EFFECTS OF SINTERING TEMPERATURE ON THE STRUCTURE, MICROSTRUCTURE AND PROPERTIES OF 0.935($Bi_{0.5}$ $Na_{0.5}$) TiO3 - 0.065$BaTiO_3$ PIEZOELECTRIC CERAMICS

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Reçu le 13/12/2009 – Accepté le 15/10/2010

Résumé

L'effet de la température de frittage des céramiques exempt de Plomb 0.935($Bi_{0.5}$ $Na_{0.5}$)TiO_3 -0.065$BaTiO_3$ a été étudié dans la gamme de température 1150°C - 1200°C. La diffraction des rayons X montre que la structure est de type perovskite avec la co-exixtence de la phase rhombohédrique et tetragonale. Des grains fines et homogènes ont été observé pour les échantillons frittés à1150 et 1160°C et une augmentation de la température de frittage à 1180-1200°C provoque une croissance significative des grains avec l'apparition des grosses grains. Les valeurs de la polarisation rémanente P_r à la température ambiante sont 27, 31, 27 et 29 $\mu C/cm^2$ pour les échantillons frittés à 1150, 1160, 1180 et 1200^0C respectivement. A la température ambiante l'échantillon fritté à1180°C présente de bonnes performances : la valeur de la constante diélectrique est de 833 à 1 KHz, un facteur de couplage électromécanique K_t de l'ordre de0.52 et un rapport k_t/k_p de l'ordre de 2.08. Il en résulte que ces céramiques peuvent être utilisés dans les applications des transducteurs ultrasonores.

***Mots clés** : Céramiques exempt de plomb, température de frittage, Propriétés piézoélectriques.*

Abstract

The influence of sintering temperature of 0.935($Bi_{0.5}$ $Na_{0.5}$)TiO_3 -0.065$BaTiO_3$ lead-free ceramics was studied from 1150°C to 1200°C. The X-ray diffraction patterns showed that all of the BNT6.5BT ceramics exhibited a single perovskite structure with the co-existence of the rhombohedral and tetragonal phase. A fine and homogeneous grains were observed for samples sintered at 1150 and 1160°C and the increase of the sintering temperature up to 1180-1200°C induces significant grain growth with the appearance of coarse grains. The values of remnant polarization P_r obtained at room temperature are 27, 31, 27 and 29 $\mu C/cm^2$ for specimens sintered at 1150, 1160, 1180 and 1200^0C respectively. At room temperature, the sample sintered at 1180°C exhibited good performances: dielectric constant was 833 at 1 KHz, thick coupling factor k_t was 0.52 and the k_t/k_p ratio was 2.08. Therefore, the ceramics can be suitable for ultrasonic transducers in commercial applications.

***Keywords** : free ceramics, sintering temperature, piezoelectric properties.*

ملخص.

درس تأثير درجة حرارة تلبيد الخزفيات الخالية من الرصاص 0.935($Bi_{0.5}$ $Na_{0.5}$)TiO_3 -0.065$BaTiO_3$ في المجال الحراري 1150°C - 1200°C . .طيف انعراج الأشعة السينية أثبت أن البنية البلورية هي بنية البروفكيست مع تداخل الطور الرباعي والطور ثلاثي الميل لجميع العينات .لوحظ في. درجة حرارة التلبيد 1150°C و 1160°C أن البنية المهجرية ذات حبيبات صغيرة ومتجانسة،أما في المجال التلبيد الحراري 1180°C - 1200°C لوحظ نمو حبيبات مع ظهور حبيبات كبيرة الحجم .في درجة حرارة الغرفة،قيم الإستقطابية الذاتيةP_r هي 27, 31, 27 و29 $\mu C/cm^2$ بالنسبة للعينات الملبدة في 1160°C ,1150°C, 1180°C و1200°C على التوالي. العينة الملبدة في درجة حرارة 1180°C تملك خصائص جيدة: ثابت عزل ذو قيمة833 عند الاهتزاز 1KHz،عامل الكهروميكانيكى Kt ذو قيمة0.52 والنسبةKt/ /Kp ذات قيمة 2.08 .إذن يمكن استعمال هذه الخزفيات في تطبيقات محول الموجات الفوق صوتية

***الكلمات المفتاحية** : الخزفيات الخالية من الرصاص. درجة حرارة التلبيد. الخصائص الكهرواجهادية.*

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The lead-based piezoelectric materials like (Pb,Zr)TiO_3 (abbreviated as PZT) are the most widely used in piezoelectric applications [1, 2]. However, these materials cause serious environmental problems because of the toxicity of the lead oxide and its high vapor pressure during the sintering process, which is adversative to the sustainable development and the environmental protection [3]. Consequently, many researches are today carried out to develop lead-free piezoelectric materials that would present so good piezoelectric properties such as PZT ceramics.

Bismuth sodium titanate ($Bi_{0.5}$ $Na_{0.5}$)TiO_3 (abbreviated as BNT) is considered to be an excellent candidate of lead-free piezoelectric ceramics [4]. The BNT ceramic exhibits a large remnant polarization $P_r = 38$ μC/cm^2, a high Curie temperature $T_c = 320$ °C and a phase transition point from ferroelectric to antiferroelectric $T_d = 200$ °C. However the use of BNT in piezoelectric application is limited by the difficulty to pole this ceramic due to its large coercive field (73 kV/cm).

To improve piezoelectric and dielectric properties of BNT ceramics, various BNT-based solid solutions have been developed [5-9]. Among these solid solutions, (1-x)($Bi_{0.5}$ $Na_{0.5}$)TiO_3 -$x$$BaTiO_3$ (BNT-xBT) system has been attracted a great deal of attention owing to the existence of a rhombohedral-tetragonal morphotropic phase boundary (MPB) near x=0.06-0.07[10].

Compared with pure BNT, the BNT-xBT ceramics reveal relatively high piezoelectric properties and low coercive field near the MPB. However, it is appeared that dielectric and piezoelectric properties depend on the ceramic process conditions and particularly on the sintering temperature. In this paper, we examine the influence of sintering temperature on the structure, microstructure and piezoelectric properties of 0.935($Bi_{0.5}$ $Na_{0.5}$)TiO_3 - 0.065$BaTiO_3$ (BNT6.5BT) lead-free ceramics.

1. EXPERIMENTAL PROCEDURE

The ceramic samples were prepared by solid state sintering from carbonates Na_2CO_3 (reagent grade, Sigma-Aldrich, 99,5%), $BaCO_3$ (reagent grade, Sigma-Aldrich, 99%),and oxides Bi_2O_3 (Aldrich, 99,9%) , and TiO_2 (Riedel-dehaen). The powders were weighed respectively according to BNT6.5BT composition then mixed by planetary milling in ethanol using agate balls as milling media for 1 h. The milled powders were calcined at 825^{0}C for 4 h in air atmosphere. After calcining, the powders were rehomogenised by planetary milling in ethanol using agate balls for 1h and then isostatically pressed. The compacted samples were sintered between 1150 to 1200^{0}C for 4 h in air atmosphere. The as-prepared samples were cut in disks shape of 12mm in diameter and 1mm in thickness.

The crystal structures of sintered ceramics were determined by means of X-ray diffractometer (RIGAKU Miniflex) using Cu Kα radiation. The microstructure of the sintered ceramics was observed with scanning electron microscope (SEM, HITACHI,S-3500N).

The specimens were polished and electroded with a silver paste and after were poled in a silicone oil bath at 60^{0}C under a DC field of 5 kV/mm for 10 min for piezoelectrics measurements. The piezoelectric coefficient d_{33} was measured using a piezoelectric d_{33}-meter (Piezotest PM 200) at a frequency of 100 Hz. The electromechanical coupling factors k_p and k_t were measured by the resonance and anti-resonance technique using an impedance analyzer (HP 4194A). Dielectric properties of samples were determined using the impedance analyzer HP 4194A at room temperature. P-E hysteresis loops were obtained by Radiant Precision Workstation ferroelectric testing system at room temperature.

2. RESULTS AND DISCUSSION

2.1. Phase structure and Microstructure

The X-ray diffraction patterns of BNT-6.5BT ceramics sintered at 1150, 1160, 1180 and 1200^{0}C respectively are shown in Figure 1.

These patterns show an almost pure perovskite structure phase whatever the temperatures with some slight amount of $Na_2Ti_3O_7$ phase. At room temperature, the $Bi_{0.5}$ $Na_{0.5}$ TiO_3 system is in rhombohedral phase and $BaTiO_3$ is in tetragonal phase.

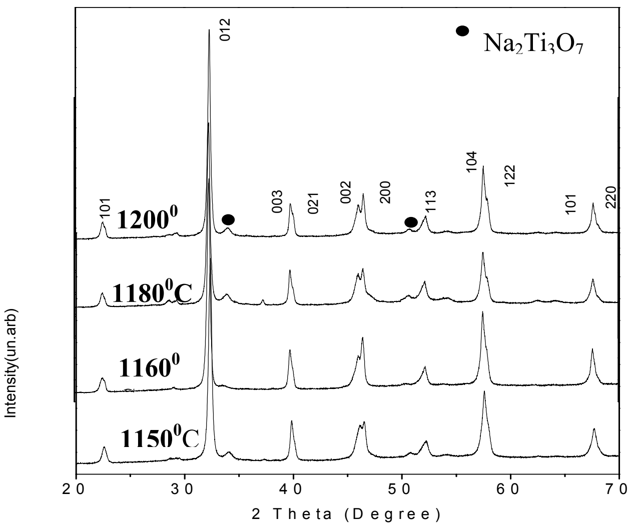

Figure 1: XRD patterns of 0.935($Bi_{0.5}$ $Na_{0.5}$)TiO_3 -0.065$BaTiO_3$ ceramics sintered at different temperatures.

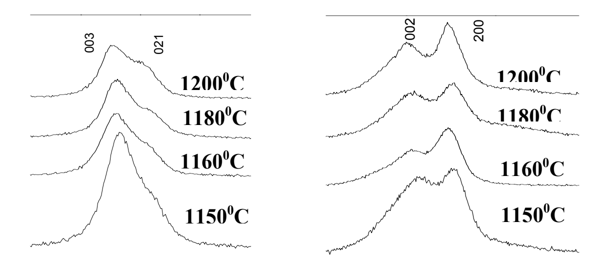

Figure 2: XRD patterns in the 2 theta ranges of 39-41^0 and 45-48^0.

According to the literature, there is a rhombohedral-tetragonal MPB in their solid solution near $0.935(Bi_{0.5}\ Na_{0.5})TiO_3$ $-0.065BaTiO_3$ composition. X-ray diffraction pattern of the composition at MPB is characterized with separated presence of two peaks to (003)/(021) at about $39{,}84^0$ and splitting of the peak to (202) planes at around $46{,}51^0$. In this work, further XRD analysis performed in the 2 theta ranges of $39\text{-}41^0$ and $45\text{-}48^0$ is shown in the figure 2. Pattern exhibits the feature of peak splits at corresponding diffraction angles, indicating co-existence of tetragonal and rhombohedral angles phases in BNT-6.5BT ceramics.

Figure 3 shows the SEM micrographs of BNT-6.5BT ceramics sintered for 4 hours at 1150, 1160, 1180 and 1200°C respectively.

All the ceramics are almost fully densified whatever the temperature. At 1150 and 1160°C, the microstructures consist of fine and homogeneous grains with an average grain size close to 1µm. Some slight porosity is observed and consists of small intergranular pores. This porosity is consistent with the value of the apparent density ρ measured by Archimedes' method. An increase of the sintering temperature up to 1180-1200°C does not favor the densification state but induces significant grain growth. This last one conducts to the appearance of coarse grains (~3-4µm). The density of all specimens is between 97.1 and 97.6%.

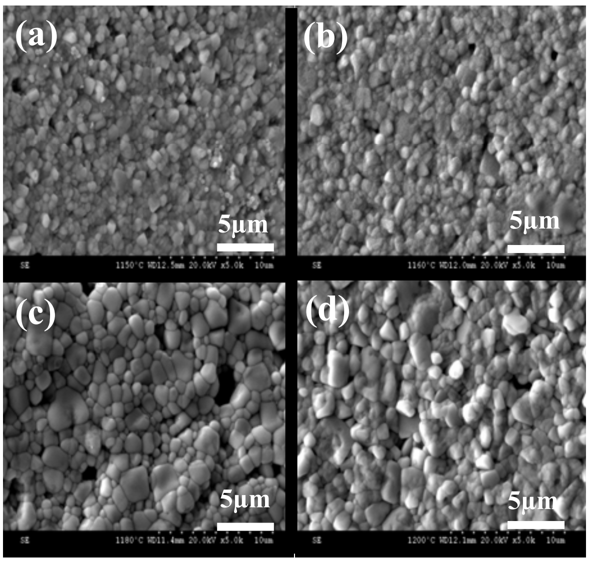

Figure 3: SEM micrographs of BNT-6.5BT ceramics sintered at (a)-1150^0C, (b)-1160^0C, (c)-1180^0C and (d)-1200^0C

2.2-Ferroelectric and piezoelectric properties

Figure 4 shows the P-E hysteresis loops of BNT-6.5BT ceramics sintered at different temperatures. Theses hysteresis were achieved at room temperature. The saturated loops confirm the ferroelectric nature of the specimens. The values of remnant polarization P_r are 27, 31, 27 and 29 µC/cm^2 for specimens sintered at 1150, 1160, 1180 and 1200^0C respectively. The specimen sintered at 1160^0C exhibits the maximum value and has the good squareness loops.

The high values of remnant polarization P_r in the system can be attributed to increase in domain wall motion that switches domains and hence affects the polarization. The coercive field values of all samples are lower than these of the $Bi_{0.5}\ Na_{0.5}\ TiO_3$ ceramics (about 73 kV/cm) at room temperature.

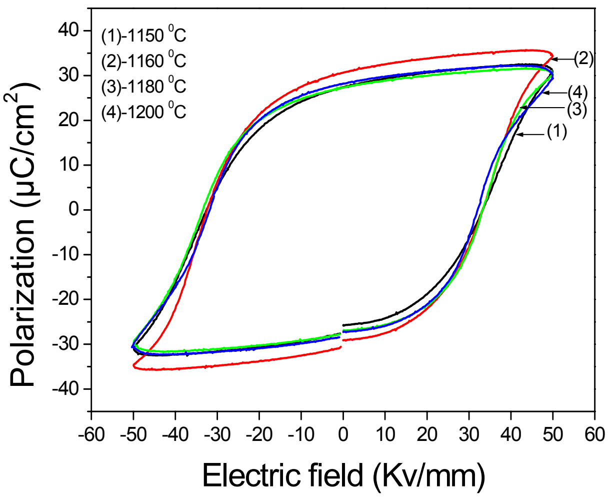

Figure 4: P-E hysteresis loops of $0.935(Bi_{0.5}\ Na_{0.5})TiO_3$ - $0.065BaTiO_3$ ceramics sintered at different temperatures

The detailed dielectric and electromechanical properties of BNT-6.5BT ceramics sintered at different temperatures are shown in table 1. The 6.5 BNT-BT ceramics sintered at different temperatures all have applicable electrical properties. The dielectric constant ε_r (1 KHz) and dielectric loss tg(δ) (1 KHz) do not have a remarkable change with sintering temperatures.

The piezoelectric coefficient d_{33}, the planar coupling factor k_p and the thick coupling factor k_t are found to be over 140 pC/N, 0.24 and 0,39 respectively for all sintering temperatures. The planar coupling factor k_p has a small change when sintering temperature is below 1200^0C. The larger k_t value is obtained at sintering temperature1180^0C and 1200^0C (0.51 and 0.52 respectively). We have calculated the ratio of $k_t/\ k_p$ because it is an important parameter for ultrasonic transducers [1]. The highest value of $k_t/\ k_p$ was found for the sample sintered at 1180^0C.This ratio ranges from 1.62 to 2.08 for the sintered samples which satisfy well the requirement for applications.

Table 1 : Dielectric and piezoelectric properties of BNT-6.5BT ceramics sintered at different temperatures.

Sintering temperature (^{0}C)	1150	1160	1180	1200
Dielectric Constant ε_r	830	910	833	864
Dielectric loss tg(δ)	0,036	0,035	0,037	0,032
d_{33} (pC/N)	141	145	148	155
K_p	0,24	0,26	0,25	0,28
K_t	0,39	0,45	0,52	0,51
K_t/K_p	1,62	1,73	2,08	1,78

Taking into account the above results, the composition near morphotropic phase boundary (MPB) have relatively high piezoelectric and electromechanical activities. It is attributed to an increase in the number of possible spontaneous polarization directions for the composition near MPB due to the coexistence of the rhombohedral and tetragonal phase [11-13].

CONCLUSION

The phase structure, microstructure and piezoelectric properties of BNT-6.5BT lead-free ceramics sintered at different temperatures were investigated. X-ray diffraction pattern indicates a pure perovskite structure with the co-existence of the rhombohedral and tetragonal phase. The ceramics exhibit good piezoelectric properties: The piezoelectric coefficient d_{33}, the planar coupling factor k_p and the thick coupling factor k_t are found to be over 140 pC/N, 0.24 and 0,39 respectively and the k_t/ k_p ratio ranges from 1.62 to 2.08.It can be believed that these ceramics can be used in piezoelectric devices.

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