfO$</em>{5.5}$</td>
<td>1385</td>
<td>4</td>
</tr>
<tr>
<td>Ba$<em>2$EuHfO$</em>{5.5}$</td>
<td>1475</td>
<td>4</td>
</tr>
</tbody>
</table>

Fig. 6.14 Variation of relative sintered density with temperature for Ba$_2$LaHfO$_{5.5}$ (a) coarse grained powder synthesised through the solid state route (b) nanoparticles synthesised through the combustion process.

This reduction in sintering temperature and time may be attributed to the enhanced kinetics due to the small degree of agglomeration and ultrafine nature of the powder.
6.7 Conclusions

A new group of complex cubic perovskite ceramic oxides with general formula $\text{Ba}_2\text{REHfO}_{5.5}$ (RE = La, Pr, Nd, and Eu) have been synthesised as nanoparticle by a modified combustion process. In the present technique, a novel method has been introduced to obtain the respective ions in solution for the combustion process. Citric acid has been used as the complexing agent instead of polyvinyl alcohol and ammonia as the fuel/oxidant in place of urea. By using the present modified combustion route nanoparticles of phase pure $\text{Ba}_2\text{REHfO}_{5.5}$ ceramic compounds could be synthesized in a single step process without the need of a calcination step. The solid combustion products thus obtained were characterized by x-ray and electron diffraction, differential thermal analysis, thermogravimetric analysis, IR spectroscopy, particle size analysis, surface area determination and high-resolution transmission electron microscopy. The x-ray diffraction studies revealed that the combustion products are phase pure $\text{Ba}_2\text{REHfO}_{5.5}$ compounds and have a complex cubic perovskite (A$_2$BB'O$_6$) structure. The high resolution transmission electron microscopic examination of the as prepared powder showed that the particles are in the range 5-50 nm. The
lattice imaging of the nanocrystalline particles are sharp and showed very little distortion, without any second phase. The nanocrystalline powders obtained through the present method could be sintered to a very high density (> 97% of the theoretical density) at relatively lower temperatures in shorter durations. Particle size reduction, better phase purity and sinterability are clear advantages of the present modified combustion process.
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