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The Effect of Milling Times and Annealing on Synthesis of Strontium Titanate Ceramics

Rahmat Doni Widodo* — Mechanical Engineering Dept., Semarang State University
Azwar Manaf — Physics Dept, University of Indonesia
Viktor Vekky R.R. — Physical Engineering Dept., Nasional University
Dony Hidayat Al-Janan — Mechanical Engineering Dept., Semarang State University

Abstract— ***Analysis of microstructure of Strontium titanate ($SrTiO_3$) phase obtained by milling and annealing of $SrCO_3$ and TiO_2 precursors. However, the material properties for strontium titanate require a careful control of crystallite structure as well as microstructure design to meet a specific application. The mixture of strontium carbonate ($SrCO_3$) and tintanium oxide (TiO_2) powders was used to obtain $SrTiO_3$ phase by using vibrator ball mill with ball to powder ratio 10:1 and heat treatment processes. The size of powder particles was determined by a laser particle analyzer (PSA). The X-ray diffraction methods were used for qualitative, quantitative phase analyses and for crystallite size and lattice distortion determination. The milling process of strontium carbonate and tintanium oxide mixture causes decrease of the mean particle size and crystallite size of involved phases. The X-ray diffraction investigations of $SrCO_3$ and TiO_2 mixture milled for 60 hours and annealed at 900°C with 24 h of holding time enabled the identification of $SrTiO_3$ phase. Annealing the sample of the particles at 900 ^{0}C has resulted in a dense compact and promoted the formation of particles containing nanocrystallites. The crystallite-growth samples of $SrTiO_3$ phase were dependent on temperature and time of their annealing.***

Keywords— particle size, crystallite size, strontium titanate, mechanical milling, annealing

I. INTRODUCTION

Alkaline earth metal titanates are becoming increasingly important in the ceramic and electronic industries where, in particular, $BaTiO_3$ and $SrTiO_3$ are widely employed. Strontium titanate ($SrTiO_3$) is a paraelectric cubic structured perovskite material at room temperature. It exhibits a large dielectric constant of ~300 of the sintered ceramics. At temperatures <105 K, its cubic structure transforms to tetragonal ferroelectric phase. Furthermore, $SrTiO_3$ (STO) has various physical properties because of its ferroelectricity, thermoelectricity with a thermal conductivity of 12 $Wm^{-1}K^{-1}$, photocatalysis and superconductivity at temperatures <20 K [1].

Piezoelectric response has been presented on STO, which exhibits a rapidly increasing piezoelectric response with decreasing temperature below 50 Kelvin; the magnitude of its response around 1 Kelvin is comparable to that of the best materials at room temperature [2]. In addition, it has good mechanical strength with the Mohs hardness of 5.5, high thermal and chemical stability, low dielectric loss, a low coefficient of thermal expansion of $9.4 x 10^{-6}$ °C^{-1}, a high melting temperature of 2080°C, a refractive index of 2.31–2.38 nearly identical to that of the diamond and semiconductor with a band gap of y3.2 eV [3,4]. STO has been applied in radio and microwave-frequency tunable capasitor device, metal-insulator-metal (MIM) capasitors [5], and dynamic random access memories (DRAMs)[6].

There were many synthesis methods applied to STO including conventional mixture oxides [7], microwave synthesis [8], mechanochemical [9], coprecipitation [10], and sol–gel [11]. The microstructure and the processing for each are quite different. The convenient method for the production of fine and nanocrystalline materials is mechanical milling by a ball-milling technique which has also being adapted to the preparation of strontium titanate. The technique is considered simple and less costly able to produce powders which compose of very fine particles in the range of single-domain particles (~1 μm) [12,13]. In solid-state synthesis, a single phase SrTiO3 could be obtained only after calcination of the reaction mixture at high temperature (1000–1200°C)[14].

In this work, we report some results of materials characterization especially particle and grain sizes which were promoted during mechanical milling and annealing of a $SrTiO_3$ ceramics. Discussion are including results of mean particle size characterization by a Laser Particle Size Analyzer and mean crystallite size determination by means of line broadening analysis employing a step scanning counting in the X-ray diffraction (XRD) apparatus.

II. EXPERIMENT METHOD

$SrTiO_3$ (coded STO) were obtained from the mixture of strontium carbonate $SrCO_3$ and tintanium (IV) oxide TiO_2 powders, by using high-energy ball milling and heat treatment processes. Stoichiometric quantities of the analytical-graded precursors $SrCO_3$ and TiO_2 with purity better than 98 % were mixed and milled in a vibratory ball mill up to 60 hours. The weight ratio of balls to milled material was 1:10. After milling process the diameter sizes of examined powder particles were determined using Particle Size Analyzer (PSA) Coulter LS100. Phase analysis and crystallite size of milled powders were carried out using the X-ray Philips diffractometer equipped with Co $K\ \alpha$ radiation. The X-ray diffraction patterns were recorded by "step-scanning" method in 2θ range from 20° to 100° and 0.005° step.

The powders were annealed in the electric chamber furnace (Thermolyne 46100C) at 550, 750, and 900°C in the air under atmosphere pressure up to 24 hours. The Rietveld analysis was performed applying High Score Plus program that is an update version for Rietveld refinement with PC and mainframe computers. The pseudo-Voigt function was used in the describing of diffraction line profiles at Rietveld refinement. The crystallite sizes and lattice distortions for $SrCO_3$ and TiO_2 also $SrTiO_3$ phases were estimated using Williamson-Hall method [15]

III. RESULT AND DISCUSSION

The diffraction patterns of $SrCO_3$ and TiO_2 precursors (Fig.1) which these were matched diffraction patterns of $SrCO_3$ and TiO_2 in *data base Inorganic Crystal Structure Database* (ICSD) number 98-016-6088 dan 98-007-6177 respectively.

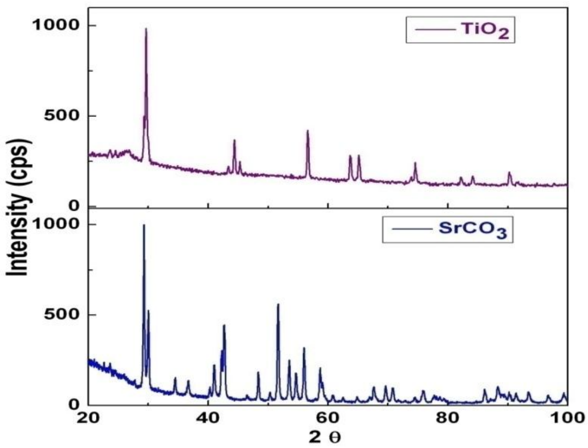

Fig.1. X-ray diffraction patterns of $SrCO_3$ and TiO_2 precursors

Fig.2 are showing results of evaluation for mean particle size of $SrCO_3$ and TiO_2 mixture up to 60 hours of milling. All the sample powders go through the four stages of the mechanical alloying process, namely: (a) initial stage; (b) intermediate stage;(c) final stage; (d) completion stage [16]. It shows that mean particle sizes of mechanically milled for $SrCO_3$ and TiO_2 mixture in initial or early stages of milling are characterized by the increase in the mean size due to incorporation of particles of component compounds. The largest mean particle size were achieved after 10 hours milling times. However, the mean particle size of $SrCO_3$ and TiO_2 mixture is ~16 μm. Extention of milling time beyond 10 hours have decreased progressively the mean size towards a settle value. Long terms of mechanical treatment during advanced stages of mechanical alloying have caused particles experiencing embitterment due to accumulation of internal stresses [17]. Continuous plastic deformations to the brittle particles should caused further reduction in particle size towards an average value of ~ 2 μm and eventually settle down to that value even if the deformation continues to grow after the duration of 60 hours milling time at completion stage.

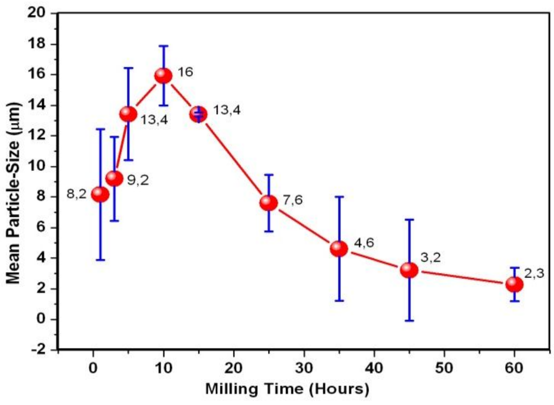

Fig.2. the mean particle size of $SrCO_3$ and TiO_2 mixture as function of milling time

In Fig.3, the comparison of diffraction patterns of $SrCO_3$ and TiO_2 mixture after 5, 15, 35 and 60 hours of milling process is shown. Identification of the diffraction peaks ensured that the all peaks are matched with that of $SrCO_3$ and TiO_2 phase. In addition, in Fig.3. shows the broadening of diffraction lines and decrease of their intensity. These effects indicate that ball milling causes decrease of the crystallite size of tested phases and leads to homogenizing the milled mixture.

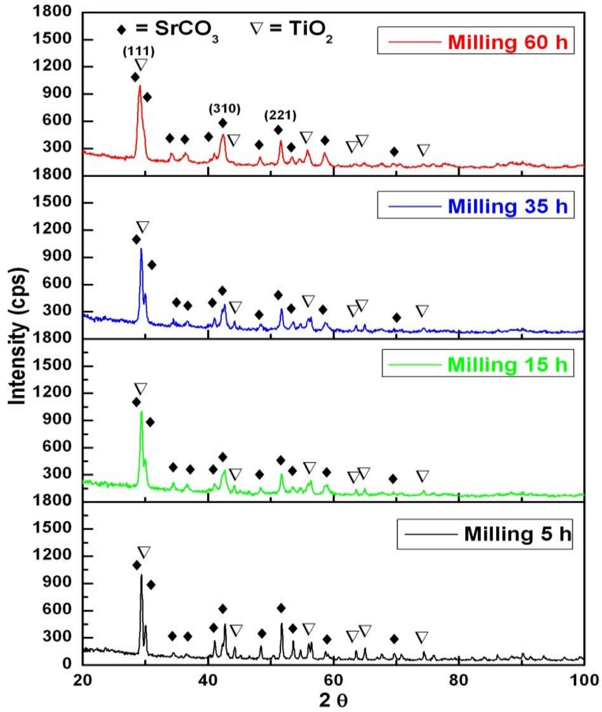

Fig.3. X-ray diffraction patterns of $SrCO_3$ and TiO_2 mixture up to 60 hours of milling

In Fig.4, as the result of milling process the mean crystallite size of $SrCO_3$ and TiO_2 phases diminishes to 17 nm and 19 nm, respectively of the milling time up to 60 hours.

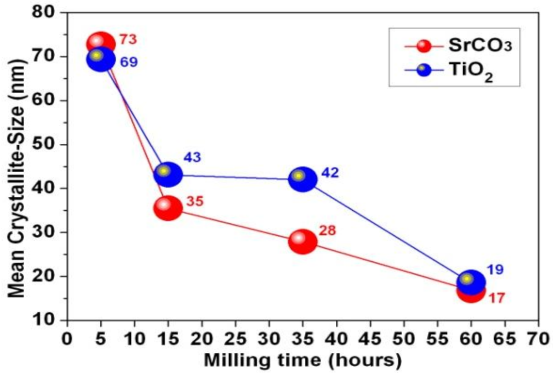

Fig.4. The mean crystallite size of $SrCO_3$ and TiO_2 mixture up to 60 hours of milling

The X-ray diffraction investigations of $SrCO_3$ + TiO_2 powder mixture milled for 60 hours and after different temperature and times of annealing treatment up to 900°C (Fig.5). The sample was crystallized to cubic strontium titanate single phase after annealing at 900◦C for twenty four hours in air.

The lattice constant calculated from the XRD data is 3.906Å that agrees with the reported XRD data in Inorganic Crystal Structure Database (ICSD) number 98-002-3076 with shaped cubic perovskite crystal structure for $SrTiO_3$. To know for sure, temperature and time of the most optimum is achieved in the transformation process into a single phase STO phase in full, then it should be tested thermal analysis. The intensity and sharpness of the X-ray diffraction (XRD) peaks of STO phase were found to increase with annealing temperature at 900 °C up to 24 hours. The increase in intensity and sharpness of the XRD peaks with annealing temperature may be attributed to the increase in the grain or crystallite size thereby increasing packing density of the samples annealed at higher temperature.

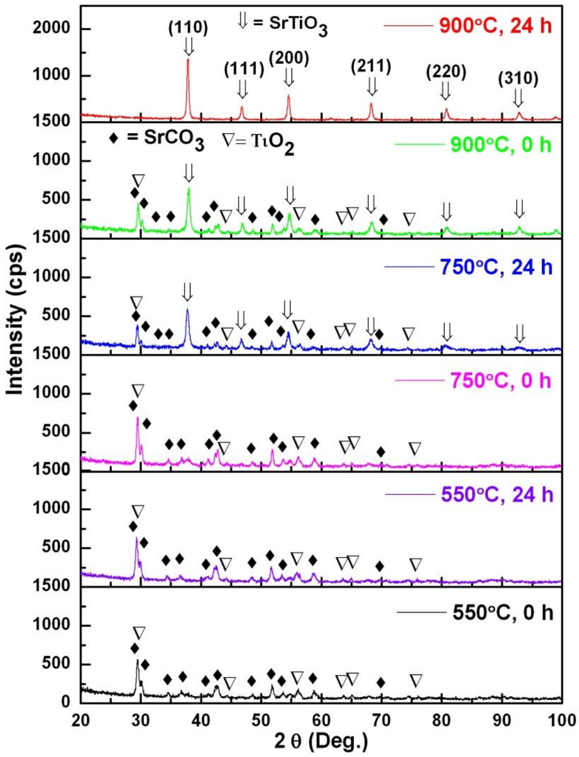

Fig.5. X-ray diffraction profile of $SrCO_3$ and TiO_2 mixture after annealing up to 900°C.

IV. Conclusions

The investigations performed on the $SrCO_3$ and TiO_2 mixture after milling and heat treatment allowed to formulate the following statements:

- High-energy milling of studied of $SrCO_3$ + TiO_2 powder mixture milled for 60 hours results in the decrease mean particle size to ~ 2 μm and crystallite size to 17 nm and 19 nm, respectively.
- Heating of the particles results in the mechanical integration of the sintering temperature of 900 °C promote the formation of crystallites with nanometer-scale size and material make the integration of mechanical and sintering the material with a particle containing nanocrystallite.
- $SrTiO_3$ ceramic has been prepared by mechanical alloying processing technique. The as fired powder was found to be amorphous and crystallized to cubic $SrTiO_3$ after annealing up to 900 °C for twenty hours. Dense ceramic samples were obtained by annealing at different temperatures and holding times.

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