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SINTERING TIME DEPENDENCE OF $BaBi_2Nb_2O_9$ CERAMICS PROPERTIES

WPŁYW CZASU SPIEKANIA NA WŁASNOŚCI CERAMIKI $BaBi_2Nb_2O_9$

The results of investigation of influence of sintering time on grain structure and ferroelectric relaxor properties are presented. The grain structure analysis performed by the scanning electron microscope (SEM) exhibits differences in grain size of the ceramics sintered for various time at the constant temperature. Namely, the grain sizes increase with the increase of the sintering time. This fact results in changes in dielectric properties. The temperature position of maximum of permittivity shifts to higher values.

Keywords: Ceramics; Dielectric properties; Relaxor ferroelectrics

W niniejszej pracy prezentowany jest wpływ czasu spiekania na strukturę ziarnistą i właściwości relaksorowe ceramiki $BaBi_2Nb_2O_9$. Analiza tej struktury, przeprowadzona przy użyciu skaningowego mikroskopu elektronowego (SEM), ujawnia różnice w rozmiarach ziaren spiekanych w różnych czasach ale w stałej temperaturze. Mianowicie rozmiary ziaren wzrastają wraz ze wzrostem czasu spieku. Ponadto długość czasu spieku ma również wpływ na zmiany własności dielektrycznych.

1. Introduction

The $BaBi_2Nb_2O_9$ (BBN) ceramics belong to Aurivilius compounds, generally described by following formula $[Bi_2O_2][A_{n-1}B_nO_{3n+1}]$. The compounds are built up by the intergrowth of Bi-O and pseudo-perovskite layers. There are promising materials and very friendly for enviroment, because they do not contain lead. BBN ceramics show behaviour characteristic for ferroelectric relaxors, namely a strong frequency dispersion of the permittivity maximum and a significant shift of its temperature with frequency, what has been presented in our earlier paper[1,2]. Analysis of the real (ε') and imaginary (ε'') part of permittivity allowed us to determine the values of Burn's temperature (T_B) and the freezing temperature (T_f) characteristic to the relaxor ferroelectrics. It is commonly known that the ferroelectric relaxors find extensive use in military, telecommunications and other applications [3, 3, 4, 5,6]. The recent tendency in miniaturization of electronic equipment caused that electric components required new materials properties. This tendency is connected with decreasing the electroceramics grain size. The main aim of these investigations is to find the correlation between the grain size and characteristic properties of ferroelectric relaxors. The way to control dimensions of grain seems to be technology of sintering ceramics. In our earlier paper we widely described influence of sintering temperature on relaxor properties of $BaBi_2Nb_2O_9$ (BBN) ceramics [7]. The other helpful factor in steering the grains size is time of sintering. The main purpose of present studies is to learn the effect of sintering time on $BaBi_2Nb_2O_9$ (BBN) ceramics properties.

2. Experimental

$BaBi_2Nb_2O_9$ ceramics were prepared by standard route using two-steps sintering process. Appropriate quantities of $BaCO_3$, Bi_2O_3, Nb_2O_5 were weighted and mixed. In the first step the conventional sintering at 950°C for 2h was carried out. Then the materials were crushed, milled and sieved. Than the materials were pressed again into cylindrical pellets and sintered at 1100°C. The time (t_s) of second sintering process was changed from 4 to 13 hours. The all obtained samples were semitransparent and they had good mechanical quality.

The grain structure and distribution of all elements throughout the grains were examined by scanning elec-

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tron microscope, (SEM), JSM-5410 with an energy dispersion spectrometer (EDS), whereas the crystallographic structure and parameters of elementary cell were determined from XRD measurements carried out using Huber diffractometer. The powder diffraction diagram was measured from 10 to 100° in 2θ with 0.02° steps and a 2 s counting time. The changes in sintering time modify also the dielectric properties of the BNN ceramics. The samples of 0.6mm thickness coated with silver electrodes were used for the dielectric measurements. The samples directly after sintering were rejuvenated by thermal treatment at 450°C prior to measurements. Consequently a part of frozen defects formed during the sintering process was recombined. The dielectric measurements were carried out on heating in the temperature range 0-450°C

using an HP4192A impedance analyser for the frequency of measuring field 0.1-1000 kHz.

3. Results

A typical scanning electron images of the BBN ceramics sintered for 4 and 13 hours are presented as example in Fig.1 indicated, that size of grain increased with the extension of sintering time. The average grain size G was determined using linear intercept method. The G value changed from 14μm to 19μm for ceramics sintered for 4 and 13 hours respectively (Fig.2). Commonly is known the fact, that for single-phase ceramics materials, the following equation can be used to present the relation between sintering time and average grain size [8]
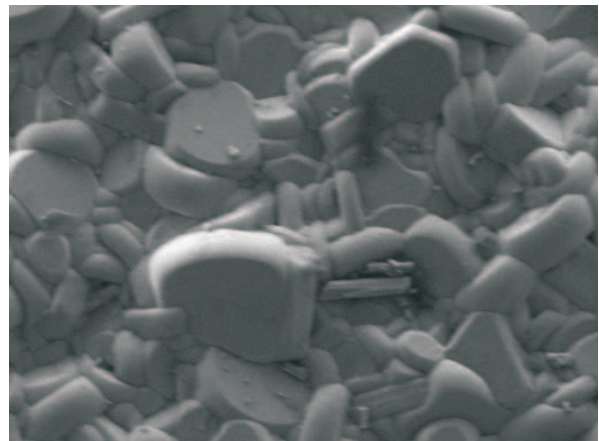
a)
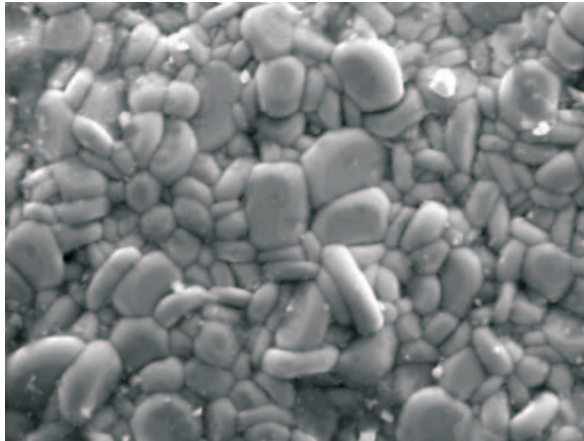
b)

Fig. 1. SEM images of $BaBi_2Nb_2O_9$ ceramics sintered for 4 and 13h time

$$G = G_o + Kt^n,$$

where G is the average grain size, G_o is the initial grain size, t is sintering time and n is the growth coefficient. The attempts of fit our results to this equations were undertaken. The satisfactory results of fitting were obtained for samples sintered during 6 and more hours (see in Fig.2). The value of n factor is equal to approximately 0.41±0.02. Theoretically the n factor should be equal to 0.5, but we have to take into consideration the existence of impurity and pores on the grain boundary, which impeded grain growth [9]. Impossibility to fit results to above mentioned relationship for samples with shorter sintering time indicated that these have purly developed grain structure with a lot of pores and not completely reacted $BaCO_3$. The above assumptions were confirmed by measurements of density, obtained by Archimedes

displacement method with distilled water. Initially, the density of samples is low and increases quickly with increasing of sintering time, later the density is practically invariable. This proves that the sintering mechanisms are different at different sintering stages: plastic flow and diffusion creep are the main sintering mechanism at initial sintering stage and last sintering stage, respectively [10].
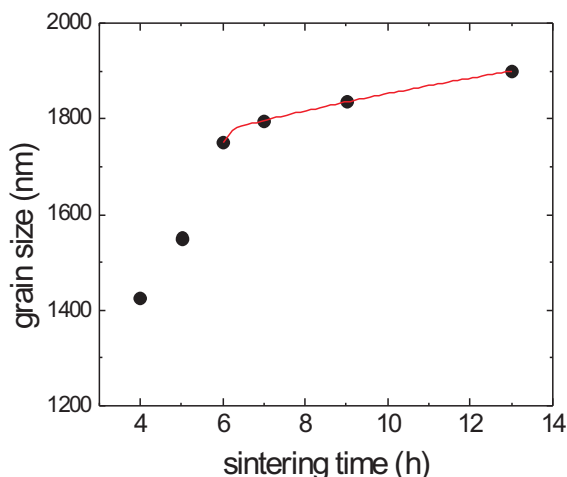
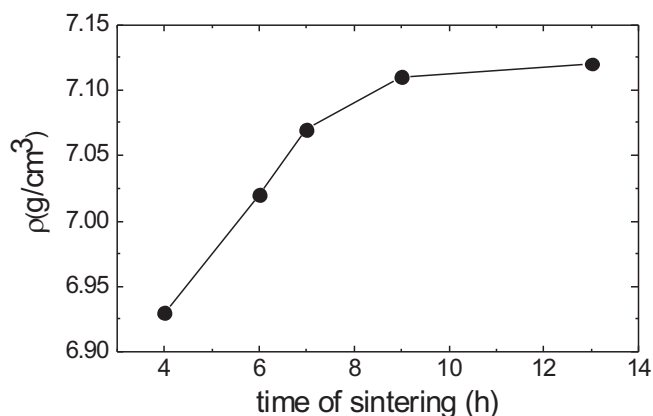Fig. 2. Influence of sintering time on average grain size of $BaBi_2Nb_2O_9$ ceramics

Fig. 3. Influence of sintering time on real density

The X-ray diffraction patterns (XRD) of ceramics sintered for 5 hours obtained at room temperature are shown, as an example, in Fig.4. The XRD profile was analyzed by using set of programs DHN Powder Diffraction System ver.2.3. The location and intensity of 32 diffraction lines were identified in the range of the measured angle. The obtained results show a good agreement with JCPDS standard number 12-0403 for $BaBi_2Nb_2O_9$.

All line indexes connected with Aurivillius structure were assigned for all investigated ceramics. For ceramics sintered by 4 and 5 hours we perceived the presence of a single very weak line for $2\theta=25.58°$ not connected with the Aurivillius structure. This line is probably connected with the strongest diffraction line of $BaCO_3$ structure (JCPDS standard No. 11-0697), what confirmed our opinion about presence of a small quantity of BaCO3. The ratio of the integral intensity of this line to the integral intensity of all the lines of diffraction pattern allowed estimating the content of the $BaCO_3$ phase at ca 1 %, 0.75% and 0.5% for ceramics sintered by 4, 5 and 6 hours, respectively. The BBN ceramics were characterized by tetragonal structure with space group I4/mmm [11, 12]. The lattice parameters obtained from X-ray patterns changed with sintering time (Fig.5). It is worth to notice, that the volume of crystallographic cell increases with time of sintering (from 4 to 9 hours). This tendency completely changes for samples sintered for 13 hours, what correlates with dielectric measurements presented below.
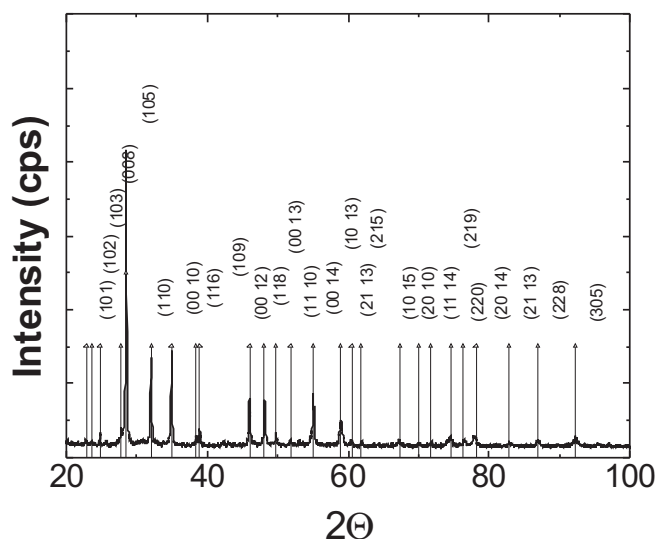

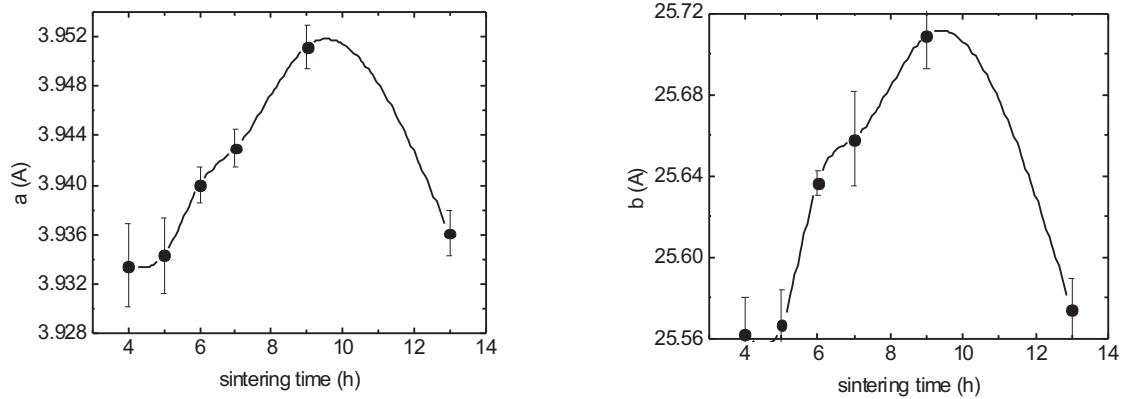Fig. 4. XRD pattern of BBN ceramics sintered for 5 hours

Fig. 5. Variation of lattice parameters (a,b and c) as a function of sintering time

Fig. 6 shows changes in the 100 kHz dielectric response with increase in sintering temperature. The temperature dependencies of the real (ε') and imaginary (ε") part of permittivity reveal a strong diffused character of phase transition for all studied BBN ceramics. The maximum value of dielectric permittivity (ε_{max}) and corresponding temperature T_m are strongly dependent on the sintering time. The changes of ε_{max} are not regular. Firstly the value of ε_{max} strongly increased and achieved maximum for ceramics sintered for 6h, what can be the result of much higher crystalline phase content in the ceramics. However, too long sintering time leads to both: creating the new defects of crystal lattice as well as to the significant reduction of ε_{max}. The change of T_m, evaluated from ε'(T) dependences at f = 100 kHz, shows linear increase with a rate 2.2°C/hour (degree per hour) of sintering.
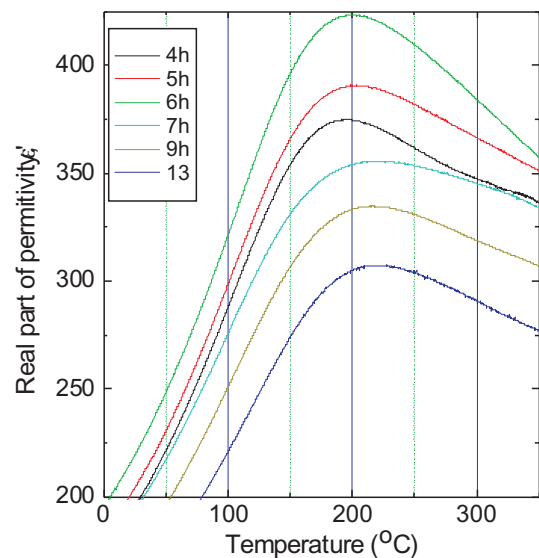

Fig. 6. Real part of permittivity as a function of temperature measured on heating at frequency of measuring field 100kHz for BBN ceramics

The degree of frequency dispersion can be described by evaluating the pressure dependence of ΔT_m value, defined as the difference between T_m measured at 0.7 and 1000 kHz, respectively. The measurement of $\Delta\varepsilon'_{max}$ dispersion can be defined in a similar manner. The ΔT_m increases linearly with a rate of 5.3° C/ hour of sintering for all investigated samples except the last samples sintered by 13 hours (Fig.7). The $\Delta\varepsilon'_{max}$ also increased from 58 to 156, respectively for samples sintered for 4 and 13 hours. The attempts of determination the freez-

ing temperature and energy of polarization fluctuations from Vogel-Fulcher relationship were undertaken . The relationship is presented below:
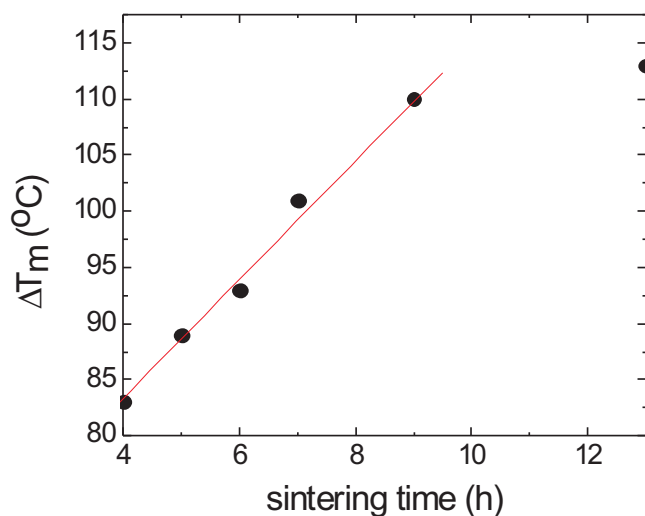

Fig. 7. Degree of frequency dispersion of $\Delta T_m = T_m(1000kHz) - T_m(0.7\ kHz)$ as a function of sintering time

$$f = f_0 \exp\left[\frac{-E_a}{k(T_m - T_f)}\right],$$

where E_a is the activation energy, T_f is the freezing temperature of polarization fluctuations, and f_o is the pre-exponential factor. The value of E_a and T_f are dependent linearly from sintering time for almost all samples (Fig.8). The activation energy and freezing temperature of samples sintered for 13 hours, significantly deviate from linear character.
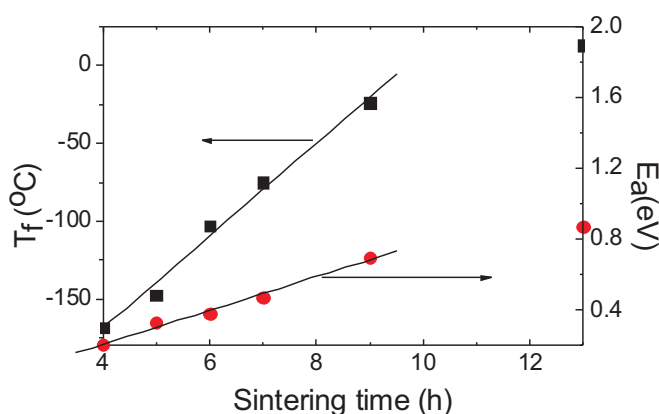

Fig. 8. The freezing temperature (T_f) and activation energy (E_a) as a function of sintering time

The presented above dielectric data together with the Sherrington and Kirkpatrick relationship were used to determine the temperature dependence of local order parameter q [13]:

$$\varepsilon' = \frac{C\{1 - q(T)\}}{T - \theta\{(1 - q(T)\}},$$

where θ is Curie-Weiss temperature, C is the Curie-Weiss constant. The value of q is equal zero at high temperature in a paraelectric phase and starts to increase when the polar clusters begin to appear on cooling – it is called Burns temperature(T_B). The difference between T_f and T_B determined the temperature range of ferroelectric relaxor behaviour. This range reduced with the increase of sintering time (Fig.9).
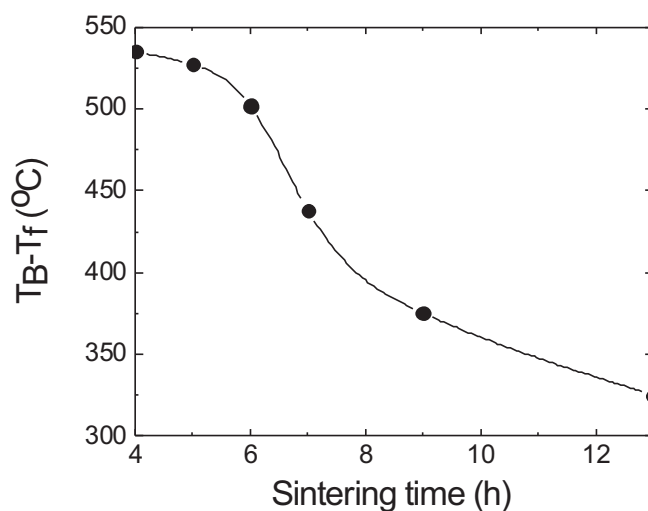

Fig. 9. The difference of T_B ad T_f vs. sintering time

4. Conclusions

The results presented above as well as results presented in our earlier paper [6] show, that there are two ways of control not only grain size, but also the dielectric and relaxor properties. The first way is a control by sintering temperature, the second way is control by sintering time. With point of view of potential application the second way seems to be more predictable, almost all characteristic values change linearly and we are able to obtain the ceramics with specified value of, for example grain size or temperature T_m or T_f.

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