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Preparation of Parium Titanates With Different Particle Size Distribution Using Modified Pechini Method

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ABSTRACT

Barium titanates is one of the most important ceramics that are widely used in the electronic industry because of its high dielectric constant, its ferroelectricity, and its piezoelectric properties. In the current study, five different batches of barium titanate powders were prepared by modifiedpechini method using the barium chloride and the titanium chloride as a starting materials in order to obtain different particle size distributions.SEM, TGA, DTA, XRD, FTIR, and other techniques have been used to characterize the prepared samples.XRD results suggested that the synthesized $BaTiO_3$has a tetragonal phase.SEM images of the prepared samples reveala polyhedron shapes, on average, also it show that there are markedinfluence of the reactant concentration on the average size of the grains,where the samples prepared from higher solution concentration tend to possess larger grain size compared to that prepared from low concentration.

Keywords: Barium Titanate, pechini method.

الملخص

تعتبر مادة تيتانات الباريوم من المواد السيراميكية المهمة التي تستعمل بشكل واسع في الصناعات الالكترونية وذلك لما تمتلكه هذه المادة من ثابت عزل عالي وايضا بسبب خواصها الفيروكهربائيةو البيزوكهربائية.في هذه الدراسة، تم تحضير خمس خلطات مختلفة لنماذج من مادة تيتانات الباريوم بواسطة طريقة بيجيني المعدلة وباستخدام مادة كلوريد الباريوم ومادة كلوريد التيتانيوم كمواد اولية وذلك للحصول على توزيعات حبيبية مختلفة،استخدمت التقنيات الاتية SEM, TGA, DTA, XRD, FTIRلغرض وصف النماذج المحضرة. اظهرت نتائج XRD انتيتانات الباريوم المحضرة تمتلك الطور الرباعي. بينما اوضحت صور SEM ان النماذج المحضرة لتيتانات الباريوم تمتلك اشكال متعددة الاوجه في الغالب، وايضا هذه النتائج اوضحت بأن هنالك تأثير ملحوظ لتراكيز المواد المتفاعلة على معدل حجم الحبيبات. حيث ان العينات المحضرة من تراكيز عالية تمتلك حبيبات كبيرة مقارنة مع العينات المحضرة من تراكيز قليلة.

الكلمات المفتاحية:تيتاناتالباريوم، طريقة بيجيني.

INTRODUCTION

Barium titanate ($BaTiO_3$) is a member of a large group of the compounds which are called the perovskite family with a general formula (ABO_3) where A refers to a cation of low charge and higher radius in comparison with B sitewhich has inversely situation. It represents one of the important electronic ceramic components which isacquired practical interest for more than 60 years. This is because it has a good characteristics, like, its relatively simple crystal structure, because it can exhibits ferroelectric properties at room temperature ,and finally, it can be easily prepared as polycrystalline ceramic. The high dielectric constant of the barium titanate make it very attractive material to be used in capacitors. Moreover, it can be employed for other application such as, medical imaging, gas lighter, ultrasonic cleaning, underwater detection and others application.(Carter& Norton, 2013) (Vijatović *et al*., 2008) (Mark, 1969).

Barium titanatehas been prepared by several method such as solid-state reaction method, sol-gel rout, co-precipitation method, hydrothermal method, mechanochemical synthesis, pechini method and others.Among these, the modifiedpechini method is an attractive method because of its simplicity, high producibility, low processing temperature, high purity, and the possibility to hold the initial stoichiometry(Vijatović *et al.,* 2008).

In view of the above, the objective of this research is to synthesize barium titanate powder with different particle size distribution using barium chloride and titanium chloride as starting materials by modifiedpechini method.

EXPERIMENTAL DETAILS

$BaTiO_3$ powder was prepared by modified pechini method according to following steps: (100ml) barium chloride solution were prepared by dissolving the specify amount of $BaCl_2$ in (100ml) of distilled water, and then put on the magnetic stirring with an average speed of (1100) rpm for(30)minute. The desired volume of titanium chloride solution was added to the solution of $BaCl_2$ under continuous stirring for additional (30) minutes.A solution of (100ml) of oxalic acid is prepared by dissolving prepared weight of $C_2H_2O_4$ in (100ml) of distilled water.This solution is then placed on magnetic stirring for (30) minute with an average speed of (1100) rpm, it then added drop by drop into the mixed solution of $BaCl_2$ and $TiCl_3$ under continuous stirring to get nutty color precipitate of barium titanyl oxalate (BTO),according to the following reaction:

$BaCl_2.2H_2O+TiCl_3+2C_2H_2O_4+2H_2O+1/2O_2 \not{BaTiO}(C_2O_4)_2.4H_2O+4HCl+1/2Cl_2$.....(1).

The precipitate (BTO) is then filtered and washed several time with distilled water and then dried at temperature 80°C for 20 hours. Finally, the precipitate (BTO) was fired at (850°C) for (2) hours with heating rate of 3 °C/min to be thermally decomposed to yield a white powder of bariumtitanate. according to the equations below:

$BaTiO(C_2O_4)2.4H_2O \longrightarrow BaTiO(C_2O_4)2 + 4H_2O$…..... (2).

$2BaTiO(C_2O_4)2 \longrightarrow Ba_2Ti_2O_5(CO_3)(CO_2) + 2CO_2 + 4CO$….....…(3).

$Ba_2Ti_2O_5(CO_3)(CO_2) \longrightarrow Ba_2Ti_2O_5(CO_3) + CO_2$ ……..…(4).

$Ba_2Ti_2O_5(CO_3) \longrightarrow 2BaTiO_3 + CO_2$…….....….(5).

Five different batches with different concentrations of barium chloride and titanate chloride were prepared in order to achieve different particle sizes as shown in the **Table 1**:

Table.1 Concentrations of the precursor solutions.

Batch No.	Concentration of Titanium Chloride	Concentration of Barium Chloride
Batch.1	0.05	0.05
Batch.2	0.1	0.1
Batch.3	0.25	0.25
Batch.4	0.5	0.5
Batch.5	0.97	0.97

RESULT AND DISCUSSION

XRD RESULT

Fig.1 showsthe result of x-ray diffraction analysis of barium titanate powder calcined at 850°C with a heating rate of 3°C/min and soaking time of (2 hours). The calculated values of d-spacing and relative intensities obtained from this pattern are given in the **Table.2**. These values indicate that the observed pattern is in good agreement with (JCPDS) Card No.(5-626) for tetragonal BaTiO3**.**

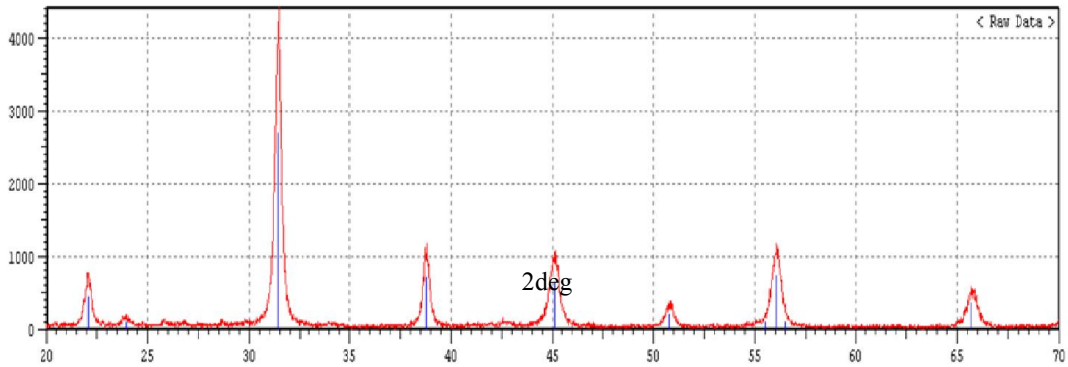


Fig.1. XRD pattern of barium titanate powder calcined at 850°C.

Table.2 XRD data of Barium titanate (BaTiO3).

2θ	*intensity*	*d-spacing*	*h k l*	*phases*
22.096	16	4.019	100	tetragonal
31.447	100	2.842	110	tetragonal
38.792	26	2.319	111	tetragonal
45.100	24	2.008	200	tetragonal
50.781	8	1.796	210	tetragonal
56.052	27	1.639	211	tetragonal
65.705	13	1.419	220	tetragonal

FTIR Result

Fig.2shows the FTIR spectrum of the prepared barium titanate powder calcined at 850 °C, the peak near 494 cm−1 characterizes the stretching vibration of Ti-O bond, it can be noticed that the CO^{-2}_3 group is characterized by absorption bands in the region 1428-1186-1118-855 cm–1.The peak at 1752 cm−1 was related to the C=O vibration modes, the small band at 2328 cm-1 was correspond to the asymmetric stretching mode of CO_2. The presence of the CO_3 group is probably due to the reaction of residual Ba^{2+} with CO^{2-} in the air (Garrido et. al., 2014).

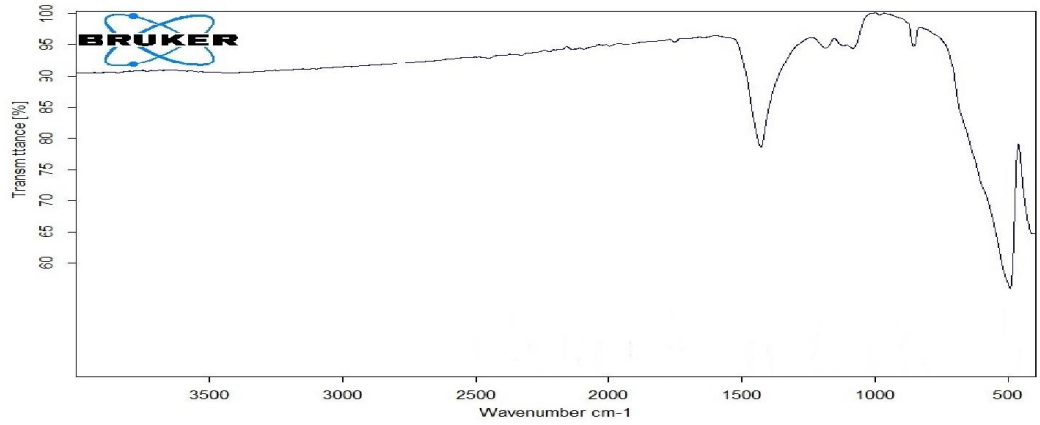


Fig.2.FTIR spectrum of barium titanate powder after calcination at 850°C.

DTA Result

Fig.3illustrates the differential thermal analysis result for a sample of barium titanate before calcination. It can be seen that there are four endothermic peaks in the DTA curve.The first endothermic peak is correspond to dehydration of barium titanyl oxalate (BTO) (loss of water) in the range of (106-178°C) which is represented by following equation:

$BaTiO(C_2O_4)_2.4H_2O \longrightarrow BaTiO(C_2O_4)_2 + 4H_2O$…….....(6)

The second peak involves the thermal decomposition of the dehydrated oxalate in the range of (295-373°C) leading to the formation of intermediate carbonate which occur in two steps according to equations (7) and (8):

$2BaTiO(C_2O_4)_2 \longrightarrow Ba_2Ti_2O_5(CO_3)(CO_2) + 2CO_2 + 4CO$…..…(7)

$Ba_2Ti_2O_5(CO_3)(CO_2) \longrightarrow Ba_2Ti_2O_5(CO_3) + CO_2$ ……..…….…(8)

the third peak indicats the result of the decomposition of the intermediate carbonate resulting in the formation of barium titanate in the range of (663-713°C) according to equation (9):

$Ba_2Ti_2O_5(CO_3) \longrightarrow 2BaTiO_3 + CO_2$…….....(9)

while the forth peak may be contributed to the decomposition of barium carbonate in the range of (773-787°C) which observed by FTIR analysis

$BaCO_3 \longrightarrow BaO+CO_2$.....(10)

These results are matching with that obtained by Callagher et al. who suggested a three-steps mechanism associated with the formation of BT from barium titanyle oxalate (Gallagher *et al.,* 1965).

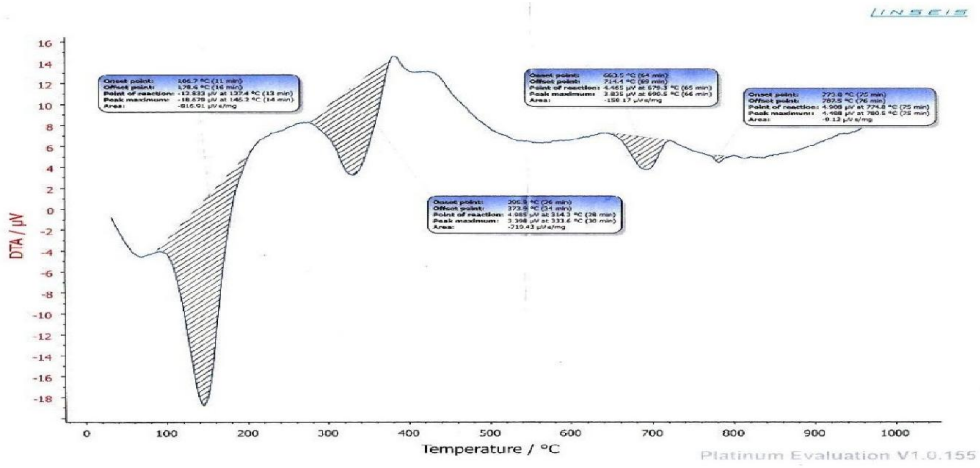


Fig.3.DTA result of barium titanatebefore calcination.

TGA RESULT

Fig.4 shows the result of thermogravimetric analysis (TGA) for a sample of bariumtitanate before calcination. A few milligrams of barium titanate powder were put in an alumina crucible and then heated under the flowing of an N2 atmosphere to 850°C with a heating rate 10°C/min.It can be observed that there are three ranges of temperature in which the weight loss of BT powder were investigated. The first loss of 10% was in the range from around 50°C to 200°C and it was attributed to dehydration of water. The second weight loss of 24% was in the range of (300-550°C) and was related to the thermal decomposition of the dehydrated oxalate. Finally, the third loss of 10% was in the range of (670-740°C) and was corresponded to the loss of carbonate group and formation of barium titanate powder, after 740°C barium titanate become stable and does not undergo any noticeable weight loss. The results of TGA are in good agreement with that obtained by (DTA) analysis. Based on these results the calcination temperature was selected to be 850°C.

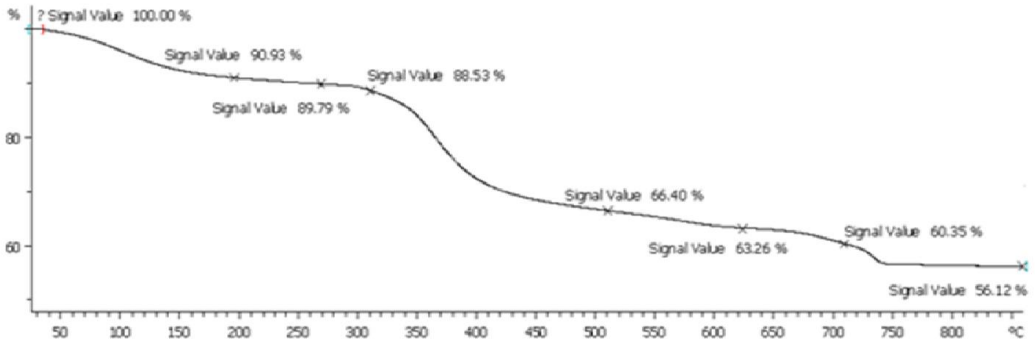


Fig.4. TGA result of barium titanatebefore calcination at 850 °C.

PSA RESULT

Fig.5(a, b, c, d, and e) show the result of analysis of particles size distribution for the calcined barium titanate powders prepared from solutions with different concentrations of (0.05, 0.1, 0.25, 0.5, and 0.97M) respectively.It can be observed that all the prepared samples has multimodal distribution. It is obvious that with increasing the concentration of the precursors solutions, the modal of the coarser particles becomes the major modal and the vice versa. This is attributed to the fact, that the precipitation procedure involve two major process which are nucleation and growth, decreasing the concentration will make the nucleation process predominant, and hence the precipitant possess large number of small particles (Skoog *et al*.2013)

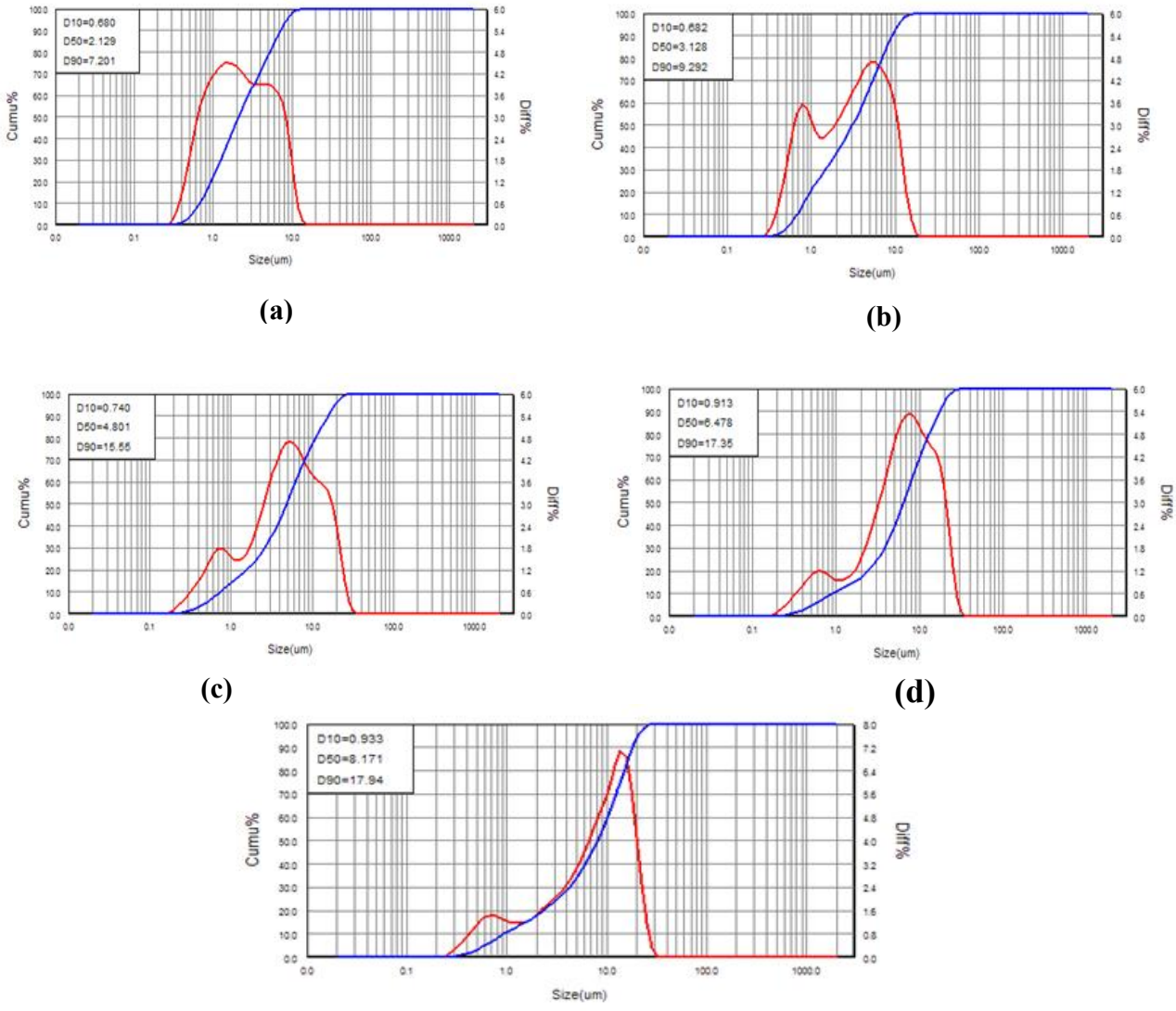


Fig.5. The particle size analysis for barium titanate powder with (a) 0.05M, (b)0.1 M (c) 0.25M, (d) 0.5M, and (e) 0.97M

The D10, D50, and D90, shown on each distribution, represent the particle size that 10%, 50%, or 90% of the sample have particle size less than them respectively. **Fig.6** shows the effect of the solution concentration on the D10, D50, and D90 values.

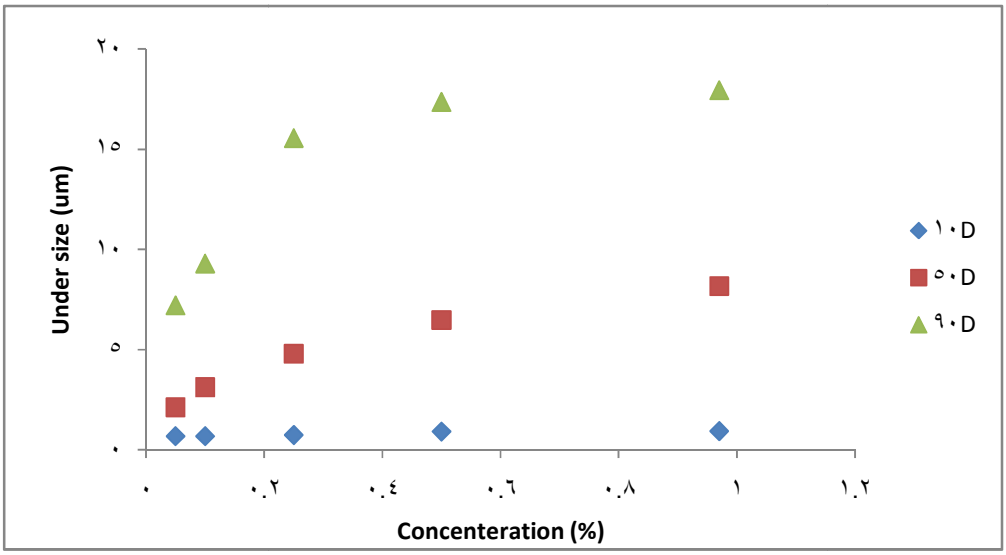
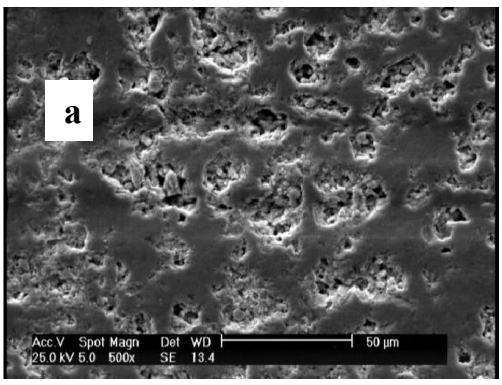


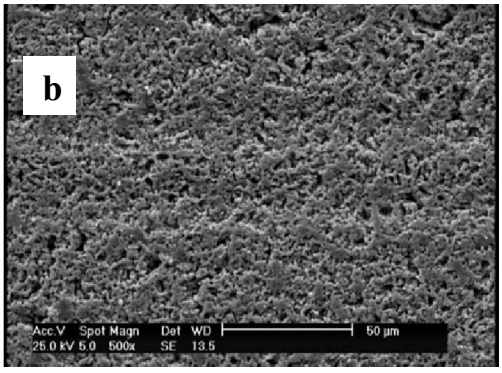
Fig.6 Show the effect of solution concentration on D_{10},D_{50},and D_{90}.

Fig.6 clearly shows that D10, D50, and D90 has the potential to represent the effect of the concentration on the particle size and particle size distribution; Thus, the values of D10, D50, and D90 was used in the current work to represent the particle size and the particle size distribution in the modeling part.

SEM RESULT

Fig.7(a, b, c, d, and e) shows the SEM micrographs of the surface of samples of barium titanate sintered at a temperature of 1200°C with the heating rate of (3.5°C/min) for a soaking time of 1h for the batches 1, 2, 3, 4, and 5 respectively.The SEM image shows that the microstructure of each sample consists of a large network of interconnected grains, these grain have a multi-faceted shape, on average, with homogenous distribution of porosity and with a nearly narrow size distribution. It can be seen that there is a clear effect of the reactant concentration on the average size of the grains and the interconnectivity of the grains.With increasing the concentration of the precursors, the grain size increases. This is due to the larger size of the prepared powder used to prepare the sintered samples. In contract, the interconnectivity increase with decrease the concentration of precursors. This is because of the finer particles size of the powder obtained at low concentration has higher surface area leading to more efficient sintering process.





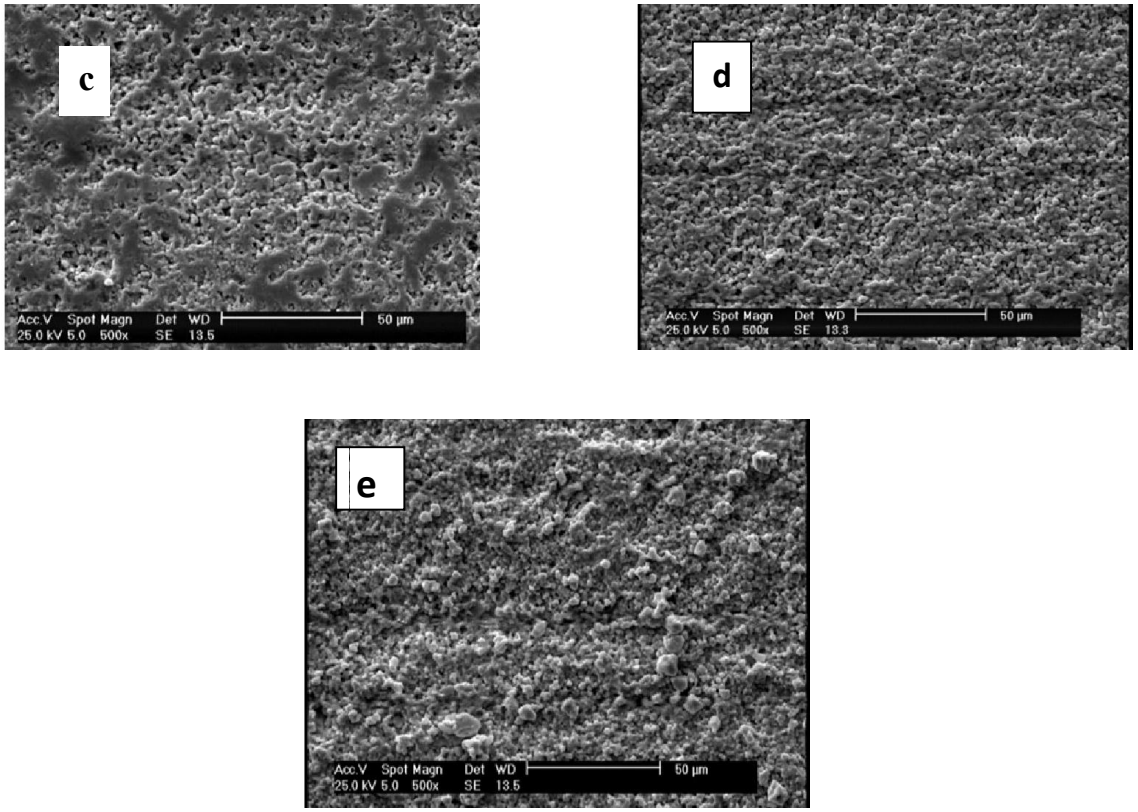


Fig.7 SEM micrographs for BT samples sintered at 1200°C for 1 hr prepared from a solution of (a)0.05 M, (b)0.1 M, (c) 0.25 M, (d) 0.5 M, and (e) 0.97 M..

CONCLUSIONS

High purityperovskite barium titanate with tetragonal phase was successfully prepared using modifiedpechini method. The results show that the particle size and the particle size distribution of BT can be controlled by adjusting the concentration of the precursors solution in the pechini method.The obtained particle size distribution are multimodal distribution. The increase of the concentration of the precursors enhances the model of the coarser particles of the account of the model of the finer particles.

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