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Structural Study of $Ba_{1-x}CaxTiO_3$ Ceramic Perovskite Material Using X-ray Diffraction Analysis

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Abstract: Ceramic perovskite material with the chemical formula $Ba_{1-x}Ca_xTiO_3$ (where x = 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) was prepared by using solid-state reaction technique for preparation of ceramic materials. X-ray diffraction results were compared with the international center for diffraction data (ICDD). Rietveld refinement using FullProf and Unit Cell programs was carried out and it was found that the structural phases of the samples with x = 0.1 and 0.2 are tetragonal belonging to P4mm space group. The sample with x = 0.3 possesses biphasic structure (tetragonal and orthorhombic) having P4mm and Pmmm space groups respectively, whereas the samples with x = 0.4, 0.5 and 0.6 have orthorhombic structure with Pmmm space group. Lattice parameters, unit cell volume, x-ray density and crystallite size for the diffraction peak (110) have been calculated for all samples and the results show the effect of Ca substitutions on the structural properties of $BaTiO_3$ ceramic perovskite. By using Powder Cell program and the refinement information, the unit cell and the crystal structure have been plotted for the sample with x = 0.1.

Keywords: Ceramic perovskite materials; $Ba_{1-x}Ca_xTiO_3$; XRD analysis; Rietveld refinement.

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1 Introduction

The mineral perovskite $CaTiO_3$ was discovered by German chemist Gustav Rose in 1839 who named it after the Russian mineralogist Lev Alexeievitch Perovsky [1], 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 $CaTiO_3$. The ideal perovskite structure has a cubic unit cell of side about (3.9 Å), with $Pm\bar{3}m$ space group and contains one formula unit [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) [2]. Substitution of Ca ions with Ba ions leads to different Curie temperature. ABO_3 materials (where A can be one of the ions Ca, Ba, Sr or Mg; and B can be one of the ions Ti, Mn, Zr or 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 [1,2]. In the preparation of these materials, deformation may occur leading to different phases like tetragonal, rhombohedral, orthorhombic, monoclinic or triclinic.

2 Experimental Procedure

Polycrystalline $Ba_{1-x}Ca_xTiO_3$ (where x = 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) ceramic samples were synthesized by standard solid-state ceramic technique. Stoichiometric amount of $BaTiO_3$ and $CaTiO_3$ were weighed and mixed in an agate mortar. The reactants were heated in air at 1000 ºC, 1300 ºC and 1350 ºC for 10 hours. Finally, the samples were pressed into

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pellets of 1 cm diameter and sintered for 5 hours at temperature of 1350 ºC. X-ray diffraction patterns were obtained using a SHIMADZU 6000 X-ray diffractometer with CuKα radiation of wavelength (λ = 1.5406 Å). The patterns were compared with the standard ICDD cards (81-0042 and 09-0365) and analysed by Rietveld refinement method using the FullProf and Unit Cell packages. The lattice parameters were calculated using the relation [3,4]:

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \tag{1}$$

For tetragonal a = b ≠ c, for cubic a = b = c and $\alpha = \beta = \gamma = 90^o$

The unit cell volume for orthorhombic structure is:

$$V = abc \tag{2}$$

And x-ray density can be calculated using the following equation:

$$\rho_{x\text{-ray}} = Z.M / V.N_A \tag{3}$$

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

Crystallite size was calculated using the peak (110) corresponding to the Bragg’s angle ($2\theta = 31.6266^o$) by using the well-known Scherer's formula:

$$D = 0.98\ \lambda / \beta \cos\theta \tag{4}$$

Where λ is CuKα radiation wavelength and β is the Full Width at Half Maximum (FWHM) measured in radians.

3 Results and Discussion

Figure (1) shows the x-ray diffraction patterns of all $Ba_{1-x}Ca_xTiO_3$ (where x = 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) samples. The patterns of the first and second samples (with x = 0.1 and 0.2) show splitting at (200) and (002) directions which is referred to tetragonal splitting with P4mm space group, whereas the third sample (with x = 0.3) possesses a biphasic structure (tetragonal + orthorhombic) with P4mm and Pmmm space groups respectively. The remaining samples (where x = 0.4, 0.5 and 0.6) show orthorhombic phase structure with Pmmm space group [5]. The crystallite size calculated using the peak broadening at (111) orientation, x-ray density and unit cell volume along with the lattice parameters are listed in table (1). The addition of impurity atoms (Ca-atom) to the parent materials causes a peak shift toward higher angles which may indicate the development of strain in materials [6], and evolution of new peaks i.e. the peak at around ($2\theta = 33^o$) in the XRD pattern of the sample with x = 0.3. The (100 %) relative intensity (I_{max}) plays an important role in understanding the structure of materials [6,7]. It can be observed that with increasing doping concentration, the peak of corresponding to 2θ around 33^o becomes stronger which may explain the structure phases of the prepared samples [8]. Additional peaks can be seen in higher doping concentration, for example ($2\theta = 51.71^o$). Figures (2a) and (2b) show the Rietveld refinement of $Ba_{1-x}Ca_xTiO_3$ (where x = 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) samples carried out using FullProf and Unit Cell packages. Figure (3) shows the variation of crystallite size as a result of calcium substitutions. It can be observed that, in general, the crystallite size increases with increasing the calcium substitutions which may indicate the increasing rate of crystallites formation [9]. Figure (4) shows the structure of unit cell for the tetragonal structure of the sample with x = 0.1 using Powder Cell program by using the information obtained from the refinement data.

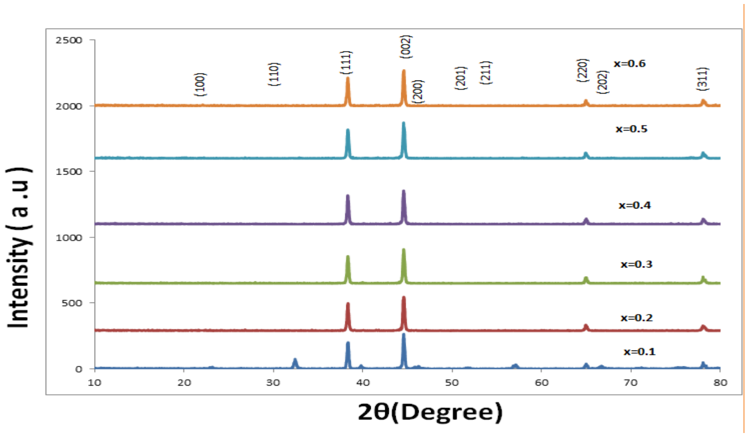


Fig. (1): XRD patterns of $Ba_{1-x}Ca_xTiO_3$ perovskite material prepared in the present study.

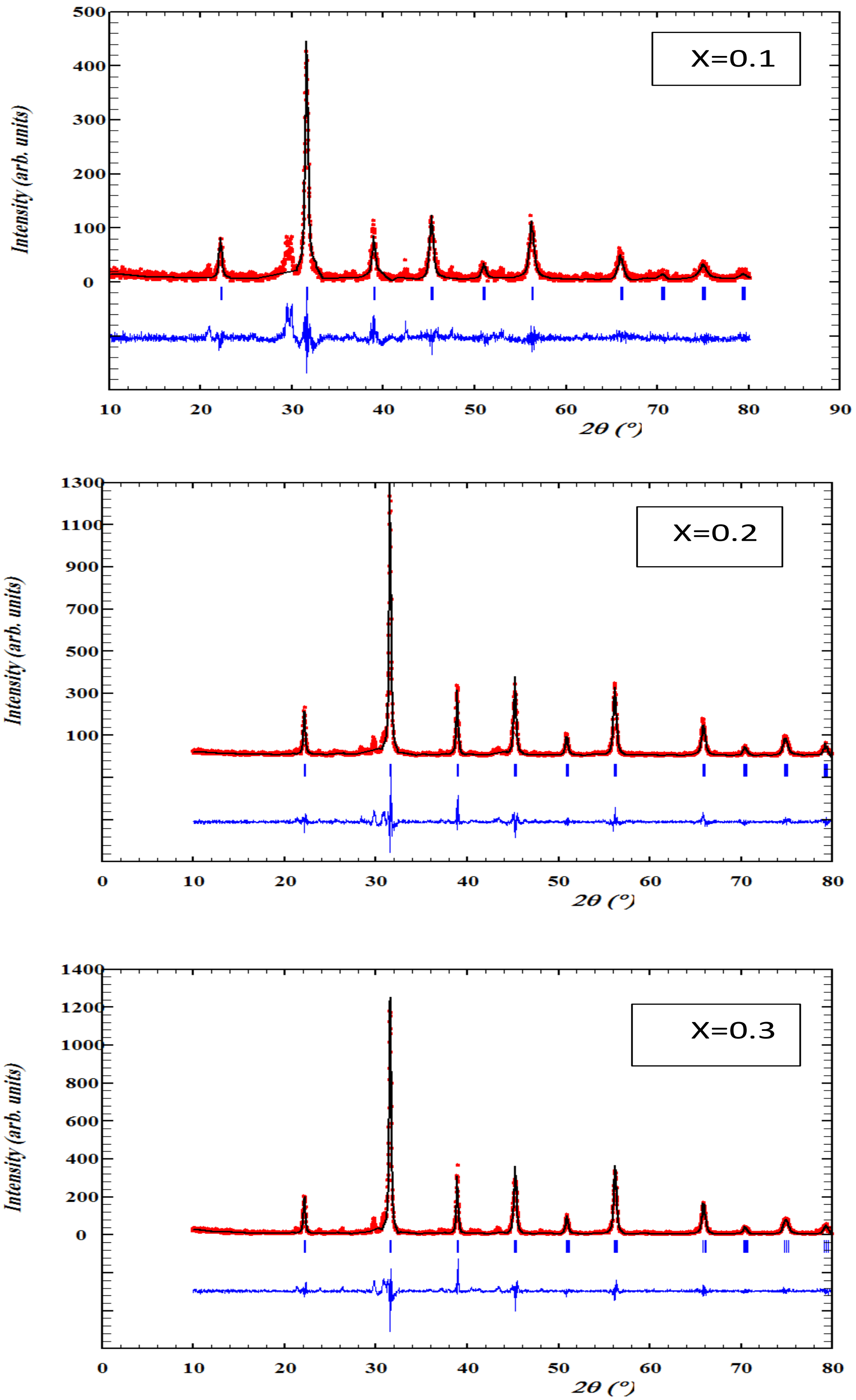


Fig. (2a): Rietveld refinement of $Ba_{1-x}Ca_xTiO_3$ samples with x = 0.1, 0.2 and 0.3 using FullProf program.

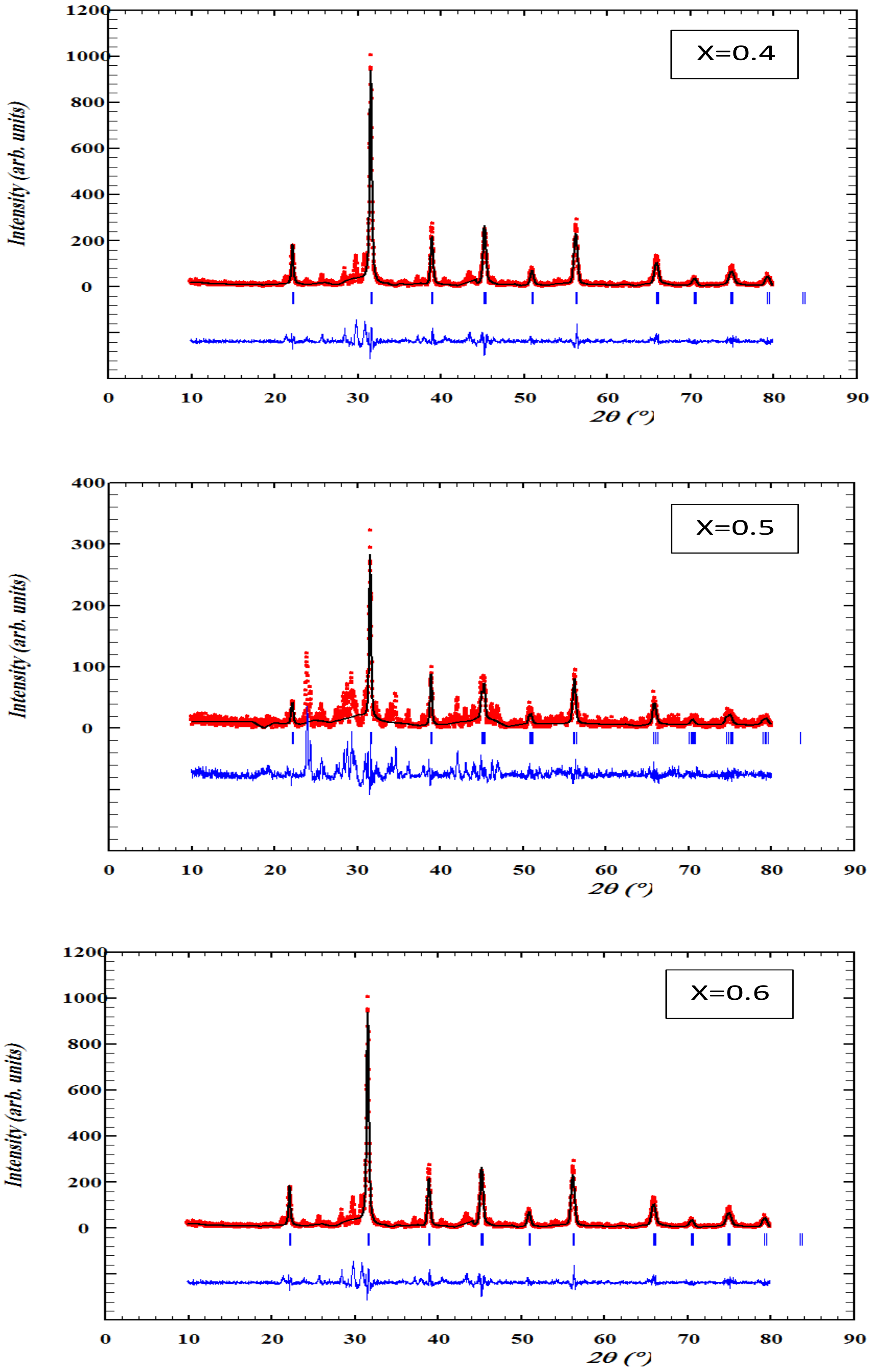


Fig. (2b): Rietveld refinement of $Ba_{1-x}Ca_xTiO_3$ samples with x = 0.4, 0.5 and 0.6 using FullProf program.

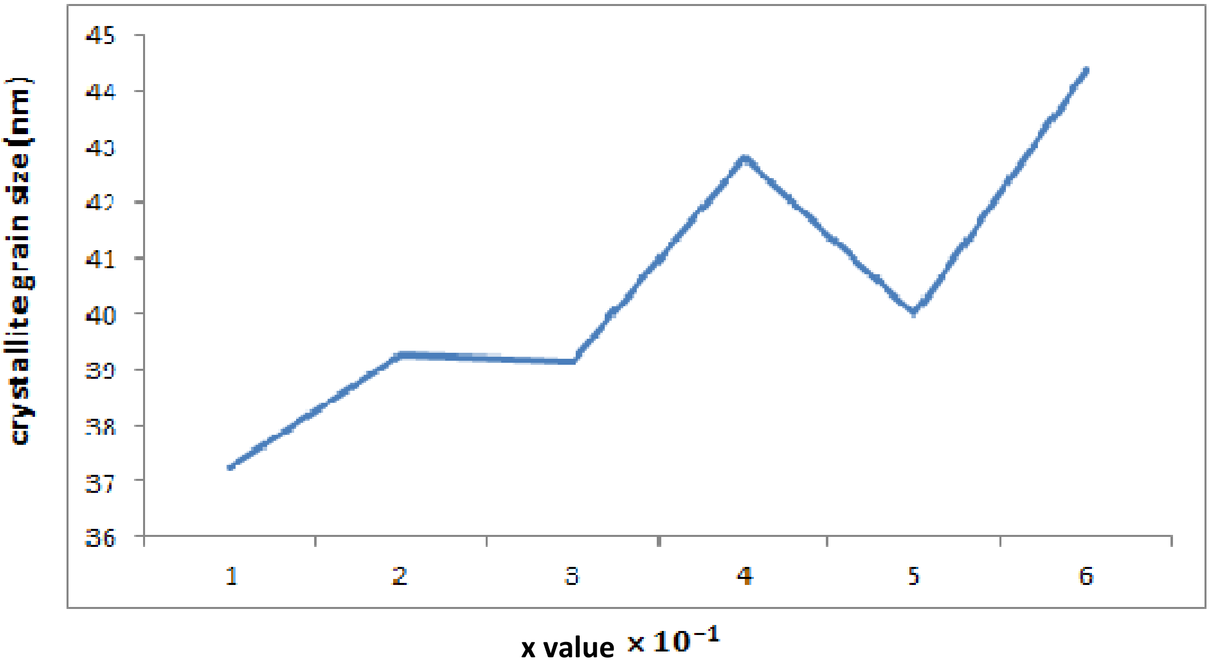
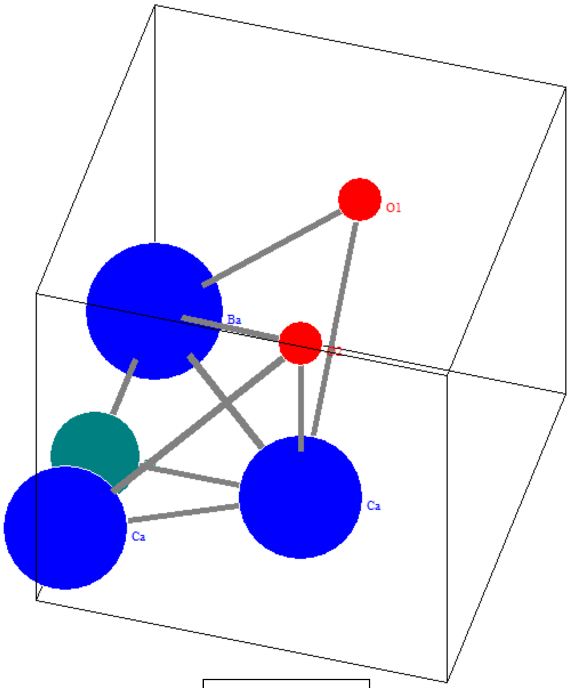


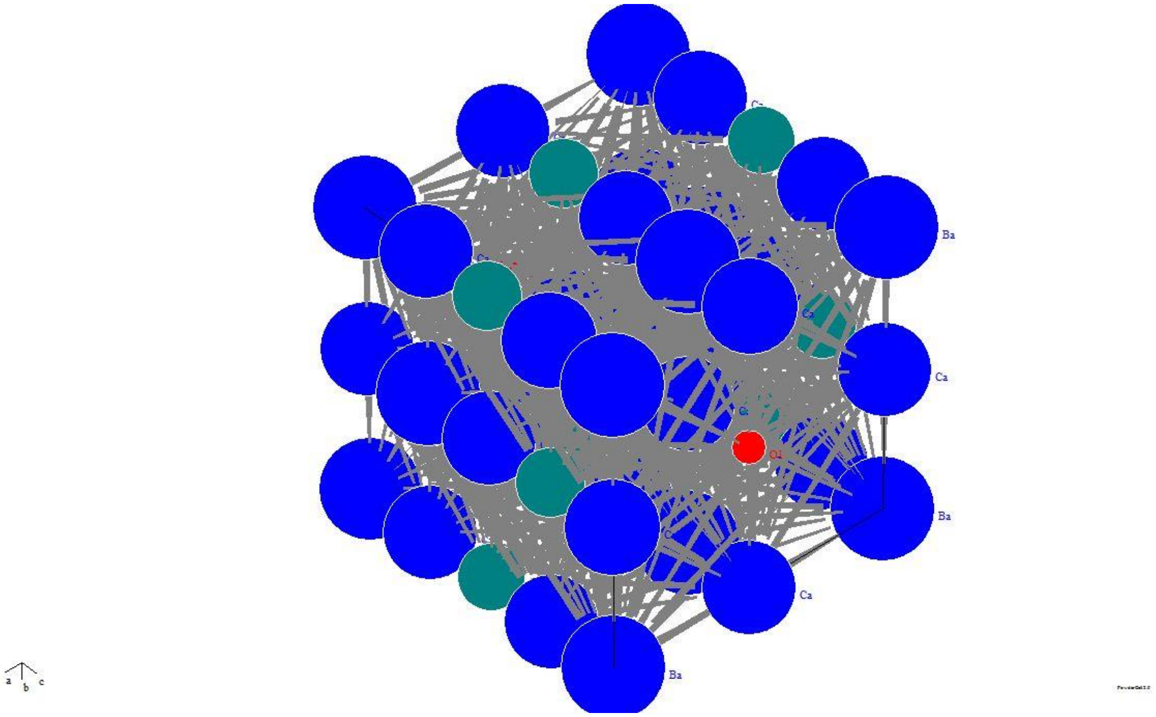
Fig. (3): Crystallite size vs. substitution calcium value (x).

Table (1): Lattice parameters and crystallite grain size for Ba$_{1-x}$Ca$_x$TiO$_3$, samples.

Sample	Structure	Space group	Unit cell volume (Å^3)	x-ray density g/cm^3	Crystallite size (nm)
X=0.1	Tetragonal a=3.98 Å c=4.098 Å, c/a=1.02	P4mm	64.771	5.728	37.26
X=0.2	Tetragonal a=3.998 Å c=4.089 Å, c/a=1.02	P4mm	65.358	6.34	39.27
X=0.3	Tetragonal, a=3.97 Å c=4.012 Å, c/a=1.o1 orthorhombic a=4.012 Å, b=3.97 Å c=2.80 Å	P4mm Pmmm	63.232 44.597	5.35	39.16
X=0.4	Orthorhombic a=13.77 Å, b=4.19 Å c=3.97 Å	Pmmm	229.054	5.32	42.81
X=0.5	Orthorhombic a=9.188 Å, b=7.89 Å c=4.18 Å	Pmmm	303.68	5.67	39.98
X=0.6	Orthorhombic a=14.17 Å, b=4.012 Å c=2.68 Å	Pmmm	152.49	5.89	44.37



a: Unit cell



b: Tetragonal structure

Fig. (4): Structure representations of tetragonal $Ba_{1-x}Ca_xTiO_3$ with x = 0.1 using Powder Cell program.

4 Conclusions

Perovskite material $Ba_{1-x}Ca_xTiO_3$ (where x = 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) was prepared successfully by using solid-state reaction technique. The diffraction data were compared with (ICDD) cards and analyzed by Rietveld refinement using FullProf and Unit Cell programs. The samples with x = 0.1 and 0.2 show single tetragonal phase with P4mm space group, whereas the third sample (with x = 0.3) shows a biphasic structure (tetragonal and orthorhombic) with P4mm and Pmmm space group respectively. The remaining samples (with x = 0.4, 0.5 and 0.6) have orthorhombic structure with Pmmm space group. Lattice parameters, unit cell volume, x-ray density and crystallite size were affected by Ca-substitutions in $BaTiO_3$ lattice due to difference of atomic radii of Calcium, Barium and Titanium.

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