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## SIGNIFICANT INCREMENT OF THE DIELECTRIC PERMITTIVITY AND DOMAIN PROPERTIES IN THE (1-x)PbTiO<sub>3</sub>-x(Na<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub> CRYSTALS

Crystals of PbTiO<sub>3</sub> and 0.9PbTiO<sub>3</sub>-0.1(Na<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub> were obtained by the flux growth method whereas crystals of (Na<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub> were growth by the Czochralski method. Raman spectroscopy and polarized light microscopy were performed at room temperature. The Raman spectra of 0.9PbTiO<sub>3</sub>-0.1(Na<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub> shown significant changes comparing to the base materials PbTiO<sub>3</sub> and (Na<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub>. A domain structure was investigated by use polarized light microscopy. Dielectric permittivity measurements were carried out in the temperature range from 20°C to 550°C and a frequency from 1 kHz to 1 MHz. These showed higher dielectric permittivity for the crystals 0.9PbTiO<sub>3</sub>-0.1(Na<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub> than the source materials PbTiO<sub>3</sub> and (Na<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub>.

The high value of dielectric constant makes it possible to applied 0.9PbTiO<sub>3</sub>-0.1(Na<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub> as efficient dielectric medium in a capacitors. The small size of the domain structure with the easy possibility of switching by application of an external electric field, give opportunities to apply these materials to FRAM memory applications. Moreover, the high sensitivity of these materials to the surrounding gases e.g. ammonia, chlorine, hydrogen, etc., allows the construction of sensor devices.

*Keywords:* perovskite, ferroelectric materials, dielectric properties, optical properties

### 1. Introduction

Crystals, ferroelectric compounds with perovskite structure ABO<sub>3</sub> are very interesting materials from application point of view.

Ferroelectric materials with a high dielectric constant and high breakdown voltage allow the building of efficient capacitors on the reduced size and high capacities which is especially important for miniaturization of electronic devices [1].

In compounds with perovskite structure occurs a piezoelectric effect (observed in the structure without the center of symmetry). Therefore, these compounds are widely used in technology (e.g. as actuators, micromechanical system, multi-layer capacitor, etc.) [2-6].

The unique possibility of switching the domain structures in ferroelectric materials, by using an electric field for this purpose, makes possible to construct modern and efficient FRAM memories [4,7-8].

The modern civilization is endangered by many factors – among other harmful gases in atmosphere, dust and smog. Searching for materials useful for modern detector devices of such toxic substances is a big challenge for protection of the environment.

An important role in the above mentioned areas is attributed to the perovskite based crystals, which show a wide range of interesting properties e.g. (1-x)PbTiO<sub>3</sub>-x(Na<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub> (hereafter referred to as (1-x)PT-x(NBT)).

The basic compound lead titanate PbTiO<sub>3</sub> (hereafter referred to as PT), well described in literature, is ferroelectric at room temperature. The phase transition, at a temperature of about 490°C, from ferroelectric tetragonal structure (P4mm) to the paraelectric phase with cubic structure (Pm3m) is accompanied by a strong change of dielectric permittivity [9,10]. The PT crystals as well as ceramics properties were extensively examined [9-15].

The second of the basic compounds, the sodium-bismuth titanate (Na<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub> (hereafter referred to as NBT) is also

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ferroelectric at room temperature. It undergoes two phase transitions: the first one at about 540-520°C from the high-temperature cubic phase to tetragonal, and the second one to rhombohedral phase at about 300-260°C [16-20].

Suitable modifications which vary the content of cations in the crystals (e.g.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$ ) influence both the temperatures of the phase transformations and their dielectric properties [21-23].

The paper [21] shows that results obtained using Raman method remain in connection with the temperature of measurement. However, the results presented in [22] refer to  $0.5\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - $0.5\text{PbTiO}_3$  ceramics.

The results of detailed investigations of the effect of influence of Pb concentration on the dielectric, thermal properties and Raman spectra of  $(1-x)(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ - $x\text{PbTiO}_3$  ceramic for  $x = 0.08$  and  $x = 0.6$  were presented in publication [23]. These studies confirmed that the dielectric, thermal and Raman spectra of  $(1-x)(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ - $x\text{PbTiO}_3$  ceramics depend strongly on the Pb concentration. The changes of Pb ions concentrations influences the phase transition temperature, thermal hysteresis, permittivity and the Raman spectra [23].

The present work is dedicated to study the influence of Na and Bi ions concentration on the dielectric and optical properties of  $(1-x)\text{PbTiO}_3$ - $x(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  crystals ( $x = 0.1$ ).

## 2. Experimental

$\text{PbTiO}_3$  and  $0.9\text{PbTiO}_3$ - $0.1(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  crystals were obtained by the flux growth method. Crystals of PT and  $0.9\text{PT}$ - $0.1\text{NBT}$  were prepared by the earlier described method [24].  $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  crystals were grown from the melts by the Czochralski method [25].

Raman spectra were recorded by Bio-Rad FTS 6000 spectrometer with a Nd-YAG laser (1064 nm) of 200 mW power. The spectra were collected in the back-scattering geometry in the frequency range  $50$ - $1000\text{ cm}^{-1}$  with a  $4\text{ cm}^{-1}$  resolution level. Only the standard edge filter was used during the Raman measurements. The measurements were carried out at ambient temperature.

Optical investigations by use a Nikon Eclipse LV 100 POL polarizing microscope were also carried out at ambient temperature.

To study the dielectric properties (dielectric permittivity) a Gwinstek Precision LCR Meter series 8110G was used. The measurements were carried out in a temperature range from  $20^\circ\text{C}$  to  $550^\circ\text{C}$  with a constant rate of temperature change of  $4^\circ\text{C}/\text{min}$  with a frequency range from  $1\text{ kHz}$  to  $1\text{ MHz}$  for heating and cooling processes respectively (the measurements results are described in the next chapter).

Crystals measuring  $1.5 \times 2\text{ mm}$  were cut using a wire saw. Then they were cleaned. For this aim, they were immersed in acetone for 5 minutes. Then they were removed and subjected to an oven-heating process at  $200^\circ\text{C}$  for a period of 60 minutes. The next step was to apply the masking frame and spray silver

electrodes. Prior to the measurements, the samples were heated up to  $550^\circ\text{C}$  and kept at this temperature for 120 minutes.

## 3. Results and discussion

The ionic radii for sodium ( $r_{\text{Na}} = 1.02\text{ \AA}$ ) and bismuth ( $r_{\text{Bi}} = 1.03\text{ \AA}$ ) are similar, however lead has a much higher radius ( $r_{\text{Pb}} = 1.37\text{ \AA}$ ). The substitution of Pb by Na/Bi causes a distortion of crystal structure and changes the force constants, thus influencing on the shapes of Raman spectra.

Fig. 1 shows the room temperature Raman spectra of the investigated specimens. The spectra for PT and NBT are consistent with those reported earlier [12,21]. Raman spectra of  $0.9\text{PT}$ - $0.1\text{NBT}$  are similar to PT, however some differences between these spectra are visible. For  $0.9\text{PT}$ - $0.1\text{NBT}$ , the Raman spectrum is slightly shifted towards higher frequencies (compared to pure PT) and in addition some of the peaks (e.g.  $150$ ,  $360$ ,  $640\text{ cm}^{-1}$ ), decrease their intensity. The peaks in the  $200$ - $300\text{ cm}^{-1}$  region are characteristic for the tetragonal phase. There appears a new, small, peak visible at about  $460\text{ cm}^{-1}$  (indicated by the arrow). The presence of this line in the spectrum may be associated with the difference in mass and ionic radius of Pb and Na/Bi and with disorder (vacancy or substitution Pb by Na or Bi) created on the A-site of  $0.9\text{PT}$ - $0.1\text{NBT}$  [22,23]. The evolution of high-frequency modes above  $650\text{ cm}^{-1}$  can be caused by increasing the average ion radius of the cations in sublattice A and by changed orientation of oxygen vacancies [26].

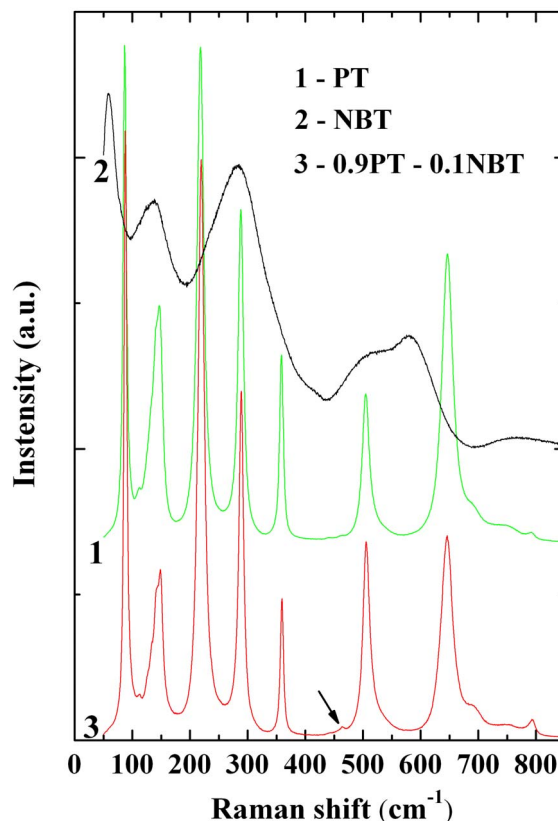


Fig. 1. Raman spectra of the  $\text{PbTiO}_3$  (1),  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  (2) and  $0.9\text{PbTiO}_3$ - $0.1(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  (3) crystals at room temperature

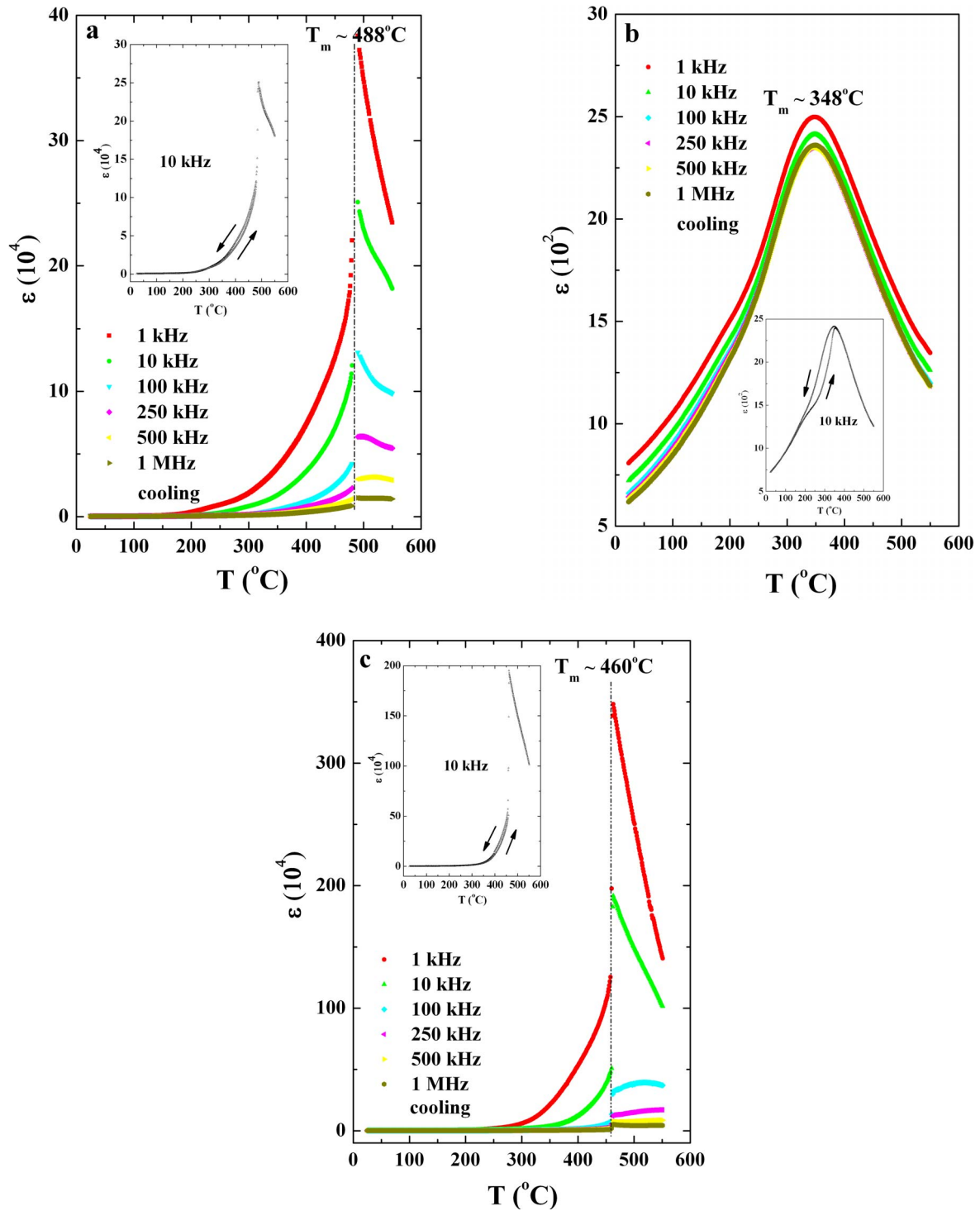


Fig. 2. Temperature/frequency dependence of the electric permittivity of the  $\text{PbTiO}_3$  (a),  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  (b),  $0.9\text{PbTiO}_3\text{-}0.1(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  (c) crystals. Insert shows temperature dependence of electric permittivity on heating/cooling at 10 kHz

Fig. 2 shows the temperature and frequency dependence of the electric permittivity ( $\epsilon$ ) for: a) PT, b) NBT and c) 0.9PT-0.1NBT. We observed a quite sharp maximum of dielectric permittivity at about  $T_m \sim 494^\circ\text{C}$  on heating and  $488^\circ\text{C}$  on cooling respectively for  $\text{PbTiO}_3$  (Fig. 2a). The observed thermal hysteresis (insert in Fig. 2a) is a consequence of the ferroelectric property with the first-order phase transition.

In the case of the second base compound of  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  (Fig. 2b) the maximum of the electric permittivity was observed

around  $T_m \sim 353^\circ\text{C}$  (heating) and  $348^\circ\text{C}$  (cooling). In contrast to PT, no sharp peak (maximum) was seen. The insert in Fig. 2b presents the temperature dependence of the electric permittivity on heating/cooling at 10 kHz, showing a large hysteresis effect. The thermal hysteresis is a characteristic feature for martensitic phase transitions and is related to large internal stress in the material [23].

Fig. 2c presents  $\epsilon(T)$  dependence (in the frequency range from 1 kHz to 1 MHz) for 0.9PT-0.1NBT, showing its similar-

ity to pure PT with a sharp maximum of the dielectric constant for  $T_m$  around  $\sim 464^\circ\text{C}$  (in heating) and  $460^\circ\text{C}$  (in cooling). It was observed that in the 0.9PT-0.1NBT the phase transition temperature is lower due to the incorporation of the Na/Bi ions. It should be emphasized that the value of dielectric permittivity

( $\epsilon$ ) in crystals 0.9PT-0.1NBT increased (in comparison to pure PT) by an order of magnitude.

Based on the description presented in the paper [27], the basic ferroelectric parameters for the study compounds were estimated. The results are shown in Table 1.

TABLE 1

Ferroelectric parameters (Curie temperature  $T_m$ , dielectric permeability at maximum temperature  $\epsilon_{r,\max}$ , dielectric loss tangent in room temperature  $\text{tg}\delta$ ,  $\Delta T_H = T_m(\text{heating process}) - T_m(\text{cooling process})$ ,  $\Delta\epsilon = \epsilon_{\max}(\text{heating process}) - \epsilon_{\max}(\text{cooling process})$ , Curie-Weiss temperature  $T_0$ , Curie constant  $C$ ) at 10 kHz of  $\text{PbTiO}_3$ ,  $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  and  $0.9\text{PbTiO}_3 - 0.1(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  crystals

Samples	Cooling process			$\Delta T_H$ [°C]	$\Delta\epsilon_H$	$T_0$ [°C]	$C$ [°C]
	$T_m$ [°C]	$\epsilon_{\max}$	$\text{tg}\delta$				
$\text{PbTiO}_3$	488	$24.8 \times 10^4$	0.22	6	$\sim 0.5 \times 10^4$	$\sim 383$	$\sim 5.1 \times 10^7$
$(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$	348	$23.9 \times 10^2$	0.04	5	$\sim 0.19 \times 10^2$	$\sim 350$	$\sim 4.2 \times 10^5$
$0.9\text{PbTiO}_3 - 0.1(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$	460	$191.4 \times 10^4$	0.11	4	$\sim 2.0 \times 10^4$	$\sim 352$	$\sim 2.3 \times 10^8$

TABLE 2

Results of electrical permittivity  $\epsilon$  for different frequencies at room temperature ( $\epsilon_{RT}$ ), maximum temperature ( $\epsilon_{\max}$ ) and loss tangent at room temperature  $\text{tg}\delta$  form examined compounds

Frequency [kHz]	$\text{PbTiO}_3$ crystals – present			$\text{PbTiO}_3$ ceramics [10]			$(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ crystals – present			$0.9\text{PbTiO}_3 - 0.1(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ crystals – present		
	$\epsilon_{RT}$	$\epsilon_{\max}$	$\text{tg}\delta$	$\epsilon_{RT}$	$\epsilon_{\max}$	$\text{tg}\delta$	$\epsilon_{RT}$	$\epsilon_{\max}$	$\text{tg}\delta$	$\epsilon_{RT}$	$\epsilon_{\max}$	$\text{tg}\delta$
1	435	$37.3 \times 10^4$	0.19	1100	4200	2.20	805	$24.9 \times 10^2$	0.04	845	$348.4 \times 10^4$	0.16
100	245	$12.9 \times 10^4$	0.26	700	2300	2.40	660	$23.5 \times 10^2$	0.04	610	$32.4 \times 10^4$	0.08
1000	160	$6.4 \times 10^4$	0.32	300	1170	2.00	615	$23.6 \times 10^2$	0.05	560	$5.1 \times 10^4$	0.05

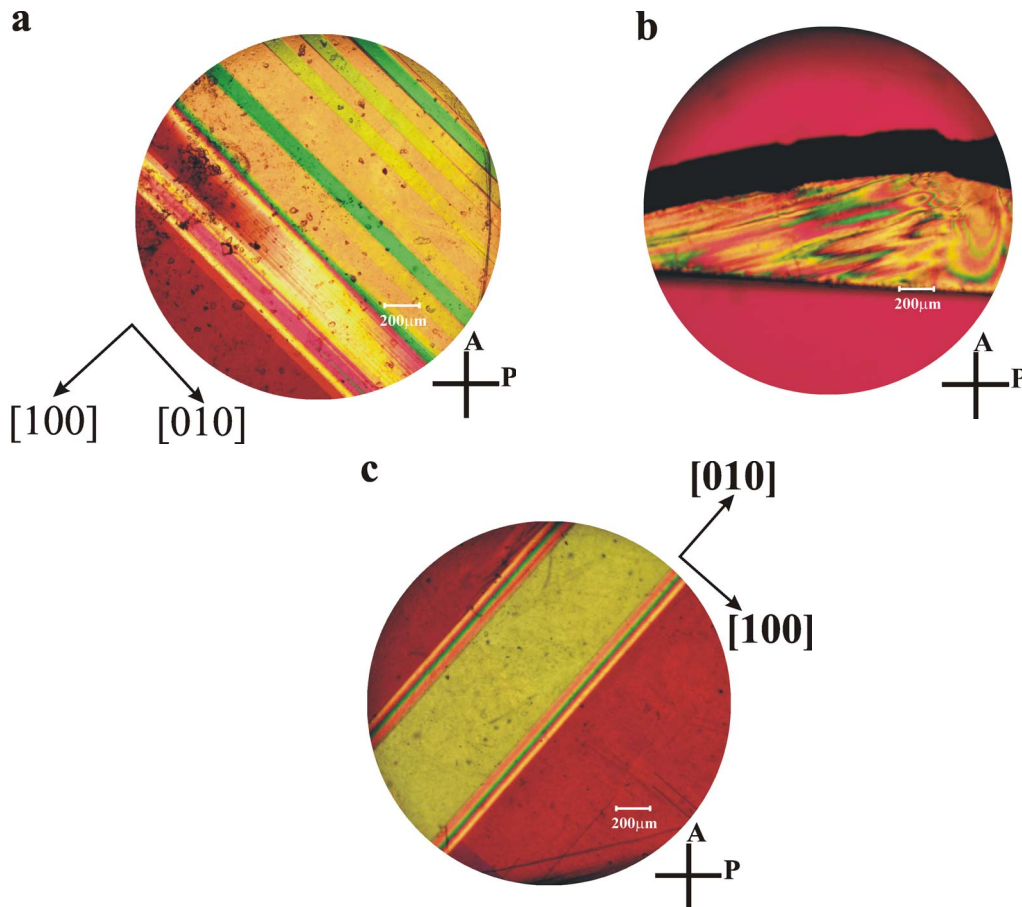


Fig. 3. Observation of domain structure in the crystallographic direction [001] of the  $\text{PbTiO}_3$  (a),  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  (b),  $0.9\text{PbTiO}_3 - 0.1(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  (c) crystals (magnification  $\times 40$ )

Fig. 3 (a-c) present the domain structure of  $\text{PbTiO}_3$  (a),  $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  (b) and  $0.9\text{PbTiO}_3-0.1(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  (c), observed in the crystal sample in polarized light at room temperature. The pictures were obtained by using the auxiliary  $\lambda$  – plate. Observations of domain structures were performed in the crystallographic directions [001]. For  $\text{PbTiO}_3$  and  $0.9\text{PbTiO}_3-0.1(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  the situation of the crystallographic axes has been depicted in the corresponding figures. It is not possible at that moment to give the precise orientation of the crystallographic axes for the  $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  sample.

In  $\text{PbTiO}_3$ , were observed domains with the three characteristic interference colours: green, purple and yellow. The particular colour corresponds to a different location of the four-fold axis of the tetragonal phase. The colour of the domain's four-fold axis parallel to the direction of polarized light doesn't change during rotation of the sample. So, during observation with the quarter wave plate the domains are constantly visible as purple. Domain sizes are of the order of  $10\ \mu\text{m}$ . A similar system of domains is observed in samples of  $0.9\text{PbTiO}_3-0.1(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ , which may indicate a similar nature of the ferroelectric phase transition to that in  $\text{PbTiO}_3$ . In contrast the crystal domain structure of  $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  reveals much smaller domains. In addition, the image of this structure is disturbed by interference effects stemming from heterogeneous stresses which appear in individual fragments of the sample (in accordance with dielectric measurements). The domain size is important for particular applications – the smaller domain dimension the easier changing its reorientation. This feature is crucial for the FRAM memory application.

#### 4. Conclusion

The  $0.9\text{PbTiO}_3-0.1(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  crystals properties presented in the article are various from the source base compounds with the perovskite structure:  $\text{PbTiO}_3$  and  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ . Searching for new functional materials, targeted for specific applications such as: capacitors, piezoelectric actuators, various types of sensors and ferroelectric memory triggers is very important from both fundamental and application point of view. The crystals materials like  $0.9\text{PbTiO}_3-0.1(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ , easy to manufacture, safe to use and cheap are desirable by modern technology.

Research conducted with Raman spectroscopy showed differences in the spectra of the crystals  $0.9\text{PbTiO}_3-0.1(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  compared to the  $\text{PbTiO}_3$ . The changes can be the result of substitution of Na/Bi ions in place of the Pb ions.

The investigations of the crystal  $0.9\text{PT}-0.1\text{NBT}$  showed a decrease of the phase transition temperature and an significant increase (by order) of the dielectric permittivity value in relation to the major compound PT. Therefore, application of the  $0.9\text{PT}-0.1\text{NBT}$  crystals as a capacitor will give measurable benefits, allowing, among others, to reduce the dimensions of electronic components due to improving parameters of the commonly used  $\text{PbTiO}_3$  compound.

Moreover, we are reporting the opportunity to change domains reorientation (in compare to PT) observed in crystals of  $0.9\text{PbTiO}_3-0.1(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  in the easier way. This effect has been confirmed by comparative optical studies of the domain structure for both compounds. In  $\text{PbTiO}_3$ , three characteristic interference colors have been distinguished, which correspond to the different location of the four-axis in the tetragonal phase. It can be assumed that, based on the preliminary tests carried out,  $0.9\text{PbTiO}_3-0.1(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$  crystals, similar to the  $\text{PbTiO}_3$ , base compound, can constitute, after further detailed research, an alternative material for FRAM type ferroelectric memories.

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