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Synthesis and Characterization of $SrBi_4Ti_4O_{15}$ by Wet Chemical Method

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Abstract

Various chemical methods such as sol-gel, solution co – precipitation, citrate gel and colloid emulsion techniques have proved to be superior to solid - state methods. Ferroelectric properties of ceramic powders depends on processing condition and technology used in the process and characteristics of the final powder.

The aim of the present work is to prepare single-phase $SrBi_4Ti_4O_{15}$ fine powders from simple salts through co-precipitation and citrate gel techniques. The XRD patterns recorded for both the materials and the particle size measurements on the pure single or Aurivillius phase were carried out using Scherrer equation. The dielectric constants are reported for the samples prepared by both the methods at frequencies 20Hz – 800kHz.

Keywords: Aurivillius family; layered oxides; ceramics; dielectric property.

Introduction

The non – volatile ferroelectric materials are used in ferroelectric random access memories (FeRAMs). Large remanent polarization, low coercive field, high Curie temperature and low the synthesizing temperature are highly desirable in FeRAM applications [1]. Bismuth layer – structured ferroelectrics (BLSFs) have attracted considerable attention [2] due to their promising fatigue – free nature. The BLSFs have a crystal structure containing interleaved bismuth oxide $(Bi_2O_2)^{2+}$ layers and pseudo-perovskite blocks which contains BO_6(The SBT belong to the Aurivillius family of layered oxides and the crystal structure is octahedral and is generally formulated as $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$. In this notation, A represents a mono-, bi- or trivalent ion, B denotes a tetra-, penta- or hexavalent ion, and m is the number of octahedral in each pseudo-perovskite block (m = 1,2,3…) [3]. $SrBi_4Ti_4O_{15}$ [4] is the typical layer-structured ferroelectrics with m = 4.

Experimental

Synthesis of $SrBi_4Ti_4O_{15}$ by co-precipitation and citrate gel methods

Titanium tetrachloride ($TiCl_4$), bismuth (III) nitrate $Bi(NO_3)_3.5H_2O$ and strontium chloride ($SrCl_2.6H_2O$) were used as the starting materials to prepare $SrBi_4Ti_4O_{15}$ by co-precipitation method. A stoichiometric amount of $SrCl_2.6H_2O$ dissolved in distilled water, $Bi(NO_3)_3.5H_2O$ dissolved in minimum amount of dilute HNO_3 to avoid precipitation of Bi ions and$TiCl_4$ dissolved in ice cold distilled water were added together to get a transparent solution. A mixture of liquid ammonia and ammonium oxalate were added to the above solution mixture with constant stirring until pH becomes greater than ten to ensure complete precipitation. After filtering, the precipitate was washed several times by using ammonium hydroxide and ammonium oxalate and dried in an oven at 100^{o}C for 12 hours. The light white precipitate was calcined at 800^{o}C for 72 hours to get phase pure sample of $SrBi_4Ti_4O_{15}$ ceramics.

For the preparation of $SrBi_4Ti_4O_{15}$ by citrate gel method, titanium tetrachloride ($TiCl_4$), bismuth (III) nitrate $Bi(NO_3)_3.5H_2O$ and strontium chloride ($SrCl_2.6H_2O$) were used as starting materials. A stoichiometric amount of $SrCl_2.6H_2O$ dissolved in distilled water, $Bi(NO_3)_3.5H_2O$ dissolved in minimum amount of dilute HNO_3 to avoid precipitation of Bi ions and $TiCl_4$ dissolved in ice cold distilled water were mixed together. The above mixture is mixed with required quantity of citric acid to get the ratio of the total metal cations to citric acid as one. Since there was no precipitation during mixing, the pH of the solution was not varied. On heating in a water bath at 100^{o}C, a light yellowish precipitate was formed after evaporation of water. Subsequently, the precipitate is decomposed in the range 150 - 900^{o}C. The precipitate initially started to swell and filled the beaker producing a foamy precursor. This foam consists of very light and homogeneous flakes of very small particle size.

Results and Discussion

The phase formation and crystallinity of the sintered samples were characterized by X- ray diffraction (Philips Analytical diffractometer). The samples were subjected to differential thermal analyzer (DTA- Linseis) in the temperature range from room temperature to 800^{o}C with the heating rate of 5^{o}C/min. The Fourier transform Infrared (FTIR) spectra of the sintered samples prepared by the co - precipitation and citrate gel methods were recorded (Perkin-Elmer 580 FTIR) by KBr technique. For the electrical property measurements, the fired powders were ground and admixed with 2 wt % polyvinyl alcohol for binding and pressed into disks at 250 Mpa. The disks were sintered for 3h at 1150^{o}C and these sintered disks were polished and coated with silver paste on both sides. The dielectric measurements were carried out at frequencies 20Hz – 800kHz using LCR meter (HP 4284A) with a signal voltage of 50mV in the temperature range 30 - 600^{o}C for the samples prepared by both the methods.

XRD Analysis for $SrBi_4Ti_4O_{15}$ prepared by co-precipitation and citrate gel methods

$SrBi_4Ti_4O_{15}$ (SBT) The JCPDS (JCPDS No: 43-0973) powder X-ray diffraction (XRD) pattern based on $Bb2_1m$ structure and the measured powder XRD pattern of $SrBi_4Ti_4O_{15}$ prepared by co - precipitation and citrate gel method are shown as Fig. 1a - c respectively. $SrBi_4Ti_4O_{15}$ is an orthorhombic structure with the lattice parameters **a** = 5.428, **b** = 5.438 and **c** = 40.94 A^o respectively. The dominant diffraction peaks of SBT matches closely both in position and relative intensities of the diffraction peaks of the JCPDS X-ray diffraction (XRD) pattern. The XRD patterns as shown in Fig.1b and 1c were obtained for the samples heated to 800°C for 72h. The precursor powder heated to 600°C showed unknown and impurity phase of SBT and the crystalline nature is improved only after heating at 700°C. The phase pure single or Aurivillius phase is obtained by calcining the sample at 800°C for 72 hours. The particle size measurement was carried out using Scherer's equation,

$D = (K\lambda) / (\beta\cos\theta)$,

where,

D is the crystalline size,

K is constant (0.9 assuming that the particle is spherical),

λ is the wavelength of the X-ray radiation,

β is the line width and

θ is the angle of diffraction.

The average particle size obtained from XRD data for co-precipitation and citrate gel methods were 120 and 140nm respectively. By comparing the particle size of the samples prepared by wet chemical techniques, it was found that the prepared ceramic powder possess particle size of smaller dimension. Thus we can conclude that the wet chemical methods are the most successful techniques for synthesizing ultra fine ceramic powders having narrow particle distribution.

SEM images of $SrBi_4Ti_4O_{15}$ powder samples sintered at 800° C by co - precipitation and citrate gel method confirms the formation of nanoparticle with an average particle size around 160 – 200nm. The observation of the appearance of (M-O) bond at 800°C in the frequency range 600 – 850 cm^{-1} in our FTIR spectra for the above sample confirm the formation of SBT [5].

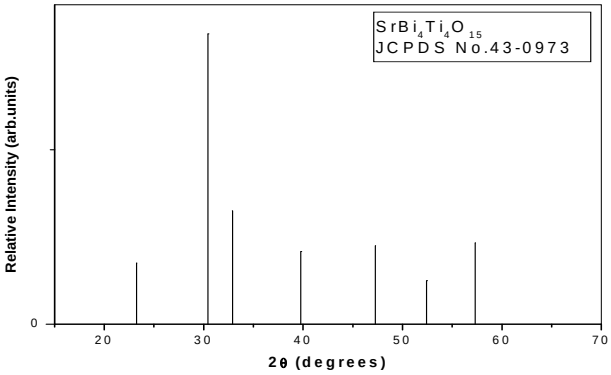

Figure 1 (a): JCPDS XRD pattern of $SrBi_4Ti_4O_{15}$.

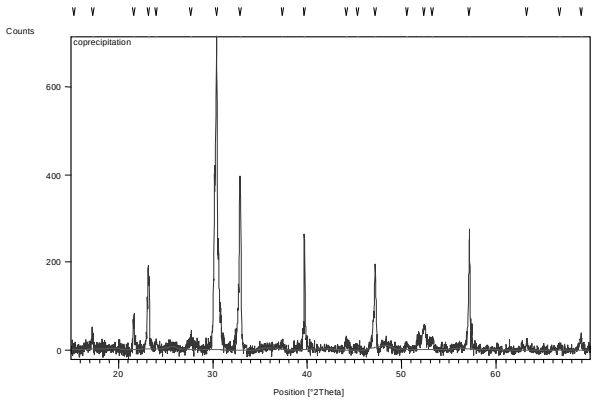

Figure 1 (b): Measured XRD pattern for $SrBi_4Ti_4O_{15}$ by co-precipitation method sintered at 800^{o}C for 72 hours.

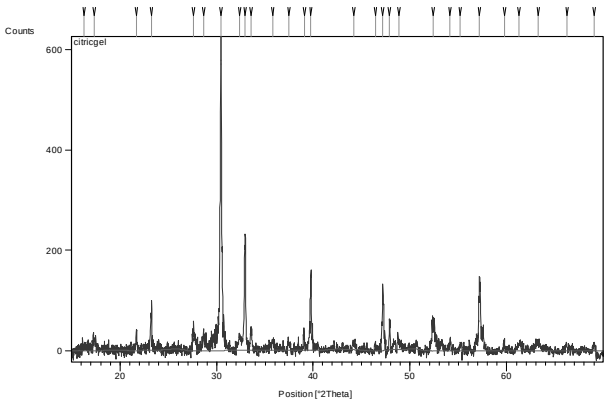

Figure 1 (c): Measured XRD pattern for $SrBi_4Ti_4O_{15}$ by citrate gel method sintered at 800^{o}C for 72 hours.

Dielectric properties of $SrBi_4Ti_4O_{15}$ by co – precipitation and citrate-gel methods

S. Ikegami et al [6] reported the Tc value as 550^{o}C for $SrBi_4Ti_4O_{15}$ (SBT), while E.C. Subbarao et al [7], Maria et al [8] and S. Kojima et al [9] have reported 530^{o}C for the same. Jun Zhu et al [4] reported the Curie temperature as 520^{o}C for SBT. Noguchi et al [10] and R.Z. Hou et al [11] have reported that there is a sharp peak of dielectric constant at Tc = 520^{o}C for $SrBi_4Ti_4O_{15}$ with the maximum dielectric constant more than 2300. Szu Hwee Ng, et al [12] reported that the dielectric constant ~2770 at a Tc of ~539 ^{o}C at 100kHz.

The temperature dependence of dielectric constant obtained at several frequencies for the sintered samples by co-precipitation and citrate-gel method are shown in Fig.2a and 2b respectively. The dielectric constant, measured at 100kHz, increases from room temperature and shows a peak at 520^{o}C. This concurs with the earlier reported value [4,10,11] of dielectric constant 2616 and 2585 for co – precipitation and citrate gel methods respectively. The narrow transition, as a function of temperature, demonstrates that the $SrBi_4Ti_4O_{15}$ is a conventional ferroelectric [12].

These measurements indicate that no relaxation effects have taken place in these compounds [8].

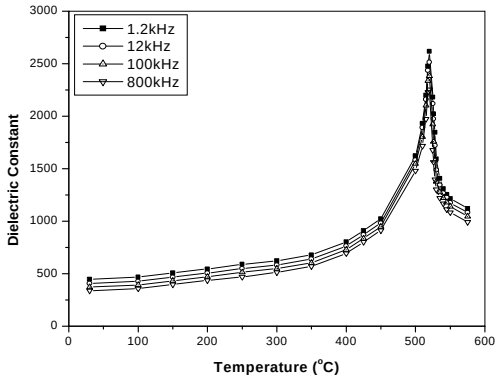

Figure 2 (a): Temperature dependent dielectric constant of $SrBi_4Ti_4O_{15}$ prepared by co – precipitation method measured at various frequencies.

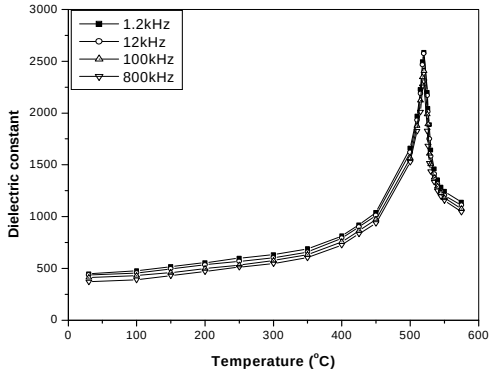

Figure 2 (b): Temperature dependent dielectric constant of $SrBi_4Ti_4O_{15}$ prepared by citrate gel method measured at various frequencies.

References

[1] B.H.Park, B.S. Kang, S.D. Bu, T.W. Noh,J.Lee,W.Jo,Lanthanum - substituted bismuth titanate for use in non-volatile memories,Nature, 401 (1999) 683.

[2] J.K.Lee, C.H. Kim, H.S. Suh, K.S. Hong, Correlation between internal stress and ferroelectric fatigue in $Bi_{4-x}La_xTi_3O_{12}$ thin films,Appl. Phys.Lett. 80 (2002) 3593.

[3] Hiroshi Irie, M. Miyayama, T. Kudo, Structure dependence of ferroelectric properties of bismuth layer – structured ferroelectric single crystals, J.Appl. Phys. 90 (2001) 4089.

[4] Jun Zhu,Xiang-yu Mao,Xiao-bing Chen, Properties of vanadium – doped $SrBi_4Ti_4O_{15}$ ferroelectric ceramics, Solid State Commn. 129 (2004) 707.

[5] Dan Xie, Wei Pan, Study on BaBi4Ti4O15 nanoscaled powders prepared by sol-gel method, Materials Lett.57 (2003) 2970.

[6] S. Ikegami, I.Ueda, Piezoelectricity in ceramics of Ferroelectric Bismuth Compounds with Layer Structure,, Jpn. J. Appl.Phys. 13 (1974) 1572.

[7] E.C. Subbarrao , A Family of Ferroelectric Compounds, J. Phys.Chem. Solids, 23 (1962) 665.

[8] Maria V. Gelfuso,Daniel Thomazini, Jose A.Eiras, Synthesis and structural, Ferroelectric, and Piezoelectric properties of $SrBi_4Ti_4O_{15}$ Ceramics, J. Am. Ceram. Soc. 82 (9) (1999) 2368.

[9] S.Kojima,R.Imaizumi,S.Hamazaki, M. Takashige, Raman study of ferroelectric bismuth layer – oxides $ABi_4Ti_4O_{15,}$ J. of Mol. Struc. 348 (1995) 37.

[10] Y. Noguchi, M.Miyayama, T. Kudo, Ferroelectric properties of intergrowth $Bi_4Ti_3O_{12}$ - $SrBi_4Ti_4O_{15,}$ Appl. Phy. Lett. 77 (2000) 3639.

[11] R.Z. Hou, X.M. Chen, La3+ substitution in four-layers Aurivillius phase $SrBi_4Ti_4O_{15}$ ceramics, Solid State Commn. 130 (2004) 469.

[12] Szu Hwee Ng, J.M. Xue, John Wang, High temperature piezoelectric strontium bismuth titanate from mechanical activation of mixed oxides, Materials chem. and phys. 75 (2002) 131.