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# Synthesis, narrow range of titanium-doping, thermal and crystal structure features of Ti (IV)-doped-bismuth-vanadates aurivillius ferroelectrics

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# ABSTRACT

Aurivillius phase with the general formula  $Bi_2SrV_{2-x}Ti_xO_9$ , where (x=0.05, 0.1, 0.2 mole) were carefully synthesized and processed by using freeze dry route depending on solution precursors and sintering temperature at 1000 °C for 8 hrs. TGA and DTA thermal analyses were performed on the green mixture of starting materials to identify the best thermal treatment for processing of Bi-Sr-V-O system. XRD – analysis of the prepared samples proved that Ti-dopant can substitute successfully within narrow range  $0.0 \le x \le 0.2$  mole. The Bi-layered perovskite structure was refined and found to be orthorhombic with space group A21am and lattice constants a=5.5195(4), b=5.5249(6),  $c=25.2837(5) A^\circ$ . SE-microscopy indicated that the average grain size found to be in between 1.3 and  $1.7\mu$ m.Furthermore, a visualized investigations were made to confirm crystal structure of Ti-substituted  $Bi_2SrV_{2-x}Ti_xO_9$  Aurivillius phase.

Keywords: Synthesis; Perovskite; X-ray; SEM; TGA & DTA; Crystal Structure.

## **INTRODUCTION**

During the last decade a lot of research has been carried out on the so-called Bi-based layerstructured ferroelectric oxides (BLSF) since these materials are excellent candidates for application as nonvolatile ferroelectric random access memory (NVFRAM). Important advantages of the BLSF-materials are the resistance to polarization fatigue up to  $10^{12}$  cycles of polarization. The bismuth – oxide layered perovskite materials such as Bi-Sr-V-O have attracted increasing attention in the research community because they are fatigue – free and lead free [1-3]. The wide spread application and commercialization of bismuth- layered perovskite ferroelectrics have been limited by drawbacks, their rather high processing temperature and their relatively low remanent polarization [4-5]. Recently, efforts have been made to enhance the properties of layered perovskite ferroelectrics by addition or substitution of alternative cations [6-8]. It's now well established that the variation of oxygen content and distribution of oxygen atoms on the lattice site strongly influence the physical and structural properties of superconducting materials and many other metallic mixed oxides [9].

Aurivillius published a series of papers [10-14] explaining the discovery of mixed metal oxides having bismuth layer alternating with perovskite structure layers, because of their ionic structural framework, Aurivillius phases exhibit great flexibility with respect to metal cation substitution. Therefore, these phases have high potential for systematic control of their properties [15].

There are different studies showing the chemical substitution such as Pb doping on Bi-O layers that can be used to improve conduction in the blocking layers and so to a large decrease in the resistivity anisotropy. The reduced anisotropy leads to improvement of the critical current in the heavy Pb-doped [16-21].

Das et al. [22] reported the improved remanent polarization of SBN and SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> this films, when a small amount of Ca cations were incorporated into A sites: Bismuth layered perovskite materials have high fatigue resistance [23] and therefore have attracted an increasing attention for non-volatile random access memory (NVRAM) application [24].

The crystal structure and chemical composition of these layered perovskites were systematically studied [25] with the general formula of  $(Bi_2O_2)^{2+}$   $(Am^{-1}BmO^3m^{+1})^{3-}$  that consisting of M-perovskite unites sandwiched between bismuth oxide layers called the family of bismuth layered structured ferroelectrics [26].

The crystal structure of  $SrBi_2Ta_2O_9$  comprises pseudo- perovskite blocks  $(SrTa_2O_7)^{2-}$  that are sandwiched between  $(Bi_2O_2)^{2+}$  layers. Sr occupies the A site of the perovskite block and Ta occupies the B-site [27].

The essential goal of the present article is to investigate low concentration range of Ti (IV)– dopings on- vanadium sites of 212 Bi-Sr-V-O Aurivillius phase which synthesized via solution route on;

- (a) Crystal structural & microstructure properties.
- (b) Thermal and processing temperature.

Furthermore a visualized studies on crystal structure data were made by means of DIAMOND IMPACT CRYSTAL package version 3.2- 2010-Germany to confirm crystal structure of titanium substituted aurivillius structure .

#### MATERIALS AND METHODS

#### **Experimental:**

The pure  $Bi_2SrV_2O_9$  and doped samples with the general formula  $Bi_2SrV_{2-x}$   $Ti_xO_9$ , where x = 0.05, 0.1, 0.2 mole were prepared by freeze dry technique and sintering procedure using the appropriate amounts nitrate solutions precursors.

The precursor (I) was the accurate molar ratios of  $Bi_2(CO_3)_3$  and  $SrCO_3$  that dissolved in few drops of conc. nitric acid giving the corresponding metal nitrates solutions. The precursor II was for  $(NH_4)_2VO_3$  and  $TiO_2$  (each purity >99%) that also dissolved in few drops of conc. nitric acid giving metal nitrates solutions. The precursors I + II were mixed together and poured into 50%

citrate/urea solution in 1L separating funnel then allow to drop into liquid nitrogen getting freeze drops of mixtures.

The resulted freeze drops forwarded to freeze dry machine with specific program of acidic water solvent for 60 hrs . The resultant reground in an agate mortar for half an hour. Then the finely ground powder was subject to firing at 800  $^{\circ}$ C for 10 hours, reground and finally pressed into pellets with thickness 0.2 cm, diameter 1.2 cm and sintered at 1000  $^{\circ}$ C for 8 hours. Then the furnace is cooled slowly down to room temperature. Finally the materials are kept in vacuum desiccator over silica gel dryer.

## **II.I-** Structural Measurements:

#### **II.I.A. X-Ray diffraction (XRD):**

The X-ray diffraction measurements (XRD) were carried out at room temperature on the fine ground  $Bi_2SrV_2O_9$  and  $Bi_2SrV_{2-x}Ti_xO_9$  systems in the range ( $2\theta = 10-70^\circ$ ) using Cu-Ka radiation source and a computerized [Steo-Germany] X-ray diffracto-meter with two theta scan technique. A visualized studies of crystal structure were made by using Diamond Molecular Structure version 3.2 package, Germany .

## **II.I.B. Scanning Electron – Microscope:**

Scanning electron microscope (SEM) measurements were carried out using small pieces of prepared samples on different sectors to be the actual molar ratios by using "TXA-840,JEOL-Japan" attached to XL30 apparatus with EDX unit, accelerant voltage 30kv, magnification 10x up to 500.000x and resolution 3. nm. The samples were coated with gold.

#### **II.II.** Thermal analyses measurements :

The thermo-gravimetric analysis (TGA) and the differential thermal analysis (DTA) measurements were carried out on the green mixtures (starting powders) of the prepared samples using a computerized Shimadzu c Japan TGA/DTA analyzer and  $Al_2O_3$  as a reference for DTA measurements.

#### **RESULTS AND DISCUSSION**

#### III.I. Phase Identification: III.I.A. X-Ray Diffraction:

The X-ray diffraction patterns of pure and Ti-doped samples with the general formula  $Bi_2SrV_{2-x}$   $Ti_xO_9$ , where x = 0.05, 0.1, 0.2 mole are shown in Fig (1<sub>a-d</sub>).

Analysis of the corresponding 20 values and the interplanar spacing d (A<sup>o</sup>) by using computerized program proved that the compound is mainly belongs to aurivillius -Bi-layered perovskite crystal structure which refined and found to be orthorhombic space group A21am, with lattice constants a = 5.5195(4), b = 5.5249(6), c = 25.2837(5) A<sup>o</sup>, that expressed by assigned peaks in major.

Single aurivillius phase of the layered perovskite structure appeared when dopant ratio is up to or equal 0.05 mole as reported in [28] for substituted aurivillius phase. The substitution of  $Ti^{4+}$  for  $V^{5+}$  in BSV would induce A-site cation vacancies in perovskite layers, which leads to an increase of internal stress for the shrinkage of unite cell volume [29]. The increasing of Ti- ions in the crystal lattice of BSV will result in strong stress, which will expel other Ti-ions from the crystal lattice of BSV. The layered perovskite structure would be more restrictive since  $(Bi_2O_2)^{2+}$  interlayeres impose a great constraint for structural relaxation. Such a structural constraint

induced from  $(Bi_2O_2)^{2+}$  interlayeres may well explain the lack of an appreciable decrease in lattice parameters with an increased amount of doping as reported in[30] for vanadium doping.



(a) pure  $Bi_2SrV_2O_9$  and Ti-doped samples (b): $Bi_2SrV_{1.95}Ti_{0.05}O_9$ , (c): $Bi_2SrV_{1.9}Ti_{0.1}O_9$ (d):  $Bi_2SrV_{1.8}Ti_{0.2}O_9$ .

From Fig.(2) it is clear that *c*-axis increases as result of substitution Ti- dopant on the bases of pauling ionic radius  $Ti^{4+}(68 \text{ pm})$  while  $V^{5+}(59 \text{ pm})$ . It is expected that *c*-axis



Fig.(2): Variation of *c-axis* as a function of Ti-content

increases as  $\text{Ti}^{4+}(68 \text{ pm})$  doping ratio increases. Furthermore,  $\text{Ti}^{4+}$  is lower in charge than V<sup>5+</sup> and as a result it is expected to decrease stress inside lattice and consequently the shrinkage factor of lattice will be increased. From Fig.(1<sub>a-d</sub>).

It is clear that the Ti- substitutions are successful in the investigated low concentration range with maximum concentration x = 0.2 mole since there is no evidence noticeable at X-ray diffract gram referring to Ti- impurity phases. This confirms that Ti-dopant can substitute in the V-sites successfully in the whole investigated range(0.05-0.2 mole ).

#### **III.I.B. Micro-Structural Properties (SEM):**

Fig.  $(3_{a -c})$  show the scanning electron micrographs recorded for pure 212-Bi-Sr-V-O system and Ti-doped having the formula Bi<sub>2</sub>SrV<sub>2-x</sub> Ti<sub>x</sub>O<sub>9</sub>, where x = 0.0, 0.05 and 0.1 mole. The average grain size of pure and Ti-doped 212-Bi-Sr-V-O system were calculated carefully and found to be in between 1.3-1.7 µm which is totally matched with those reported in the literatures [31-32].



Fig. (3<sub>a-c</sub>): SE-micrograph images recorded for pure and some selected Ti-doped 212-Bi-Sr-V-O system: where (a): Bi<sub>2</sub>SrV<sub>2</sub>O<sub>9</sub>, (b): Bi<sub>2</sub>SrV<sub>1.95</sub>Ti<sub>0.05</sub>O<sub>9</sub> and (c): Bi<sub>2</sub>SrV<sub>1.8</sub>Ti<sub>0.2</sub>O<sub>9</sub>

Fig  $(3_a)$  for pure Bi-212 shows that the high content of bismuth results in attraction for the grain with each others and porous appeared between the grains due to bismuth evaporation.

For sample with Ti-doping (0.05,0.1 mole), the Ti- ions connect to grain with other, the increasing of Ti- concentration leads to increase of grain size from 1.3  $\mu$ m for pure Bi-212 to 1.7  $\mu$ m for doped samples x = 0.05 and 0.3 respectively.

From Fig.  $(3_{a-c})$  one can notify that there is no sharp differences in the grey colouration that reflects homogeneity and the quality of processing of 212-Bi-Sr-V-O regime. Furthermore, TiO<sub>2</sub> does not detected in the grain boundaries which emphasis that Ti-ions substitute successfully on the crystal lattice on the vanadium sites in the investigated range.

The white particles zone in the SEM-image is due to Bi-excess show a small fraction of metallic Bi segregation. A possible explanation is the lack of oxygen during thermal

decomposition. As a consequence  $Bi^{3+}$  is reduced to Bi. Upon further heating this Bi is oxidized again to  $Bi^{3+}$  and incorporated in the  $SrBi_2V_2O_9$  perovskite structure [33].

#### **III.II.** Thermal Analyses measurements:

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out in the temperature range from room temperature to 850°C at a heating rate of 10 °C min<sup>-1</sup> on the green mixture of pure 212-BiSrVO and some selected Ti -doped samples with the general formula  $Bi_2SrV_{2-x}Ti_xO_9$ , where x= 0.1, 0.2 mole.

From TGA/DTA curves as shown in Fig ( $4_{a-c-e}$ ), the TGA analysis can be divided into four steps, the first step occupies the region from room temperature till 230°C for which the weight loss occurred is attributed to the humidity and decomposition of (NH<sub>4</sub>)<sub>2</sub>VO<sub>3</sub> into NH<sub>3</sub> and vanadium oxide.



 $\label{eq:Fig.4a-c-e} Fig.(4_{a-c-e}): Thermogravimetric (TGA) and differential thermal analyses(DTA) curves recorded for green mixture of pure and some selected Ti-doped 212-Bi-Sr-V-O system where (a): Bi_2SrV_2O_9, (c): Bi_2SrV_{1.95}Ti_{0.05}O_9$ 

The second region from 230°C to 400°C in which  $Bi_2(CO_3)_3$  is decomposed into  $Bi_2O_3$  and  $CO_2$ . The third region of temperature from 400-660 °C at which weight loss occurred is due to partial decomposition of SrCO<sub>3</sub> incorporated with high temperature solid state initial phase formation reaction. The fourth step occupying in the range 660-850 °C is due to final decomposition of SrCO<sub>3</sub> and the final formation of solid state oxide [34-36]. The endothermic peaks above 400°C in DTA curves correspond to solid state reaction formation [37].

#### III.III. Molecular Structure Visualization of $Bi_2SrV_{2-x}Ti_xO_9$ :

A visualization study made is concerned by matching and comparison of calculated and theoretical data of atomic positions ,bond distances , oxidation states and bond torsion on the crystal structure formed see Tables 1-3. The study exhibited good fitting between experimental and theoretical data .

Atom	Atom	x	у	z	d A <sup>o</sup>
Sr1 Bi1	Sr1 Bi1	0.226	0.751	0.5	0.2649
	01	0.69	0.788	0.5	2.3051
Sr2 Bi2	O3	0.477	1.006	0.7489	2.282
	03	0.023	1.006	0.7489	2.282
	O3	-0.023	0.994	0.7489	2.3906
	03	0.523	0.994	0.7489	2.3906
V1 Ti	V1 Ti	0.231	0.2549	0.58668	0.2097
	O4	0.477	0.481	0.5706	1.7422
	O2	0.284	0.302	0.6589	1.8321
	05	0.422	-0.046	0.585	1.8624
	O4	0.023	0.481	0.5706	1.887
	05	0.078	-0.046	0.585	1.9664
01	01	0.19	0.212	0.5	0.6623
	V1 Ti	0.269	0.2549	0.58668	2.1989
	V1 Ti	0.231	0.2549	0.58668	2.2303
	Sr1 Bi1	0.726	0.249	0.5	2.3051
	O4	0.477	0.481	0.5706	2.4873
O2	O2	0.216	0.302	0.6589	0.3753
	V1 Ti	0.269	0.2549	0.58668	1.8321
	V1 Ti	0.231	0.2549	0.58668	1.8534
03	03	0.477	0.506	0.2489	0.2624
	Sr2 Bi2	0.75	0.7646	0.20155	2.282
	Sr2 Bi2	0.25	0.2354	0.20155	2.3906
O4	O4	0.477	0.481	0.5706	0.3292
	V1 Ti	0.731	0.7451	0.58668	1.7422
	V1 Ti	0.769	0.7451	0.58668	1.887
	01	0.69	0.788	0.5	2.4873
	05	0.422	0.954	0.585	2.4892
05	05	0.422	-0.046	0.585	0.9994
	V1 Ti	0.731	-0.2549	0.58668	1.8624
	05	0.922	0.046	0.585	1.8986
	V1 Ti	0.769	-0.2549	0.58668	1.9664
	04	0.477	0.481	0.5706	2.4892

Table.1.Selected bond lengths inside unit cell of Bi <sub>2</sub>	SrV <sub>2-x</sub> Ti <sub>x</sub> O <sub>9</sub> aurivillius phase
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Atom	Atom	Coordinates	d A <sup>o</sup>
Sr1 Bi1	Sr1 Bi1	0.5-x, y, z	0.2649
	01	1-x, 1-y, z	2.3051
Sr2 Bi2	03	1-x, 1.5-y, 0.5+z	2.282
	O3	-0.5+x, 1.5-y, 0.5+z	2.282
	O3	0.5-x, 0.5+y, 0.5+z	2.3906
	O3	x, 0.5+y, 0.5+z	2.3906
V1 Ti	V1 Ti	0.5-x, y, z	0.2097

	O4	1-x, 1-y, z	1.7422
	O2	x, y, z	1.8321
	O2	0.5-x, y, z	1.8534
	O5	1-x, -y, z	1.8624
	O4	-0.5+x, 1-y, z	1.887
01	01	0.5-x, y, z	0.6623
	V1 Ti	x, y, z	2.1989
	V1 Ti	0.5-x, y, z	2.2303
	Sr1 Bi1	1-x, 1-y, z	2.3051
	O4	1-x, 1-y, z	2.4873
O2	O2	0.5-x, y, z	0.3753
	V1 Ti	x, y, z	1.8321
	V1 Ti	0.5-x, y, z	1.8534
O3	O3	1-x, 1-y, z	0.2624
	Sr2 Bi2	1-x, 1.5-y, -0.5+z	2.282
	Sr2 Bi2	x, -0.5+y, -0.5+z	2.3906
O4	O4	1-x, 1-y, z	0.3292
	V1 Ti	1-x, 1-y, z	1.7422
	V1 Ti	0.5+x, 1-y, z	1.887
	01	1-x, 1-y, z	2.4873
	O5	1-x, 1-y, z	2.4892
O5	O5	1-x, -y, z	0.9994
	V1 Ti	1-x, -y, z	1.8624
	O5	1.5-x, y, z	1.8986
	V1 Ti	0.5+x, -y, z	1.9664
	V1 Ti	0.5-x, y, z	2.2354

Table .3. Selected bond angles of some selected atoms in	inside unit cell of of Bi <sub>2</sub> S	brV2.xTixO9
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Atom 1	Atom 2	Atom 3	Angle 123^
01	V1 Ti	Sr1 Bi1	95.335
01	V1 Ti	O4	43.103
01	V1 Ti	Sr1 Bi1	100.681
01	V1 Ti	O4	46.764
01	Sr1 Bi1	04	65.045
O2	O2	V1 Ti	87.41
O2	02	V1 Ti	80.919
O2	V1 Ti	V1 Ti	6.491
03	03	Sr2 Bi2	111.489
03	03	Sr2 Bi2	62.649
03	Sr2 Bi2	Sr2 Bi2	118.524
O4	O4	V1 Ti	164.529
04	04	V1 Ti	167.297
O4	O4	V1 Ti	13.03
04	04	V1 Ti	10.825
04	V1 Ti	01	59.591
04	V1 Ti	05	54.847

O4	V1 Ti	01	59.435
O4	V1 Ti	05	59.556
O4	V1 Ti	01	144.364
O4	V1 Ti	05	120.015
04	V1 Ti	01	142.511
O4	V1 Ti	05	116.453
05	V1 Ti	05	63.036
05	V1 Ti	O4	164.477
05	05	V1 Ti	57.581
05	05	V1 Ti	145.943
05	05	V1 Ti	148.955
05	V1 Ti	O4	43.798
05	V1 Ti	O4	43.788
05	V1 Ti	O4	46.701

Fig.5<sub>a</sub> shows zoom in XRD-profile of aurivillius phase with the general formula  $Bi_2SrV_{2-x}$   $Ti_xO_9$  measured in the range (2 $\theta$  =30-35 °). The blue circles refer to the 212- aurivillius phase which compared with visualized XRD-profile that constructed depending up on lattice coordinates of pure  $Bi_2SrV_{2-x}$   $Ti_xO_9$  aurivillius phase as shown in Fig.<sub>5b</sub>. The comparison of fundamental lines of peak positions in Figs.<sub>5a,5b</sub> in the selected range (2 $\theta$  =30-35 °) indicated that there are good fitting between peak positions located in between 2 $\theta$  =30-35 ° in both diagrams.



Fig.5a:High resolution XRD-profile of Aurivillius phase having the general formula  $Bi_2SrV_{2-x}$  $Ti_xO_9 (2\theta = 30-35^{\circ})$ 



Fig.5b: Visualized XRD-of aurivillius Bi<sub>2</sub>SrV<sub>2</sub>O<sub>9</sub> phase .

It is well known that the crystal structure of  $Bi_2SrM_2O_9$  comprises pseudo- perovskite blocks  $(SrM_2O_7)^{2-}$  that are sandwiched between  $(Bi_2O_2)^{2+}$  layers as shown in Figure  $6_a$  and  $6_b$ . Sr

occupies the A site of the perovskite block and M occupies the B-site ,The B-sites could be Nb or Ta as reported in [27] .

It was suggested that the existence of  $V^{5+}$  at the *B*-site in the pseudo-perovskite layers reduces the electromechanical coupling coefficients which consistent with [38].

The structural formula of the aurivillius phase is generally described as  $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$ , which consists of pseudo-perovskite  $(A_{m-1}B_mO_{3m+1})^{2-}$  layers interleaved with  $(Bi_2O_2)^{2+}$  layers along the *c*-axis. The *A* site is composed of a mono-, di-, or trivalent metallic ion, the *B* site contains a tetra-, penta-, or hexa-valent metallic ion, and *m* is the number of  $BO_6$  octahedra in the pseudo-perovskite layers (m=1-5) [39].

In the present investigations A-sites are Bi and Sr atoms while B-sites is penat-valent vanadium atom and consequently represents  $VO_6$  octahedra as shown in Figs.6<sub>a</sub>.

The unit cell of aurivillius phase was visualized as clear in  $Fig.6_b$  with minimum number of atoms which is 60 atoms.



Fig.<sub>6b</sub>: Perovskite layered structure of Bi<sub>2</sub>SrM<sub>2</sub>O<sub>9</sub> aurivillius phase (M=V<sup>5+</sup>)



Visualized Lattice with 60 atoms

Fig.<sub>6b</sub>: Filled unit cell diagram of Bi<sub>2</sub>SrM<sub>2</sub>O<sub>9</sub> aurivillius phase (M=V)

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Tables.1,2 and 3 show the calculated bond distances and bond angles of some selected bonds and angles inside unit cell of visualized aurivillius Ti-doped phase .

The analysis of these listed data indicated that the B-O bond distances where is B-sites are (VTi) ions are matched with those reported in literatures as [40] with maximum bond length for VTi- $O_5$  which is 1.9623(4) A<sup>o</sup> and minimum one is for VTi- $O_4$  which equal to 1.7421 A<sup>o</sup> respectively.

The analysis of calculated bond angles of  $VO_6$  poly-octahedral indicated that Ti-substitutions in the vanadium sites does not caused any kind of distortion on the poly –hedral formed and there are no torsion on the most of angles which reflects the charge suitability and ionic radius fitting between Ti-dopant and vanadium ion .

It was observed that there are three kinds of oxygen-VTi-oxygen angles namely  $O_1-V-O_4$  43.103°,  $O_4-V-O_1$  &  $O_4-V-O_5$  maximum 59.5912 and 54.847 minimum

And finally third type which is  $O_4$ -V- $O_1$ ,  $O_4$ -V- $O_5$  with angles  $144.3641^{\circ \text{ max.}}$  and  $116.4532(1)^{\circ \circ \circ \circ}$  min. The differences in values of angles that belong to the same environment are due to the inter-coupling and repulsion force caused by the neighboring oxygen atoms .

#### CONCLUSION

The conclusive remarks can be summarized as following ;

1- X-ray diffraction proved that the compounds is mainly belong to aurivillius -Bi-layered perovskite crystal structure which refined and found to be orthorhombic space group A21am, with lattice constants a = 5.5195(4), b = 5.5249(6), c = 25.2837(5) A<sup>o</sup>.

2- Ti-dopant can substitute in the V-sites successfully in the whole investigated range ( 0.05 -  $0.2\ {\rm mole}$  ) .

3- Synthesis by Freeze dry technique yield to structure quality with moderate homogeneity as proved in SEM & EDX analysis.

4- Thermal analyses TGA & DTA indicated that the best processing temperature is above 850  $^{\rm o}{\rm C}$   $\pm$  10 .

5- Visualization of molecular structure of Ti-doped 212-SBV-aurivillius phase confirmed the suitability and fitting of titanium dopings in the investigated range.

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