INFLUENCE OF SINTERING TEMPERATURE ON PHASE FORMATION AND OPTICAL PROPERTIES OF LEAD-FREE FERROELECTRIC Bi_{0.5}Na_{0.5}TiO_3 MATERIALS

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ABSTRACT

Pb(Zr,Ti)O_3 based ferroelectric materials have been widely used in electronic devices even though they were banned due to the toxicity of lead on health and environment. Among the lead-free ferromagnetic materials, Bi_{0.5}Na_{0.5}TiO_3 has received much attention because their ferroelectric and piezoelectric characteristics are comparable to Pb(Zr,Ti)O_3. In this report, Bi_{0.5}Na_{0.5}TiO_3 was fabricated by sol-gel method. The influence of fabricating conditions such as gelization, sintering temperature on crystallinity was studied. The result showed that Bi_{0.5}Na_{0.5}TiO_3 was in single phase when compensation amount of Na in gelization is 40 mol%; sintering temperature higher than 800 °C and sintering time is 2 h. The bandgap of Bi_{0.5}Na_{0.5}TiO_3 which estimated from absorption spectroscopy is in the range of 3.01 - 3.18 eV.

Keywords: Bi_{0.5}Na_{0.5}TiO_3, sol-gel, optical properties, lead-free, ferroelectric.

1. INTRODUCTION

Pb(Zr,Ti)O_3 based ferroelectric materials (PZT) have been widely used in daily life, science and technology [1]. Although PZT has good ferroelectric and piezoelectric characteristics, PZT-based materials have a serious problem due to the high amount of Pb (60 %) which can affect ecosystem and human health. According to the World Health Organization (W.H.O) report, lead has a harmful effect on children, especially on the mental development. This report also shows that about 600000 new cases of child patients having fluence on the mental development, 143000 deaths are related to lead poisoning every year [2]. In Vietnam, according to the news of the Ministry of Natural Resources and Environment, the environmental pollution related to
Influence of sintering temperature on phase formation and heavy-metals containing Pb in the traditional villages such as a lead recycling village of Dong Mai, Chi Dao, Hung Yen (Vietnam) is quite alarming. The blood tests of 335 children in this village show that 207 children have been lead poisoning [3]. Therefore, removing poisonous elements in electronics devices is really necessary.

To encourage the development of the new ferroelectric material which is friendly environmental and do not affect human health, many laws of ban and restriction of using electronics devices containing poisonous element such as Pb were enacted by EU, Japan, Korea and China etc [4]. However, PZT-based ferroelectric materials have excellent ferroelectric and piezoelectric properties which make it not be ready to replace by other lead-free materials. Jo’s survey about the market of ferroelectric and piezoelectric ceramics is presented in Fig. 1 in which the market share for PZT-based ceramics is very high, around 94.5%. The survey also shows that the lead-free piezoelectric ceramics only makes up a very small market share for applications [1].

From the upward tendency of lead-free piezoelectric ceramics, Bi$_{0.5}$Na$_{0.5}$TiO$_3$ based ceramics has been focused attention due to their properties which are comparable with traditional materials based on PZT-based [4]. Lead-free ferroelectric Bi$_{0.5}$Na$_{0.5}$TiO$_3$ ceramic was fabricated for the first time by two Soviet scientists (Smolenskii and Agranovskaya) in 1959 [5]. The ferroelectric property of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ was announced by Smolenskii’s group [6]. Bi$_{0.5}$Na$_{0.5}$TiO$_3$ has perovskite structure with a remanent polarization of 34 $\mu$C/cm$^2$ at room temperature and the Curie temperature of 320°C [6]. The theoretical calculation for Bi$_{0.5}$Na$_{0.5}$TiO$_3$ suggests this material has a wide direct bandgap of 1.97 eV [7]. The experimental results from Parija et al. show that the bandgap is around 2.94 eV [8]. Another suggestion from Wang et al. is that the bandgap varies in a range of 2.82 eV and 2.92 eV, depending on the concentration of NaOH in hydrothermalization [9]. Kushawaha et al. found that Bi$_{0.5}$Na$_{0.5}$TiO$_3$ has the good photocatalytic and antibacterial abilities [10]. Additionally, Ai et al. confirmed that Bi$_{0.5}$Na$_{0.5}$TiO$_3$ has a better detoxification of NO$_x$ compared to a commercial material of TiO$_2$ P25 (Degussa) [11]. The ability to H$_2$ evolution from water with an evolution rate of 325.4 $\mu$molh$^{-1}$ gcat$^{-1}$ by using a 500W Xe lamp was studied by Wang et al. [9]. Lin et al. found that the photocatalytic property of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ can be improved by treatment of metyl orange [12].

Recently, besides the study of ferroelectric, piezoelectric and insulating properties, Bi$_{0.5}$Na$_{0.5}$TiO$_3$ has been futher studied in the other directions as photocatalysis, water splitting and antibacterial ability. This is due to the existence of spontaneous ferroelectric domains which

![Figure 1](image_url). The survey of the market share for electronics devices using lead-free piezoelectric ceramics (a) and using ferroelectric and piezoelectric materials in common [1] (License Number #3762260532932).
can reduce the possibility of electron-hole pair recombination, making the photocatalytic efficiency very high [13]. Kang et al. found that the phase formation, ferroelectronic and insulating properties of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ film synthesized by sol-gel method strongly depended on the primary ratio of Bi/Na because these elements are easy to evaporate during gelization and annealing processes [14]. However, these reports about the evaporating amount of Na during gelization, the influence of sintering temperature on the phase information and optical properties of this material have not been performed in a systematic manner.

In this report, lead-free ferroelectric material Bi$_{0.5}$Na$_{0.5}$TiO$_3$ was synthesized by sol-gel method. The result shows that the single-phase Bi$_{0.5}$Na$_{0.5}$TiO$_3$ material is obtained when the compensating amount of Na is above 40% and the annealing temperature is higher than 800°C. The bandgap of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ varies with the change of the Na amount and the annealing temperature.

2. EXPERIMENT

Bi$_{0.5}$Na$_{0.5}$TiO$_3$ was synthesized by sol-gel method in which the precursors are bismuth nitrate (Bi(NO$_3$)$_2$·5H$_2$O), sodium nitrate (NaNO$_3$), tetraisopropoxytitanium (IV) C$_4$Ti$_2$H$_{28}$O$_7$ and the solvents are acetic acid (CH$_3$COOH) and acetylacetone (CH$_3$COCH$_2$COCH$_3$). The Bi(NO$_3$)$_2$·5H$_2$O and NaNO$_3$ materials were first dissolved in deionised water and acetic acid. The solution was stirred at room temperature in 1 hour to completely dissolve the salts of Bi(NO$_3$)$_2$·5H$_2$O and NaNO$_3$. When the solution became transparent, the solvent of acetylacetone was added to prevent Bi$^{3+}$ ions from reverse precipitation and form C$_4$Ti$_2$H$_{28}$O$_7$-dissolved environment. The C$_4$Ti$_2$H$_{28}$O$_7$ amount was suitably calculated before adding into the solution which was then stirred in 1 day until it became transparent. After that, the solution was dried at a temperature of 110°C to form gel. Dried gel was annealed in air at different temperatures from 500 °C to 1000 °C for 2 hour then furnace cooled. The Na residual amount was varied from 0 to 50 mol% to investigate the influence on the phase information. Structural phase of sample was studied by X-ray diffraction using the wavelength of CuK$\alpha$ (1.5406 Å), the 2θ angles from 20 to 70° and the step of 0.02°. The morphology was monitored by scanning electron microscope (SEM) and the optical properties were studied by UV-visible absorption spectroscopy.

3. RESULT AND DISCUSSION

Figure 2 shows XRD pattern of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ sample annealed at 800 °C in air for 2 h with different compensated amount of Na. Bi$_{0.5}$Na$_{0.5}$TiO$_3$ has a single phase with rhombohedral structure when the Na amount is above 40%. In case of amount of Na less than 40%, the gel-forming vaporization results in the lack of a necessary amount of Na, hence the new phase of Bi$_2$Ti$_2$O$_7$ is formed to. This observation is in a good agreement with the report of Kang et al. [14]. In addition, when the Na amount in range of 10 - 30 mol%, other impurity phases are observed and difficult to observe to identify the origin of these phases.

The influence of sintering temperature on the phase formation was illustrated on XRD patterns (Fig. 3) of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ with the Na amount of 40 mol% at different sintering temperatures from 500 to 1000 °C for 2 h in air. Fig. 3 shows that, after sintering at 500 °C, some diffraction peaks related to a parasite phase of Bi$_2$Ti$_2$O$_7$ are observed in addition to the peak of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ phase. The intensity of Bi$_{0.5}$Na$_{0.5}$TiO$_3$-phase peak increases with an increase of sintering temperature; meanwhile, the intensity of Bi$_2$Ti$_2$O$_7$-phase peak decreases. At
temperature above 800 °C, most of peaks related to Bi$_2$Ti$_3$O$_7$ phase are removed and only some peaks from Bi$_{0.5}$Na$_{0.5}$TiO$_3$ are left. At 1000 °C, no observation of parasite phase suggests that Bi$_{0.5}$Na$_{0.5}$TiO$_3$ is stable. As a result, the phase-formation temperature of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ should be in range of 800 - 1000 °C.

Figure 2. XRD patterns of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ sample annealed at 800 °C for 2 hours in air with different Na compensated amounts.

Figure 3. XRD patterns of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ sample with the Na amount of 40 mol% at different sintering temperatures from 500 °C to 800 °C for 2 hours in air.

The effect of sintering temperature on the morphology of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ having 40 mol% Na amount was studied at different temperatures: 500 °C, 600 °C, 900°C and 1000 °C, seen Fig 4(a)-(d). The result shows that the particle grain size is small and uniform. When increasing sintering temperature to 600 °C, particles have a tendency of forming cubic shape with larger size as compared to the 500 °C sintered sample. At 900°C, particles were sintered and cubic structure was destroyed. This trend was observed more clearly at the sintering temperature above 1000 °C. In conclusion, the sintering temperature plays a very important role in controlling the structure of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ which influences on the Bi$_{0.5}$Na$_{0.5}$TiO$_3$ development in applications related to H$_2$ splitting and also for photocatalysis [7].

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Figure 4. The morphology of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ samples with the same Na amount of 40 mol% annealed at (a) 500 °C, (b) 600 °C, (c) 900 °C and (d) 1000 °C for 2 h in air.

Figure 5. (a) absorption spectra of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ sample and (b) the dependence of $(\alpha hv)^2$ on the photon energy ($h\nu$) corresponding to different Na amounts from 0 to 50 mol%.

Figure 5 shows absorption spectra of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ sample corresponding to different Na amounts. From Fig. 5, the sample has an absorption edge of 420 nm when Na amount varies from 10 to 40 mol%. In case of no Na compensation, beside absorption edge of 420 nm, there is another absorption edge of 520 nm. In $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ sample with 50 mol% Na compensated amount, a new small absorption edge of 450 nm was detected. This appearance is expected to be related to the absorption edge of $\text{Bi}_2\text{Ti}_2\text{O}_7$ or contaminants in case of no or too high Na-compensated amount. Fig. 6(b) shows the relation between $(\alpha hv)^2$ and the photon energy ($h\nu$) in $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ samples corresponding to different Na-compensated amount varying in range of 0 - 50 mol%. The bandgap ($E_g$) is determined by interpolating the linear part of the plot of $(\alpha hv)^2$ versus $h\nu$. The bandgap value is estimated around 3.05 - 3.18 eV.
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TỔM TẮT

ÁNH HƯỞNG CỦA NHIỆT ĐỘ NUNG THIỆU KẾT ĐẾN VIỆC TÀO PHA VÀ TÍNH CHẤT QUANG CỦA VẬT LIỆU SẮT ĐIỆN KHÔNG CHỈ Bi_{0.5}Na_{0.5}TiO_{3}

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Vật liệu sinter điện nén Pb(Zr,Ti)O$_3$ đã và đang được ứng dụng rộng rãi trong các lĩnh vực điện tử mạch sử dụng điện do tình dục hai của nguyên tố chất (chiём khoảng ~ 60% khối lượng) để sản xuất và môi trường. Trong số các họ vật liệu sinter điện không chất được nghiên cứu phát triển thì vật liệu sinter điện không chất Bi$_{0.5}$Na$_{0.5}$TiO$_3$ được quan tâm do chúng có các đặc trung sient điện và áp điện so sánh được với vật liệu nén Pb(Zr,Ti)O$_3$. Trong báo cáo này, vật liệu Bi$_{0.5}$Na$_{0.5}$TiO$_3$ được chế tạo bằng phương pháp sol-gel. Các điều kiện anh hướng từ điều kiện công nghệ chế tạo như quá trình gel hóa, quá trình trung tiêu kết khi pha kết tinh của vật liệu được khảo sát. Kết quả nghiên cứu cho thấy vật liệu sinter điện không chất Bi$_{0.5}$Na$_{0.5}$TiO$_3$ do pha cấu trúc khí hàm lượng Na bù trong quá trình gel hóa tới ưu khoảng 40 mol.% và nhiệt độ nung tạo pha là trên 800 °C trong khoảng thời gian 2 giờ ngoài không khí. Kết quả phân tích phổ hấp thụ cho thấy đồ rộng vùng cảm của vật liệu Bi$_{0.5}$Na$_{0.5}$TiO$_3$ có giá trị trong khoảng từ 3,01 - 3,18 eV.

*Từ khóa:* Bi$_{0.5}$Na$_{0.5}$TiO$_3$, sol-gel, tính chất quang, sinter điện không chất.