Titanium doping effect and structural properties of titanium-(IV)-doped-Bi-Sr-Vanadate ferroelectric

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ABSTRACT

The perovskite samples with general formula Bi\textsubscript{2}SrV\textsubscript{2-x}Ti\textsubscript{x}O\textsubscript{9}, where (x= 0.05, 0.1, 0.2, 0.3, 0.6) were carefully synthesized and processed by using solid state reaction route and sintering temperature at 900°C for 25 hrs. TGA and DTA thermal analyses were carried out on the green mixture to identify the best thermal treatment for processing of Bi-Sr-V-O system. Structural investigations by using XRD – analysis of the prepared samples proved that Ti-dopant can substitute successfully until x= 0.45 mole on the Bi-layered perovskite crystal structure. SE-microscopy indicated that the average grain size was found to be in between 1.25 and 1.66 \( \mu \)m. Ti-dopings have slight to moderate effects on both ESR-signals and conduction mechanism of Ti-doped Bi-Sr-VO regime ferroelectric ceramic. Infrared absorption spectra recorded for Ti-doped samples show broad band characteristics to different M-O-M vibrational modes.

INTRODUCTION

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\textsuperscript{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\textsuperscript{4-5}. Recently, efforts have been made to enhance the properties of layered perovskite ferroelectrics by addition or substitution of alternative cations\textsuperscript{6-8}.

It’s now well established that the variation of oxygen content and distribution of oxygen atoms on the lattice site strongly influences the physical and structural properties (e.g. electrical conductivity) at high-temperature. Superconductors and many other metallic oxides\textsuperscript{9}.

The discovery of high temperature superconductors has attracted much attention for their technological application such as superconducting quantum interference devices (SQUID). The high Tc ceramic superconductor, the Bi –based system has been studied because of its high critical temperature especially with the partial substitution of Pb in Bi and Sr sites since it promotes the stabilization of 2223 phase when grown from 2212 phase\textsuperscript{10-11}.

Aurivillius published a series of papers\textsuperscript{12-14} 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\cite{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\cite{16-18}.

It’s shown that the Sn doping in Bi-system superconductors does not change the Tc significantly\cite{19-20}. Shrivastava et al.\cite{21} found that the incorporation of La cations into A sites up to 50% continuously decreased the Curie temperature in SBN ferroelectric ceramics.

Das et al.\cite{22} reported the improved remanent polarization of SBN and SrBi$_2$Ta$_2$O$_9$ thin films, when a small amount of Ca cations were incorporated into A sites: Bismuth layered perovskite materials have high fatigue resistance\cite{23} and therefore have attracted an increasing attention for non-volatile random access memory (NVRAM) application\cite{24}.

The crystal structure and chemical composition of these layered perovskites were systematically studied\cite{25} with the general formula of (Bi$_2$O$_2$)$_{2+}$ (Am$^{1-}$BmO$^{3-}$)$_m$, consisting of m-perovskite units sandwiched between bismuth oxide layers called the family of bismuth layered structured ferroelectrics\cite{26}, where A and B two types of cations that enter the perovskite unite A is Bi$^{3+}$, Ba$^{2+}$, Sr$^{2+}$, and B is Ti$^{4+}$, Ta$^{5+}$, and m=1-6 layered perovskite strontium tantalite is a member of bismuth layer-structured ferroelectrics.

The crystal structure of Sr Bi$_2$Ta$_2$O$_9$ comprises pseudo-perovskite blocks (SrTa$_2$O$_7$)$_2$ that are sandwiched between (Bi$_2$O$_2$)$_{2+}$ layers. Sr occupies the A site of the perovskite block and Ta occupies the B-site\cite{27}.

The essential goal of the present article is to investigate wide range of Ti – dopings on vanadium sites of 212 Bi-Sr-V-O regime on:

(a) Structural & microstructure properties.

(b) Thermal and processing temperature.

(c) Spectroscopic properties (IR, ESR).

(d) Conduction behaviour of 212-Bi-Sr-V-O, system.

**EXPERIMENTAL**

The pure Bi$_2$SrV$_2$O$_9$ and doped samples with the general formula Bi$_2$SrV$_{2-x}$Ti$_x$O$_9$, where x = 0.05, 0.1, 0.2, 0.3, 0.6 mole were prepared by conventional solid state reaction route and sintering procedure using the appropriate amounts of Bi$_2$(CO$_3$)$_3$, SrCO$_3$, (NH$_4$)$_2$VO$_3$ and TiO$_2$ (each purity >99%). The mixture was ground in an agate mortar for one hour. Then the finely ground powder was subject to firing at 800 °C for 10 hours, reground and finally pressed into pellets with thickness 0.2 cm, diameter 1.2 cm and Sintered at 900 °C for 30 hours. Then the furnace is cooled slowly down to room temperature. Finally the materials are kept in vacuum desiccator over silica gel dryer.

**Structural measurements**

(a) X-ray diffraction (XRD)

The X-ray diffraction measurements (XRD) were carried out at room temperature on the fine ground Bi$_2$SrV$_2$O$_9$ and Bi$_2$SrV$_{2-x}$Ti$_x$O$_9$ systems in the range (2θ =10-70°) using Cu-Kα radiation source and a computerized [Bruker Axs-D8 advance] X-ray diffractometer with two theta scan technique.

(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 700,000x and resolution 3. nm. The samples were coated with gold.

**Conductivity measurements**

The DC-electrical conductivity of the samples was measured using the two terminals DC-method. The pellets were inserted between spring loaded copper electrodes, A KEITHLEY 175 multimeter (ASA) was employed from room temperature up to 500K. The temperature was measured by a calibrated chromel-alumel thermocouple placed firmly at the sample. Measurements were conducted in such a way that at each temperature, sufficient time was allowed to attain thermal equilibration.

**Thermal analyses measurements**
The thermogravimetric 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 Japan TGA/DTA analyzer and Al₂O₃ as a reference for DTA measurements.

**Solid infrared absorption spectral measurements**

The IR absorption spectra of the prepared samples were recorded using “Nexus 670 FT IR spectrometer” in the range 500-2500 cm⁻¹ using pure KBr matrix.

**Electron paramagnetic resonance measurements**

The electron spin resonance spectra (ESR) were recorded at room temperature for the prepared samples using at x-band frequencies on a “Bruker- ELEXSYS E 500 Germany” spectrometer at the National Research Center, Egypt.

**RESULTS AND DISCUSSION**

**Phase identification**

**(a) X-ray diffraction**

The X-ray diffraction patterns of pure and Ti-doped samples with the general formula Bi₂SrV₂ₓTiₓO₉, where x = 0.05, 0.1, 0.2, 0.3, 0.6 mole are shown in Figure (1 a-f).

Analysis of the corresponding 20 values and the interplanar spacing d (Å) by using computerized program proved that the compound is mainly belong to distorted perovskite type with hexagonal crystal form see Figure 1g, that expressed by assigned peaks. The unite cell dimensions were calculated using parameters of the most intense X-ray reflection peaks and found to be a= 5.8804 Å, b= 7.304Å and c= 212Å for the pure Bi₂Sr-V-O.

**Figure 1**: Hexagonal crystal structure of Bi-Sr-Vanadates

Single phase of the layered perovskite structure appeared when Ti is up to or equal 0.05. The substitution of Ti⁴⁺ for V⁵⁺ 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. 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 (Bi₂O₂)²⁺ interlayers impose a great constraint for structural relaxation. Such a structural constraint induced from (Bi₂O₂)²⁺ interlayers may well explain the lack of an appreciable decrease in lattice parameters with an increased amount of vanadium doping.

From Figure 2 It is clear that C-axis increases as result of substitution Ti dopant on the bases of ionic radius it is expected that C-axis increases as Ti⁴⁺ doping ratio increases.

Furthermore, Ti⁴⁺ is lower in charge than V⁵⁺ and as a result it is expected to decrease stress inside lattice and consequently the shrinkage factor of lattice will be increased.
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From Figure (1), it is clear that the Ti-substitutions are successful in the most of investigated range even at high concentration x=0.6 mole since there is no evidence noticeable at X-ray diffractogram referring to Ti impurity phase. This confirms that Ti-dopant can substitute in the V-sites successfully in the whole investigated range.

(b) Microstructural properties (SEM)

Figure (3) shows the scanning electron micrographs recorded for pure 212-Bi-Sr-V-O system and Ti-doped having the formula Bi$_2$SrV$_{2-x}$Ti$_x$O$_9$, where x= 0.1, 0.3 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 1.5-1.9 µm which is totally matched with those reported in the literatures[31-33].

Figure (3) 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 (0.1,0.3), the Ti-ions connect to grain with other, the increasing of Ti concentration leads to increase of grain size from 1.58 µm in pure Bi-212 to 1.901 µm and 1.981 µm for x = 0.1 and 0.3 respectively (Figure 2).

From Figure (3) 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$_2$ can not be detected in the grain boundaries which emphasis that Ti-ions substitute successfully on the vanadium sites.

(c) 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$^{-1}$ on the green mixture of pure 212-BiSrVO and some selected Zr doped samples with the general formula Bi$_2$SrV$_{2-x}$Ti$_x$O$_9$, where x= 0.1, 0.3 mole.

From TGA/DTA curves as shown in Figure (4), 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$_4$)$_2$VO$_3$ into NH$_3$ and vanadium oxide.

The second region from 230°C to 400°C at which Bi$_2$(CO$_3$)$_3$ is decomposed into Bi$_2$O$_3$ and CO$_2$. The third region of temperature from 400-660°C at which weight loss occurred is due to partial decomposition of SrCO$_3$ 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 SrCO3 and the final formation of solid state oxide[33-35].

The endothermic peaks above 400°C in DTA curves correspond to solid state reaction formation[33].

Electron paramagnetic resonance measurements

Figure (5) explain the electron spin resonance
(ESR) signals recorded for pure Bi212 and some selected Ti doped samples with x = 0.1, 0.3 mole.

strong coupling between Ti4+ ion that substitutes V5+ ion successfully at low dopant concentration Figure 6. These results of ESR proved that the anisotropy occurred as a result of Ti-doping where \( g_{\text{eff}} \) varies as function of x value\(^{[36-37]}\).

**DC-Electrical conductivity measurements**

Figure (7a) displays the variation of dc-electrical conductivity as a function of reciprocal of absolute temperature for various Ti4+ dopings.

The data from Figure (7a) exhibit conducting and semiconductor behavior since the conductivity increases as the temperature rise in case of conductor and the conductivity decrease as the temperature rise in case of semiconductor\(^{[38]}\).

Figure (8a) show the relation between the energy gap (E\( _g \)), number of e\(^-\) in conduction band (N\( _{cb} \)) for Ti-doped in which the E\( _g \) and N\( _{cb} \) increase as the ratio of
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Ti doping increases from $x = 0.05$ till $x = 0.6$ high concentration.

\[ \rho = \rho_0 e^{-\Delta E_d / KT} \]

\[ N_{ob} = AT^{3/2} e^{-\Delta E_d / 2KT} \]

Figure 7a: The variation of DC- electrical conductivity as a function of temperature for (b) Bi$_2$SrV$_{1.95}$Ti$_{0.05}$O$_9$

Figure 7b: The variation of DC- electrical conductivity as a function of temperature for (c) Bi$_2$SrV$_{1.9}$Ti$_{0.1}$O$_9$

Figure 7c: The variation of DC- electrical conductivity as a function of temperature for (d) Bi$_2$SrV$_{1.8}$Ti$_{0.2}$O$_9$

Figure 7d: The variation of DC- electrical conductivity as a function of temperature for (e) Bi$_2$SrV$_{1.7}$Ti$_{0.3}$O$_9$

Figure 7e: The variation of DC- electrical conductivity as a function of temperature for (f) Bi$_2$SrV$_{1.6}$Ti$_{0.4}$O$_9$

Figure 7f: The relation between $E_{gap}$ and Ti doped
Solid infrared absorption spectral measurements

The infrared absorption spectra of pure $\text{Bi}_2\text{SrV}_2\text{O}_9$ and their Ti doped in the range of 500-2500 cm$^{-1}$ are shown in Figure 9.

CONCLUSION

In summary, $\text{Bi}_2\text{SrVO}_x$ ceramics doped with various $x$-values were prepared by the solid state reaction method. X-ray diffraction proved that the compounds have distorted perovskite structure with hexagonal crystal form and the Ti substitutions are successfully even at high concentration $x=0.6$ mole. The ferroelectric properties of the layered perovskite have been significantly enhanced with Ti doping. The DC-electrical conductivity show conducting metallic and semiconducting behavior. The IR spectra display that the system belongs to deficient perovskite structure and extra oxygen atom ($O_{\gamma\pm\zeta}$).

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