Sonochemical preparation and refinement of ultra-fine powders of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$

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Abstract

Perovskite structure based ceramic have a characteristic property of substitution in the “A” site of the ABO$_3$ structure. Sonochemical synthesis of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ has been carried out by ultrasound irradiation and then followed by heat treated of 800 °C for two hours. The resulted powders have been characterized by its powder diffraction pattern. X-ray data has been indexed and refined using RIETICA software. The h, k, l values for different lattice planes have been generated from the experimental data. The calcium substituted perovskite crystallizes in orthorhombic symmetry with space group Bmmb (63). The calculated and observed values of corresponding intensities, 2, were shown a good agreement ($R_p$ and $R_w$ less than 7%). The obtained unit cell parameters have been calculated as $a=7.591(9)$, $b=7.690(5)$, and $c=7.735(6)$. This research was showed that sonochemical process was became the potential method of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ preparation.

Keywords: Perovskite, Ca$_{0.5}$Sr$_{0.5}$TiO$_3$, x-ray data

Introduction

Perovskite form of Ca-substituted SrTiO$_3$ solid solution were also have attracted interest for diversity of structural state and phase transition which they display in responses to changing temperature and composition (Carpenter, 2007).

Perovskite-type compounds had synthesized by solid state reactions and it giving the polycrystalline form of samples. The starting materials are then usually simple binary oxides or pure elements reacted at relatively high temperatures. This synthesis technique involves problems due to the fact that certain starting oxides (e.g. PbO) may vaporize (Feofilov et al., 2007). Hydrothermal synthesis techniques have been applied to manufacture nanopowders perovskite. Powders and thin films with controlled levels of dopants have been prepared with the Sol-Gel technique using metal alkoxides as precursors (Hreniack et al., 2004). Thin films of ferroelectric materials have been successfully prepared by physical vapor deposition (Takeuchi et al., 2003).

Recently, sonochemical method has been employing in order synthesis novel material. It is very simple technique and can be used to prepared oxide materials in very low temperature. The other fact is is that the product of reaction generated with ultrasonic wave could be obtained in the form of amorphous nanoparticles (J. C. Yu et al., 2003 and C. Kurniawan, 2008).

While the solution are irradiated by ultrasonic wave, there were the creation, growth and collapse of a bubble that formed in the liquid. The implosion of the bubbles could raise local temperature up to 5000K and with cooling rate of $10^{11}$ K/s. This phenomenon leads to the chemical bond breaking of the reactants and the formation of amorphous particles (Suslick, 1999).

The structure of perovskite-type compounds having crystal structures that related to the mineral perovskite CaTiO$_3$. In the ideal form the crystal structure of cubic ABX$_3$ perovskite can be described as consisting of corner sharing [BX$_6$] octahedra with the A cation occupying the 12-fold coordination site formed in the middle of the cube of eight such octahedra. The ideal cubic perovskite structure is not very common and also the mineral perovskite itself is slightly distorted. The perovskite family of oxides is probably the best studied family of oxides. The interest in compounds belonging to this family of crystal structures arise in the large and ever surprising variety of properties exhibited and the flexibility to accommodate almost all of the elements in the periodic system. Pioneering structural work on perovskites were conducted by Goldschmidt et al in the 1920’s that formed the basis for further exploration of the perovskite family of compounds. Distorted perovskites have reduced symmetry, which is important for their magnetic and electric properties. Due to these properties, perovskites have great industrial importance, especially SrTiO$_3$ (C. Kurniawan, 2008).

The idealized cubic structure is realized in SrTiO$_3$. The latter can be described as Sr$^{2+}$ and O$^{2-}$ ions forming a cubic close packed lattice with Ti$^{4+}$ ions occupying the octahedral holes created by the
oxygen. The perovskite structure has a three dimensional net of corner sharing [TiO$_3$] octahedra with Sr$^{2+}$ ions in the twelve fold cavities in between the polyhedral.

The objective of the present study was to explore the sonochemical method on preparation of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ and its lattice parameter determination by the method Le Bail refinement of X-Ray diffraction pattern.

Materials and Methods

The samples of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ were prepared as follow. In a conical flask, 0.015 mol Sr(OH)$_2$, and 0.015 mol Ca(OH)$_2$ were diluted on aquaDM and then were added into ethanolic solution of 0.030 mol titanium isoproxipoxide (TiIPP). The solution then were irradiated with ultrasonic wave produced by ultrasonic cleaning bath (Branson, Model 2210) for 2 h. The ratio of water and etanol was 1:1 of total volume 60 mL. The white precipitates were filtrated and washed with 0.1M HOAc followed with etanol thoroughly. The powders were dried in an oven at 100 °C.

Ultrasound sound wave radiation was used to initiate the reaction of precursor to obtained Ca$_{0.5}$Sr$_{0.5}$TiO$_3$. At the time of mixing Sr(OH)$_2$ and Ca(OH)$_2$ with water, the container became hot. This showed that dissolving process was releasing a heat (exo)thermic. The small solubility in water (about 2.25 gram/100 gram water) were caused the targeted product indistinguishable from its precursors. During the sonication, the solution was stirred up by the wave resulted from the vibrated transducer (47 kHz) and the temperature of water bath was increased about 5–8 °C.”}

The X-ray diffraction (XRD) patterns were collected using X-Pert PANalytical PW3373 diffractometer (Cu Kα radiation equipped with accelerator). The resulting pattern then were refined by using Rietica177 to obtained the compatibility of space group and its cell parameter. The temperature in the lab, where the experiments were performed was at around 29 °C with minimum humidity of 95 %.

Results and Discussion

Results from the powder X-ray diffraction measurement on the Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ heated at 100 and 800 °C are shown in Figure 1.

From the Figure 1 we could see the existence of the quite striking difference. The sample that only was treated with sonochemical and then was heated in the temperature of 100 °C, it did not have the peak of perovskite that emerged. This was significant that the product that prepared only by using sonochemical was still having amorphous form of perovskite and TiO$_2$ phase. The presence of TiO$_2$ is reasonable since TiIPP undergo the hydrolysis faster than other precursor at the lower value of pH.

As it superheated of 800 °C for two hours, the X-ray diffraction pattern of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ was shown that the intensity of TiO$_2$ peak is very small. Definitely, it proved that the sonochemical method which followed by heat treatment was effective to reduce the reaction time of the preparation of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$.

The other impurity is CaO, as it resulted from the untreated Ca(OH)$_2$ which has lower solubility on water.

The estimated crystallite size of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ by using Debye-Scherrer formula:

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

where d is particle size, θ is diffraction angle, λ is the X-ray wavelength and B is the full width at half maximum (FWHM) of the respected peak. The calculated crystallite sizes of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ is shown in Table 1. It can be seen that the crystallite sizes of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ ranged from 20 to 35 nm with the average sizes 27.60 nm.

Table 1 Crystallite size (D) calculated by using Debye-Scherrer formula.

<table>
<thead>
<tr>
<th>Peak no.</th>
<th>hkl*</th>
<th>2θ</th>
<th>FWHM</th>
<th>D (nm)</th>
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<tr>
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<td>68.68</td>
<td>0.4896</td>
<td>19.64</td>
</tr>
</tbody>
</table>

*indexed as it had a good agreement with SG Bmmb and Z=8.

The SEM images of ultra-fine powder of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ that were sonochemically prepared and annealed at 800 °C is shown in Figure 2. The particles tend to form aggregates with homogenous diameters.
Those images were shown the undisstinguished morphology of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ and its precursors. This might be consistent with the crystallite size data obtained from the XRD measurement. Since the average particle size does not change so much, it will give relatively same morphology of the grains.

The calculated and observed values of corresponding intensities, 20, show a good agreement with space group Bmmb (#63) with Z=8. The final weighted $R_p$ and $R_w$ factors were found less than 7%, respectively, which confirm that the refinement is acceptable (Clegg, 1998).

When temperature increased, crystal structure of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ changes from orthorhombic to tetragonal (I4/mcm) at around 300 °C and then to cubic phase (Pm3m) at around 650 °C (C.J. Ball et al, 1998). It is possible that after heated at 800 °C, Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ particles did not change into the orthorhombic structure, instead it becomes stable with the cubic structure at room temperature.

Conclusions

Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ ultra-fine powders have been prepared by sonochemical method. The Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ then were heated at temperatures 100 °C and 800 °C for about 2 h in order to study the effect of heat treatment to the Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ particles. Crystallite size tends had a good uniformity as heating temperature increased. The lattice parameter values are suggested that perovskite Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ are in orthorhombic phase with space group Bmmb.

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References


