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Short communication

Synthesis of nanocrystalline $Sn_{0.2}Zr_{0.8}TiO_4$ by the citrate gel method

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Abstract

A gel was formed when a aqueous solution of $ZrOCl_2$, $SnOCl_2$, $TiOCl_2$ and citric acid in stoichiometric ratio is heated on a water bath. This gel on decomposition at 873 K produced nano crystallites of the ternary oxide, $Sn_{0.2}Zr_{0.8}TiO_4$. The conventional solid state ceramic method yields the same compound at 1173 K only. The average particle size of the samples prepared by the citrate method as studied by transmission electron microscopy (TEM) is 50 nm.

Keywords: A. Powders: chemical preparation; B. X-ray methods; D. ZrO_2; D. TiO_2

1. Introduction

Microwave dielectric ceramics have important applications in communication technology, e.g. cellular phones. The requirements for this application are a high dielectric constant (>40) at microwave frequency, a low dielectric loss (Q >5000, Q = 1/tan) and near zero temperature coefficient of resonance frequency for temperature stable circuits [1–3]. The size of the dielectric resonator is inversely proportional to its dielectric constant. For the past 20 years, systems such as $Ba(Sr,Ta)O_3$, $MgTiO_3$–La_2O_3–TiO_2–Nd_2O_3, $BaTiO_3$–TiO_2 and (Sn,Zr) TiO_4 [3–5] were investigated and found to have reasonably acceptable properties. Among these $Sn_{0.2}Zr_{0.8}TiO_4$ has been already used in commercial devices as a dielectric resonator because of its optimum properties. The reported values [5] of the dielectric constant ~40, the quality factor ~5000 and the temperature coefficient of resonant frequency ~50 ppm are for this system. The three methods that are employed to reduce the sintering temperature of this compound are low melting glass additions, chemical processing and smaller particle sizes of starting materials. Ultrafine powders prepared by chemical methods with particle size less than 50–100 nm referred to as nanocrystalline powders can have significantly enhanced sintering rates and decreased sintering temperatures due to high driving force of densification. The various chemical methods include hydrothermal, sol–gel [5] and co-precipitation [6] have been employed for this purpose.

Here, we report a simple citrate gel process of for the preparation of nanocrystalline powders of $Sn_{0.2}Zr_{0.8}TiO_4$. This method is commonly used for preparation of complex oxides [7–10] and not yet reported for the preparation of these powders. This process involves complexation of metal ions by poly functional carboxyl acids such as citric acid or tartaric acid having one hydroxyl group. On heating this mixture, the solvent (water) evaporates resulting in increased viscosity. On complete removal water, the mixture is a polymeric gel and its constituents mixed at atomic level. This resin on heating at higher temperature produces the respective oxides. The only drawback of this method is the residual carbon, if present can possibly deteriorate the dielectric properties.

2. Experimental

$ZrOCl_2$, $TiCl_4$, $SnCl_4$ and citric acid used for the preparation of microwave dielectric are of AR grade. Required quantity of $ZrOCl_2$ was weighed and dissolved in a solution containing stoichiometric amount of $TiOCl_2$ and $SnOCl_2$, which were prepared by diluting $TiCl_4$, and $SnCl_4$

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solutions with ice cold distilled water. This solution mixture is mixed with citric acid and heated on a water bath. The ratio of total metal cations to citric acid is one. Since there was no precipitation during mixing, the pH of the solution was not varied. On heating on a water bath at 373 K a yellowish gel was formed after evaporation of water. Subsequently, the gel is decomposed at various temperatures ranging from 423 to 973 K in air. The heating rate employed was 10 K/min and kept for 4 h. The gel initially started to swell and filled the beaker producing a foamy precursor. This foam consists of homogeneous flakes of very small particle size.

Various techniques such as XRD (Philips PW 1710 Diffractometer) and BET surface area measurements (Nova 1200 instrument using BET analysis) were employed to characterize these powders. For lattice parameter and interplanar distance (*d*) calculation, the samples were scanned in the 2θ range of 10–80° for a period of 5 s in the step scan mode. Silicon was used as an internal standard. Least squares method was employed to determine the lattice parameters. The transmission electron spectroscopy (TEM) picture was recorded with JEOL model 1200 EX instrument at the accelerating voltage of 100 kV. The fine powders were dispersed in amyl acetate on a carbon coated TEM copper grid. The samples were analyzed for the presence of carbon by microanalysis technique on a CARLO ELBA EA-1108 analyzer.

For comparison, samples are also prepared by standard solid state technique. The corresponding oxides are weighed in required ratio and mixed well in an agate mortar using acetone for 2 h. The mixed powders were fired at 1373 K for 24 h with intermittent grinding at room temperature.

3. Results and discussion

The citric acid added acts as a complexing agent. The mixture of citric acid and bismuth nitrate solution forms a gel on heating on a water bath which decomposes at higher temperatures >423 K. During calcinations process, a black fluffy mass (foam–like) is formed which occupies large volumes of the furnace. As the temperature increases, the black mass turns to white in colour with the removal of carbon. Samples calcined at 773 K for 20 min shows less than 1% of carbon. At higher temperatures of calcination no carbon was found to present (found by microanalysis technique).

Fig. 1 shows the XRD for the samples heated at 873 K and peaks can be indexed based on orthorhombic unit cell of $ZrTiO_4$ ceramics. However, there is small shift in d-lines corresponding to Sn substitution in the lattice. No impurity lines were observed. The orthorhombic unit cell parameters calculated by least aquare method for this sample are $a = 4.807$ Å, $b = 5.035$ Å and $c = 5.463$ Å. The ionic radius of Sn^{4+} being less than the Zr^{4+}, the unit cell parameters decreased with stannate substitution. Sn substitution is known [4] to inhibit the Zr–Ti ordering transformation that $ZrTiO_4$ undergoes at temperatures below 1573 K. It is also stated [4] that the role of Sn is to stabilize the interface between Zr rich and Ti-rich domains, which form during the cation ordering transformation. In the case of samples prepared by ceramic technique, the phase was formed only at 1373 K after prolonged heating. The surface area of calcined powders is found to be 80 m^2/g. The average particle size is found to be 50 nm as illustrated in TEM photograph (Fig. 2) taken for the powder sample. The particles are found to be spherical in shape. The crystallite size measurements were also carried out using the Scherrer equation, $D = k\,\lambda/\beta\cos\theta$ where D is the crystallite size, k is a constant (=0.9 assuming that the particles are spherical), λ is the wavelength of the X-ray radiation, β is the line width (obtained after correction for the instrumental broadening) and θ is the angle of diffraction. The average particle size obtained from XRD data is 80 nm.

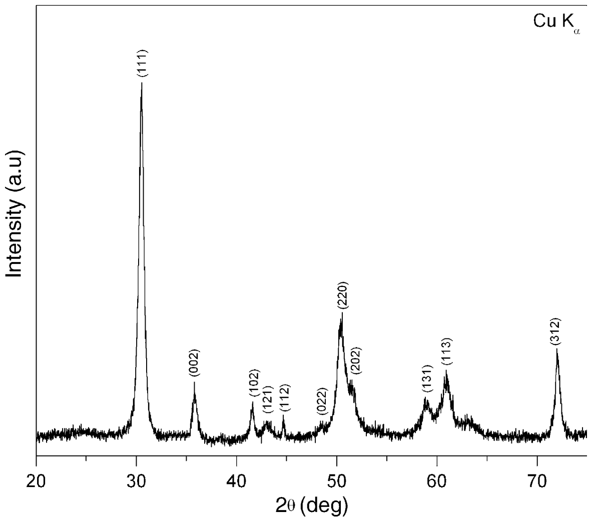

Fig. 1. The XRD of $Sn_{0.2}Zr_{0.8}TiO_4$ powder clacined at 873 K.

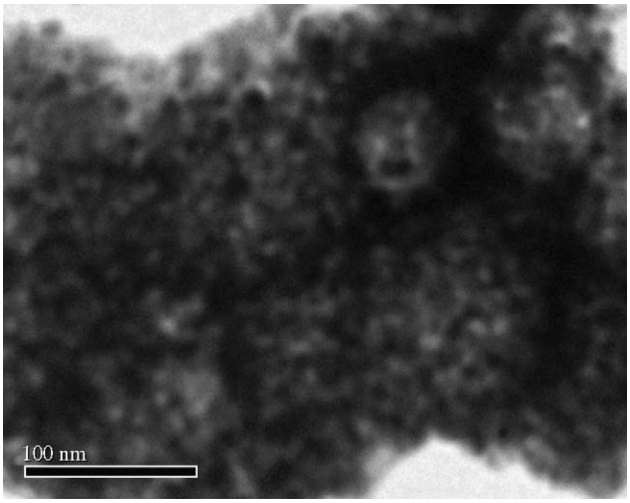

Fig. 2. TEM picture of $Sn_{0.2}Zr_{0.8}TiO_4$ powder clacined at 873 K.

4. Conclusion

A simple citrate gel process was elucidated to prepare microwave dielectric $Sn_{0.2}Zr_{0.8}TiO_4$ at 873 K. The average particle size of these powders was found to be 50 nm.

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