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Synthesis of Nano-Crystalline $Zr_{0.8}Sn_{0.2}TiO_4$ Powder by Choline-Chloride-Malonate Deep Eutectic Solvents

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Abstract

Chloride-malonate deep eutectic solvent (Cm-DES) was applied to synthesize nano-crystalline $Zr_{0.8}Sn_{0.2}TiO_4$ ceramic powder by using $Zr(CH_3COO)_4$, $SnCl_2•2H_2O$ and $Ti(OCH_3CH_3)_4$ as raw materials. The nano-crystalline $Zr_{0.8}Sn_{0.2}TiO_4$ powder was obtained at 450 °C, dramatically lower than that by solid state reaction. Meantime, the grain size of as-synthesized $Zr_{0.8}Sn_{0.2}TiO_4$ powder at 450 °C is 10.7 nm. In the synthesized process, Cm-DES, as a solvent and template, affects the synthesis process and the time required for synthesis is greatly reduced. These results show that the Cm-DES is suitable and prospective for the synthesis of nano-crystalline $Zr_{0.8}Sn_{0.2}TiO_4$ ceramic powder, which could contribute to reduce energy consumption and time cost.

1. Introduction

Deep eutectic solvents (DESs) is a new type of solvents like ionic liquids [1, 2], which is cheap, eco-friendly and prepared easily, just from the concurrent melting of two simple species. Based on the advantages such as easy synthesis, cost-saving, and high solubility of metal salts, DESs has been widely used in various fields, such as gas adsorption [3], ferroelectrics [4, 5] and so on. However, as far as the literature is concerned, there is no report on the synthesis of microwave dielectric ceramic powders by DESs. In this work, $Zr_{0.8}Sn_{0.2}TiO_4$ powder was synthesized by the Chloride-malonate deep eutectic solvent (Cm-DES) and the effect of calcination temperature on the phase composition, grain size and microstructure of as-synthesized powder was investigated.

2. Experimental

$Zr_{0.8}Sn_{0.2}TiO_4$ powder was prepared by the Cm-DES using high-purity materials including $Zr(CH_3COO)_4$ (Zr,15.0-16.0%), $SnCl_2·2H_2O$ (≥98.0%), and Titanium isopropoxide (TiO_2, 27.5-28.2%) which were purchased from Sinopharm Chemical Reagent Co., Ltd, China. The chloride-malonate DES (Cm-DES) were prepared using choline chloride (98.0-101.0%) and malonate (≥98.0%) with molar ratio of 1:1, then the mixture was mechanically stirred in a bath (80 °C) until clear solution formed. Stoichiometric $SnCl_2·2H_2O$ and $Zr(CH_3COO)_4$ solutions were added to Cm-DES (20 ml) successively. The mixture was then heated to 90°C and stirred until clear solution formed. And then stoichiometric titanium isopropoxide was added to the mixture solution and stirred vigorously. The obtained gel was dried, ground, and calcined at 250-650 °C for 2h. X-ray diffraction (D8 Bruker Advance) patterns of the as-synthesized powders were obtained with Cu Ka radiation (λ=0.1541 nm) from 20 ° to 80 ° with a step of 0.02 ° at room temperature. The morphology was characterized using TEM (JEM-2100). The mean grain sizes were characterized by Nano Measurer 1.2 program.

3. Results And Discussion

Fig. 1 shows the XRD patterns of $Zr_{0.8}Sn_{0.2}TiO_4$ powders calcined at various temperatures. Some glass phases were detected for the powder calcined at 250 °C, but the diffraction peaks corresponding to $Zr_{0.8}Sn_{0.2}TiO_4$ (PDF No.81-2214) appear from 350 °C. The intensity of diffraction peaks for the powder calcined at 450 °C is much higher and increases with elevating calcination temperature. This means that well-crystallized $Zr_{0.8}Sn_{0.2}TiO_4$ powders can be achieved by the Cm-DES at 450 °C, a temperature much lower than that in other preparation methods [6-10]. Generally speaking, high temperature (>1050 °C) is needed to prepare $Zr_{0.8}Sn_{0.2}TiO_4$ ceramics by traditional solid state reaction, which limits its application in new fields such as LTCC. The high calcination temperature and coarse grain size of $Zr_{0.8}Sn_{0.2}TiO_4$ ceramic powders prepared by solid state reaction may be detrimental to the Qf value of the obtained $Zr_{0.8}Sn_{0.2}TiO_4$ ceramics. Furthermore, no second phase was detected in all the powder samples synthesized by this Cm-DES method with higher calcination temperature (≥ 450 °C). The mean grain size of the $Zr_{0.8}Sn_{0.2}TiO_4$ powder prepared by the Cm-DES at 450 °C is around 6.6 nm (calculated by Scherer formula), which is significantly smaller than that by solid state reaction.

Fig. 2 shows HRTEM images and mean grain sizes of as-synthesized powders at different calcination temperatures. The powder calcined at 350 °C is spherical, and the grain boundary between grains is obvious, as shown in Fig. 2A; The powder calcined at 450 °C is also spherical, however its grain size is increased significantly. With the further increase of calcination temperature, the grain size of the powder sample increases monotonously, agglomeration becomes more serious, and the particle shape changes from spherical to irregular polyhedron (600 °C, Fig. 2D). In addition, the mean grain sizes of the powder samples obtained at different calcination temperatures were calculated by Nano Measurer 1.2 program, as shown in Fig. 2E. Although the grain size of the as-synthesized powders increases with the increment of calcination temperature and remains unchanged when the calcination temperature is above 550 °C, the maximum grain size within the experimental temperature range is only 13.7 nm, the mean grain size is far smaller than that obtained by solid state reaction method.

The formation mechanism of $Zr_{0.8}Sn_{0.2}TiO_4$ phase in Cm-DES was also discussed. For the synthesis of $BaTiO_3$, Boston *et al*. [4] presented that the key to the formation of $BaTiO_3$ phase was the reaction with metal chlorides. We tried to synthesize $Zr_{0.8}Sn_{0.2}TiO_4$ and $BaTiO_3$ directly from metal chlorides. Unfortunately, no $Zr_{0.8}Sn_{0.2}TiO_4$ and $BaTiO_3$ phase were not detected in the calcined powders, as shown in Fig. 3. On the contrary, $Zr_{0.8}Sn_{0.2}TiO_4$ and $BaTiO_3$ powders were obtained by adding the same metal chlorides into Cm-DES, mixing and stirring evenly, and calcining at the same temperatures. These results indicate that Cm-DES can not only be used as solvent to dissolve the metal chlorides mentioned above, but also promote the formation of $Zr_{0.8}Sn_{0.2}TiO_4$ and $BaTiO_3$. Generally, there are some interactions, including hydrogen bonding and electrostatic interactions in the DESs. The -C=O groups of malonic acids are mostly free in the eutectic mixture and the –OH groups are strongly associated with the Cl^- of choline chloride through hydrogen-bonding interactions [11], which is key because hydrogen bonds lower the lattice energy of choline chloride and the melting point of the eutectic mixture. Herein, Cm-DES exists as a transparent, colorless liquid at room temperature. After the dissolution of $SnCl_2{\cdot}2H_2O$, $Zr(CH_3COO)_4$, and

titanium isopropoxide in the Cm-DES at 90 °C, the color of the liquid mixture changes from colorless to yellow, corresponding to the formation of the MCl_x^-. That is to say, the metal ions are primarily absorbed in the Cm-DES cluster at the expense of the partial destruction of the hydrogen-bonded framework of Cm-DES and the hydrogen-bond between –OH (choline) and ···chloride (metal salt) forms. Similar phenomena were detected by Thorat *et al*. [11] and Abbott *et al*. [12], respectively. During the calcination, these MCl_x^- metal ions could present at higher temperature and accelerate the decomposition of Cm-DES to produce some light substances such as CO, methane, and ethane. [11], which lower the Gibbs free energy (ΔG) of the formation of $Zr_{0.8}Sn_{0.2}TiO_4$. The oxidation of these substances also promote the formation of $Zr_{0.8}Sn_{0.2}TiO_4$ at lower temperature. Meantime, the grain size of $Zr_{0.8}Sn_{0.2}TiO_4$ particles is very small due to the template confinement effect of hydrogen bonding network in Cm-DES.

Table 1 Comparison of characteristics $Zr_{0.8}Sn_{0.2}TiO_4$ powders synthesized by various methods

Methods	Calcination temperature/ °C	Dwelling time/h	Grain size /nm	Secondary phase	Ref.
Solid state reaction	1050	2	-	TiO_2	[10]
Hydrothermal	150-230	2	100	TiO_2/SnO_2	[13]
Sol-gel	250/450/700	0.5/0.5/0.5	10-20	-	[7]
Co-precipitation	800	4	200	-	[8]
Ultrasonic spray pyrolysis	700	-	100-200	-	[6]
Cm-DES	450	2	13.7	-	This work

As we all know, $Zr_{0.8}Sn_{0.2}TiO_4$ is a typical microwave dielectric ceramic material which has been commercialized for a long time. At present, the development of 5G communication is in full swing, and the problems of energy efficient utilization and environmental sustainable development are becoming increasingly prominent. As one of the key supports of 5G communication, how to prepare $Zr_{0.8}Sn_{0.2}TiO_4$ microwave dielectric ceramics with low cost, short process, time saving and low energy consumption has become particularly critical. Table 1 lists the typical results carried out for the synthesis of $Zr_{0.8}Sn_{0.2}TiO_4$, including hydrothermal, sol-gel, co-precipitation and ultrasonic spray pyrolysis. Solid state reaction (SSC) is widely used to prepare the $Zr_{0.8}Sn_{0.2}TiO_4$ powder/ceramic with oxides such as ZrO_2, SnO_2 and TiO_2. While it needs solid phase diffusion with a long diffusion distance before the reaction with each other, herein high heating temperatures and long dwelling time were needed, resulting in some disadvantages such as high energy consuming and undedirable metaphases. Conventional solution chemical methods such as hydrothermal, co-precipitation, sol-gel, and ultrasonic spray pyrolysis method are also developed

to prepare $Zr_{0.8}Sn_{0.2}TiO_4$ powder/ceramics. Aqueous/liquid states precursor materials were employeed in these solution chemical methods to solve the problems like hard diffussion and long diffussion distances. Unfortunately, special and expensive instruments like high pressure vessels and sonic device limit the application in batch production. In contrast, the synthesis of $Zr_{0.8}Sn_{0.2}TiO_4$ powder by Cm-DES reported in this work is low-cost, short process, time-consuming and energy-saving.

4. Conclusions

The nano-crystalline $Zr_{0.8}Sn_{0.2}TiO_4$ ceramic powder was synthesized by Cm-DES at such low temperature as 450 °C. The synthesis temperature is much lower than that for the traditional solid state reaction, reducing time and energy consumption. The corresponding $Zr_{0.8}Sn_{0.2}TiO_4$ ceramic powders exhibit well crystallized and the mean grain size is 10.7 nm at 450 °C. In the synthesis process, Cm-DES, as dissolvent materials, react media and template, can promote the $Zr_{0.8}Sn_{0.2}TiO_4$ synthesis at lower temperature. Cm-DES process is low-cost, short process, time-consuming and energy-saving, which make it a prospective, cost-saving, and sustainable process for the preparation of microwave dielectric ceramics.

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Figures

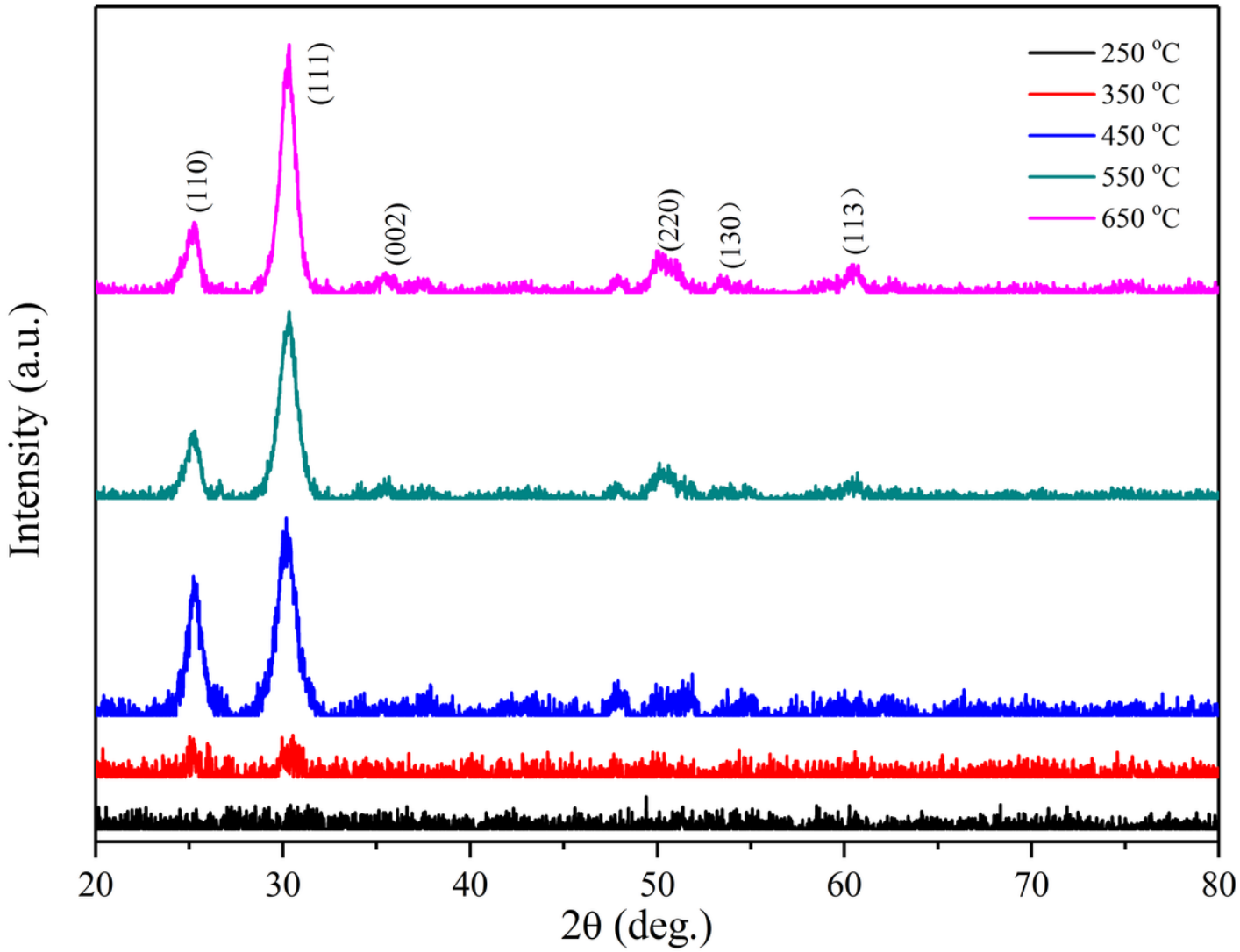

Figure 1

X-ray diffraction patterns of the as-synthesized powders by chloride-malonate deep eutectic solvent calcined at various temperatures.

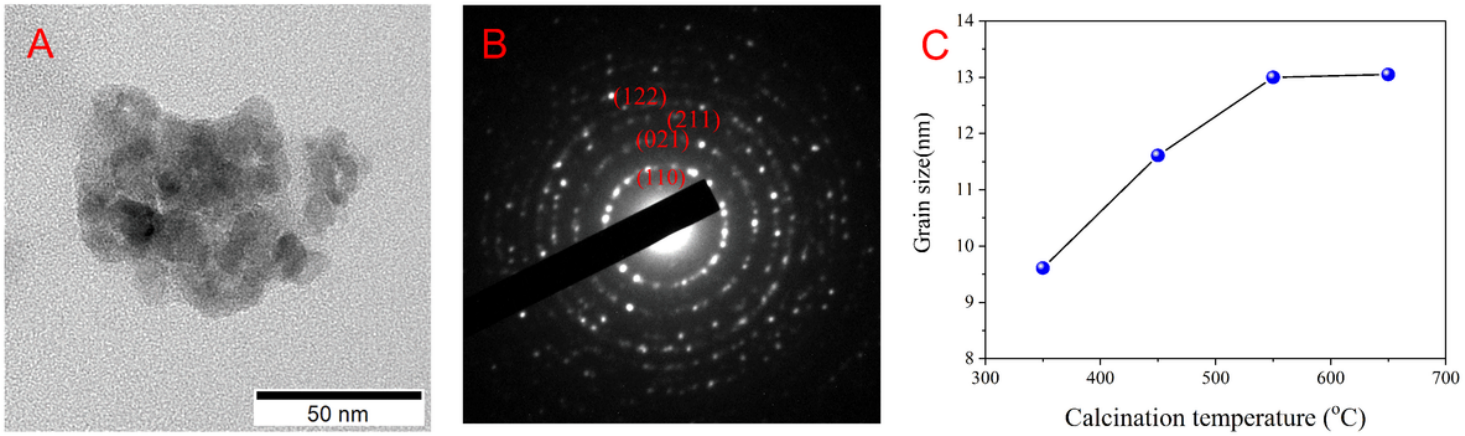

Figure 2

HRTEM images of as-synthesized powders by chloride-malonate deep eutectic solvent calcined at (A) 350 °C, (B) 450 °C, (C) 550 °C and (D) 650 °C, respectively, and (E) the corresponding mean grain sizes.

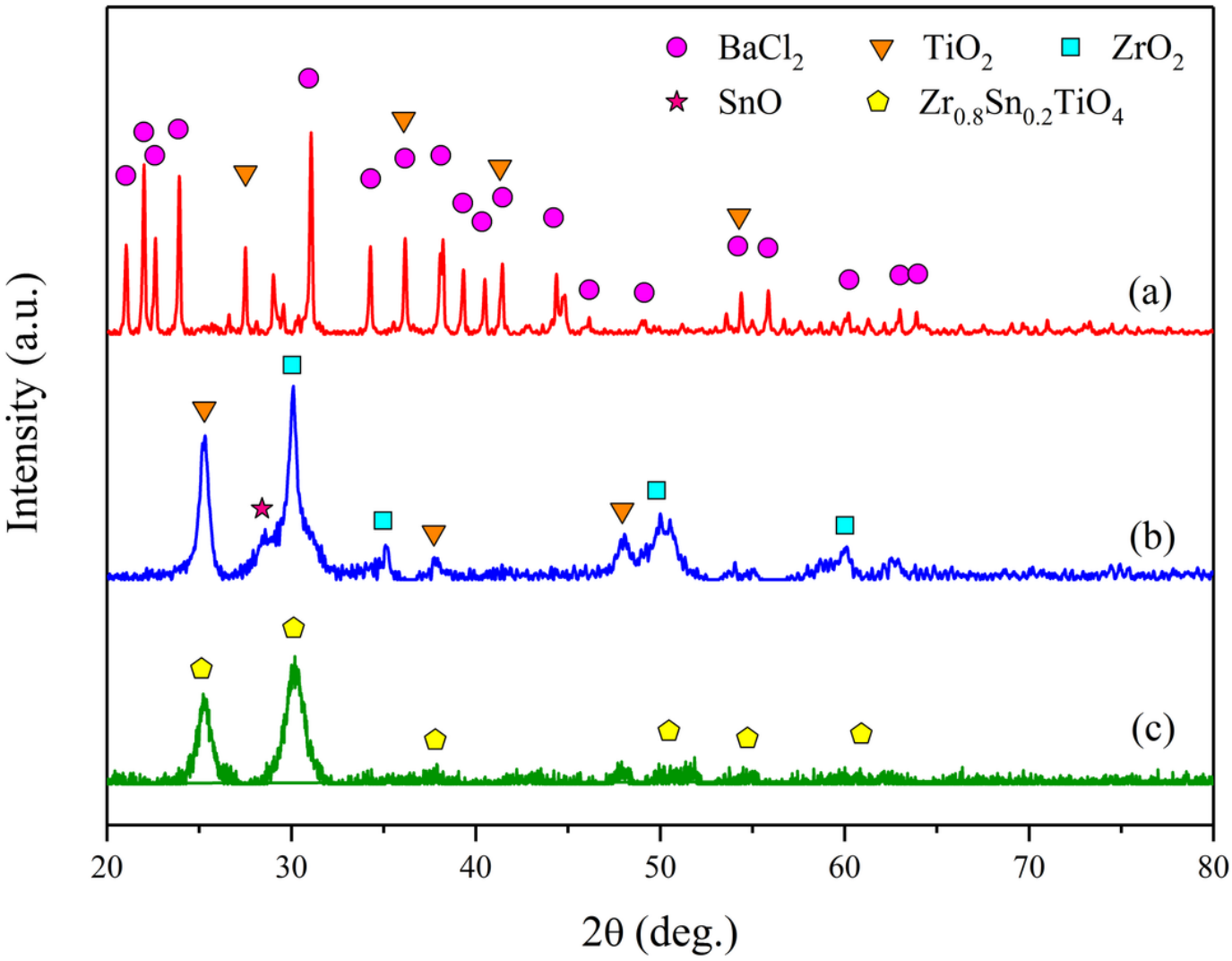

Figure 3

Typical X-ray diffraction patterns of (a) the BaO-TiO2 powder synthesized by solid state reaction (SSC) at 950 °C, (b) the ZrO2-SnO-TiO2 powder synthesized by SSC at 450 °C, and (c) the as-synthesized Zr0.8Sn0.2TiO4 powders by chloride-malonate deep eutectic solvent calcined at 450 °C.