SYNTHESIS AND CHARACTERIZATION OF Ca DOPANT EFFECT ON $PbCaTiO_3$ POWDERS

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Abstract

The purpose of this work was to synthesize $Pb_{1-x}Ca_xTiO_3$ (x = 0, 0.1, 0.2, 0.3 wt%) in the form of powder phase by solid state mixed oxide technique and to study the structural properties of this laboratory-made $PbCaTiO_3$ specimen by a systematic analysis of XRD and SEM for the potential applications in the ferroelectric devices. From XRD results, $PbCaTiO_3$ powders were significantly formed with tetragonal symmetry. According to SEM results, these $PbCaTiO_3$ powders were composed of regular and sphere grains with sizes ranging from (278.5 nm-433.75 nm) for various x contents. The $PbCaTiO_3$ powders were quite suitable for cost effective and uncomplicated trends of ferroelectric materials such as random access memory (RAM).

Keywords: $PbCaTiO_3$, solid state mixed oxide technique, X-ray diffraction (XRD) and Scanning Electron Microscope (SEM)

Introduction

The science and technology of nanostructured materials is advancing at a very rapid pace. Nowadays, the preparation and functionalization of one-dimensional nanostructured materials has become one of the most important roles of the nanotechnology. Nanotechnology is employed in many different electronics communications, and computing applications, providing smaller, faster, and more portable systems. In general, the size of a nanoparticle spans the range between 1 and 100 nm. Metallic nanoparticles have different physical and chemical properties from bulk metals, properties that might prove attractive in various industrial application are the simplest form of structures with sizes in the nm range. In principle, any collection of atoms bonded together with a structural radius of < 100 nm can be considered a nanoparticle.

Nanoparticles can be in the form of nanocrystals, nanopowders, or nanoclusters, and the particles act as a bridge between bulk materials and atomic or molecular structures. Nanoparticles have a very high surface area to volume ratio, which provides a great driving force for diffusion, particularly at high temperature.

A perovskite is any material with the same type of crystal structure known as the perovskite structures with the oxygen in the face centers. Perovskite-type materials can be represented by their general formula as ABO_3 where, A and B are any two different sized cations and B is the anion bonding them. Most of the perovskites contain oxygen as the anion. Hence, perovskite oxides can be presented by their general formula as ABO_3. Perovskite type oxide materials are important for electronic applications since they exhibit diverse physical properties such as super conductivity, dielectricity, ferroelectricity and magnetism.

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Experimental Procedure

Starting Materials

The materials used in this study were Lead Oxide (PbO), Calcium Oxide (CaO) and Titanium Dioxide (TiO2) with different molar ratio of calcium. Figure 1 shows the Starting materials.

Calcium Oxide (CaO) Titanium Oxide (TiO_2) Lead Oxide (PbO)

Figure 1 Starting materials

Preparation of $Pb_{1-x}Ca_xTiO_3$ powders

Calcium (x = 0 g, 0.1 g, 0.2 g, 0.3 g) doped lead titanate $PbTiO_3$ was successfully prepared by solid state reaction method. Lead oxide (PbO), calcium oxide (CaO) and titanium dioxide (TiO_2) were weighed with digital balance and mixed with desired stoichiometric composition of $PbCaTiO_3$ powders. The mixture was ground by agate mortar to become a homogeneous mixture. The mixed $PbCaTiO_3$ powders were calcined at 800 °C for 1.5 h in furnace and reground with agate mortar. The reground $PbCaTiO_3$ powders passed through 100, 250 and 400 mesh sieves. Finally, homogeneous $PbCaTiO_3$ powders were obtained. In this section, the structural properties of $PbCaTiO_3$ powders were characterized by X-ray diffraction method (XRD). Figure 2 showed the block diagram of preparation of $PbCaTiO_3$ powders with different x contents.

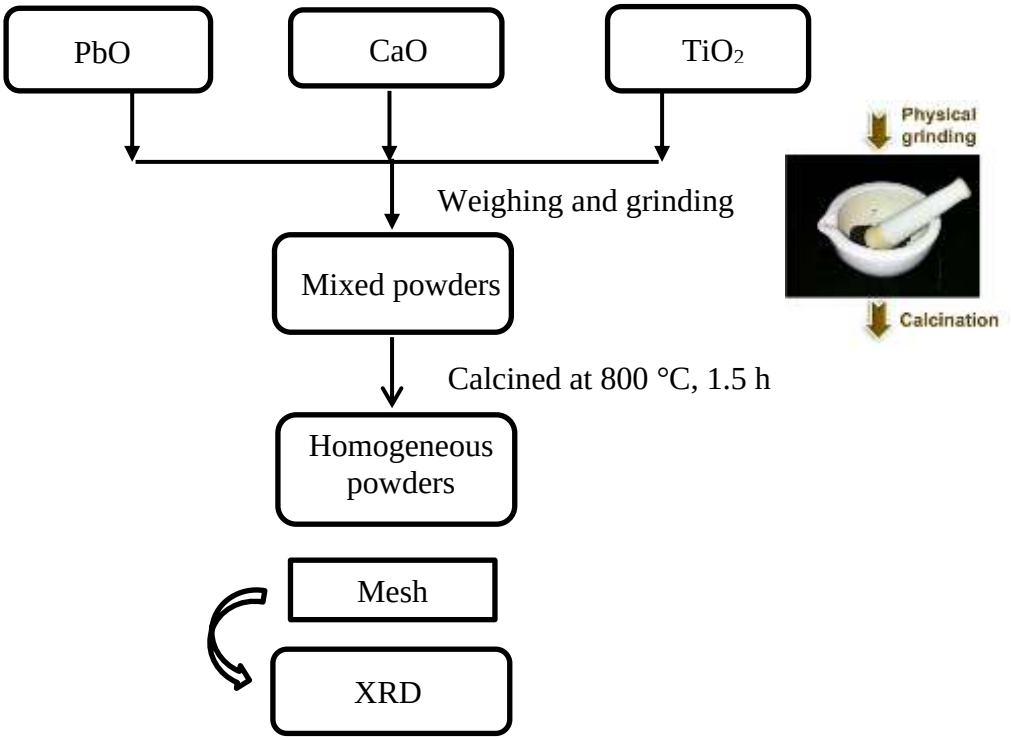


Figure 2 The block diagram of preparation of PCT nanoparticles with different x contents

Results and Discussion

XRD analysis of $PbCaTiO_3$ powders

X-ray diffraction technique (XRD) is a powerful technique for determination of crystal structure. It provides simple nondestructive information on the nature of intermetallic and crystal phase usually in a very short time. The great deal of the crystallographic information of crystalline $PbCaTiO_3$ powder has been studied by crystallite size. The XRD patterns of $PbCaTiO_3$ specimens were perovskite type with tetragonal structure as shown in figure 3 (a-d). There are several diffractions of the standard peaks which were scanned within the diffraction angles range from 10° to 70°. Some extra peaks were formed on all XRD profile and they could not be identified. PCT powders were obtained and examined its phase formation by X-ray diffractometer using Cu-K_α radiation with wavelength of 1.54056 Å. All the peak heights and peak positions were in good agreement with the JCPDS (Join Committee on Powder Diffraction Standards) in 49-0863 > $PbCaTiO_3$ library file. The average crystallite-sizes were 29.872, 25.253, 24.827, 28.019 nm for various x contents respectively. For the powder, 2θ, FWHM values and crystallite sizes were given in Table 1-2. The lattice parameter (a, b and c) and lattice distortion (lattice strain) c/a of dominant peaks were described in Table 3. Thus, the PCT powders were successfully obtained by solid state reaction method with tetragonal structure.

The crystallite size was calculated using a well-known Debye Scherrer's formula in equation:

$$G=\frac{0.899\times\lambda}{FWHM\times\cos\theta} \quad (1)$$

where,

G = crystallite size
λ = 1.54056 Å for Cu K_α
FWHM = full width at half maximum at dominant peak
θ = Bragg angle.

Table 1 Structural Properties of $Pb_{1-x}Ca_xTiO_3$ Powders for (x = 0 , 0.1wt %)

Sr No.	(h kl)	2 θ (deg)	FWHM (deg)	Observed Crystallite Size (nm)	Sr No.	(h kl)	2 θ (deg)	FWHM (deg)	Observed Crystallite Size (nm)
1	(001)	21.205	0.262	33.700	1	(001)	21.252	0.327	27.030
2	(100)	22.581	0.200	44.100	2	(100)	22.571	0.238	37.120
3	(101)	31.300	0.249	35.500	3	(101)	31.309	0.270	32.710
4	(110)	32.269	0.232	38.000	4	(110)	32.311	0.300	29.430
5	(111)	39.039	0.246	35.900	5	(111)	39.056	0.250	35.300
6	(002)	43.447	0.378	23.400	6	(002)	44.037	0.575	15.360
7	(200)	46.347	0.262	33.700	7	(200)	46.343	0.301	29.340
8	(102)	49.490	0.585	15.100	8	(102)	49.926	0.532	16.590
9	(201)	51.594	0.288	30.600	9	(201)	51.587	0.440	20.050
10	(210)	52.223	0.367	24.100	10	(210)	52.219	0.407	21.690
11	(112)	55.239	0.386	22.800	11	(112)	55.415	0.440	20.050
12	(211)	57.053	0.297	29.700	12	(211)	57.100	0.342	25.840
13	(202)	65.487	0.376	23.500	13	(202)	65.653	0.416	21.220
14	(220)	67.675	0.314	28.110	14	(220)	67.669	0.360	24.530
Average crystallite size				29.872	15	(003)	68.250	0.396	22.290
						Average crystallite size			25.235

Table 2 Structural Properties of $Pb_{1-x}Ca_xTiO_3$ Powders for (x = 0.2, 0.3 wt%)

Sr No.	(h kl)	2 θ (deg)	FWHM (deg)	Observed Crystallite Size (nm)	Sr No.	(h kl)	2 θ (deg)	FWHM (deg)	Observed Crystallite Size (nm)
1	(001)	21.252	0.329	26.840	1	(001)	21.408	0.703	12.560
2	(100)	22.558	0.244	36.200	2	(100)	22.561	0.231	38.220
3	(101)	31.97	0.281	31.440	3	(101)	31.272	0.276	31.980
4	(110)	32.227	0.255	34.620	4	(110)	32.210	0.289	30.560
5	(111)	39.026	0.283	31.180	5	(111)	39.080	0.228	38.800
6	(002)	43.944	0.626	14.100	6	(002)	43.880	0.640	13.790
7	(200)	46.325	0.300	29.400	7	(200)	46.293	0.249	35.500
8	(102)	49.915	0.584	15.120	8	(102)	50.039	0.252	35.100
9	(201)	51.548	0.383	23.100	9	(201)	51.534	0.311	28.370
10	(210)	52.203	0.319	27.710	10	(210)	52.125	0.284	31.120
11	(112)	55.441	0.495	17.830	11	(211)	57.013	0.310	28.470
12	(211)	57.054	0.331	26.690	12	(202)	65.760	0.417	21.190
13	(202)	65.443	0.511	17.270	13	(220)	67.552	0.473	18.650
14	(003)	67.149	0.549	16.080		Average crystallite size			28.019
Average crystallite size				24.827					

Table 3 Lattice parameters and c/a ratios of various x contents for $Pb_{1-x}Ca_xTiO_3$ Powders

x contents (wt%)	Lattice Parameter (Å)		Tetragonality c/a
	a	c	
x = 0	3.9162	4.1804	1.0674
x = 0.1	3.9170	4.1602	1.0621
x = 0.2	3.9218	4.1624	1.0613
x = 0.3	3.9313	4.1412	1.0534

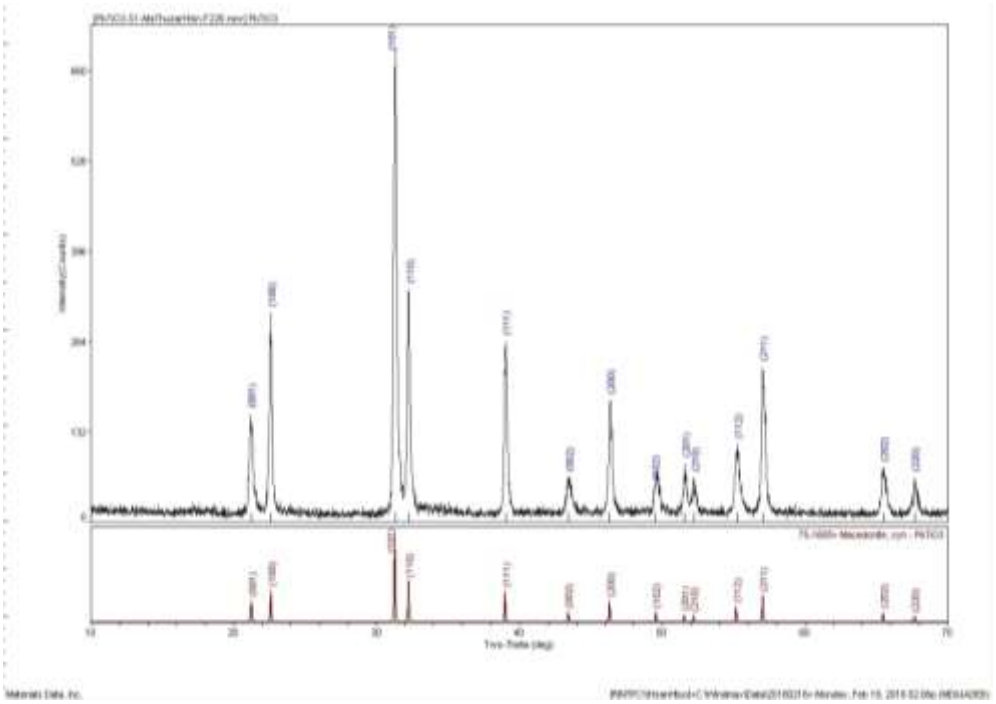


Figure 3 (a) The XRD patterns of $PbCaTiO_3$ powders (x = 0 wt%)

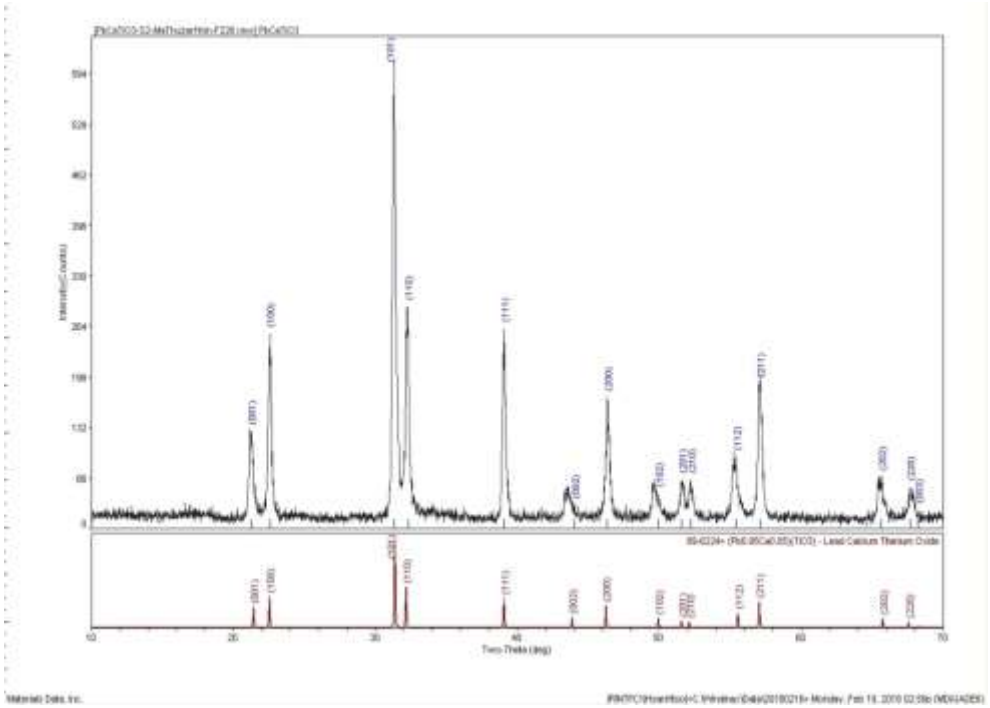


Figure 3 (b) The XRD patterns of $PbCaTiO_3$ powders (x = 0.1 wt%)

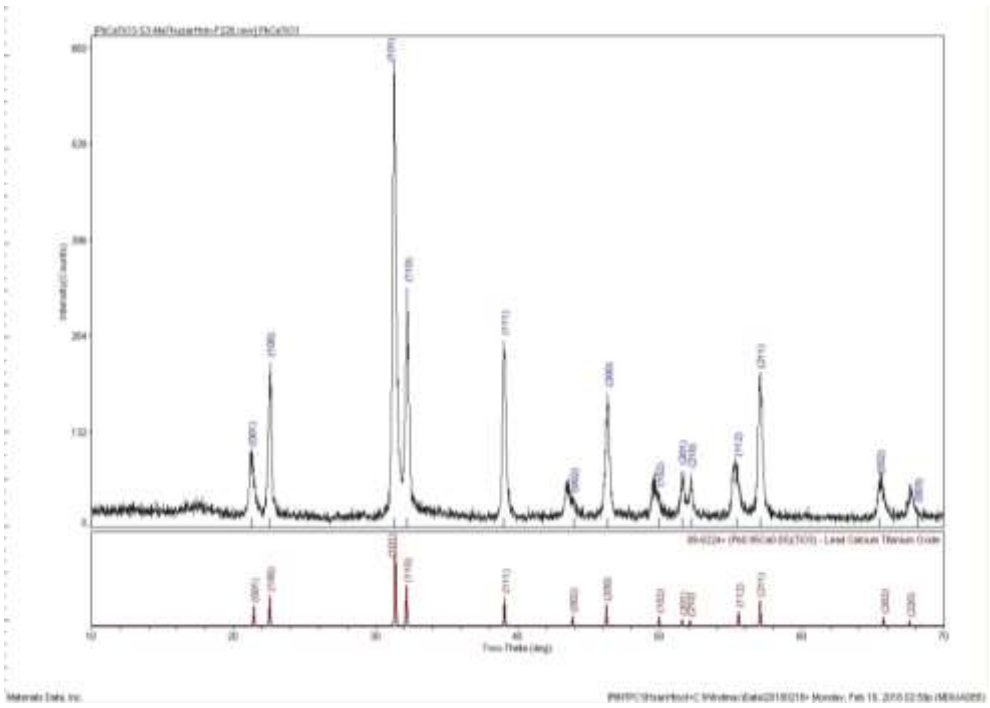


Figure 3 (c) The XRD patterns of $PbCaTiO_3$ powders (x = 0.2 wt%)

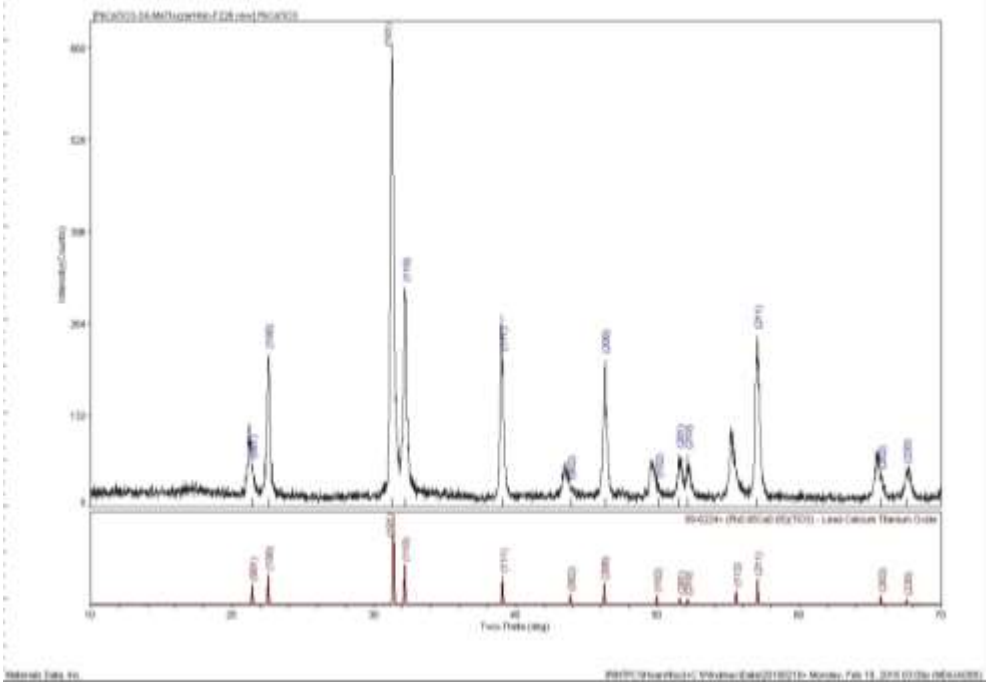
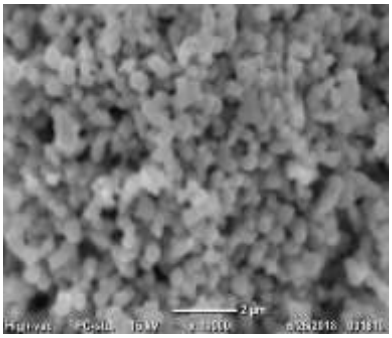


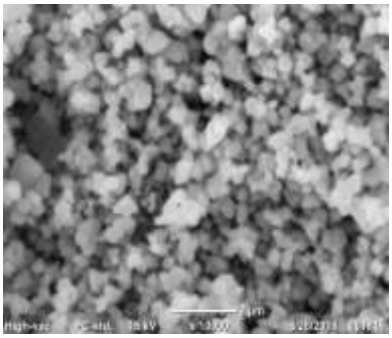
Figure 3 (d) The XRD patterns of $PbCaTiO_3$ powders (x = 0.3 wt%)

SEM Analysis of $Pb_{1-x}Ca_xTiO_3$ powders

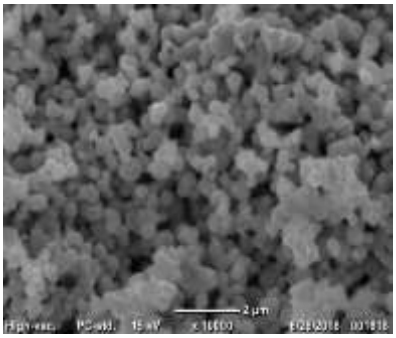
$PbCaTiO_3$ powders were obtained successfully by solid state reaction method. The microstructural properties of $PbCaTiO_3$ powder were observed by using Scanning Electron Microscopy (SEM). Materials evolutions were obtained grain size, surface roughness and pore distribution. Figure 4 (a-d) showed the SEM photographs of $PbCaTiO_3$ crystalline powder at calcined temperatures 800 °C. As detail analysis of SEM micrograph, it looked crack-free and little dense. Porosity and grain growth pattern were significantly observed on SEM images. These images were smooth and seemed to be front-oriented and the grain distribution was uniform but some of grain sizes were slightly larger. According to SEM results, these $PbCaTiO_3$ powders were composed of regular and sphere grains with sizes ranging from (278.5 nm-433.75 nm) for various x contents.



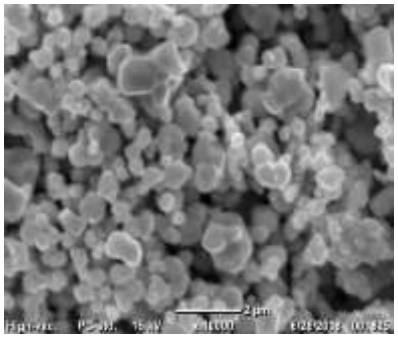
(a) (x = 0 wt%, Average grain size = 278.5 nm)



(b) (x = 0.1 wt%, Average grain size = 324.25 nm)



(c) (x = 0.2 wt%, Average grain size = 333 nm)



(d) (x = 0.3 wt%, Average grain size = 433.75 nm)

Figure 4 (a-d) SEM photographs of $PbCaTiO_3$ crystalline powder (x = 0, 0.1, 0.2 and 0.3 wt%) at calcined temperatures 800 °C

Conclusion

$Pb_{1-x}Ca_xTiO_3$ powders with different x contents were successfully prepared by solid state reaction method. In the XRD analysis, crystallite sizes of several peaks were 29.872 nm, 25.253 nm, 24.827 nm, 28.019 nm for various x contents respectively. From XRD results, the crystal structure of the prepared $PbCaTiO_3$ powders was perovskite type with tetragonal symmetry. According to SEM analysis results, $PbCaTiO_3$ powders were smooth, sphere, and uniform grain with sizes ranging from (278.5 nm-433.75 nm) for various x contents. As these research data, the $PbCaTiO_3$ powders were quite suitable for cost effective and uncomplicated trends of ferroelectric materials such as random access memory (RAM).

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