

Solid State Synthesis of Barium Strontium Titanate at 850°C from mechanically activated BaCO₃-SrCO₃-TiO₂ mixture.

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Abstract

The influence of mechanical activation on the solid state reaction to synthesis Ba_{0.70}Sr_{0.30}TiO₃ was studied. Thermal analysis of the raw materials and the activated BaCO₃-SrCO₃-TiO₂ mixture was carried out. Phase analysis of the activated BaCO₃-SrCO₃-TiO₂ mixtures as a function of calcination temperature was studied. The mechanical activation did not induce any chemical reaction among the raw material prior to calcination, but it has an enormous effect in reducing the calcination temperature, hence accelerated the formation of Ba_{0.70}Sr_{0.30}TiO₃. Thermal analysis showed the decomposition process of the activated mixture started at temperature as low as 600-700°C as compared to 900-1000°C for the raw materials. In calcination process, single phase Ba_{0.70}Sr_{0.30}TiO₃ had been successfully synthesized at 850°C, which was 200-300°C lower than the conventional solid state reaction.

1. Introduction

Ba_{1-x}Sr_xTiO₃ or barium strontium titanate is a piezoelectric ceramic that has numerous important applications in electronic devices. The unique properties such as high dielectric constant, low dissipation factor, low leakage current and composition dependent Curie temperature has positioned Ba_{1-x}Sr_xTiO₃ as a technological demanding and commercially important material. Ba_{1-x}Sr_xTiO₃ is widely used as capacitor, positive temperature coefficient (PTC), stress sensor and integrated capacitor in dynamic random access memory (DRAM). By these reasons, the synthesis and processing of Ba_{1-x}Sr_xTiO₃ to improve the performance and processability is the key scientific interest among scientists and researchers.

The conventional method of synthesizing Ba_{1-x}Sr_xTiO₃ involved mixing the raw materials, namely BaCO₃, SrCO₃ and TiO₂ in desired stoichiometrical ratio, followed by high temperature solid state reaction or calcination to form single phase Ba_{1-x}Sr_xTiO₃, the temperature required can easily exceeded 1000°C. Although this method is simple and straight forward, it often contributed to compositional inhomogeneous and particle coarsening effect [1]. The high energy consumption to synthesis Ba_{1-x}Sr_xTiO₃ at elevated temperature made this method less cost-effective as well.

Co-existent of different phases was expected if lower calcination temperature applied [2]. Indeed for the mentioned limitations of conventional solid state reaction, these raw materials have to be effectively processed to produce highly homogeneous mixture in term of composition and particle size [3]. Hence, intimate mixing of the raw materials is of vital importance.

Several chemistry based synthesis method have been successfully developed to produce Ba_{1-x}Sr_xTiO₃ powder. Sol-gel and co-precipitation techniques were among the common methods used, however heat treatment ranging from 700-900°C on the precursor leading to the formation of Ba_{1-x}Sr_xTiO₃ remained necessary [4-6]. Furthermore, these methods often involved multiple-step processing, costly inorganic or organometallic raw materials [7], special care in handling and disposing the chemicals was necessary. Comparing to solid state reaction synthesis, chemistry based method always associate with high manufacturing cost, low production yield, complicated processing flow and environmental unfriendly, which was unsuitable for large scale production.

The term of 'mechanical activation' is used to describe those processes which were affected by mechanical energy and which increased chemical reactivity of the system without modifying or changing its chemical composition [8]. The concept of mechanical activation was adopted from mechanical alloying process which was developed to produce oxide dispersion strengthened (ODS) alloy and nanocrystalline materials. The intrinsic advantage of mechanical activation process is that solid state reaction is activated due to mechanical energy that lead to the improvement of chemical reactivity of the raw materials, hence reduced the calcination temperature [9]. Synthesis of electroceramics such as CaTiO₃, SrTiO₃ and BaTiO₃ by mechanical activation method had been made possible by researchers [10-12]. The relative ease of producing cost effective mechanical activation-derived electroceramics with good homogeneity will be the key driving force in propelling this technique.

In this work, preparation of Ba_{0.70}Sr_{0.30}TiO₃ powder from mixture of BaCO₃-SrCO₃-TiO₂ which undergoes mechanical activation and calcination process was reported.

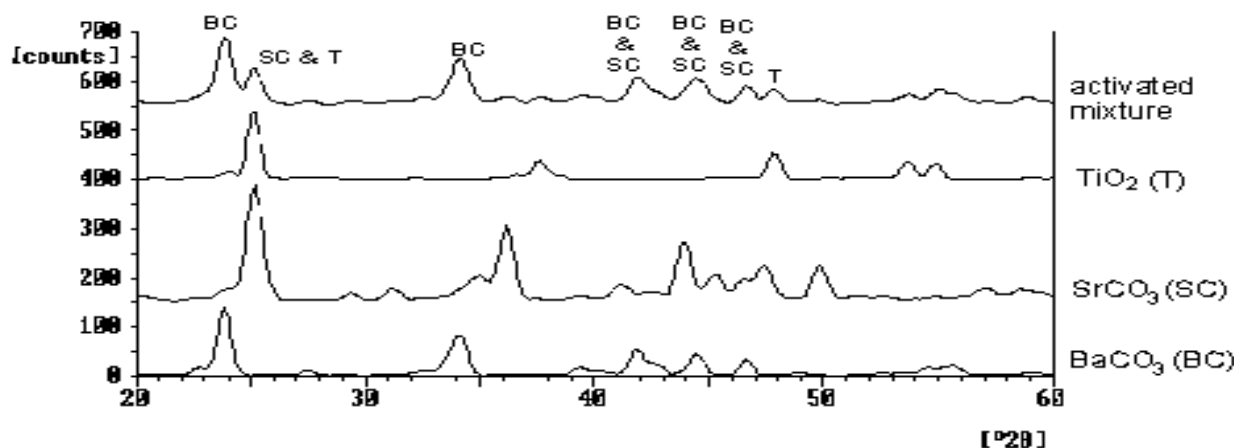


Fig. 1: XRD pattern of BaCO_3 , SrCO_3 , TiO_2 and activated BaCO_3 - SrCO_3 - TiO_2 mixture

2. Experimental

Commercially available BaCO_3 (99+% purity, Merck), SrCO_3 (99+% purity, Merck) and TiO_2 (99+% purity, Merck) powder were used as the raw materials. The chemicals were weighed, corresponding to the stoichiometrical composition of $\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$. The mechanical activation operation was carried out using Retsch RM100 autogenous mortar grinder system. The milling medium was made of sintered corundum. The BaCO_3 - SrCO_3 - TiO_2 mixture was activated for 60 mins. Thermal-gravimetry or TG analysis (model: Linseis) was performed on the inactivated raw materials of BaCO_3 and SrCO_3 as well as the activated BaCO_3 - SrCO_3 - TiO_2 mixture. The heating rate was set at $10^\circ\text{C}/\text{min}$ from room temperature to 1200°C . The particle morphology of the raw materials and the activated mixture were examined by transmission electron microscope, TEM (CM12, Phillips). The activated mixtures were calcined at temperature ranging from 750 - 900°C (step of 50°C) for 3 hours in air. X-ray diffraction (XRD) analysis was performed (Cu- $K\alpha$, PW1710, Phillips) on the raw materials, activated mixture and calcined activated mixture.

3. Results and discussion

The XRD patterns of respective raw materials and the activated mixture were shown in Fig. 1. Each XRD patterns of the raw materials: BaCO_3 , SrCO_3 and TiO_2 , were clearly belong to witherite phase of BaCO_3 (JCPDS file no. 05-0378), strontianite phase of SrCO_3 (JCPDS file no. 05-0418) and anatase phase of TiO_2 (JCPDS file no. 21-1272). For the activated mixture, all the XRD peaks were attributed to BaCO_3 , SrCO_3 and TiO_2 . The most intense peak observed at 2θ of 23.835° was corresponded with BaCO_3 , agrees well with the mixture's composition where BaCO_3 contributed approximately 63% of the total weight of the mixture. The peak at 2θ of 25.175° was attributed to SrCO_3 and TiO_2 , the peaks overlap with each other as the 2θ angle were very close for both SrCO_3 and TiO_2 . The XRD pattern of the activated mixture indicated the existence of all the raw materials; no other phase was detected

since the mechanical activation process did not induce any chemical reaction to the mixture.

Fig. 2 showed the comparison of the most intense peak for the activated mixture and the inactivated BaCO_3 , the activated mixture has a broader peak compared to BaCO_3 . The peak broadening effect, which was known as Scherrer formula indicated that the milled mixture has a smaller crystallites size, which was in agreement with the function of mechanical activation in reducing the particle size [13].

The morphology of the raw materials and the activated mixture was shown in TEM micrograph in Fig. 3. The particles of BaCO_3 and SrCO_3 were elongated particles, with both particle size of about 1 - $2\ \mu\text{m}$. TiO_2 particles were highly agglomerated and appeared to be spherical with particle size about $100\ \text{nm}$, the smallest among the raw materials. The activated mixture in Fig. 3(d) appeared to be agglomerated as well, suspected to cause by the large surface area to volume ratio [14]; as the result of mechanical activation process. The particles size of the activated mixture was ranging from 50 - $400\ \text{nm}$, with a mixture of spherical and elongated particles. The large elongated particles of BaCO_3 and SrCO_3 observed in Fig. 3(a) and Fig. 3(b) was not detected after being activated for 60 mins; it agreed with the XRD pattern in Fig. 2 which proven the particle size reduction.

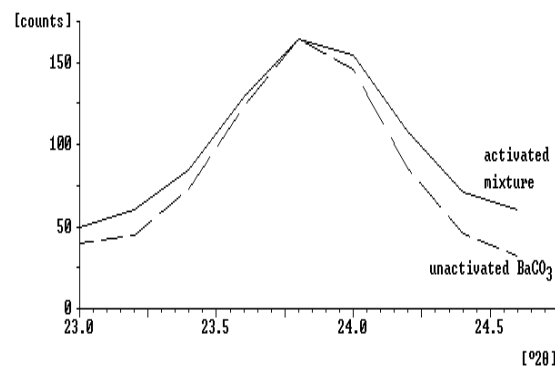


Fig. 2: Peak broadening effect of activated mixture compare to inactivated BaCO_3

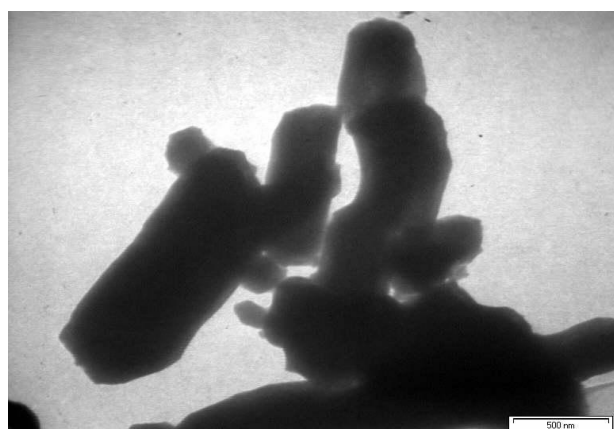
Fig. 4 showed the TG patterns of the inactivated BaCO_3 and SrCO_3 as well as the activated BaCO_3 - SrCO_3 - TiO_2 mixture. The TG curves were in the same scale but being shifted on the vertical axis for clarity of comparison. A massive weight loss was observed in all the samples but the weight loss process started at different range of temperature. The weight loss was due to the decomposition process which happened at an elevated temperature to produce oxides and CO_2 gas. As observed, the decomposition process for the activated mixture happen at a much lower temperature (in the region of 600 - 700°C) compared to the inactivated BaCO_3 and SrCO_3 (in the region of 900 - 1000°C). The decomposition process for the activated mixture completed at about 1050°C , however the weight loss of both BaCO_3 and SrCO_3 had not stabilized though the temperature reached 1200°C .

Clearly, mechanical activation had reduced the particle size of BaCO_3 - SrCO_3 - TiO_2 mixture thus creating larger surface area which increased the reactivity of the solid system. This enables decomposition process happens at a much lower temperature, in another word, accelerates the entire process to completion at a shorter duration.

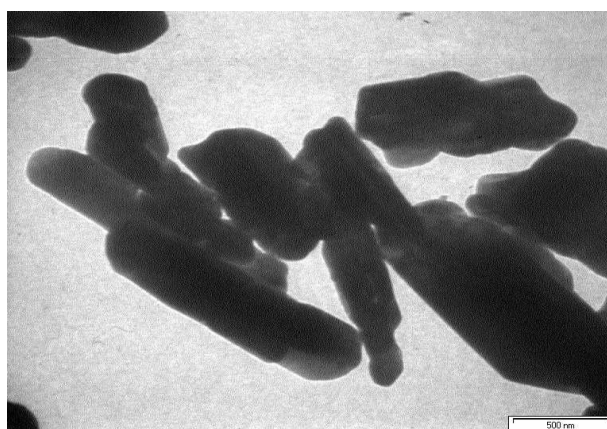
The TG curve of the activated mixture helps to establish the estimated calcination temperature. As

mentioned earlier, the TG was set to ramp at $10^\circ\text{C}/\text{min}$ without allowing any dwell time in between; however in normal condition, calcination was done at an elevated temperature and remained at that temperature for certain duration before cooling it down to room temperature. In the TG curve for activated mixture, it was observed that massive weight loss happened at 700 - 1000°C . In order to identify the thermal event in this region, several calcination processes (at 750°C , 800°C , 850°C and 900°C) were performed.

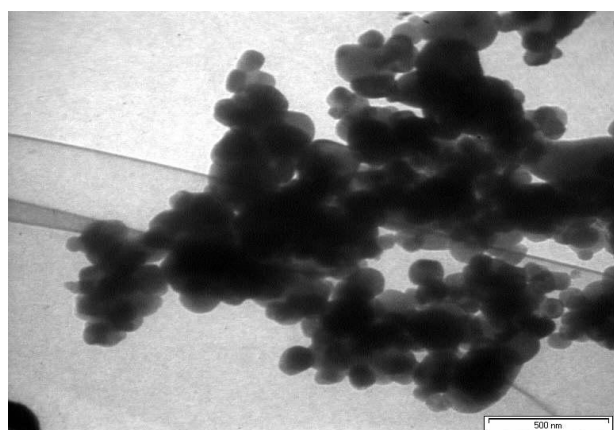
The XRD patterns of the activated mixture as a function of calcination temperature were shown in Fig. 5; the dwell time at each temperature was 3 hours. Comparing the XRD pattern of the uncalcined activated mixture to that of the sample calcined at 750°C , the intensity of major peaks for uncalcined activated mixture at 2θ of 23.835° and 25.175° which were corresponding to BaCO_3 , SrCO_3 and TiO_2 ; were significantly reduced as most of the carbonates were decomposed and reacted with TiO_2 to form $\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$. The appearance of the most intense peak at 2θ of 31.795° which were not seen in the uncalcined activated mixture was attributed to the formation of $\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$ phase. Based on the XRD phase analysis, at 750°C , co-existence of $\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$, BaCO_3 , SrCO_3 and TiO_2 were found.



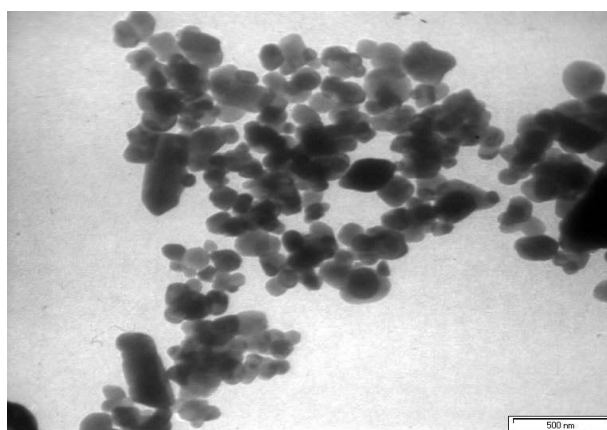
(a) BaCO_3



(b) SrCO_3



(c) TiO_2



(d) activated BaCO_3 - SrCO_3 - TiO_2 mixture

Fig. 3: TEM micrographs of the raw materials and BaCO_3 - SrCO_3 - TiO_2 activated mixture

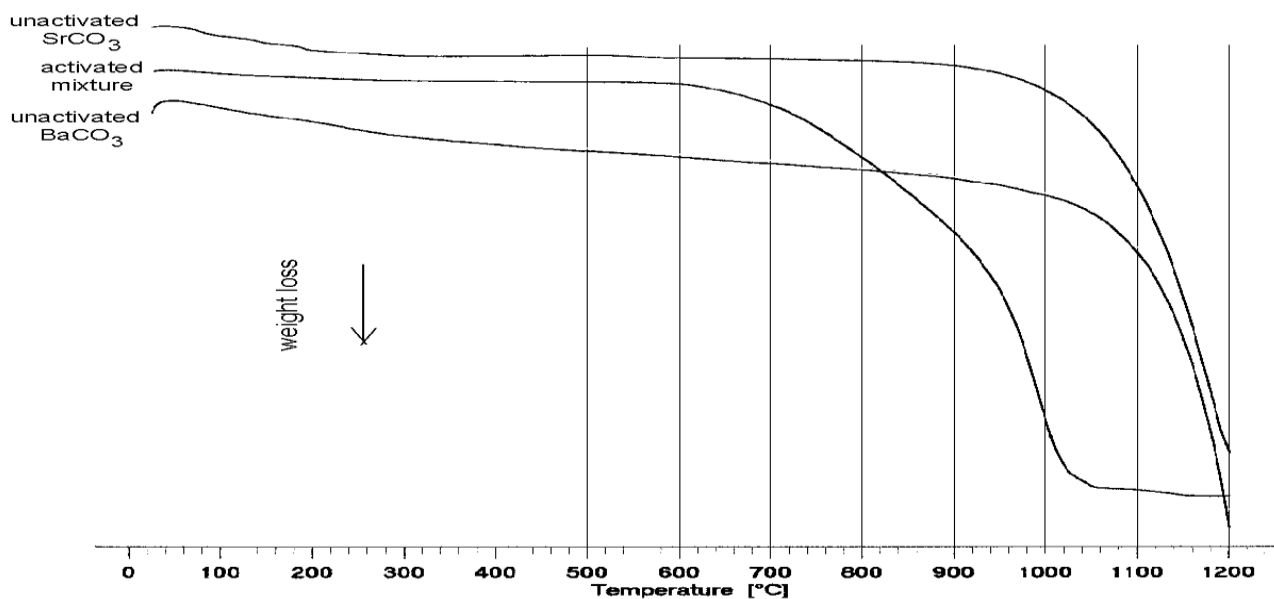


Fig. 4: TG curves of inactivated BaCO_3 and SrCO_3 compared to the activated mixture

For the activated mixture calcined at 800°C , the appearance of new peaks at 2θ of 22.100° and 51.180° show further evidence on the existence of $\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$ phase. The minor peak at 2θ of 23.995° was attributed to remnant BaCO_3 ; peaks which corresponded to SrCO_3 and TiO_2 phases were no longer detected. Further increase in calcination temperature to 850°C resulting the formation of single phase $\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$. No significance difference in the XRD pattern for the activated sample calcined at 900°C compared to 850°C .

The formation of single phase $\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$ at 850°C was significantly lower than those required by conventional solid state reactions which were normally set at $1050\text{--}1150^\circ\text{C}$ [15-16], and almost comparable with chemistry based methods that annealed at $700\text{--}800^\circ\text{C}$ [4-6]. However the processing flow employed by mechanical activation method was similar with conventional solid state reaction and much simpler as compared to the chemistry based methods. From the observation in Fig. 2 and Fig. 5, the low formation temperature for $\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$ was benefited from the refined powder as a result of the mechanical activation.

Fig. 6 showed the XRD patterns of the activated mixture and a control sample (only mixed using spatula) calcined at 850°C for 3 hours. All the peaks from the controlled sample could be easily attributed to the raw materials. However, at the same temperature, single phase $\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$ had been successfully synthesized from the mechanically activated mixture. The $\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$ synthesized was in cubic structure since tetragonal structures of barium strontium titanate will

show a split peaks at (200) plane. The formation of cubic structure was agreed well with those synthesized by either conventional solid state reaction [16] or chemistry based method [17] for the same composition. The cubic structure was contributed by the Sr^{2+} incorporation into the BaTiO_3 structure, where smaller ionic radius Sr^{2+} (1.16 nm) replaced larger ionic radius Ba^{2+} (1.36 nm) causing shrinkage to the unit cells. It is consistent with the fact that BaTiO_3 is in tetragonal structure and SrTiO_3 is in cubic structure at normal condition.

Although preparation of others electroceramics powder using mechanical activation processing has been reported, but the preparation of $\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$ via mechanical activation was limited. Based on literature studies on other electroceramics synthesized via mechanical activation, it was also possible to use other raw materials to synthesized $\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$, namely BaO-SrO-TiO_2 mixture and $\text{Ba(OH)}_2\text{-Sr(OH)}_2\text{-TiO}_2$ mixture by mechanochemical synthesis (without calcination process). However, both mixtures have to be prepared and activated for long hours in control atmosphere to prevent the formation of carbonates when the oxides were exposed to air.

Furthermore any formation of carbonate in the mixture will require heat treatment to preserve single phase $\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$. Prolonged mechanical activation could also lead to unnecessary contamination from the milling medium [18]. As for $\text{BaCO}_3\text{-SrCO}_3\text{-TiO}_2$ mixture, the carbonates were stable in air atmosphere, though calcination was required; but to author's opinion, it is the most feasible method in the point of processability.

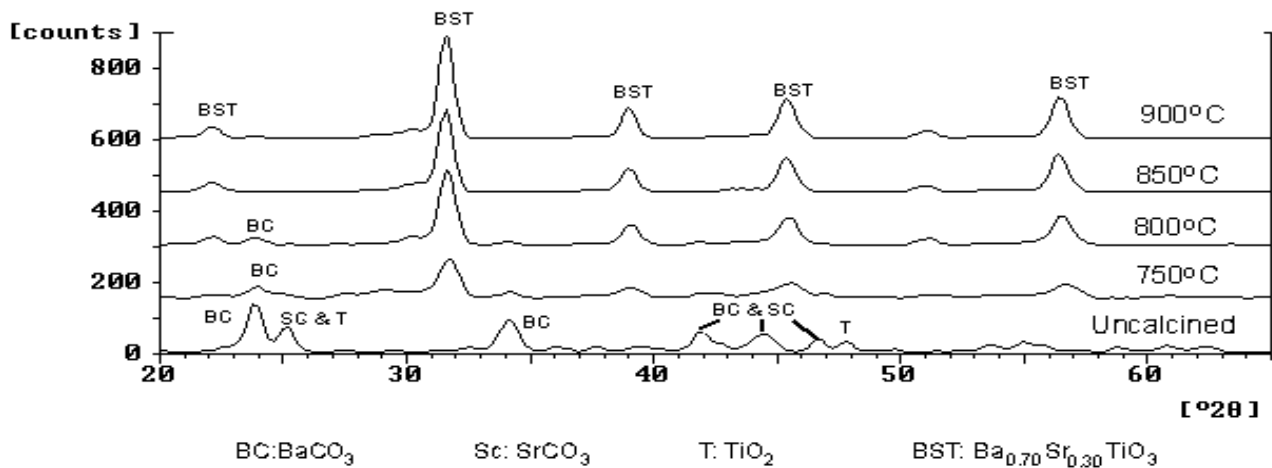


Fig. 5: XRD patterns of activated mixture calcined at 750°C to 900°C for 3 hours

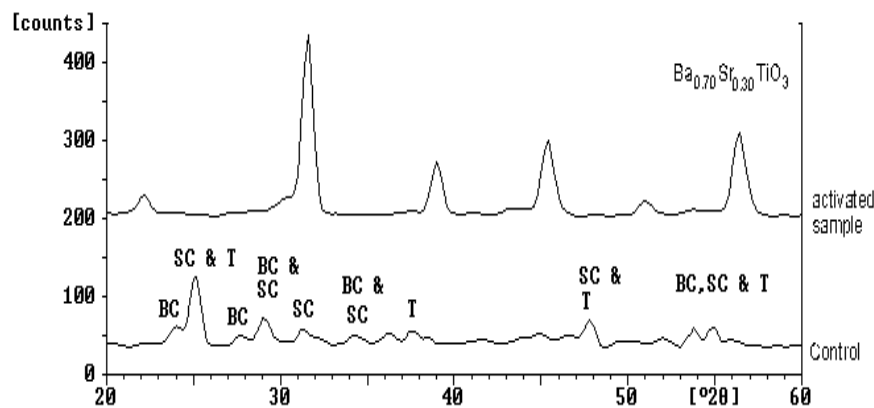


Fig. 6: XRD patterns of the activated mixture and control (mixed by using spatula) calcined at 850°C for 3 hours

4. Conclusion

Mechanical activation process has been successfully applied to the $\text{BaCO}_3\text{-SrCO}_3\text{-TiO}_2$ mixture in order to lower the calcination temperature for single phase $\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$ formation. Single phase $\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$ was successfully synthesized by calcining the activated mixture at temperature as low as 850°C, which was 200-300°C lower than conventional method and it was comparable to $\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$ synthesized by chemistry based methods. Besides shortening the overall calcination process, it was also beneficial in preventing particle coarsening due to high temperature processing.

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References

1. Maison, W., Kleeberg, R., Heimann, R.B. and Phanichphant, S., "Phase content, tetragonality, and crystallite size of nanoscaled barium strontium

titanate synthesized by catecholate process: effect of calcination temperature.", *J. Eur. Ceram. Soc.*, Vol. 23, (2003), 127-132.

2. Teoh, W.T., Ahmad Fauzi, M.N. and Zainal, A.A., "Formation of barium strontium titanate powder by solid state reaction using different calcination temperatures.", *Malaysian Journal of Science*, Vol. 21A, (2002), pp. 109-111.
3. Berbenni, V., Marini, A. & Bruni G., "Effect of mechanical milling on solid state formation of BaTiO_3 from $\text{BaCO}_3\text{-TiO}_2$ (rutile) mixtures.", *Thermochimica Acta.*, Vol. 374, (2001), pp. 151-158.
4. Kholam, Y.B., Bhoraskar, S.V., Deshpande, S.B., Potdar, H.S. and Pavaskar, N.R., "Simple chemical route for the quantitative precipitation of barium-strontium titanyl oxalate precursor leading to $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ powders.", *Mater. Lett.*, Vol. 4079, (2002), pp. 1-9.
5. Suasmoro, S., Pratapa, S., Hartanto, D., Setyoko, D. and Dani, U.M., "The characterization of mixed titanate $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ phase formation from oxalate

- coprecipitated precursor.”, *J. Eur. Ceram. Soc.*, Vol. 20, (2000), pp. 309-314.
6. Nayak, M., Lee, S.Y. and Tseng, T.Y., “Electrical and dielectric properties of $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ thin films prepared by a hydroxide-alkoxide precursor-based sol-gel Method.”, *Mater. Chem. & Phys.*, 77, (2002), pp. 34-42.
 7. Lee, S.E., Xue, J.M., Wan, D.M. & Wang, J., “Effects of mechanical activation on the sintering and dielectric properties of oxide-derived PZT.”, *Acta Mater.*, Vol. 47 No. 9, (1999), pp. 2633-2639.
 8. Juhasz, A.Z. and Opoczky, L., *Mechanical Activation of minerals by grinding-pulverizing and morphology of particles*, West Sussex, Ellis Horwood, 1990.
 9. Stojanovic, B.D., “Mechanochemical synthesis of ceramic powders with perovskite structure.”, *J. Mater. Proc. Tech.*, Vol. 143-144, (2003), pp. 78-81.
 10. Mi, G.M., Saito, F., Suzuki, S and Waseda, Y., “Formation of CaTiO_3 by grinding from mixtures of CaO or $\text{Ca}(\text{OH})_2$ with anatase or rutile at room temperature.”, *Powder Technol.*, Vol. 97, (1998), pp. 178-182.
 11. Berbenni, V., Merini, A. and Bruni, G., “Effect of mechanical activation on the preparation of SrTiO_3 and Sr_2TiO_4 ceramics from the solid state system $\text{SrCO}_3\text{-TiO}_2$.”, *J. Alloys and Compounds*, Vol. 329, (2001), pp.230-238.
 12. Brzozowski, E. and Castro, M.S., “Lowering the synthesis temperature of high purity BaTiO_3 powders by modifications in the processing conditions.”, *Thermochimica Acta*, Vol. 298, (2003), pp. 123-129.
 13. El-Eskandarany, E.S., *Mechanical Alloying for Fabrication of Advanced Engineering Materials*. New York, Noyes Publications, 2001.
 14. Lu, S.W., Lee, B.I., Wang, Z.L. and Samuels, W.D., “Hydrothermal synthesis and structural characterization of BaTiO_3 nanocrystals.”, *J. Cryst. Growth*, Vol. 219, (2000), pp. 269-276.
 15. Thakur, O.P., Prakash, C. & Agrawal, D.K., “Dielectric behavior of $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{TiO}_3$ ceramics sintered by microwave.”, *Mater. Sci. Eng.*, Vol. 96, No. 3, (2002), pp. 221-225.
 16. Su, B. & Button, T.W., “The processing and properties of Barium Strontium Titanate thick films for use in frequency agile microwave circuit applications.”, *J. Eur. Ceram. Soc.*, Vol. 21, (2001), pp. 2641-2645.
 17. Noh, T.Y., Kim, S.W. & Lee, C., “Chemical preparation of Barium-Strontium Titanate.”, *Bull. Korean Chem. Soc.*, Vol. 16, No. 2, (1995), pp. 1180-1184.
 18. Suryanarayana, C., “Mechanical alloying and milling”, *Prog. Mater. Sci.*, Vol. 46, (2001), pp. 1-184.