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Effect of Ca Substitution on Structural properties of $Ba_{1-x}Ca_xTiO_3$ Nano Compound Synthesis by Sol-Gel Method

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ABSTRACT: Nano perovskite compound ($Ba_{1-x}Ca_xTiO_3$), where ($X = 0, 0.2, 0.4, 0.6, 0.8$), was prepared by using chemical sol-gel route. X-ray diffraction results were compared with the international center for diffraction data (ICDD). Rietveld refinement using *foolproof*, and powder cell programs was carried out and it was found that the structural phases of the samples with ($X = 0$) and ($X = 0.2$) are tetragonal phase belongs to ($P4mm$) space group, and other samples with ($X = 0.4, 0.6$ and 0.8), possess biphasic structure (tetragonal and orthorhombic), belongs ($P4mm$) and ($Pmmm$), space groups respectively, Lattice parameters, unit cell volume, c/a ratio, x-ray density and grain size for the diffraction peak (101) have been calculated for all samples, and the results show that (Ca^{+2}) ions, substitutions in ($Ba_{1-x}Ca_xTiO_3$), Nano compound were effected of structural properties, and By using Powder Cell program and the refinement information, the unit cell and the crystal structure for prepared compound $BaCaTiO_3$ have been plotted.

Keywords: sol-gel; $Ba_{1-x}Ca_xTiO_3$; XRD analysis; Rietveld refinement

I. INTRODUCTION

Perovskite is the mineral name of calcium titanate ($CaTiO_3$), which was discovered by German chemist Gustav Rose in 1839 who named it after the Russian mineralogist Lev Alexeievitch Perovskiy, since then, the name "perovskite" has been applied to many compounds, synthetic and natural, that have similar structure. Perovskite in general refers to a family of compounds whose structures are related to that of the mineral perovskite $CaTiO_3$ [1]. Its simplest structure is cubic [2]. Ordered perovskites are of great interest due to the flexibility of introducing them into the composition. In fact, having multiple cations at a particular site allows ions of greater or lesser oxidation state to be incorporated into the composites. Ordering of these cations affects the symmetry of the structures, and further the bulk properties of the material [3, 4].

One of the most interesting perovskites is $BaTiO_3$ whose ferroelectric nature has gained its attention as a high dielectric material. Substitution at both A- and B-sites (at ABO_3 perovskite ceramics) has been made in attempt to make these materials more technologically useful. Upon cooling from high temperature, $BaTiO_3$ undergoes a cubic paraelectric to tetragonal ferroelectric phase transition at (303 K) [5, 6].

ABO_3 materials, where (A can be one of the ions Ca, Ba, Sr, Mg and B can be one of the ions Ti, Mn, Zr, Sn with A-ion having larger ionic radius than B-ion) exist in structurally different forms which are broadly classified into perovskite and limonite on the basis of tolerance factor [6, 7]. So when preparation ABO_3 materials, substitution process cause deformation leading to formed different phases, like tetragonal, orthorhombic, monoclinic or triclinic.

II. Materials and method

The polycrystalline ($Ba_{1-x}Ca_xTiO_3$), where ($X = 0, 0.2, 0.4, 0.6, 0.8$), Nano powder samples, were prepared by using sol-gel method, and Barium acetate ($C_4H_6BaO_4$), Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$), Titanium isopropoxide $Ti\{OCH(CH_3)_2\}_4$, acetic acid ($C_2H_4O_2$) and 2-methoxy ethanol ($C_3H_8O_2$), and distilled water, as a raw materials, the molar ratio (1: 1 mol) for each of the (Ba, Ca: Ti), respectively, for all prepared sample, after weighted the amounts of each used raw materials for each sample, all of the Barium acetate ($C_4H_6BaO_4$), dissolved in the appropriate

amount of acetic acid($C_2H_4O_2$) and Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$), in appropriate amount of distilled water,also Titanium isopropoxide $Ti\{OCH(CH_3)_2\}_4$ havebeen mixingwith an appropriate quantity 2-methoxyethanol($C_3H_8O_2$), and all separately using a magnetic stirrer,and then mixed three solutions in a large beaker heat-resistant (Pyrex) with adjusting theacid function (pH) until reaching approximately (5) with the addition of distilled water at room temperature and then raised the reaction temperature to ($120^\circ C$) and this temperature was fixedin the preparation of all samples, until gasesbeganescalate and continued interaction with stirring, untilthe liquid (sol)turning togels form, after thatthe beakerput in an oven pre-heated at a temperature ($120^\circ C$) for (2h),todrying the gel and to ensure to it get the heat from all sides,which ensures quick drying and then turn off the oven and leave it,to the next day to cool down after that, the dry gel was extracted from the oven and then grinding in an agate mortar, and collectingpowder,was admitted to the oven for two hours at a temperature ($900^\circ C$) for the calcination purpose and obtain the required phase, and all samples prepared in the same steps.

The structural properties was studied by using a SHIMADZU6000, X-ray diffractometer with, ($CuK\alpha$), radiation of wavelength ($\lambda = 1.5406 \text{ \AA}$), The obtained, X-ray diffraction patterns of the samples, compared with the standard ICDD cards (81-0042), and then X-ray diffraction patterns, were analyzed by fullprof and Unit Cell packages, which depending on Rietveld refinementto find out the phase and space group, The lattice parameters of prepared samples, was calculated by using the relation [8].

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \dots\dots\dots (1)$$

For tetragonal $a = b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$

d:the distance between two levels parallel consecutive inside the crystal .

(hkl): Miller index.

The unit cell volume fortetragonal structure was calculated by using the relation.

And theoretical density(ρ_{x-ray}) was calculated by the following equation [].

$$\rho_{x-ray} = \frac{zM_{wt}}{N_A V} \dots\dots\dots (3)$$

Where Z is number of molecules per unit cell, M is the atomic mass of the compound, and N_A is Avogadro's number.

The grain size (D_{sh}), was calculated by using Scherer's equation, and the peak (101) [8].

$$D_{sh} = \frac{k\lambda}{\beta \cos \theta} \dots\dots\dots (4)$$

Where λ is $CuK\alpha$ radiation wavelength, and β is the Full Width at Half Maximum (FWHM), measured in radians

III. Results and Discussion

In figure (1), the x-ray diffraction patterns of all $Ba_{1-x}Ca_xTiO_3$, where ($X = 0, 0.2, 0.4, 0.6$ and 0.8) series (C) samples , shows compliance with the global standard cards ,the card number (81-0042), belonging to the space group (P4mm), which indicated formation and the presence of tetragonal phase in All samples ,as well as observed through X-ray diffraction patterns of series (C) samples,that the process of substitution ion (Ba^{+2}), by ion(Ca^{+2}), at the ratios of ($X = 0$), ($X = 0.2$), did not cause the presence of additional phases in the samples (C0,C1), while it was noted that the process of substitution with ratios ($X = 0.4, 0.6, 0.8$) in the samples (C2, C3,C4), was led to appearance a new peak in the X-ray diffraction spectrum of these samples approxemintly at the position ($2\theta = 33^\circ$) , its strength increases, with (X) ratio, or ion(Ca^{+2})concentration in the $Ba_{1-x}Ca_xTiO_3$, Nano compound, with remains the main peak of tetragonal phase, which means appearance orthorhombic phase as secondary phase with tetragonal phase, in (C2, C3,C4) samples ,so we concluded that samples(C2, C3,C4),possesses a biphasic structure (tetragonal + orthorhombic) with P4mm and Pmmm space groups respectively, due to substitution process ,this results has good agreement with [9] research, the results of Rietveld refinement X-ray diffraction spectrum of $Ba_{1-x}Ca_xTiO_3$ samples, like Reliability factors, space groups and phases were listed in table (1), Which confirmed the space groups and phases results, whereas figure (2), shows the structure of unit cell for tetragonal structure of ($BaCaTiO_3$) with atoms of elements position, and their atomic coordinates using Powder Cell program by using the information obtained from the refinement data, were listed in the table (2).

The calculated results of unit cell parameters,(c/a) ratios,x-ray density and unit cell volume were listed in table (3),through the results we were noted that the unit cell parameters, x-ray density and unit cell volumes decreased

with increases of with (X) ratio, or ion(Ca²⁺)concentration ,in Ba_{1-x}Ca_xTiO₃ Nano compound samples, this behavior was due to the difference between ionic radius of (Ca²⁺)and (Ba²⁺) ,whereas(Ca²⁺) had the smaller ionic radius, furthermore the results in table (3), exhibited that,(c/a) ratios were more than (1), which were noted to formed the tetragonal phase in all samples ,and this behavior shows a good agreements with a lot research’s like [10,11].

The results of grain size (D_{sh}),of Ba_{1-x}Ca_xTiO₃ where (X =0, 0.2, 0.4, 0.6 and 0.8) series (C) samples, that calculated by using Scherer's equation, listed in table (4), (D_{sh}) results exhibited that grains size was in Nano scale range, and substitution(Ba²⁺) ions by(Ca²⁺) , in Ba_{1-x}Ca_xTiO₃ samples ,causes to reduces grain size values with increases (X) values, by means(Ca²⁺)concentration ,and this noted behavior was due to the difference between ionic radius of (Ca²⁺)and (Ba²⁺) ,whereas(Ca²⁺) had the smaller ionic radius than(Ba²⁺) ion, and Because the (Ca²⁺) ions occupys positions of (Ba²⁺) ions in the lattice, all that’s led to create the small distance between the ions and increase the Coulomb force which effect on the grain size as shown in figure (3).

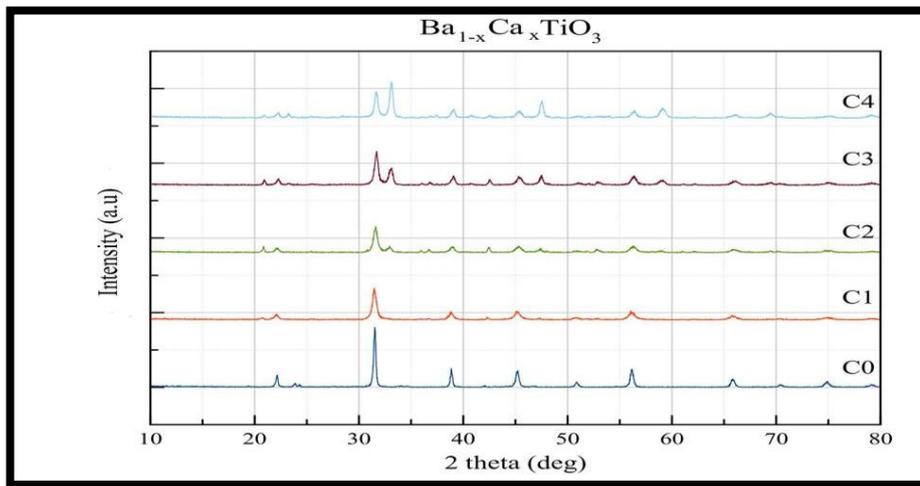


Fig. (1): XRD patterns of Ba_{1-x}Ca_xTiO₃ prepared by sol-gel

Table (1) Reliability factors, space groups and phases of Ba_{1-x}Ca_xTiO₃ prepared by sol-gel

sample	Ca content (X)	R _p	R _{wp}	R _{exp}	χ ²	GOF	Space group	phase
C0	0.0	35.7	46.6	39.6	3.33	1.82	P4mm	Tetragonal
C1	0.2	23.6	32.6	27.4	2.80	1.67	P4mm	Tetragonal
C2	0.4	29.4	36.7	29.60	3.52	1.87	P4mm+P mmm	Tetragonal+orthorhombic
C3	0.6	36	42.1	28.64	2.16	1.47	P4mm+P mmm	Tetragonal+orthorhombic
C4	0.8	36.1	42.3	28.4	2.42	1.55	P4mm+P mmm	Tetragonal+orthorhombic

Table (2) Atoms positions of BaCaTiO₃

Atom	BaCaTiO ₃		
	X	Y	Z
Ba	0	0	0
Ca	0	0	0
Ti	0.5	0.5	0.5
O1	0.5	0.5	0.5128
O2	0.5	0	0.486

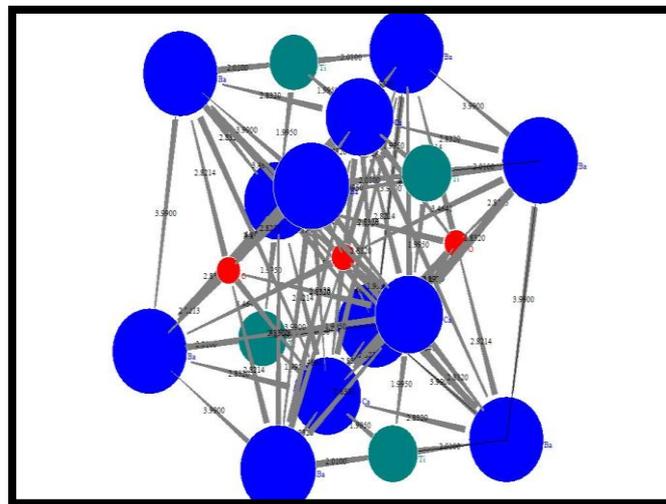


Figure (2) atoms positions and bond length of BaCaTiO₃

Table (3) lattice parameters, volume, x-ray density, of Ba_{1-x}Ca_xTiO₃ prepared by sol-gel

sample	Ca content(X)	a(Å)	c(Å)	c/a	V(Å ³)	$\rho_{x\text{-ray}}$ (g/cm ³)
C0	0.0	4.0017	4.0250	1.0058	64.4547	6.0077
C1	0.2	4.0001	4.0078	1.00192	64.12800	5.5346
C2	0.4	3.9979	4.0028	1.00122	63.97757	5.0428
C3	0.6	3.9889	4.0011	1.00305	63.66279	4.5604
C4	0.8	3.9811	3.9951	1.00351	63.31896	4.0751

Table (4) Grain size of Ba_{1-x}Ca_xTiO₃ prepared by sol-gel.

Sample	Ca content (X)	D _{sh} (nm)
C0	0.0	42.2000
C1	0.2	19.2221
C2	0.4	17.2023
C3	0.6	15.9947
C4	0.8	15.7553

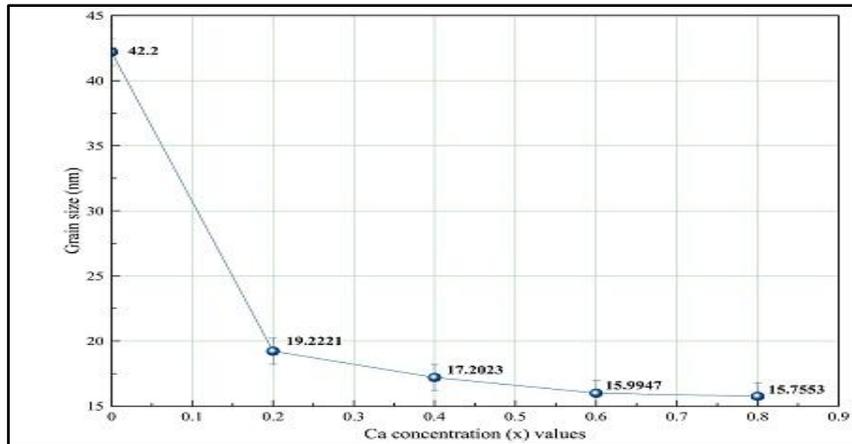


Figure (3) Grain size vs. substitution Calcium concentration value (x).

IV. CONCLUSION

The polycrystalline ($Ba_{1-x}Ca_xTiO_3$), where ($X=0,0.2,0.4,0.6,0.8$), Nano compound was successfully prepared by sol-gel method, The diffraction data were compared with (ICDD) cards, and analyzed by Rietveld refinement ,using Foolproof and Unit Cell programs, The samples with ($X = 0$) and ($X=0.2$), shows single tetragonal phase, with (P4mm) space group ,while the others samples with ($X=0.4,0.6$ and 0.8), shows a biphasic structure (tetragonal and orthorhombic) , with (P4mm) and (Pmmm) space group respectively , all of the structural parameters just like lattice parameters ,c/a ratio ,lattice volume ,x-ray density and grain size, were effect by Calcium (Ca^{+2}) ions ,substitution in $Ba_{1-x}Ca_xTiO_3$ Nano compound , because of difference in ionic radii between Calcium(Ca^{+2}) ions, Barium(Ba^{+2}) ions.

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