A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 59 2014 Issue 1
DOI: 10.2478/amm-2014-0001

M. ADAMCZYK*, L. KOZIELSKI*, R. ZACHARIASZ*, M. PAWEŁCZYK**, L. SZYMCZAK***

STRUCTURAL, DIELECTRIC SPECROSCOPY AND INTERNAL FRICTION CORRELATION IN $BaBi_2Nb_2O_9$ CERAMICS

KORELACJE POMIĘDZY STRUKTURĄ, SPEKTROSKOPIĄ DIELEKTRYCZNĄ I TARCIEM WEWNĘTRZNYM W CERAMICE $BaBi_2Nb_2O_9$

The research presented in this paper concerns $BaBi_2Nb_2O_9$ (BBN) which is the member of the Aurivillius family and seems to be interesting from the point of view of its potential applications in storage media. Our investigations focused on temperature dependence crystal structure and mechanical properties of this ceramics as well as on the dielectric properties of samples. Correlation between positions of the maximum of the real part of electric permittivity and the behavior integral width of diffraction lines XRD versus temperature had been discussed based of the presence of polar nano-regions with orthorhombic distortion in macroscopic tetragonal matrix.

Keywords: Relaxor ferroelectrics, mechanical properties, ceramics

Wyniki badań przedstawionych w niniejszej pracy dotyczą ceramiki $BaBi_2Nb_2O_9$ (BBN), która należy do rodziny materiałów o strukturze Aurivillius'a. Materiały te są bardzo interesujące z punktu widzenia zastosowań w urządzeniach elektronicznych. Przeprowadzone badania umożliwiły określenie temperaturowych zmian struktury krystalicznej oraz własności mechanicznych badanej ceramiki. Otrzymane zależności porównano z wynikami badań dielektrycznych. Stwierdzone korelacje pomiędzy położeniami maksimów na wykresie temperaturowej zależności rzeczywistej części przenikalności elektrycznej a zachowaniem całkowej szerokości połówkowej linii dyfrakcyjnych zostały przedyskutowane z uwzględnieniem obecności nano-obszarów polarnych o dystorsji rombowej w tetragonalnej makroskopowej matrycy.

1. Introduction

Bi-layered perovskites have recently attracted a great interest due to their potential technological importance for a diverse range of applications. In particular, the $BaBi_2Nb_2O_9$ (BBN) seems to be interesting from the point of view of its potential applications in storage media. Hitherto the investigations focused on two main aspects, i.e. specification of crystal structure and description of the specific dielectric behaviour of this ceramics [1-3]. S.M. Blacke et al. [3] examined X-ray and neutron data and suggested that the $BaBi_2Nb_2O_9$ was tetragonal with the space group I4/mmm. Futher investigations carried out by R. Macquart et al [4], showed the presence of a phase transition at room temperature. They suggested that phase transition from an I4/mmm structure to the ferroelectric I4mmm occurs. The investigations were carried out from 20 K up to 500K and temperature dependence of lattice parameters didn't show any anomalies. Moreover, Ismunadar et al [5] showed that Ba ions entered not only the perovskite blocks but also $(Bi_2O_2)^{2+}$ layers resulting in inhomogeneous distribution of Ba ions and local charge imbalance in the layered structure. Based on XRD measurements they proved that in BBN ceramics 15-20% of Ba^{2+} ions are located in the $(Bi_2O_2)^{2+}$ layers. This structural disorder is inherently connected with the dielectric behavior of this ceramics. The frequency dependence of the dielectric response demonstrates typical behavior for relaxor ferroelectrics, namely the maximum of the real part of the dielectric permittivity (ε'_{max}) is strongly dispersive and shifts to higher temperatures with an increase in the frequency [6]. A broad dielectric relaxation in the BBN compound may occur due to a higher chemical disorder (corresponding to higher random field) and this might be responsible for the relaxor behavior in the BBN [7]. In other words, the positional static disorder of Bi and Ba cations is responsible for ferroelectric relaxor behavior through the formation of nanoregions with different structural disorder levels. The XRD investigations reported in this paper confirm the existence of such nanoregions. Furthermore, the presence of them are the cause of specific behavior of temperature characteristic of mechanical losses $(Q)^{-1}$ and Young's modulus (E), which is described below.

The aim of this work is the comparison of the results of temperature variation of dielectric permittivity (described in our previous papers [8, 9]) to mechanical losses and XRD investigations. Such comparison for BBN ceramics has not been available until now.

* DEPARTMENT OF MATERIALS SCIENCE, UNIVERSITY OF SILESIA, ŚNIEŻNA 2, 41-200 SOSNOWIEC, POLAND
** WYŻSZA SZKOŁA TECHNOLOGII INFORMATYCZNYCH, MICKIEWICZA 29, 40-085 KATOWICE, POLAND
*** INSTITUTE OF PHYSICS, UNIVERSITY OF SILESIA, UNIWERSYTECKA 4, 40-007 KATOWICE, POLAND

2. Experimental

The $BaBi_2Nb_2O_9$ ceramics were prepared using the conventional mixed-oxide processing technique. Stoichiometric amounts of $BaCO_3$, Bi_2O_3 and Nb_2O_5 reagents were weighed and mixed. Thermal synthesis of the pressed mixture was carried out at 950°C for 2 h. Then the crushed, milled and sieved materials were again pressed into cylindrical pellets. The samples were prepared for XRD, dielectric measurements and mechanical loss measurements in the plate – like shape of the following dimensions: length – 40 mm, width – 10 mm, thickness – 3 mm. Next the samples were sintered at 1100°C for 6 h and then cooled to room temperature for 12 h. The obtained ceramics were semitransparent. The specimens were polished and coated with silver paste electrodes.

Preliminary X-ray investigations were carried out on ceramics samples at room temperature, using a Huber diffractometer (focused in the Zeeman-Bohlin focusing system, monochromatize $CuK_{\alpha 1}$ radiation). The diffraction spectrum was measured from 19° to 100° in 2θ with a 0.05° step and analyzed using a set of programs, i.e. the DHN powder Diffraction System ver. 2.3. X-ray measurements were carried out in order to describe the temperature variation of crystal lattice parameters. They were performed using high-resolution Siemens D5000 diffractometer (focused in Bragg-Brentano focusing system, filtred CuK_α radiation) in a wide temperature range (from 20°C to 460°C).

Internal friction (Q^{-1}) and Young's modulus (E) were measured as a function of temperature at frequencies in the range from 100 Hz to 1500 Hz (with step 1 Hz) [10, 11]. Internal friction was computed from the logarithmic decrement of exponentially damped harmonic oscillations. Young's modulus (E) was calculated from the well – known relationship [10]:

$$E = 94.68\left(\frac{l_r}{h}\right)^3 \frac{m_d}{b} f_r^2 [\mathrm{Pa}], \qquad (1)$$

where l_r – sample lenght, h – thickness, b – width, and m_d – mass of vibrating part of the sample. The resonant frequency f_r was measured in a vacuum. Internal friction was measured as a function of temperature with the heating rate of 3°C/min.

Dielectric measurements of the real (ε') and imaginary (ε'') parts of the permittivity vs. temperature were carried out on heating by using the impedance analyzer HP4192A. The sample was rejuvenate by thermal treatment at 723 K prior to measurements to allow recombination and relaxation of part of the frozen defects, formed during the sintering process.

3. Results and discussion

3.1. XRD phase studies

The X-ray diffraction pattern (XRD) of the BBN ceramics obtained at room temperature is shown in Fig. 1.

The results show good agreement with the JCPDS standard number 12-0403 for the $BaBi_2Nb_2O_9$. All of the line indexes related to the Aurivillius structure were assigned. The occurrence of two very weak lines for 2θ = 25.58° not connected with the Aurivillius structure is caused by the presence of a vestigial quantity of $BaCO_3$ since this line corresponds to the strongest diffraction line of the $BaCO_3$ structure (JCPDS standard No. 11-0697).

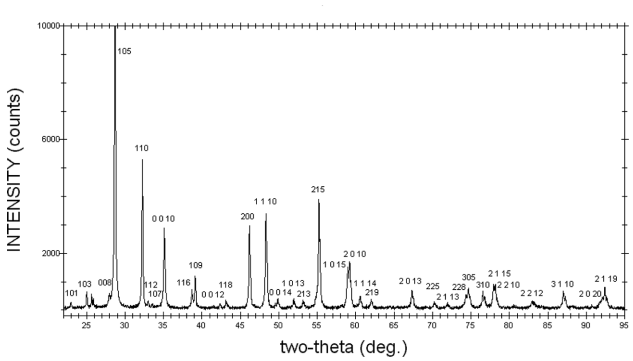

Fig. 1. The XRD pattern of BBN ceramics

The lattice parameters obtained from the X-ray pattern were a = b = 3.9406±0.0006 Å, and c = 25.6378±0.0059 Å. These results are in good agreement with the results reported in [5]. The results obtained in this work allowed determination of temperature changes of lattice parameters. Cursory look at the behavior of lattice parameters of the tetragonal unit cell during increasing of temperature did not reveal the existence of structural phase transition. The growth of the parameters is connected with the classical thermal expansion (Fig. 2 a and b).

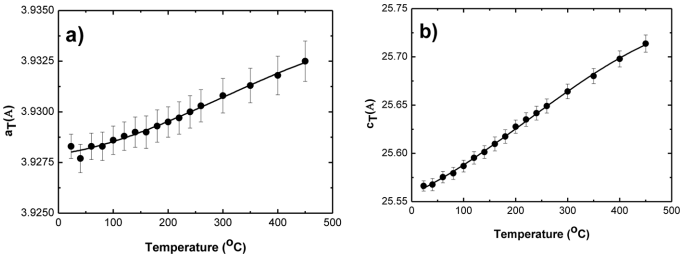

Fig. 2. Variation of the lattice constants as a function temperature

However a more thorough analysis of these relationship (especially c_T(T)) revealed that this increase is not linear. This observation is clearly demonstrated in Fig.3. The maximum connected with the inflexion point on the curve c_T(T) occurs in the vicinity of 200°C.

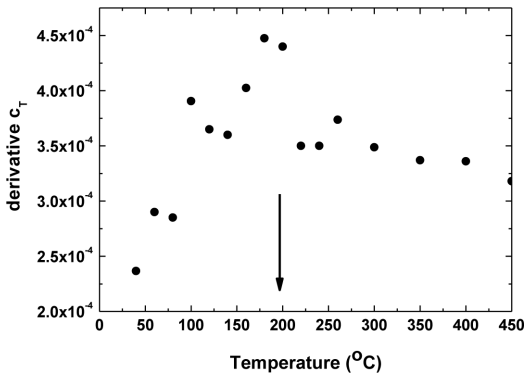

Fig. 3. Derivative of temperature variation unit cell c parameter evaluation

Moreover the integral width of diffraction lines (i.e. the integral intensity of line divided by maximum intensity) show

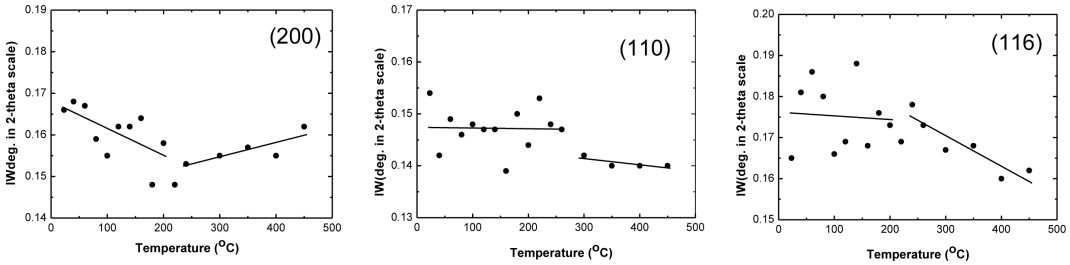

Fig. 4. Integral width of diffraction lines

an anomaly in close vicinity to 200°C (see Fig. 4). Namely in absence of phase transition should increase monotonically with temperatures increasing. In the case of BBN ceramics the character of change is just opposite. The integral width of diffraction line 200 achieved minimum in the vicinity of 200°C and next linear increase.

The evolution in crystallographic structure, take place in the temperature range of 200°C-240°C, which is in good agreement with the results obtained in mechanical and dielectrical relaxation.

3.2. The temperature dependence of Young's modulus and mechanical loss Q^{-1}

The variations of internal friction (Q^{-1}) and Young's (E) modulus as a function of temperature for BBN ceramics are shown in Fig. 5. Figure 5b indicates the value of Young's modulus at room temperature is equal to 77 GPa.

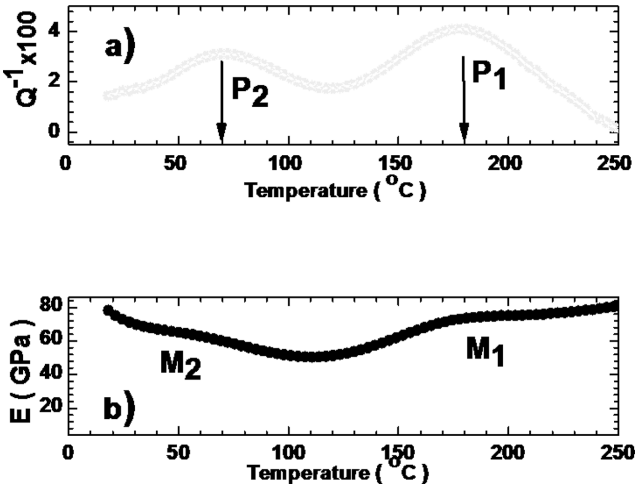

Fig. 5. Internal friction Q^{-1} (a) and Young's modulus E (b) vs. temperature for $BaBi_2Nb_2O_9$ ceramics

Internal friction curves shown in Fig. 5a exhibits two broad peaks. The P_1 peak appears at 180°C and the P_2 peak-insignificantly smaller – appears at 71°C. These peaks are closely connected with fine variations in temperature dependence of Young's modulus. The scale of the anomaly is very small, but this phenomenon is observed not only in BNN ceramics, but also in other materials (e. g.-PZT ceramics [12]). The temperature of the first anomaly, so-called M_1, is shifted towards higher temperatures, whereas the temperature of the second anomaly, M_2, is slightly lower than P_2. It is worth to notice that the temperature of the P_1 peak is slightly lower than the range where the anomaly of the lattice parameter measured by XRD method was observed.

3.3. The temperature dependence of the real and imaginary parts of permittivity

The characteristics $\varepsilon'(T)$ and ε'' (T) for a number of frequencies are shown in Fig. 6. These characteristics, and in particular ε' (T) curves, reveal strongly broadened phase transition. Moreover, the obtained results confirmed the relaxor ferroelectrics behavior of the investigated ceramics, including strong frequency shift of the permittivity maximum (ε'_{max}) and visible shift of peak's temperature (T_m) with frequency (Fig. 6b).

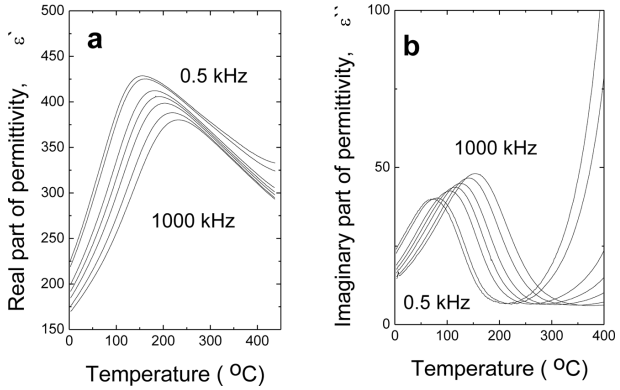

Fig. 6. Real (a) and imaginary (b) parts of permittivity (ε) as a function of temperature measured at several frequencies. The curves were measured at different frequencies: 7, 10, 50, 100, 200, 500, and 1000 kHz [8]

It should be emphasized that the temperature range in which the ε' (T) curves reaches a strong diffuse transmittance maximum is in good agreement with the temperatures at which the anomalous behavior of the integral width of diffraction lines and of internal friction peaks are observed.

4. Discussion

The first results concerning the temperature changes of dielectric properties $BaBi_2Nb_2O_9$ ceramics were obtained by E.C. Subbarao [13]. The results revealed strong diffuse character of permittivity maximum, which is the consequence of chemical disorder in crystal lattice, caused mainly by barium and bismuth ions. Namely the ions exchange their positions – the barium ions enter into bismuth oxide layers and replace the bismuth ions. The bismuth ions occupy, in turn, the free space in the perovskite blocks [5, 1]. In final effect the "average" macroscopic structure is tetragonal, but this structure contains the polar nano-regions with orthorhombic distortion, which cause the relaxor – type ferroelectric properties. These polar

nano-regions (clusters) are present even at high temperatures and make noticeable influence on the dielectric permittivity.

The results of X-ray measurements confirmed above mentioned thesis. Based on this idea of clusters with orthorhombic distortion existing in tetragonal matrix, the abnormal behavior of integral width of some diffraction lines mentioned above (in particular 200 line) becomes easy to explain. The anomalies are created by the gradually disappearance of the clusters with orthorhombic distortion and change of their symmetry from orthorhombic to tetragonal. Also the departure from linear character of the lattice parameter c(T) is in good agreement with the thesis.

It should be emphasized, that the changes occurring in ceramics $BaBi_2Nb_2O_9$ around 200°C are not classically understood phase transition, but the only structural changes associated with the disappearance of a significant amount of nano-regions with the orthorhombic distortion, which existence is due to lattice disorder.

Disappearance of some nano-regions (in which chemical disorder significantly reduces the local value of Curie temperature) caused, that the remaining polar cluster are surrounding by paraelectric matrix. The depolarization field associated with the spontaneous polarization P_s of such regions tends to the compensated state by two possible ways. One of them, consists of the formation of locally compensated polydomain structure. As a result, the participation of domain walls in a bulk of sample increase, but the change is not significant, because of their low content in the sample volume. The second way is connected with the screening polarization P_s by free electron and ion space charges from the surrounding medium – the existence of this possibility is confirmed by thermal depolarization currents observed in those ceramics at temperatures significantly higher than the temperature of permittivity maximum (T_m) [8, 9]. The process bears responsibility for an increase in internal friction around the temperature of 180°C (peak P_1).

The explanation of the second internal friction peak (P_2) is more complicated. Its temperature position corresponds to the broadened temperature range of the maximum of ε'' (T) function. Temperature dependence of mechanical properties in Bi-layered perovskites, especially $SrBi_2Ta_2O_9$ [14] are identified with a peak situated far from the phase transitions, as a stress-induced oxygen-vacancy relaxation. However, in the case of the BBN ceramics, the temperature of the second peak (P_2) is too low to be associated with this phenomenon. The origin of the second peak requires more detailed investigations in future.

5. Conclusions

The temperature characteristic of the lattice constant, dielectric permittivity and mechanical loss measurements are presented. The temperature position of the internal friction peak (P_1) corresponds with the position of the maximum in the real part of electric permittivity and with the variation of the integral width of diffraction lines XRD as a function of temperature. The results confirm the presence polar nano – regions with different structural distortion level in BaBi2Nb2O9 ceramics, caused by ions disorder in crystal lattice.

Acknowledgements

Authors are very grateful to dr hab. Andrzej Molak for helpful discussion and remarks.

This work was supported by the Polish Ministry of Science and Higher Education (Grant no N N507 504338).

REFERENCES

[1] Y. Shimakawa, Y. Kubo, Y. Nakagawa, S. Goto, T. Kamiyama, H. Asano, F. Izumi, Crystal structure and ferroelectric properties of $ABi_2Ta_2O_9$ (A=Ca, Sr, and Ba), Phys. Rev. B **61**, 6559 (2000).

[2] A.L. Kholkin, M. Avdeev, M.E. Costa, J.L. Baptista, Dielectric relaxation in Ba-based layered perovskites, Applied Physics Letters **79**, 662 (2001).

[3] S.M. Blake, M.J. Falconer, M. McCreedy, P. Lightfoot, Cation disorder in ferroelectric Aurivillius phases of the type $Bi_2ANb_2O_9$ (A=Ba, Sr, Ca), J. Mater. Chem. **7**, 1609 (1997).

[4] R. Macquart, B.J. Kennedy, T. Vogt, Ch.J. Howard, Phase transition in $BaBi_2Nb_2O_9$: Implications for layered ferroelectrics Phys. Rev. B **66**, 212102 (2002).

[5] Ismunadar, B.J. Kennedy, Effect of temperature on cation disorder in $ABi_2Nb_2O_9$ (A=Sr, Ba), J. Mater. Chem. **9**, 541 (1999).

[6] C. Miranda, M.E.V. Costa, M. Avdeev, A.L. Kholkin, J.L. Baptista, Relaxor properties of Ba-based layered perovskites, J. Europ. Ceram. Soc. **21**, 1303-1306 (2001).

[7] D. Nuzhnyy, S. Kamba, P. Kuzel, S. Veljko, V. Bovtun, M. Savinov, J. Petzelt, H. Amorin, M.E. Costa, A.L. Kholkin, Ph. Boullay, M. Adamczyk, Dynamics of the phase transitions in Bi-layered ferroelectrics with Aurivillius structure: Dielectric response in the terahertz spectral range, Physical Review B **74**(13), 134105 (2006).

[8] M. Adamczyk, Z. Ujma, M. Pawełczyk, Dielectric properties of $BaBi_2Nb_2O_9$ ceramics, Journal of Materials Science **41**(16), 5317 (2006).

[9] M. Adamczyk, Z. Ujma, M. Pawełczyk, L. Szymczak, L. Kozielski, Influence of sintering conditions on relaxor properties of $BaBi_2Nb_2O_9$ ceramics, Phase Transitions **79** (6/7), 435 (2006).

[10] D. Czekaj, A. Zarycka, A. Lisińska-Czekaj, J. Czuber, Mechanical properties of piezoceramic thin films, LI Otwarte Seminarium z Akustyki, Gdańsk – Sobieszewo 6-10.09.2004.

[11] A. Zarycka, B. Bruś, R. Zachariasz, M. Czerwiec, J. Ilczuk, Application of measurements of internal friction amplitude dependences for tests of ceramic materials, Physica Status Solidi A **205**, 1120 (2008).

[12] H. Frayssignes, M. Gabbay, G. Fantozzi, N.J. Porch, B.L. Cheng, T.W. Button, Internal friction in hard and soft PZT-based ceramics, Journal of the European Ceramic Society **24**, 2989 (2004).

[13] E.C. Subbarao, A family of ferroelectric bismuth compounds, Journal of Physics and Chemistry of Solids **23**, 665 (1962).

[14] J.S. Zhu, K. Chen, W. Li, F. Yan, Y.R. Dai, X.M. Lu, Y.N. Wang, Mechanical ad dielectric investigation on point defects and phase transition in ferroelectric ceramics, Materials Science and Engineering A **442**, 49 (2006).

Received: 20 September 2013.