Design and modify the combustion synthesis method to synthesize ceramic oxide powders

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Electronic ceramics are widely used as elements and components in industries such as electrical engineering, electronics, and information. They not only have become the main stream in the advanced ceramics market, but also have been developed well in applications with respect to both scope and magnitude. Overall, ceramic oxides are the most important ones among these electronic ceramic materials [1]. The conventional method for preparing ceramic oxide powders is to perform the solid-state reaction of oxides and carbonates. These starting materials are mixed at a specific composition ratio and then calcined in the air or oxygen atmosphere at a high temperature for a long time. Intermittent grinding is required to obtain phase-pure and homogeneous product powders. Although this method is relatively simple, the conventional solid reaction process is time-consuming and energy intensive. Recently, a variety of wet-chemical methods have also been reported to be effective in generating ultrafine and more homogeneous powders of ceramic oxides [2–4]. However, complex schedules and low production rate are the common problems of the wet-chemical methods.

Fortunately, the drawbacks of these methods as mentioned above could be partially eliminated by using the combustion synthesis method, which has been applied to synthesis of various high performance materials including ceramics, intermetallics, and composites [1, 5]. Various advantages such as low processing cost, energy efficiency, and high production rate [6] are among the benefits of the combustion synthesis method. With regard to the combustion synthesis of ceramic oxide, the general procedure is to use corresponding metal powder to be mixed thoroughly with metal oxides in a proper ratio, and then press them to get the reactant compact. The compact is ignited in an oxidizing atmosphere and ceramic oxide products are thus obtained after combustion [1, 7–9]. This indicates that the metal powder is the fuel whereas the oxidizing agent is oxygen. Both materials cause combustion and results in high temperature with phase transformation to obtain the final product. However, the reaction needs to be conducted under a required oxygen pressure. At this operating point, the events of melting of metal, coalescence of melt, and grain growth of as-synthesized product may occur due to the combustion reaction arising out of high temperature (about 1400–1600 °C). Such adverse factors may decrease the simplicity of procedure, lower the reaction converse, and reduce the product quality. Therefore, the combustion synthesis method can be further improved significantly.

One approach that can be used in the examination of gun powder reaction. The weight ratio of gun powder is 75% saltpeter, 10% sulfur, and 15% charcoal. As soon as it is ignited, a rapid (but over-simplified) reaction takes place [10]:

$$2KNO_3 + S + 3C \xrightarrow{\Delta} K_2S + N_2\uparrow + 3CO_2\uparrow$$

Combustion of gun powder does not need any external oxygen, because the oxidizing agent KNO_3 can provide a large quantity of oxygen enough to complete the reaction. It should be noted that the three ingredients of gun powder are solid and, among them, potassium nitrate acts as an oxidant whereas sulfur and charcoal act as fuels. With this in mind, we have come up with an idea to develop a new combustion synthesis method for synthesizing oxide ceramic powders. The idea is that mixtures composed of metal nitrates to be added with suitable fuel powders in an appropriate ratio are to be ignited and completely burnt to form ceramic oxides. In a sense, gun powder can generate a lot of gases when burned. If such application is utilized in the synthesis of ceramic powders, gaseous products can be released via the combusting reactants and are conducive to heat loss through convection, resulting in rapid reduction of product temperature. On a practical level, it is suggested that fine powders could be produced due to the prevention from both the growth of grains and the agglomeration of particles. As stated above, the theory for improving the combustion synthesis methods has been established accordingly.

Using suitable raw materials in combustion synthesis ensures the stability of the chemical composition and high quality of products. More importantly, it must be readily available and convenient to be used. In addition, it should react non-violently and produce nontoxic gases. In the beginning, this research selects citric acid, urea, and glycine to be the fuels to confirm both the feasibility of our proposal and the applicability of using these three organic compounds. Some of their properties from the literatures [11, 12] are listed in Table I. On the other hand, metal nitrates are utilized in the present work because of their dual role of being

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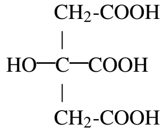
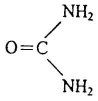
TABLE I Some properties of organic compounds used in this study

Properties	Organic component Critic acid	 Urea	 Glycine
Structural formula	 $\begin{array}{c} CH_2\text{-}COOH \\ \vert \\ HO\text{—}C\text{—}COOH \\ \vert \\ CH_2\text{-}COOH \end{array}$		$H_2N\text{—}CH_2\text{—}COOH$
Molecular weight (g/mol)	192.1	60.1	90.1
Heat of combustion (kJ/g)	10.2	10.5	13.0
Decomposition temperature (°C)	175	135	262

the cation sources and the oxidant. Analytical-grade organic compounds and metal nitrates were used as raw materials in this study.

Firstly, this research focused on synthesizing $Ni_{0.5}Zn_{0.5}Fe_2O_4$ to be our target product. $Ni_{0.5}Zn_{0.5}Fe_2O_4$, a soft magnetic material, can be used in the manufacturing of multilayer chip inductors (MLCIs). The products are synthesized by an amount of 25 g per batch. The following illustrates the operation procedure. First, measure the required quantity of metal nitrates and put it in the crucible. Then, add organic fuel of which it has an "equivalent stoichiometric ratio" with respect to metal nitrates. Afterward, stir and mix them completely. Here, the definition of the "equivalent stoichiometric ratio" indicates that the oxygen content of oxidant can be completely reacted to oxidize/consume the organic fuel exactly [13]. As a result, the combustion process can produce CO_2, H_2O, and N_2 gases without the necessity of getting oxygen from outside. Taking metal nitrates (oxidant) and glycine (fuel) to be reactants in synthesizing Ni-Zn ferrite as an example, the following is its stoichiometric chemical reaction:

$$\begin{aligned} &0.5Ni(NO_3)_2{\cdot}6H_2O + 0.5Zn(NO_3)_2{\cdot}6H_2O \\ &\quad + 2Fe(NO_3)_3 \cdot 9H_2O + \frac{40}{9}NH_2CH_2COOH \\ &\xrightarrow{\Delta} Ni_{0.5}Zn_{0.5}Fe_2O_4 + \frac{80}{9}CO_2 + \frac{316}{9}H_2O \\ &\quad + \frac{20}{9}N_2 \quad (\sim 45 \text{ moles of gases produced}) \end{aligned}$$

Metal nitrates possess hygroscopicity, consequently, they can easily absorb moisture and then become slurry. Therefore, the reactants can be mixed homogeneously during the stirring process. This slurry mixture was heated using a hot-plate at ∼100 °C to dehydrate itself thoroughly. The dried mixture (hereafter should be termed as precursor) possesses the characteristics of combustion. And it can be ignited to start combustion reaction by using mini gas burner or hot-plate. By doing so, flames and smoke are produced, and the products left behind are voluminous and fluffy. The flow chart of the process is shown in Fig. 1. Thermogravimetric analysis (TGA) (TA Instruments, SDT 2960, USA) for precursors formed with respect to using various organic fuels was carried out at a heating rate of 10 °C/min in static air. Phase formation of the product was identified by using X-ray diffraction (XRD) (SIEMENS D5000, Germany) with Cu K_α radiation. Morphological features of the product were imaged by transmission electronic microscope (TEM) (Hitachi H-7100, Japan). Moreover, powder surface area was measured by using a single point BET (Micromeritics, ASAP 2010, USA) nitrogen adsorption method. Furthermore, Perkin-Elmer CHN elemental analyzer (Model: 2400(II), USA) and an inductively coupled plasma-atomic emission spectrometer ((ICP-AES) (Jarrell-Ash, ICAP 9000, USA) were used to measure the carbon and metallic cation contents in the as-synthesized powders. Also, a vibrating sample magnetrometer (VSM) (Toei, VSM-5, Japan) was used to determine the saturation magnetization (M_s) of the sintered ferrite (900 °C/2 hr) at room temperature.

Fig. 2 shows the XRD patterns of the products synthesized using various organic fuels. As indicated by the characteristic peaks of Ni-Zn ferrite, the Ni-Zn ferrite could be produced using each of the organic fuel studied here. Notably, there exists a broadening phenomenon in this graph in terms of characteristic peaks. These occurrences can be attributed to the fact that the product powder is relatively fine. The product synthesized using glycine seemed to contain single-phased Ni-Zn ferrite because only the characteristic peaks of Ni-Zn ferrite were observed. While using urea and citric acid as organic fuels, the XRD patterns indicate that there exist other diffraction peaks caused by impurities in the as-synthesized products.

Fig. 3 shows the TGA plot of the various precursors prepared with different organic fuels. In this work, it is our judgment to define an initiation temperature (T_{in}) as a temperature when sample weight starts changing rapidly during chemical reaction. For example, when using glycine as an organic fuel in this experiment, a significant weight loss started to be observed as temperature reached at 165 °C, indicating that the chemical reaction took place very rapidly (i.e., the slope of weight loss–temperature curve is very steep). At around 180 °C, the remaining weight was only ∼16% of its original weight, and then the slope began to level off gradually. When using urea as an organic fuel, its T_{in} was around 165 °C, but the change of weight loss was much flatter as compared with glycine. There was not a significant change observed until the temperature

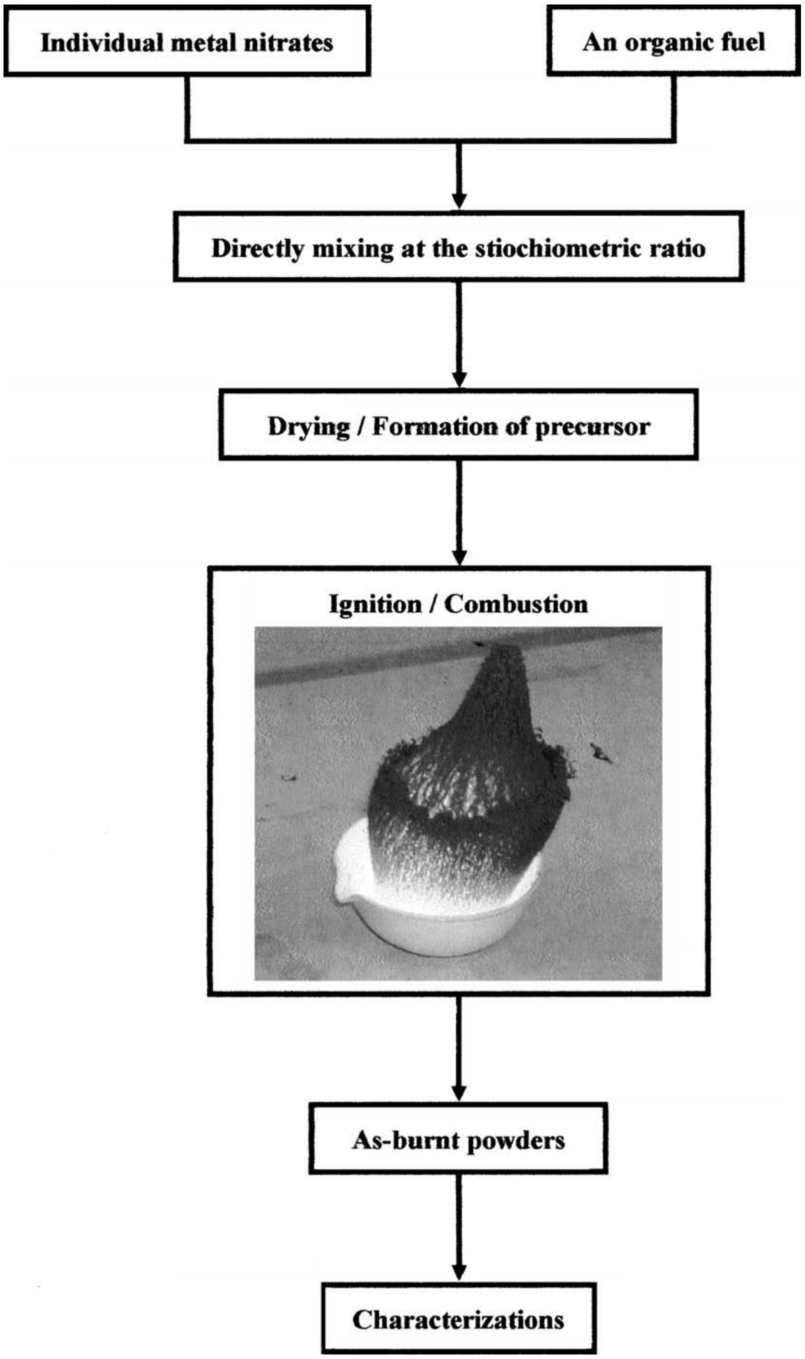


Figure 1 Flow chart for the synthesis of ceramic oxide powder using this proposed combustion method.

reached 280 °C at which its weight reduced to 18% of its original weight. When using citric acid in this work, the theomogravimetric analysis of precursor indicates that it was quite peculiar; that is, as the precursor was heated, thermal decomposition started right away. From the curve of theomogravimetric analysis, it is observed that there appears a phenomenon of three-stage weight loss. Obviously, this belongs to a multi-stage reaction. The weight loss was not stopped until the temperature reached 500 °C (final weight reduced to ∼17% of its original weight). When comparing citric acid with other organic fuels its slope is relatively flat, indicating that the reaction is more moderate. This result is consistent with the combustion phenomenon of using citric acid as a fuel—combustion reaction of the precursor is in a smoldering mode. It can be inferred that citric acid with its low combustion heat is the cause that contributes to this result. Moreover, the results obtained using thermogravimetric analysis indicated that the two organic fuels used beforehand (urea and glycine) containing amine group can be decomposed to produce ammonia at a relatively low temperature. In other words, reaction between ammonia and the NO_x from the decomposed metal nitrates took place and it is written in the following [14]:

$$\begin{aligned} &4x\mathrm{NH}_{3(g)} + 10\mathrm{NO}_{x(g)} \\ &\quad \rightarrow (5 + 2x)\mathrm{N}_{2(g)} + 6x\mathrm{H}_2\mathrm{O}_{(g)} + 2x\mathrm{O}_{2(g)} \end{aligned}$$

The energy released from the redox reaction is thus supplied to accelerate the whole combustion reaction.

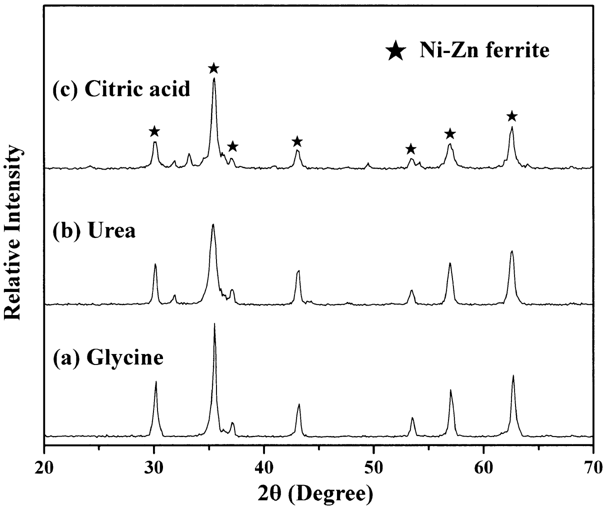


Figure 2 XRD patterns of the as-synthesized products prepared by using various organic fuels: (a) glycine, (b) urea, and (c) citric acid.

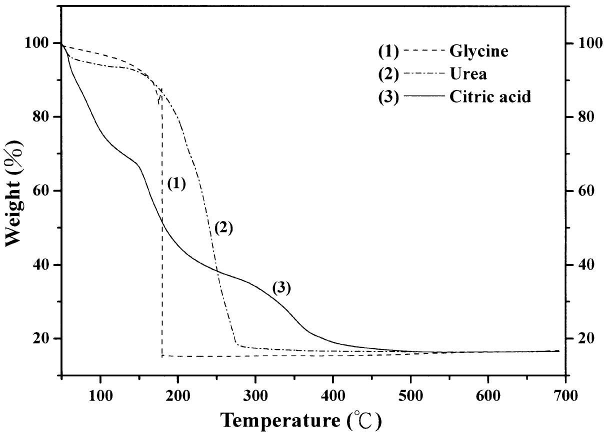


Figure 3 Typical TGA curves of the precursors prepared by using various organic fuels.

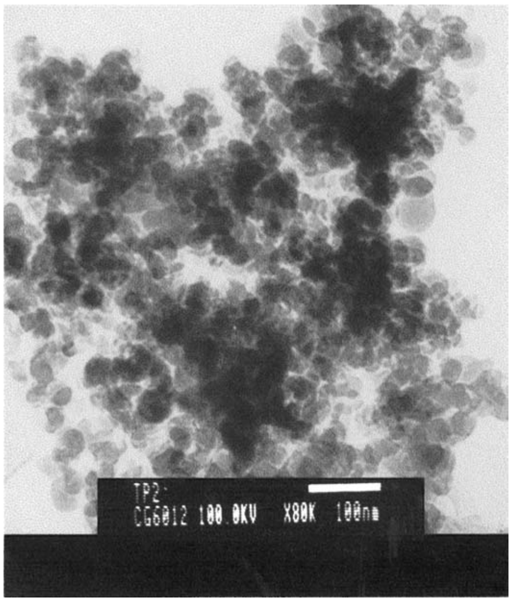


Figure 4 TEM photograph of the synthesized $Ni_{0.5}Zn_{0.5}Fe_2O_4$ powder prepared by using glycine as fuel.

Table II lists the analytical results obtained from Ni-Zn ferrite products synthesized by using various organic fuels. According to calculation using Scherer formula [15], all products obtained in this work are nanocrystalline with their sizes ranging between 20.2 and 38.7 nm. The surface area of the synthesized product are in the range 32.1–48.5 m^2/g. Since the heat released during combustion is relatively low for citric acid and urea (see Table I), the combustion reaction is incomplete. The carbon content of the products synthesized using these two fuels is higher than that using glycine. From the result of the analysis using an ICP spectrometer, the measured Ni:Zn:Fe cation ratio in the as-synthesized $Ni_{0.5}Zn_{0.5}Fe_2O_4$ was nearly equal to the required ratio, indicating that the products possess good chemical homogeneity. The M_s values of the sintered Ni-Zn ferrites are in the range of 55.8–62.4 A m^2/kg, which are comparable with those obtained by other methods [7, 8, 16, 17].

Fig. 4 shows a TEM photograph of the as-synthesized Ni-Zn ferrite produced by using glycine as the fuel. The sizes of the spherical particles are homogeneously distributed ranging from 30 to 40 nm, which is about the same as the sizes estimated by using the XRD method. It also reveals that the particles are dispersed with negligible agglomeration, and thus the as-synthesized product possesses higher surface area compared with those synthesized by using urea and citric acid as the fuels.

Fig. 5 shows XRD patterns utilizing the proposed method to synthesize different types of ceramic oxides. As can be seen, pure ZnO (a type of semiconductor ceramics) and $LiCoO_2$ (to be used as the electrode of fuel cell) can be directly synthesized from this method. However, when using this method to synthesize $SrFe_{12}O_{19}$ (a type of hard magnetic material) and $YBa_2Cu_3O_{7-x}$ (a type of superconductor), in addition to the target product produced, there exist other by-products in the as-synthesized product. These two as-synthesized powders were calcined at 1200 °C/2 hr and 900 °C/12 hr respectively, to obtain pure phase $SrFe_{12}O_{19}$ and $YBa_2Cu_3O_{7-x}$ (the XRD patterns of both calcined products are also inserted in Fig. 5). Evidently, this method can be widely employed to synthesize different ceramic oxide powders.

We have utilized an indicative and precursory experiment strategy to prove the feasibility of our proposed

TABLE II Particular properties of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ synthesized by this proposed combustion synthesis method

Fuel	Crystallite size (nm)	Surface area (m^2/g)	Carbon content (wt%)	Ni:Zn:Fe (molar ratio)	M_s (A m^2/kg)
Glycine	38.7	32.1	1.53	0.500:0.471:1.922	62.4
Urea	20.2	48.5	3.82	0.500:0.483:1.936	57.2
Citric acid	22.7	44.1	5.75	0.500:0.490:1.947	55.8

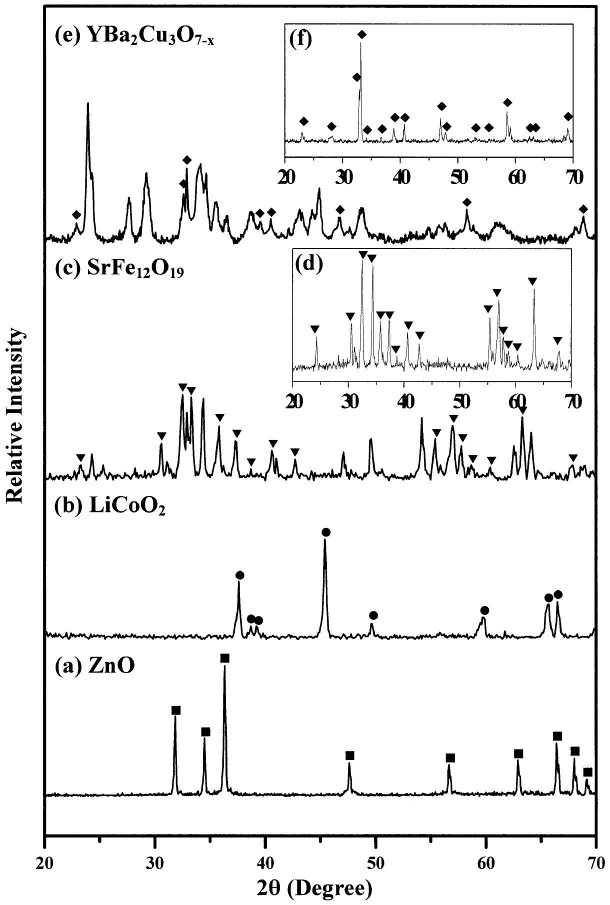


Figure 5 XRD patterns of other ceramic oxides prepared by using glicine as fuel: (a) as-synthesized ZnO, (b) as-synthesized $LiCoO_2$, (c) as-synthesized $SrFe_{12}O_{19}$, (d) as-synthesized $SrFe_{12}O_{19}$ calcined at 1200 °C/2 hr (inset), (e) as-synthesized $YBa_2Cu_3O_{7-x}$ and (f) as-synthesized $YBa_2Cu_3O_{7-x}$ calcined at 900 °C/12 hr (inset).

method. By using metal nitrates and organic fuels as reactants, combustion synthesis reaction would take place to produce ceramic oxide powder after proceeding with steps of mixing, dehydrating, and ignition directly. Although certain initial products need further calcination procedure to attain pure phase product, however, this proposed method possesses advantages such as time-saving, easy to operate, energy-saving, and widely-expandable in different applications when comparing with other methods. Moreover, this method can be expected to be one of the suitable methods for mass production of ceramic oxide powder. Other associated studies such as the effects of both molar ratio of fuel-oxidant and combustion temperature, the investigation of reaction mechanism, the characteristic analysis of products, etc. are being further investigated.

Acknowledgment

Support for this research by the National Science Council of the Republic of China under Grant No. NSC 91-2214-E-014-002 is gratefully acknowledged.

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Received 17 November 2003
and accepted 1 April 2004