# Advanced ceramics: Combustion synthesis and properties

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**Abstract.** Fine-particle ceramic powders such as chromites, manganites, ferrites, cobaltites, aluminas ($\alpha$-$Al_2O_3$, $Cr^{3+}$/$Al_2O_3$, zirconia-toughened alumina, mullite and cordierite), ceria, titania, zirconia ($t$, $m$, $c$ and PSZ), dielectric oxides ($MTiO_3$, PZT and PLZT) as well as high $T_c$ cuprates have been prepared by the combustion of redox compounds or mixtures. The combustion-derived oxide materials are of submicron size with a large surface area and are sinteractive.

**Keywords.** Combustion synthesis; metal oxides; ceramics.

## 1. Introduction

Traditionally, the word ceramics is associated with clay-based products such as bricks, tiles, pottery, table ware, sanitary ware and glass. Naturally occurring minerals like sand, quartz, bauxite, feldspar etc are used in the manufacture of these materials. Advanced ceramics differ from conventional ceramics in their high-mechanical strength, fracture toughness, wear resistance, refractory, dielectric, magnetic and optical properties. Advanced ceramics or fine ceramics are high value-added inorganic materials produced from high purity synthetic powders to control microstructure and properties. Wet-chemical routes (Segal 1989) e.g. coprecipitation, sol-gel, spray-dry, freeze-dry etc are usually employed to prepare advanced ceramic powders having submicron size, narrow size distribution and absence of particle agglomerates. However, these methods are quite involved, require long processing time, costly chemicals and special equipment. Therefore, there is a need for an alternative to the wet-chemical methods.

## 2. Combustion synthesis

Many researchers have attempted to use the heat generated by exothermic chemical reactions in the synthesis of high-temperature ceramic materials. Aluminothermite process,

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe,$$
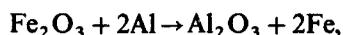
pioneered by Goldschmidt (1898) was used to prepare metals and alloys (Carlson 1973). Walton and Poulos (1959) synthesized a number of refractory cermets: oxide-boride, oxide-carbide and oxide-silicide. More recently, Merzhanov used the exothermic reaction between the elements (metal-fuel and nonmetal-oxidizer) to produce a host of materials: borides, carbides, carbonitrides, cermets, chalcogenides, hydrides, nitrides, oxides and silicides (Merzhanov 1993). This process, popularly known as self-propagating high-temperature synthesis (SHS), is also called furnaceless or fire synthesis.

Here, we present the results of a modified combustion process (low temperature initiated, self-propagating, gas-producing, exothermic reaction) for the synthesis of ceramics employing redox compounds and mixtures. The term combustion covers smouldering (heterogeneous) flaming (homogeneous gas phase) as well as explosive reactions. The rate of combustion determines the nature of reaction i.e. decomposition, deflagration or detonation. Synthesis of ceramic oxides is achieved by smouldering and flaming reactions.

### 2.1  *Preparation of oxides by the combustion of redox compounds*

Hydrazine and its derivatives (mono methyl, unsymmetric disubstituted methyl hydrazines and hydrazides) are well-known energetic rocket fuels. Hydrazine being a endothermic compound ($\Delta H_f = +12\,\text{kcal mol}^{-1}$) could explode if not properly handled or controlled. The strategy for using hydrazine and its derivatives as fuels for combustion synthesis of ceramic oxides involves complexation with appropriate metal ions. Thus, the explosivity of metal hydrazines, $M(N_2H_4)^{2+}$ containing oxidizing anions like nitrate and perchlorate could be controlled by replacing the oxidizing anions in the complex by reducing groups like formate, acetate and oxalate. These complexes have low ignition temperature ($< 300°C$) and once ignited decompose autocatalytically to yield fine particle oxides. Mixed oxides like ferrites and cobaltites have been prepared by the combustion of these metal hydrazine precursors (Patil 1986, 1991).

Hydrazine has a great affinity for carbondioxide and forms hydrazine carboxylic acid, $N_2H_3COOH$. Hydrazine carboxylate anion, $N_2H_3COO^-$, is a bidentate ligand and forms a variety of crystalline complexes with metal ions, e.g. $M(N_2H_3COO)_2$, $M(N_2H_3COO)_2\cdot XH_2O$, $M(N_2H_3COO)_2(N_2H_4)_2$ and $N_2H_5M(N_2H_3COO)_3\cdot H_2O$ where $M = Mg$, Ca, Cr, Mn, Fe, Co, Ni, Cu or Zn. These complexes and their solid solutions have low ignition temperatures ($120–300°C$) and decompose/combust in the presence of air autocatalytically with the evolution of $NH_3$, $H_2O$ and $CO_2$ to yield fine particle oxides. A large number of technologically important oxide materials have been prepared by the combustion of these redox compounds. These include $\gamma$-$Fe_2O_3$ (Ravindranathan and Patil 1986), cobalt doped $\gamma$-$Fe_2O_3$ (Suresh et al 1989a), $CeO_2$ (Mahesh et al 1986) and mixed metal oxides like cobaltites, $MCo_2O_4$ (Ravindranathan et al 1987a), ferrites, $MFe_2O_4$ (Ravindranathan and Patil 1987b), Ni–Zn ferrites (Ravindranathan and Patil 1987c; Suresh and Patil 1992), Mn–Zn ferrites (Suresh et al 1989b), Mg–Zn ferrites (Manoharan and Patil 1989), manganites, $MMn_2O_4$ (Arul Dhas and Patil 1993a) and $ZrO_2$, $TiO_2$ and $ZrTiO_4$ (Sekar and Patil 1993). Fine particle properties like specific surface area and average agglomerated particle size (Stokes diameter) of the simple and mixed metal oxides prepared by the combustion of hydrazine carboxylate precursors are summarized in table 1. The surface area values of the metal oxide powders are in the range of $4–140\,\text{m}^2/\text{g}$, which is much larger than those obtained by the conventional ceramic method. The combustion-derived powders have narrow size distribution with average agglomerate particle sizes being in the range of $0.5–5\,\mu\text{m}$. The fine particle nature of the combustion-derived powders is attributed to the low exothermicity of the combustion reaction and evolution of large amount of gases ($NH_3$, $H_2O$, $CO_2$) which help to dissipate the heat thereby preventing the oxides from sintering.

**Table 1.** Properties of oxide materials prepared by the combustion of redox compounds.

| Redox compound | Product | Surface area ($m^2/g$) | Av. aggl. size ($\mu m$) |
|---|---|---|---|
| $M(hc)_2$ | $MO, M_2O_3(M = Mg, Mn$ to $Zn)^\dagger$ | — | — |
| $M(hc)_2 \cdot 2H_2O$ | $MO, M_2O_3(M = Mg, Mn$ to $Zn)^\dagger$ | — | — |
| $Ln(hc)_3 \cdot 3H_2O$ | $Ln_2O_3(Ln = $ rare earths$), CeO_2$ | 90 | 0·76 |
| $MO(hc)_2 \cdot 2H_2O$ | $MO_2(M = Ti$ and $Zr$ and their ss) | 13–114 | 0·8–1·6 |
| $M(hc)_2(N_2H_4)_2$ | $MO, M_2O_3(M = Mg, Mn$ to $Zn)^\dagger$ | 7–34 | 2–5 |
| $N_2H_5M(hc)_3 \cdot H_2O$ | $MO, M_2O_3(M = Mg, Mn$ to $Zn)^\dagger$ | 18–75 | 2–5 |
| $(N_2H_5)M_{1/3}Fe_{2/3}(hc)_3 \cdot H_2O$ | $MFe_2O_4(M = Mg, Mn, Co$ to $Zn)$ | 26–140 | 1–5 |
| $N_2H_5M_xZn_{1-x}Fe_2(hc)_3 \cdot 3H_2O$ | $M_xZn_{1-x}Fe_2O_4(M = Mg, Mn$ and $Ni)$ | 4–140 | 1–5 |
| $(N_2H_5)M_{1/3}Co_{2/3}(hc)_3 \cdot H_2O$ | $MCo_2O_4(M = Mg, Mn, Co$ to $Zn)$ | 12–116 | 0·8–4·2 |
| $(N_2H_5)M_{1/3}Mn_{2/3}(hc)_3 \cdot H_2O$ | $MMn_2O_4(M = Co$ and $Ni)$ | 20–76 | 0·7–5 |
| $M_{1/3}Mn_{2/3}(hc)_2 \cdot 2H_2O$ | $MMn_2O_4(M = Mg$ and $Zn)$ | 27–60 | 1·9–5 |
| $PbMO(OH)_2(hc)_2 \cdot H_2O$ | $PbMO_3(M = Ti$ and $Zr$ and their ss) | 20–43 | 0·5–1 |

Note hc = $N_2H_3COO$, ss = solid solution, $^\dagger Fe_2O_3$ forms $\gamma$-phase.

Although the preparation of fine particle oxides by the combustion of redox compounds is quite simple and attractive, it has certain limitations. First, it takes several days to prepare the metal hydrazine carboxylate precursors. Secondly, the yield of the oxide is only $\simeq 20\%$. Finally, not all metals form hydrazine carboxylate complexes and therefore it was not possible to prepare other oxides like aluminas and chromites which are formed at fairly high temperatures ($> 1000°C$). This has been achieved by using flaming reactions employing metal nitrates and energetic fuels like urea and hydrazides.

## 2.2 *Preparation of oxides by the combustion of redox mixtures*

Redox mixtures like $KNO_3 + C + S$ (gun powder) once ignited undergo self-propagating, gas-producing exothermic decomposition. Similar exothermic reactions of redox mixtures are used in rocket propellants e.g. $NH_4ClO_4$–$Al$–$CTPB$. These redox mixtures containing metallic ingredients (Mg, Al) are known to give metal oxides as undesired products of combustion. This phenomenon has now been exploited to actually synthesize metal oxides by the combustion of stoichiometric mixtures of metal nitrates (oxidizer) and urea/hydrazine-based fuels.

The stoichiometric composition of the metal nitrate (oxidizer) and fuel redox mixtures was calculated based on the total oxidizing and reducing valency of the oxidizer and the fuel which serve as a numerical coefficient for stoichiometric balance such that the equivalence ratio, $\Phi_e$ is unity, i.e. $O/F = 1$ and the energy released is maximum (Jain *et al* 1981). In propellant chemistry, the species $M^{2+}, M^{3+}, M^{4+}, C$ and $H$ are considered to be reducing with corresponding valencies $+2, +3, +4, +4$ and $+1$. Elemental oxygen is considered to be an oxidizing species with valency $-2$. The valency of nitrogen is considered to be zero. According to this oxidizing and reducing valencies of the fuels such as urea ($CH_4N_2O$, U), carbohydrazide ($CH_6N_4O$, CH), tetra formyl *tris*-azine ($C_4H_{16}N_6O_2$, TFTA), oxalyl dihydrazide ($C_2H_6N_4O_2$, ODH), maleic hydrazide ($C_4H_4N_2O_2$, MH), and malonic dihydrazide ($C_3H_8N_4O_2$, MDH) are $+6, +8, +28, +10, +16$, and $+16$ respectively.

2.2a *Preparation of oxides*: Stoichiometric amount of metal nitrate (oxidizer) and fuel when ignited $\simeq 350-500°C$ undergo self-propagating, gas-producing combustion reaction (smouldering or flaming) (temp. $900-1500°C$) to yield voluminous metal oxide in less than 5 min. The high *in situ* temperature ($\simeq 1500°C$) attained during the combustion synthesis of $\alpha$-$Al_2O_3$ using $Al(NO_3)_3$-urea mixture has been attributed to the gas phase reaction of combustible decomposition products of urea (CO, HNCO, $NH_3$) and the aluminium nitrate (nitrogen oxides). A number of advanced ceramic oxide materials (table 2) have been prepared by the combustion of metal nitrate-urea/hydrazide fuels. These include: (i) refractory oxides such as $\alpha$-alumina (Kingsley and Patil 1988), ruby (Kingsley *et al* 1988, 1990a), metal aluminates (Kingsley *et al* 1990b), othoaluminates and aluminium garnet (Kingsley *et al* 1990c), ceria (Sekar *et al* 1990), zirconia (Arul Dhas and Patil 1992), pyrochlore zirconates (Arul Dhas and Patil 1993b), metal chromites (Manoharan *et al* 1990, 1992a; Gopichandran and Patil 1992a); (ii) low-thermal expansion coefficient materials like mullite (Gopichandran and Patil 1990), cordierite (Gopichandran and Patil 1993); (iii) toughened ceramics such as partially stabilized zirconia (PSZ) (Arul Dhas and Patil 1992), zirconia-alumina composites (Kingsley and Patil 1990d; Arul Dhas and Patil 1993c); (iv) magnetic materials like $\gamma$-$Fe_2O_3$ (Suresh and Patil 1993), spinel ferrites, othoferrites and iron garnet (Suresh *et al* 1991); (v) dielectric oxides such as $MTiO_3$, $MZrO_3$, PZT, PLZT (Sekar *et al* 1992a, b); (vi) high $T_c$ cuprates $La_{2-x}Sr_xCuO_4$ (Manoharan *et al* 1992b; Gopichandran and Patil 1992b) and (vii) miscellaneous oxides like spinel manganites (Arul Dhas and Patil 1993a), perovskite manganites and nickelates (Manoharan and Patil 1993).

The particulate properties such as surface area and particle size of oxide materials prepared by the combustion of redox mixtures are summarized in table 2. The surface

**Table 2.** Properties of oxides prepared by the combustion of redox mixtures.

| Oxides | Surface area[†] (m²/g) | Av. aggl. size (μm) |
|---|---|---|
| $\alpha$-$Al_2O_3$ | 8(U) | 4 |
| $MAl_2O_4$(M = Mg, Co, Ni, Cu and Zn) | 1–85 (U, CH) | 1–6 |
| $t-ZrO_2/Al_2O_3$ | 3–65 (U, CH) | 3–5 |
| $3Al_2O_3·2SiO_2$ (mullite) | 12–45 (U) | 4–8 |
| $Mg_2Al_4Si_5O_{18}$(cordierite) | 45–135 (U) | 10–15 |
| $Y_3Al_5O_{12}$ | 3–7 (U) | 2–5 |
| $MCr_2C_4$(M = Mg, Fe, Co, Ni, Cu and Zn) | 13–70 (U, TFTA) | 0·5–2 |
| $LnCrO_3$(Ln = La, Pr, Nd, Sm, Gd, Dy and Y) | 6–35 (TFTA) | 0·4–5 |
| $LnFeO_3$(Ln = La, Pr, Nd, Sm, Gd, Dy and Y) | 4–90 (ODH, TFTA) | |
| $MFe_2O_4$(M = Mg, Fe, Co, Ni, Cu and Zn) | 20–100 (ODH, TFTA) | 2–8 |
| $La_2(Sr)CuO_4$ | 3–5 (TFTA, MH) | 0·6–3 |
| $Y_3Fe_5O_{12}$ | 10–90 (ODH) | 1–5 |
| $\gamma-Fe_2O_3$ | 45(MDH) | 1·78 |
| $ZrO_2$, PSZ | 3–13 (CH) | 0·8–2·5 |
| $Ln_2Zr_2O_7$(Ln = La to Dy) | 4–20 (CH, U) | 0·4–4 |
| $MTiO_3$ (Ca, Sr, Ba and Pb) | 4–30 (TFTA, ODH) | 0·7–1·15 |
| $CeO_2$ | 14–90 (U, TFTA, CH, ODH) | 0·6–1·7 |
| $MMn_2O_4$(M = Mg, Co, Ni, Cu and Zn) | 30–60 (MH) | 0·6–1 |

[†]Fuels used for the combustion are indicated in the parentheses.

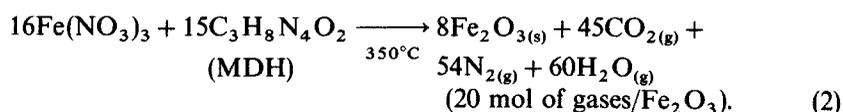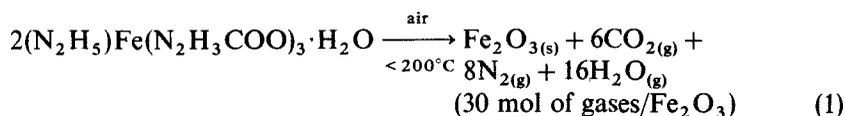**Table 3.** Comparison of properties of oxides prepared by the combustion of redox compounds (A) and redox mixtures (B).

| | Properties | | | |
|---|---|---|---|---|
| | Surface area (m²/g) | | Particle size ($\mu$m) | |
| Oxide | A | B | A | B |
| $CeO_2$ | 90 | 14–90 | 0·76 | 0·6–1·7 |
| $\gamma - Fe_2O_3$ | 75 | 45 | 2·54 | 1·78 |
| $MFe_2O_4(M = Mg, Mn \text{ to } Zn)$ | 26–140 | 20–100 | 1–5 | 2–8 |
| $Ni_{1-x}Zn_xFe_2O_4$ | 48–108 | 85–95 | 1–5 | 1–5 |
| $MCo_2O_4(M = Mg, Mn \text{ to } Zn)$ | 12–116 | 1–45 | 0·8–4·2 | 0·5–3 |
| $MMn_2O_4 (M = Mg, Co \text{ to } Zn)$ | 20–76 | 30–60 | 0·7–5 | 0·6–1 |
| $MTiO_3(M = Ca, Sr, Ba \text{ and } Pb)$ | 18–42 | 19–30 | 0·47–0·54 | 0·7–0·9 |
| PZT | 20–43 | 19–30 | 0·5–1 | 0·7–1·1 |
| PLZT | 29 | 30 | 0·52 | 0·53 |

area values of the metal oxide powders prepared by the combustion of redox mixture are in the range of 2–135 m²/g. The average agglomerate particle sizes of these powders are in the range of 0·6–15 $\mu$m.

## 2.3 *Comparison of properties of oxides prepared by the combustion of redox compounds and mixtures*

Only few oxides could be prepared by both the processes. These include, cobaltites, ferrites and dielectrics ($PbZr_{0.53}Ti_{0.47}O_3$, PZT etc.) which are formed at low temperature ($< 1000°C$). A comparative account of properties of oxides prepared by both combustion processes is given in table 3. It can be seen that the surface area of the oxide powders prepared by the combustion of redox compounds are higher than those obtained by the combustion of redox mixtures. This is because redox compounds undergo flameless (smouldering) combustion whereas redox mixture burns with a flame. Consequently, the average agglomerate particle size (light scattering sedimentation method) of the oxide powders prepared by the combustion of redox mixtures is lower than that of oxide powders obtained by the combustion of redox compounds. The marked difference in surface area and particle size in both the processes can be explained by the amount of gaseous products that are evolved during combustion. For example, the combustion synthesis of $\gamma$-$Fe_2O_3$ by both the methods can be represented as:

$$2(N_2H_5)Fe(N_2H_3COO)_3 \cdot H_2O \xrightarrow[<200°C]{air} Fe_2O_{3(s)} + 6CO_{2(g)} + 8N_{2(g)} + 16H_2O_{(g)}$$
$$(30 \text{ mol of gases/} Fe_2O_3) \qquad (1)$$

$$16Fe(NO_3)_3 + 15C_3H_8N_4O_2 \xrightarrow{350°C} 8Fe_2O_{3(s)} + 45CO_{2(g)} +$$
$$(\text{MDH}) \qquad 54N_{2(g)} + 60H_2O_{(g)}$$
$$(20 \text{ mol of gases/} Fe_2O_3). \qquad (2)$$

The combustion of redox compound (equation (1)) liberates 30 moles of gaseous products whereas redox mixture gives only 20 moles (equation (2)). It is interesting to note that combustion of redox compound yields low temperature phase ($\gamma$-$Fe_2O_3$), whereas combustion of redox mixture gives usually a high temperature phase ($\alpha$-$Al_2O_3$, $\alpha$-$Fe_2O_3$ etc). However by changing the fuel one could alter the energetics of the redox mixture and prepare various metastable phases.

## 3. Sintering and microstructure

Sintering behaviour of the combustion derived powders was studied by crushing the as-synthesized powders in an agate mortar and pelletizing under 20–70 MPa uniaxial cold pressing. Typically $ZrO_2$, $Al_2O_3$ and $Al_2O_3$–$ZrO_2$ composite when sintered at 1300–1650°C for 4 h achieved $\simeq 99\%$ theoretical density. The scanning electron
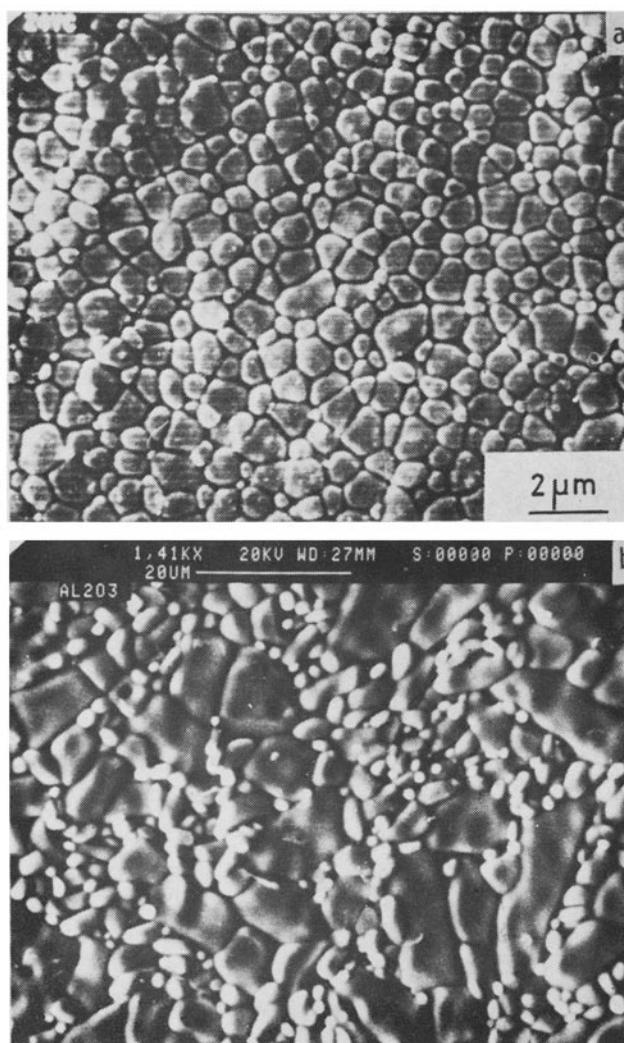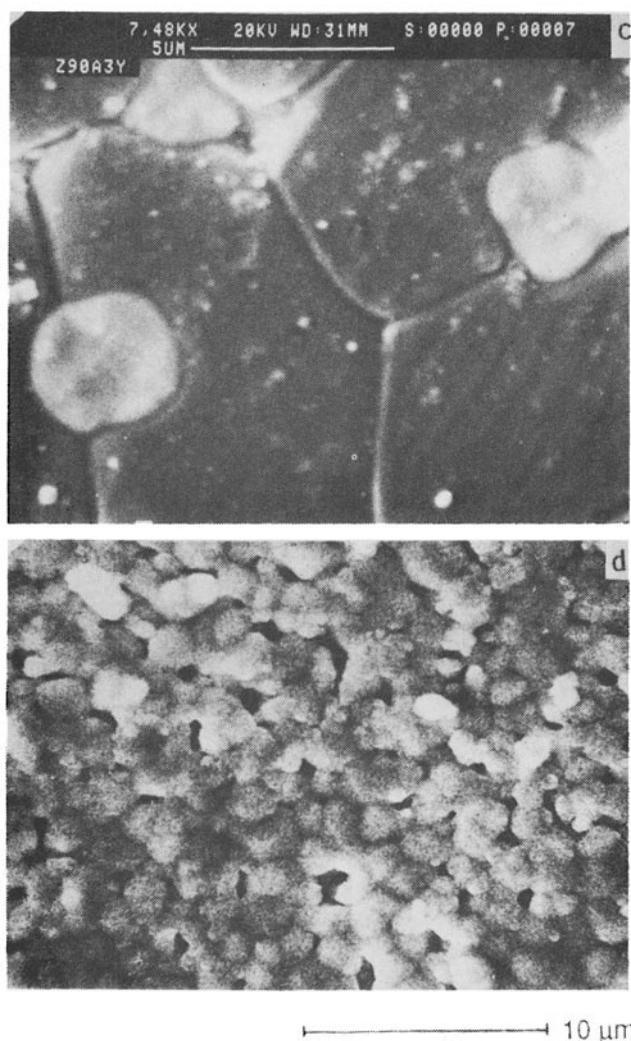


Figure 1a–b.

**Figure 1.** SEM micrographs of the surfaces of sintered pellets: (a) $ZrO_2$ (1250°C, 4 h), (b) $Al_2O_3$ (1650°C, 4 h), (c) $Al_2O_3$–$ZrO_2$ composite (1650°C, 4 h) and (d) PZT (1200°C, 1 h).

microscope (SEM) micrograph of sintered $Y_2O_3$ stabilized $ZrO_2$, $Al_2O_3$, $Al_2O_3$–$ZrO_2$ composite and PZT are shown in figure 1. The microstructure of $ZrO_2$ with 4 mol% $Y_2O_3$ (figure 1a) sintered at 1250°C reveals fine-grained microstructure and the grains are almost equiaxed with an average grain size of 1 to 3 $\mu$m. The microstructure of $Al_2O_3$ (figure 1b) sintered at 1650°C shows nearly pore-free nature and occasionally the presence of exaggerated grains is noticed. Exaggerated grain growth could be avoided by adding a small amount of impurities such as MgO, $Y_2O_3$, $TiO_2$ etc. Microstructure of $Al_2O_3$ with 10 wt% $ZrO_2$ composite (figure 1c) sintered at 1650°C shows alumina grains (black contrast) with linear grain boundaries and pore-free nature of the body. Zirconia grains (white contrast) are almost equiaxed with 1–2 $\mu$m

**Table 4.**  A comparison between solution combustion and Merzhanov's SHS.

| SHS | Solution combustion |
|---|---|
| Gasless solid state (i.e. solid → solid) process | Gas-producing solution (i.e. solution → solid) process |
| Heterogeneous | Homogeneous or heterogeneous |
| Flame temperature > 2000°C | Flame temperature ≥ 1000°C |
| Self-propagating only if the adiabatic temperature (Tad) is > 1800°C | Self-propagating even when the flame temperature > 900°C |
| Powders could be sintered to high density by simultaneous application of pressure | Compacted and sintered to near theoretical density at low temperatures |
| Commercialized | Yet to be commercially exploited |

size and occupy the grain boundaries of large alumina grains. Microstructure of PZT (figure 1d) also shows uniform grain growth with an average grain sizes of $2 \mu m$.

## 4.  Conclusions

The combustion process described here has several advantages over the other methods in terms of simplicity, cost effectiveness, energy saving, purity and homogeneity. The main differences between Merzhanov's SHS and the combustion process described here (solution combustion) are given in table 4.

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