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Void species determination of $Ba_{1-x}Ca_xTiO_3$ ceramics with FSDP-related XRD

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ABSTRACT

Void species nanostructure is studied in $Ba_{1-x}Ca_xTiO_3$ ceramics using X-ray diffraction with respect to first sharp diffraction peak (FSDP-related XRD). The FSDP parameters such as the interlayer separation, quasi-periodic in nature with an effective periodicity R , correlation length L , over which such periodicity is maintained, of atomic-density fluctuations, regardless of the precise atomic origin of such fluctuations, were calculated using general expressions. Void-based model may be a very useful experimental tool to study the above nanostructural peculiarities in crystalline solids. The present work is aimed to clarify methodological possibilities of this approach with calcium-modified barium titanate ceramics for the first time. In this paper we have reported for the first time, the effect of doping concentration of calcium on $BaTiO_3$ on different parameters like structural correlation length, periodicity, nano-void diameter, the first coordination sphere radius, the magnitude of scattering vector, etc.

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1. Introduction

Physical properties of a material depend on the microstructure and therefore, by controlling the microstructure, material properties can be tailored. Isovalent-substituted $BaTiO_3$ are promising candidates and have been actively studied. Among them, Ca-doped $BaTiO_3$ (i.e., $Ba_{1-x}Ca_xTiO_3$) crystals are considered to be one of the foremost potential candidates for the lead-free electro-optic modulators and memory devices [1]. Various applications of these ceramics have been cited in author's previous paper [2].

In ceramics, processing differences create inhomogeneous binder distribution in the materials, which can cause the formation of regions with differing densities and voids. Dark regions in the image are due to defects such as closed voids, pockets of binder, or agglomerates. Defects such as voids or agglomerates usually have different magnetic susceptibilities [3]. This difference causes artifacts in the image. Due to their mechanical, thermal, and chemical stability, high-performance ceramics have a range of properties, which makes it possible in many fields to go beyond the limits of use of various classes of materials nowadays available. In spite of this favorable starting situation, the worldwide endeavors to introduce this new group of materials have suffered some setbacks in both conventional applications and in new technologies. The ultimate reason is that these materials are very brittle. After the introduction of fracture

mechanics, designers in many fields have learned how to handle brittle materials and how to exploit the potential of their properties in components subject to extreme loadings. Materials scientists have also been very successful in developing ceramics with high strength and fracture toughness characteristics. Small and very small defects, such as micropores and cracks, as well as any other chemical and physical in-homogeneity, in the structure can cause catastrophic failure of the components due to high brittleness [4]. The intrinsic and extrinsic mechanisms of polymer degradation, like formation of volatile degradation products and involatile carbonaceous residue, the transport of volatile species (e.g. residual solvents, plasticizers, etc.) and degradation products through both empty and binder-filled pores [5], may be important issues in controlling the void species.

2. Theory

The FSDP parameters such as the interlayer separation, quasi-periodic in nature with an effective periodicity (R), and correlation length (L), over which such periodicity is maintained, of atomic density fluctuations, regardless of the precise atomic origin of such fluctuations, are calculated using the general expressions [6]:

$$R = \frac{2\pi}{S} \quad (1)$$

where S is the magnitude of the scattering vector and is given by

$$S = \frac{4\pi \sin \theta}{\lambda} \quad (2)$$

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Table 1
Nano-void species of calcium modified BaTiO₃ ceramics (Ba_{1-x}Ca_xTiO₃).

Samples	2θ(°)	β (Å)	S (Å ⁻¹)	R (Å)	L (Å)	r (Å)	D (Å)	d (Å)	E
I	22.3618	0.2400	3.1052	2.2043	26.1908	2.4899	2.3279	1.5182	1.23001
II	22.4053	0.1920	3.1109	2.0206	32.7385	2.4853	2.3237	1.5154	1.22999
III	22.4532	0.1920	3.1166	2.0169	32.7385	2.4808	2.3194	1.5127	1.23002
IV	22.5182	0.2640	3.1256	2.0111	23.8098	2.4736	2.3127	1.5083	1.22999
V	22.5261	0.3120	3.1247	2.0116	20.1468	2.4743	2.3134	1.5087	1.22998
VI	22.5039	0.2400	3.1231	2.0127	26.1908	2.4756	2.3146	1.5095	1.23000
VII	22.5288	0.2400	3.1264	2.0106	26.1908	2.4730	2.3121	1.5079	1.23001
VIII	22.5038	0.2400	3.1231	2.0127	26.1908	2.4756	2.3146	1.5095	1.23001

corresponding to the position of the FSDP, and

$$L = \frac{2\pi}{\beta} \quad (3)$$

where β is the full width at half maximum (FWHM) of the FSDP.

The refined XRD data and the calculated FSDP parameters are shown in Table 1.

3. Materials and method

Barium calcium titanate ceramics, with the formula Ba_{1-x}Ca_xTiO₃, with x ranging from 0.0 to 0.5, were prepared by conventional solid state reaction technique. High purity (more than 99%) starting powders of BaCO₃, TiO₂, and CaCO₃ were mixed with the addition of alcohol, and ball milled for 2 h at 300 rpm in a planetary ball mill (Fritsch, Pulverisette 5") in zirconia medium. The powders of the compounds were conventionally calcined at 1280 °C for 5 h in an electrical furnace. The X-ray powder diffraction profiles of the ball milled samples were recorded using Ni-filtered Cu K α radiation from a highly stabilized and automated Philips X-ray generator (PW 1830) operated at 30 kV and 20 mA. The generator is coupled with a Philips X-ray powder diffractometer consisting of a PW 3040 MPD controller, goniometer of radius 200 mm, and a proportional counter. For this experiment, 1° divergence slit and 1 mm receiving slit were used. The step-scan data of step size 0.02° and step scan 0.6 s were recorded for the entire angular range 20°–80°.

4. Results and discussion

One can see (Fig. 1) that the FSDP for various calcium modified BaTiO₃ ceramics is around $2\theta \approx 22.3618^\circ$, $2\theta \approx 22.4053^\circ$, $2\theta \approx 22.4532^\circ$, $2\theta \approx 22.5182^\circ$, $2\theta \approx 22.5261^\circ$, $2\theta \approx 22.5039^\circ$, $2\theta \approx 22.5288^\circ$ and $2\theta \approx 22.5038^\circ$ corresponding to the scattering vectors 3.1052, 3.1109, 3.1166, 3.1256, 3.1247, 3.1231, 3.1264 and 3.1231 Å⁻¹, respectively. The magnitude of FWHM of the FSDP of samples I ($x=0$), II ($x=0.05$), III ($x=0.1$), IV ($x=0.2$), V ($x=0.25$), VI ($x=0.3$), VII ($x=0.4$), and VIII ($x=0.5$) are 0.2400, 0.1920, 0.1920, 0.2640, 0.3120, 0.2400, 0.2400, and 0.2400, respectively.

The interlayer separation with an effective periodicity (R), (the atom–void distance [7]) and the correlation length (L) are calculated using Eqs. (1)–(3) and found to be 2.2043 and 26.1908 Å for sample-I. For all other samples including sample-I, these values are presented in Table 1. This means that periodicity of $R \approx 2.2043$ Å in sample-I is necessary to give the FSDP at the observed value of scattering vector $S \approx 3.1052$ Å⁻¹ and the real space quasi-periodicity takes place along the correlation length of $L \approx 26.1908$ Å.

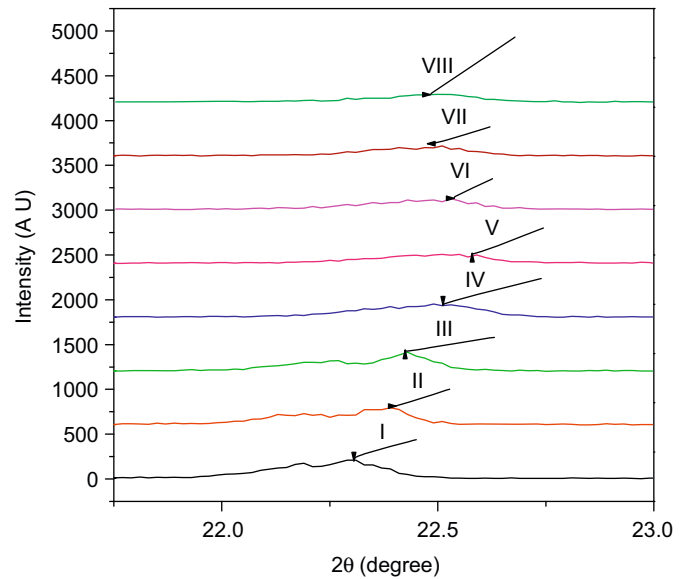


Fig. 1. XRD pattern of first sharp diffraction peak.

In case of sample-II, the FSDP is found around $2\theta \approx 22.4053^\circ$ with a scattering vector 3.1109 Å⁻¹. The magnitude of FWHM of the FSDP is equal to 0.1920. The repetitive distance (R) and the structural correlation length (L) are found to be equal to 2.0206 and 32.7385 Å, respectively.

Analytically, the FSDP position S and nano-void diameter D can be represented as [8,9]:

$$S = \frac{2.3\pi}{D} \quad (4)$$

where D is the nano-void diameter and found to be equal to 2.3279, 2.3237, 2.3194, 2.3127, 2.3134, 2.3146, 2.3121, and 2.3146 Å, respectively.

The inter-atomic correlation, a characteristic distance of second or third neighbour inter-atomic distributions is given by the well known formula [10]:

$$2r \sin \theta = 1.23\lambda$$

$$\text{or, } r = \frac{1.23\lambda}{2 \sin \theta} \quad (5)$$

where r is the first coordination sphere radius, θ is the scattering angle, λ is the X-ray diffraction wavelength, and the co-efficient 1.23 is known as the Ehrenfest's number.

Eq. (5) can be represented as

$$S = \frac{2.46\pi}{r} \quad (6)$$

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