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The phase and dielectric properties of the Sol – gel $BaTiO_3$ $_c$eramics

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ABSTRACT

A sol-gel acetate process was used to synthesize $BaTiO_3$ ceramics, using Sb as dopant. Sintering was performed in a temperature range of 1200 to 1300°C for 4 h. The XRD analysis revealed that $BaTiO_3$ ceramics indicated tetragonal structure at these temperatures. With an increase in Sb contents, dielectric measurements of $BaTiO_3$ ceramics exhibited a decrease in dielectric constant and a shift in the Curie temperature (T_c) towards the low temperature. At 1 and 3 wt% of Sb contents, T_c was shifted near room temperature. These results had an important role for the application of various devices operated in envelopment at normal temperature.

Keywords: Sb-doped $BaTiO_3$, Sol-gel process, X-ray diffraction, Dielectric properties.

INTRODUCTION

Ferroelectric barium titanate ceramics are widely utilized to manufacture electroceramics due to their excellent dielectric and piezoelectric properties. As a result, they are employed in various application such as multilayer capacitors, thermistors, dynamic random access memory (DRAM), piezoelectric transducers, optical devices, gas sensors, infrared detectors, etc [1-4]. These devices are achieved in ferroelectric state, which occurs around Curie temperature (T_c). In general, they work at room temperature, so the T_c of the ferroelectric materials should also be at room temperature. It is widely known the T_c of $BaTiO_3$ is about 120°C but it can be modified to correspond with a given application by adjusting the composition and the ceramic microstructure, or doping which substitutes into either Ba or Ti sites or both. Two types of dopants , one is acceptor ions which have a lower valence than the ions they replace (e.g. 1+ ions for Ba^{2+}, 3+ ions for Ti^{4+}) and the other is donor ions which have a higher valence than the ions they replace (e.g. 3+ ions for $Ba^{2+,}$ 5+ ions for Ti^{4+}) [5-7]. Many experiments revealed that Sb-donor dopant is the most widely accepted one for the modification of $BaTiO_3$ or other ferroelectric materials for various applications. Such, most experiments tend to study positive temperature coefficient of resistivity (PTCR) behaviour of modified $BaTiO_3$ since Sb doping can achieve semiconducting of $BaTiO_3$ which enhances the PTCR effect [8-11]. Besides, Xu et al.[12] studied pyroelectric properties of (Mn, Sb) doped –$Pb(Zr,Ti)O_3$ thin film, they found that doping with Mn and Sb into Pb(Zr, Ti)O_3 not only decreased the Curie temperature (T_c) from 350°C to 175°C, but also enhanced IR responsivity significantly. Nowadays, pyroelectric properties of ferroelectric materials have also received much attention for application of infrared detectors because of their properties such as high response in the infrared wavelength range and ability to operate at room temperature without expensive cooling systems. Most of the compounds with a lead (Pb) component [13-15] were paid great attention in the field of pyroelectric infrared detector because of their good properties, such as giving a large pyroelectric coefficient and high response in the infrared wavelength range. These days, healthy and safe environment are necessities for life. Meanwhile lead-free compounds have to be considered and urged to be developed. With suitable properties, ferroelectric $BaTiO_3$ material has received great attention for this purpose. As described earlier, doping with Sb element affected semiconducting, T_c shift and pyroelectric properties increment of ferroelectric materials. However, the effects of Sb doping on dielectric properties of $BaTiO_3$ by sol - gel process are not well known. Therefore, in this work, we prepared modified $BaTiO_3$ by the sol – gel method using acetic acid as a chelating agent and using Sb as dopant. The aim of this work was to investigate the effect of Sb doping on the dielecteic properties of $BaTiO_3$ to determine their suitability for various applications near room temperature. We also investigated the phase evolution and dielectric properties of both undoped and doped $BaTiO_3$ after various doping contents and firing conditions.

MATERIALS AND METHODS

Barium oxide, titanium (IV) isopropoxide, conc. acetic acid, methanol and dried n-butanol were used as material sources. Ba- solution was obtained from dissolving BaO (10.22 g) into 80 cm^3 of acetic acid and 50 cm^3 of methanol. In order to obtain a molar ratio of Ti/Ba = 1, stable Ti-solution was prepared by adding 20 cm^3 titanium (IV) isopropoxide into 50 cm^3 of dried n-butanol. The solution of barium and titanium were mixed and heated at 80 °C on a hot plate while stirring continuously for 2 h. After 2 h, 20 cm^3 of distilled water was added to the mixed solution to form a gel. The gel was dried in an electric oven at 110 °C for 48 h, the white powder precursor was obtained. The dopant of Sb was weighted up to 1, 3, 5, and 7 weight% of dried precursors and mixed together in an agate motar. The mixed powders were grounded and then calcined in air at a temperature ranging from 400 to 1300°C for 4 h to yield $BaTiO_3$. After that, the calcined powder was pressed by uniaxial pressure pressing at a pressure of 2 tons into pellets 10 mm in diameter and 4 mm thick. The pellets were sintered in air at temperatures of 1200 to 1300°C for 4 h. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to analyze the phase transformations of the dried powder precursors which were heated up to a temperature of 1200°C with a heating rate of 10°C/min. Phase evolution of the $BaTiO_3$ was characterized by X-ray diffraction (XRD) (CuK_α radiation). The dielectric properties of the sintered samples were measured at various temperatures as a function of various frequencies, using LCZ meter (Hewlet Packard Model 4192A). Before the dielectric measurements, the surfaces of the sintered samples were polished with sandpaper and conducting silver paint was applied on both surfaces to make an electrode.

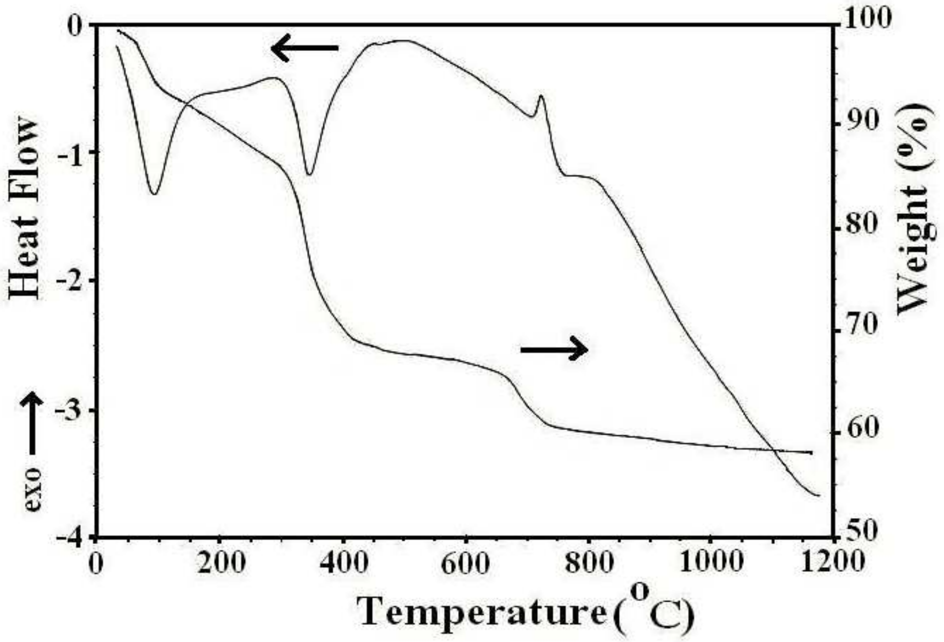
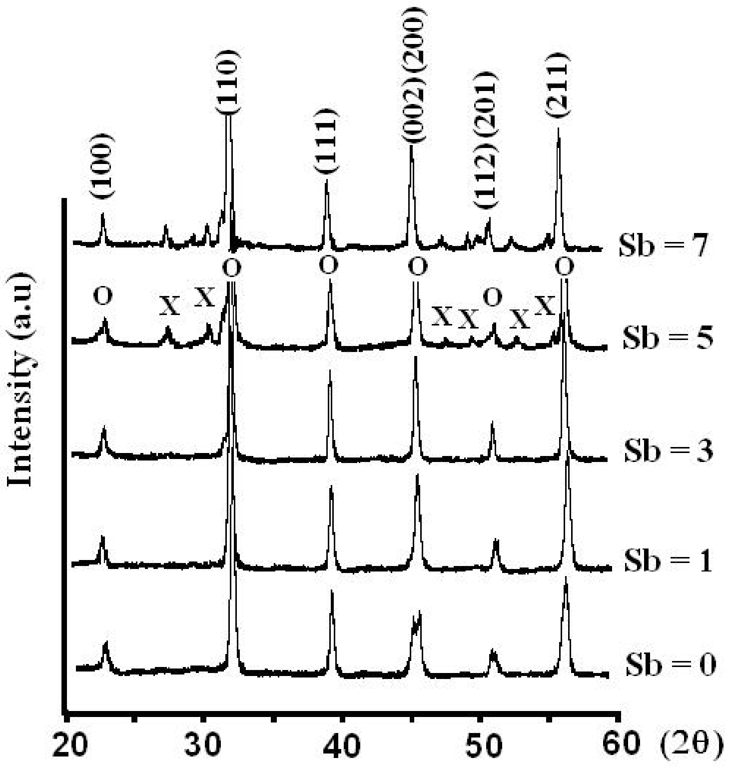
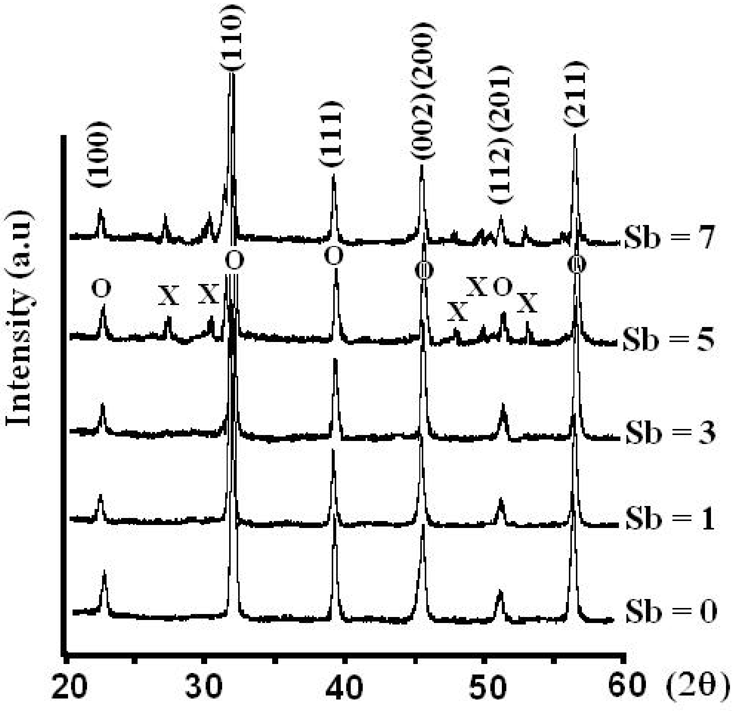


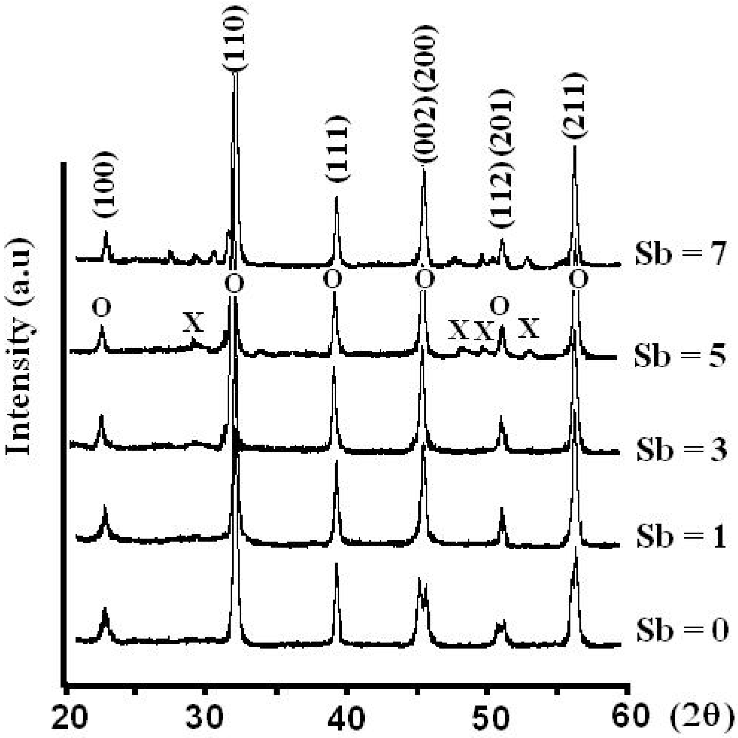
Fig. 1 DSC/TGA of the doped $BaTiO_3$ at 3 wt% Sb



(a) 1200°C



(b) 1250°C



(c) 1300°C

Fig. 2 XRD patterns of the doped $BaTiO_3$ sintered at (O = $BaTiO_3$, X = secondary phase); (a) 1200°C, (b) 1250°C, (c) 1300°C

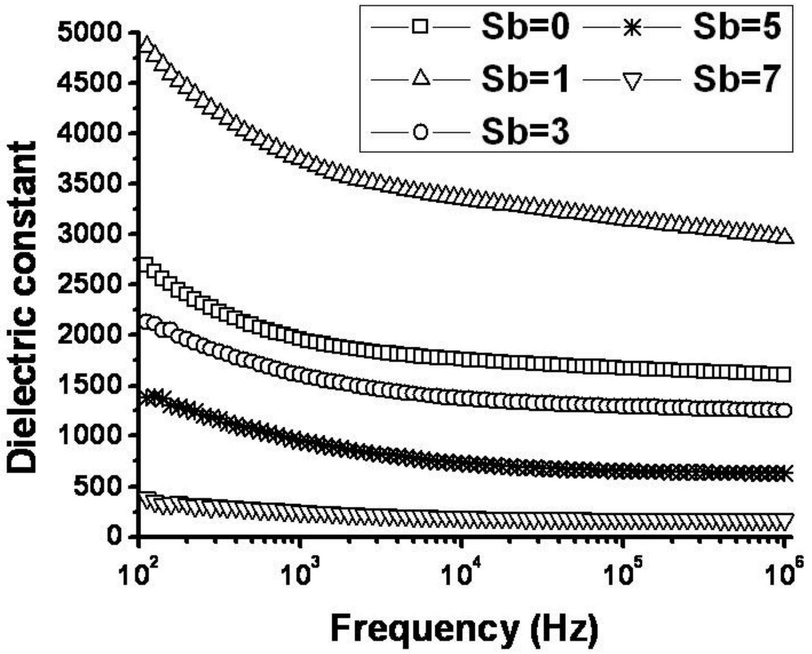
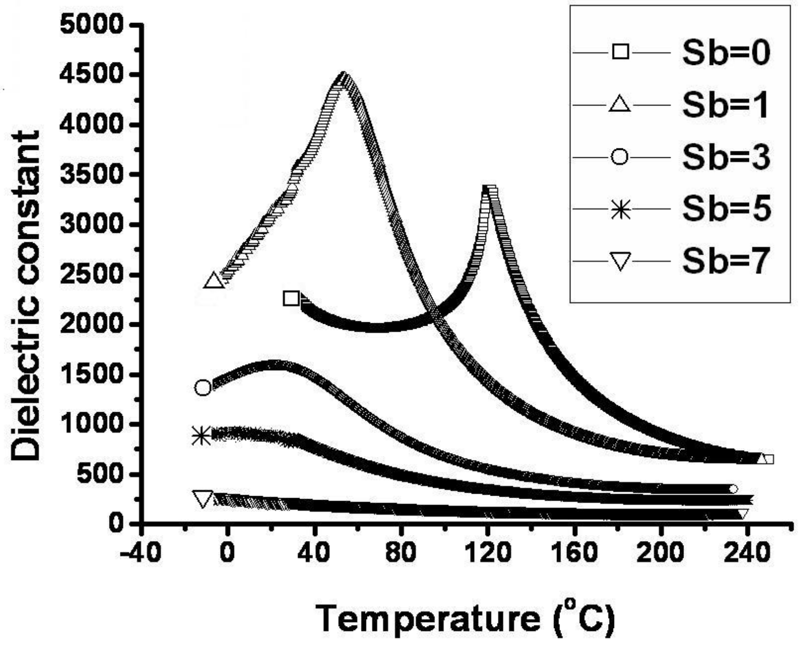
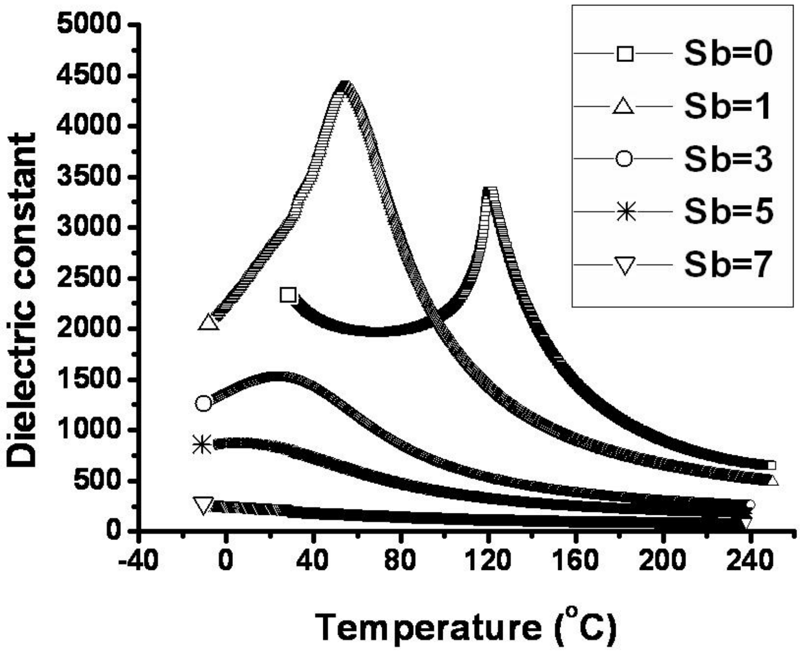


Fig. 3 Dielectric constant Vs frequencies measured at the room temperature (28 ^{o}C)



(a)



(b)

Fig. 4 Dielectric constant Vs temperature of the doped $BaTiO_3$ sinter at 1250°C for 4 h and measured at the frequencies of (a) 1 kHz (b) 1 MHz.

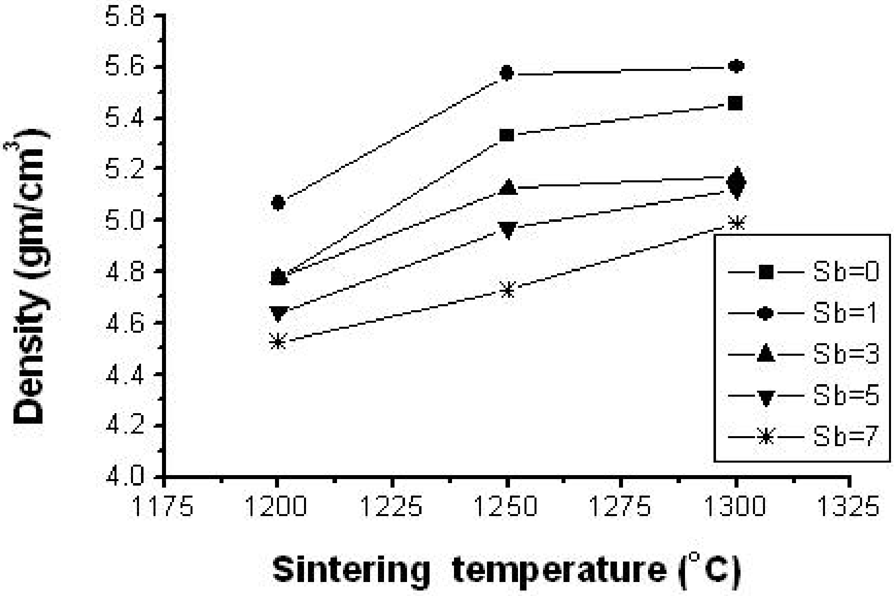


Fig. 5 The density of the doped $BaTiO_3$ related to both various sintering temperatures and various Sb contents.

Sb content (wt%)	1 kHz					1 MHz				
	Dielectric constant		Loss tangent		T_c (°C)	Dielectric constant		Loss tangent		T_c (°C)
	T_R	T_c	T_R	T_c		T_R	T_c	T_R	T_c	
0	1970	3500	0.1550	0.0082	120	1600	3350	0.0233	0.0090	120
1	3740	4500	0.1403	0.0102	53	2970	4370	0.0469	0.0125	53
3	1590	1600	0.1851	0.0120	23	1250	1530	0.0235	0.0141	25
5	960	-	0.2999	-	-	630	-	0.0248	-	-
7	250	-	0.3638	-	-	170	-	0.0256	-	-

Table 1. Dielectric values of the Sb-doped $BaTiO_3$ at room temperature (T_R = 28 °C) and Curie temperature (T_c), measured at 1 kHz and 1 MHz.

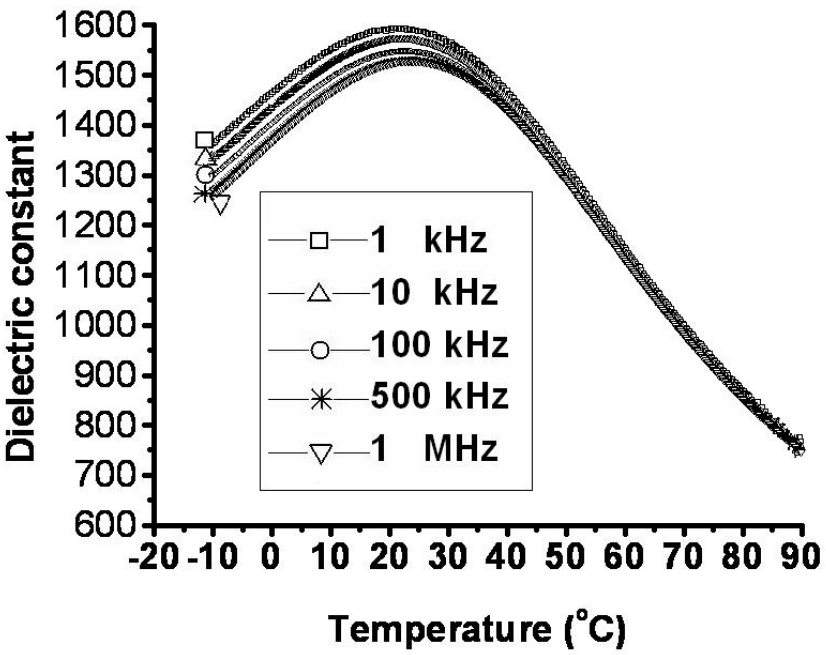


Fig. 6 The dielectric constant v.s both various temperatures and various frequencies of the doped $BaTiO_3$ with 3 wt% Sb sintered at 1250°C for 4 h

RESULTS AND DISCUSSION

3.1 Thermal analysis

Fig. 1 shows the DSC/TGA thermogram obtained from the dried precursors of 3 wt% of Sb-doped $BaTiO_3$ to 1200°C. The results showed the behavior of change with heat treatment in three steps. They could be explained that evaporation of water occurs in the first step below 250^{o}C, corresponding to endothermic peak with 10% weight loss. Loss of remnant organics or decomposition of acetate group to form barium carbonate accompanied by an endothermic peak in the second step at about 350^{o}C with 20% weight loss located at 250^{o}C to 500^{o}C. Finally, the decomposition of barium carbonate and titanium oxide followed with the reaction between fresh nuclei to form $BaTiO_3$ was observed in exothermic peak at about 600^{o}C to 750^{o}C with 6% weight loss. From DSC data, it implied that this preparation process can produce $BaTiO_3$ at lower temperature, compared with that prepared from a solid state reaction process which uses high heat treatment (>1200^{o}C) [4,16-17] due to its lower chemical activity. On the other hand, the fine particles obtained from this process [18-22] had a significant role on the reaction and due to their higher reactivity, the processes of calcination occur completely at a lower temperature.

3.2 X-ray diffraction analysis

Fig. 2(a)-2(c) show a series of the X-ray diffractograms from the $BaTiO_3$ ceramics sintered at 1200 to 1300^{o}C. The XRD patterns were analyzed based on the Joint Committee on Powders Diffraction Standard (JCPDS), card No.75-2122. In these temperature range, single – phase was only found in the undoped sample with a tetragonal structure, neither $BaCO_3$ nor TiO_2 was observed by this technique the diffraction peaks are corresponded to $BaTiO_3$. This result is in good agreement with that reported by Baorang et al.,[23] Murugaraj et al.,[24] and Chaput et al.,[25] although they prepared by using different methods. Furthermore, increase in sintering temperature to 1300^{o}C, $BaTiO_3$ with tetragonal structure was well formed which observed from the split of (002) and (200) peaks. Generally, these peaks are used for analysis of the tetragonal $BaTiO_3$. This indicates that the higher temperature sintering affected the increase of tetragonality of $BaTiO_3$, resulting in the higher values of the tetragonal percentage compared with lower ones. Moreover, the split of the (002) and (200) peaks were slightly separated as the sintering temperatures increased. It is asserted that no significant change in the XRD patterns were observed for the sample sintered at these temperature ranges. For analysis of the phase of Sb-doped $BaTiO_3$ (Fig.2), there are a few changes in the X- ray peaks due to the results in the variation of both the sintering temperatures and the Sb concentrations. When the amount of the Sb doping increased from 1 to 7 wt%, the diffraction peaks of secondary phase were also increased but had no effect on the split of (002) and (200) peaks. As a result, the $BaTiO_3$ ceramics doped below 3 wt% Sb were still the single phase with tetragonal structure which observed from X-ray line-broadening at $2\theta \approx 45^o$. But the split of (002) and (200) peaks in our XRD patterns at this doping level was not easy to distinguish due to their overlap, indicating of low degree of tetragonality. Even more overlapping of the peaks was seen on the undoped $BaTiO_3$ samples. Whereas, increase of the doping levels was higher than 3 wt% Sb, diffraction peak around a 2θ of 45^o slightly sharps, which could not observe the split of the (002) and (200) peaks. This implies that the doped $BaTiO_3$ ceramics change from tetragonal to pseudocubic. This result corresponds to the report of Wada et al.,[26] that a broad (200) peak which could not split into (002) and (200) peaks was a pseudocubic structure, resulting in a stable temperature dependence of dielectric constant; this was confirmed again by the dielectric analysis. Besides, the doped ceramics over 3 wt% of doping level could not obtain the single phase; this is due to the small amount of liquid phase of dopant a result of the presence of secondary phase which is formed by melted eutectics in $BaTiO_3 – Sb_2O_3$ systems.

3.3 Dielectric properties

Fig. 3 shows the dielectric constant related to frequencies of the $BaTiO_3$ ceramics. The analysis of all the $BaTiO_3$ ceramics was performed at room temperature. The result indicates that the dielectric constant decreased as frequency increased from 100 Hz to 1 MHz. Generally, the dielectric constant at the low frequency is higher than those obtained at the high frequency. The decrease in dielectric constant is due to the dipoles which cannot follow the alternation of the applied ac electric field which gets higher frequencies and then the total orientation polarization will be less at higher frequencies. Fig. 4(a) and 4(b) show the variation of dielectric constant of $BaTiO_3$ ceramics as a function of various Sb contents, temperatures and frequencies. It is expected that a ferroelectric – paraelectric phase transition temperature (Curie temperature,T_c) of the $BaTiO_3$ modified with Sb can be adjusted toward room temperature, including the dielectric constant is also improved for the pyroelectric voltage figure-of-merit. The results show that the doped-sample derived from 1 wt% Sb showed higher dielectric constant at T_c than undoped $BaTiO_3$ for all frequencies. This may be due to the degree of tetragonality of the doped samples showed higher, (Fig 2) and that probably resulted in higher dielectric constant which is due to higher polarization. The higher value of dielectric constant may possibly also strongly depend on the higher density of the sample due to the occurrence of liquid phase in $BaTiO_3$-Sb_2O_3 system between sintering process, the easier high density is obtained (the highest density ≈ 93% for the sample doped with 1 wt% Sb and sintered at 1250^{o}C for 4 h) which is shown in Fig. 5. Whereas, increasing the Sb concentrations over 1 wt% the dielectric constant values of $BaTiO_3$ are decreased. Typical values of the maximum dielectric constant of Sb-doped $BaTiO_3$ sintered at 1250^{o}C for 4 h were 3500, 4500 and 1600 for doping with 0, 1 and 3 wt%, respectively, at the measured frequency of 1 kHz. For at the measured frequency of 1 MHz, typical values of the dielectric constant of Sb-doped $BaTiO_3$ sintered at 1250^{o}C for 4 h were 3350, 4370 and 1530 for doping with 0, 1 and 3 wt%, respectively. Additionally, it can also be observed from the graph of the Fig.6 that the value of the dielectric constant at T_c slightly decreased with an increase in the frequency. Typical values of the dielectric constant of $BaTiO_3$ at 3wt% Sb sintered at 1250^{o}C for 4 h were 1600, 1570, 1550, 1540 and 1530 at the measured frequency of 1 kHz, 10 kHz, 100 kHz, 500 kHz and 1 MHz, respectively. The decreased in the dielectric constant at the Curie temperature indicates that the addition of Sb leads to changes in the dielectric properties. This can be explained that the doped $BaTiO_3$ had pseudocubic structure which corresponded to the report of Wada et al.,[26] and could well confirm the XRD result. For the dielectric – temperature analysis (Fig 4(b)), the results show that the amount of Sb had a significant role on the variation of the Curie temperature of $BaTiO_3$ ceramics. The increase in amount of Sb_2O_3 could shift the Curie temperature towards the lower temperature regions. These were T_c=120^{o}C, 53^{o}C and 25^{o}C for doping with 0, 1 and 3 wt% Sb, respectively. These measurements are limited with our equipment, the low temperature (<-10^{0}C) cannot be measured. When the Sb-doping levels were more than 3 wt%, resulting in a stable temperature dependence of dielectric constant; it indicates that the doped $BaTiO_3$ had pseudocubic. However, in the present work the lowing of dielectric constant related to temperature of Sb-doped $BaTiO_3$ is more complex, so it should also consider the influence of dopants as described earlier. So the reason for the decrease of Curie temperature in the $BaTiO_3$-Sb_2O_3 system can be understood from the microscopic point of view. The Sb substitution may enable replacement on Ba^{2+} ion sites which will decrease the bond covalency, affecting to the decrease of T_c, with similar result to substitution by La^{3+} or Sr^{2+} on the Ba^{2+} site [27,28]. While Ray et al.,[29] also reported the same result of a decrease of Curie temperature but with Fe^{3+}- Ti^{4+} substitution in $BaTiO_3$. Therefore, the amount of Sb ions and their valence states will affect the decrease of Curie temperature. Although higher doping level of Sb could decrease Curie temperature, whereas the value of loss tangent slightly increased. The dielectric measuring results of samples sintered at 1250 ^{o}C for 4 h are summarized in Table 1. From the data in Table.1, the value of loss tangent of all samples decreased with an increase in frequency which was in range of 0.3638 (for doping with 7 wt% Sb and at room temperature) and 0.0009 (for doping with 1 wt% Sb and at T_c). However, the loss tangent of $BaTiO_3$ with higher doping levels is little higher. From the experiment data, the doped $BaTiO_3$ showed lower dielectric constant at the Curie temperature than the undoped $BaTiO_3$ and the Curie temperature decreased as doping levels increased. It is concluded that the addition of Sb can change both the dielectric constant and Curie temperature. In particular, the low values of both the dielectric constant and Curie temperature are desired to improve the pyroelectric voltage figure-of-merit at low temperature [12,27,30]. Therefore, in this work the $BaTiO_3$ doped with 3 wt% Sb it was expected that it should have the highest pyroelectric response and should be a potential candidates as an infrared sensor, humidity sensor, gas sensor, etc., in which they could operate at near room temperature.

CONCLUSION

The sol-gel modified $BaTiO_3$ in the present work could obtain $BaTiO_3$ ceramics with a difference of both dielectric constant and T_c. The doped-sample derived from 1 wt% Sb showed higher dielectric constant at T_c than undoped $BaTiO_3$. The higher value of dielectric constant may possibly strongly depend on the higher density of the sample. By increasing doping level to the 3 wt% of Sb, the dielectric constant showed lower dielectric constant at T_c than undoped $BaTiO_3$ and the Curie temperature could be decreased to near room temperature. In particular the decrease of the dielectric constant was well fitted for improvement of the pyroelectric voltage figure-of-merit. In this work, the $BaTiO_3$ ceramics doped with 3 wt% Sb with the low values of both dielectric constant and T_c should be suitable candidates for fabrication of various devices which could operate at low temperature or near room temperature such as humidity sensor, gas sensor, infrared sensor, etc.

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