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Investigation of ultrasonic, dielectric and piezoelectric properties of the xLMT - (1-x)BT ceramics with x=0.025, 0.05, 0.075, 0.1

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Abstract

Ultrasonic, dielectric and piezoelectric studies of lead free ceramic system structures of (1-x) $BaTiO_3$-$xLa(Mg_{1/2}Ti_{1/2})O_3$ (BT-LMT) are presented in this contribution. It was shown, that such materials with x=0.025, 0.05, 0.075 and 0.1 LMT content undergo phase transitions and exhibit piezoelectric effect in the low temperature phases. Anomalies of ultrasonic velocity and attenuation at phase transitions have been observed in these materials. Measurements of temperature dependencies of ultrasonic velocity and attenuation revealed anomalies related to phase transitions in these materials. It was shown that, at room temperature and under DC bias electric field, these ceramics behave as a piezoelectrics because of electrostriction.

Keywords: piezoelectric ceramics, elastic properties, piezoelectric properties, dielectric properties.

Introduction

Lead-free perovskite relaxors are promising for environment-friendly application in electroacoustic devices [1]. A number of relaxors have been derived from barium titanate (BT) [2]. Low-loss dielectric perovskite $La(Mg_{1/2}Ti_{1/2})O_3$ (LMT) was found to be an appropriate end member to form relaxor compositions based on BT. Particular solid solutions of the BT-LMT systems were recently prepared. It was shown that BT ceramics doped with 2.5 mol% of LMT exhibit the typical features of both the ferroelectric and the relaxor [3], while BT-10% LMT demonstrates solely relaxor properties [4]. Dielectric investigations of BT-LMT performed by macroscopic methods (average over many grains) and on nanoscale level (in a single grain) have proved the presence of polar nanoregions in the ceramics at temperatures above the dielectric permittivity peak [4, 5]. Recently, homogeneous ceramics (1-x)$BaTiO_3$ - $xLa(Mg_{1/2}Ti_{1/1})O_3$ ((1-x)BT - xLMT) of the compositions x = 0.025, 0.05, 0.075 and 0.1 were obtained. X-ray diffraction studies [6] have revealed the tetragonal *(P4mm)* perovskite structure for compositions with x<0.025 and the cubic *(Pm3m)* for x > 0.05 at room temperature. Relaxor state in the (1-x)BT-xLMT system appears when three ferroelectric phase transitions (as in pure BT) merge into one diffuse transition at $x > 0.05$. At the same time, the (1-x)BT-xLMT ceramics acquire the relaxor features continuously with x. The continuous crossover from ferroelectric to relaxor behavior observed in (1-x)BT-xLMT was explained by a cluster model of relaxors. Usually relaxors, e.g PMN-PT, are strong piezoelectrics and exhibit electrostriction-induced piezoelectricity at room temperature [7]. Therefore it is of interest to study elastic and piezoelectric properties of BT-LMT ceramic system. In this contribution, we present the results of experimental ultrasonic and piezoelectric investigations of BT-LMT ceramics with different composition. The investigations of temperature dependencies of ultrasonic attenuation, velocity and piezoelectric properties revealed the anomalies at diffuse phase transitions. The electrostriction induced piezoelectric effect had been observed at room temperature in BT-LMT ceramic plates.

Experimental

Ultrasonic velocity and attenuation measurements were carried out by computer controlled pulse-echo equipment [8, 9]. Ultrasonic system allowed us to measure delay intervals less than 0.2 ns, therefore the precise relative ultrasonic velocity measurements were possible. Piezoelectric measurements were performed on home made automatic resonance-antiresonance apparatus [9-12]. The calibration of absolute sound velocity at required stabilized temperature was performed by precise measurement of electromechanical antiresonance frequencies. Silicone oil was the material for making acoustic bonds.

The dielectric measurements of BT-0.025LMT ceramics were performed by a computer controlled LCR meter HP 4284A in the frequency range 20 Hz to 1MHz, by the coaxial (frequency range 300 kHz to 3 GHz) and the waveguide (8 – 12 GHz) dielectric spectrometers [12]. All measurements were made at cooling with a rate of 1K/min in the temperature interval of 500 – 100 K. Samples of different size, satisfying technical requirements were used for every mentioned frequency range. Silver paste was used for contacts.

Results and discussion

Temperature dependence of the real and imaginary parts of the dielectric permittivity of BT-0.025LMT ceramics are presented in the Fig.1. As it is possible to see, there are three phase transitions as in pure BT. Only these phase transitions are shifted to lower temperatures, compared with BT. Also, below the first phase transition at 320K, typical relaxor properties are observed. The real part of the dielectric permittivity is strongly frequency dependent below 320 K and imaginary part at low frequencies is nearly frequency independent. This is also confirmed by frequency dependence of the real and imaginary parts of dielectric permittivity (Fig.2). From the results presented in the Fig. 1 and Fig. 2, we see, that we have relaxor, which in the low temperature phase shows another two phase transitions. In the Fig. 3 the temperature dependence of the real and imaginary parts of dielectric permittivity of 0.05 LMT-BT sample are presented. These temperature dependences differ

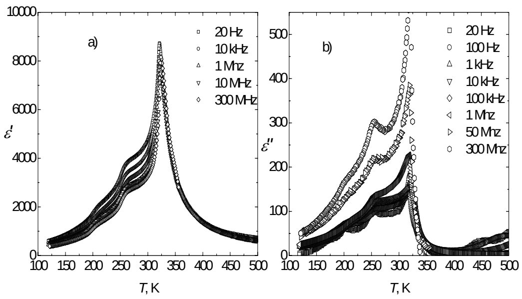

Fig. 1. **Temperature dependence of the real (a) and imaginary (b) parts of dielectric permittivity at different frequencies of BT-0.025LMT**

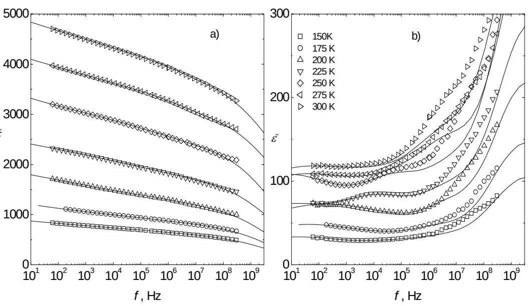

Fig. 2**. Frequency dependences of the real (a) and imaginary (b) parts of the dielectric permittivity measured in different temperatures. Lines are the best fits with the obtained distribution of the relaxation times for BT-0.025LMT**

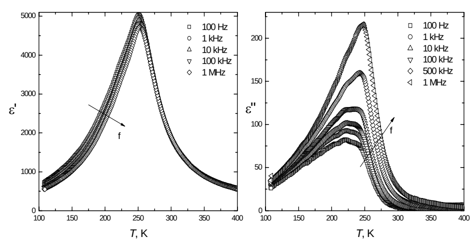

Fig.3. **The temperature dependence of the real (a) and imaginary (b) parts of dielectric permittivity at different frequencies of BT-0.05LMT**

significantly from the results presented in the Fig.1. As we can see, in the temperature dependence of the real part of dielectric permittivity we can clearly distinguish only one phase transitions: at about 250 K. More interesting results are obtained from ultrasonic measurements.

The ultrasonic velocity and attenuation measurements were carried out in BT-LMT ceramic samples, cut from rectangular bars and polished so, that two opposite sides were parallel. Length of the samples along longitudinal ultrasonic wave propagation direction was about 0.5 cm. The absolute ultrasonic velocity and attenuation values were measured at room temperature from a delay time and amplitude of three consecutive reflected in the sample echoes with 2% precision. After, we measured only variation of delay time and amplitude of first echo on temperature. Dependencies of ultrasonic velocity v and attenuation α were measured at 10 MHz frequencies in cooling run. Ultrasonic velocity decreased with temperature decreasing and reached broad minima (Fig.4). For BT-LMT with 2.5% LMT in velocity dependence two broad minima were observed, which are related to the phase transitions from rhombohedral to orthorhombic phase in the vicinity T_1=220 K, then to tetragonal phase near T_2 = 250 K. The velocity anomaly that is related to tetragonal-cubic phase transition merges to one close to T_2. Nevertheless, the broad attenuation maximum that is related to this transition is seen at T_3 =

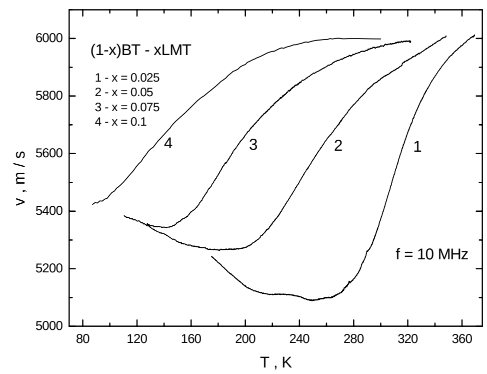

Fig.4. **The temperature dependencies of longitudinal ultrasonic velocity measured in unpolarised BT-LMT ceramics at 10 MHz frequencies**

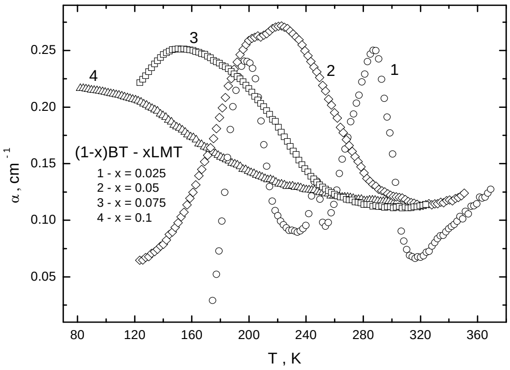

Fig.5 **The temperature dependencies of longitudinal ultrasonic attenuation measured in unpolarised BT-LMT ceramics at 10 MHz frequencies**

290 K (Fig.5). From such ultrasonic behaviour (broad elastic anomalies shifted to lower temperatures) one can conclude that phase transitions in this 2.5% LMT ceramic compound are already influenced by internal strains and shows relaxor features. With increasing of LMT content the dependencies *v=f(T)* and *α=f(T)* shifts to lower temperatures, but two attenuation broad peaks for *x*=0.05 still can be resolved. For compounds with x > 0.05 only one ultrasonic velocity minimum and corresponding to it attenuation maximum remains, and that shows fully relaxor behaviour. Therefore from ultrasonic measurements the conclusion of gradual crossover from ferroelectric to relaxor behaviour in BT-LMT ceramics [5] was confirmed.

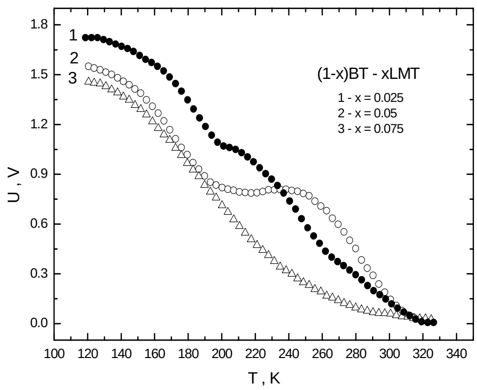

Fig.6. **The temperature dependence of electric signal detected by BT_LMT ceramic plates**

By direct measurements of electric signal from BT-LMT piezoelectric transducer, it was shown, that piezoelectric effect exists in ceramics with compositions 0.025<x <0.1 in temperature range below 312 K (Fig.6). In this experiment, the exciting 10 MHz lithium niobate transducer was attached to one end of quartz buffer and to another end the thin BT-LMT plate was glued. The plate was cut from the same bar, which was used in ultrasonic experiment. Measurements were carried out in heating after polarizing the ceramic samples at T>350 K. The temperature dependence of detected by such transducer roughly represents the temperature dependence of piezoelectric modulus of BT-LMT plate. For 2.5% LMT ceramic the two anomalies at T_1=220 K and T_2=260 K are seen. The signal vanishes at the temperature T>350 K. This corresponds to ultrasonic velocity and attenuation behaviour and represents the sequence of three phase transitions in 2.5% LMT compound. For ceramic with x=0.05 the change of slope and saturation in the dependence of detected piezoelectric signal was observed near 220K where saturation in ultrasonic velocity exists (see Fig.4). For ceramic with x=0.075 only gradual increase of detected ultrasonic signal with temperature decreasing is seen in Fig.6 (curve3) and that indicates complete evolution from ferroelectric to relaxor properties. As one can see from Fig.6, at room temperature the electromechanical

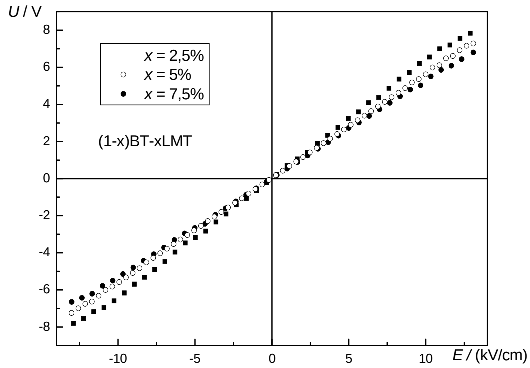

Fig.7. **Dependencies of electric signal detected by BT-LMT plates with different composition on DC bias electric field**

conversion is very small for all investigated BT-LMT ceramic materials. This situation changes with DC electric field applied to the BT-LMT plates. In this case, plate worked as ultrasonic transducer and an AC voltage appeared and increased with increasing DC field. Consequently, electrostriction-induced piezoelectricity was observed in these materials (Fig.7). The negative values of voltage show only a change of the direction of polarization in a sample. After the reversal of the DC electric field the phase of detected 10 MHz signal have changed by 180° degrees. This was clearly seen on the screen of an oscilloscope, where the received radio pulse was displayed. It is necessary to note, that detected by BT-LMT electrostrictive ultrasonic transducer signal in DC electric field depends on time and slightly increases with time (Fig.8). To our opinion, such behaviour is caused by the migration and reorientation of defects or polar nanoregions and can be related to memory effects observed earlier in other ceramic materials [13-14]. Also free charges can cause the redistribution of electric field and change effective DC field, which is responsible for

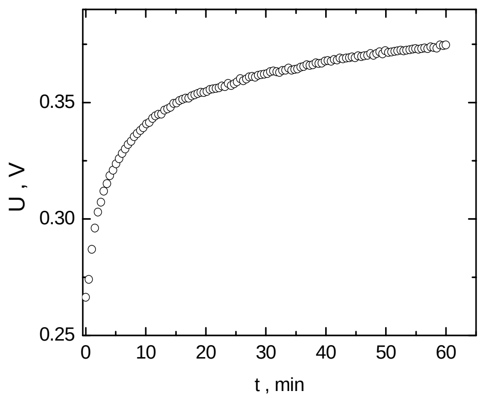

Fig.8. **The time dependence of ultrasonic signal detected by BT-LMT plate. The applied DC field was 20 kV/cm.**

the electrostriction induced piezoelectric effect. The electrostriction induced piezoelectric behaviour was also proven by the resonance-antiresonance method.

Conclusions

The temperature dependencies of longitudinal ultrasonic velocity and attenuation in BT-LMT ceramics revealed anomalies, which are indication of phase transitions in these materials. Composition dependencies of ultrasonic anomalies reflect the evolution from ferroelectric to relaxor behaviour. The electrostriction induced by DC bias field piezoelectric effect was observed in BT-LMT ceramics at room temperature and dependencies of electromechanical coupling coefficients on DC bias field for longitudinal excitations were measured. We have shown that thin plates BT-LMT ceramics can effectively excite and detect ultrasonic waves.

Acknowledgements

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References

1. **Barhi F., Simon A., Khemakhem H. and Ravez J.** Classical or relaxor ferroelectric behaviour of ceramics with composition $Ba_{1-x}Bi_{2x/3}TiO_3$. Phys. Stat. Sol. (a). 2001. Vol 184. P. 459-464.
2. **Ravez J. and Simon A.** Some solid state chemistry aspects of lead-free relaxor ferroelectrics. J. Solid State Chem. 2001. Vol.162. P 260-265.
3. **Salak A. N., Shvartsman V. V., Seabra M. P., Kholkin A. L. and Ferreira V. M.** Ferroelectric-to-relaxor transition behaviour of $BaTiO_3$ ceramics doped with $La(Mg_{1/2}Ti_{1/2})O_3$. J. Phys.: Condens. Matter. 2004. Vol. 16. P. 2785-2794.
4. **Salak A. N., Seabra M. P. and Ferreira V. M.**. Relaxor behavior of the $0.9BaTiO_3$–$0.1La(Mg_{1/2}Ti_{1/2})O_3$ solid solution**.** J. Amer. Ceram. Soc. 2004. Vol 87. P. 216-220.
5. **Salak A. N., Seabra M. P. and Ferreira V. M.** Evolution from ferroelectric to relaxor behavior in the (1-x)$BaTiO_3$ - x$La(Mg_{1/2}Ti_{1/2})O_3$ system. Ferroelectrics. 2005. Vol. 318. P. 185–192.
6. **Avdeev M., Seabra M. P. and Ferreira V. M.** Crystal structure of dielectric ceramics in the $La(Mg_{0.5}Ti_{0.5})O_3$-$BaTiO_3$ system. J. Mater. Res. 2002. Vol. 17. P. 1112-1117.
7. **Sherrit S., Catoiu G. and Mukherjee B. K.** The characterization and modelling of electrostrictive ceramics for transducers. Ferroelectrics. 1999. Vol. 228. P. 167-178.
8. **Valevičius V., Samulionis V. and Banys J.**. Ultrasonic dispersion in the phase transition region of ferroelectric materials. J. Alloys and Compounds. 1994. Vol. 211/212. P. 369-373.
9. **Samulionis V., Valevičius V., Banys J. and Brilingas A.** Ultrasonic studies of incommensurate phase transitions. J. de Physique IV. 1996. Vol. 6. P. 405-408.
10. **Samulionis V., Vysochanskii Yu. and Cajipe V.** Ultrasonic and piezoelectric investigation of $Sn_2P_2S_6$ type photosensitive ferroelectric-semiconductor crystals. Ferroelectrics. 2003. Vol. 295. P. 21-30.
11. **Samulionis V. and Banys J.** Ultrasonic and piezoelectric studies of new layered ferroelectric compounds of $Sn_2P_2S_6$ family. J.Europ. Cer. Soc. 2005. Vol. 25. P. 2543 – 2546.
12. **Samulionis V., Banys J. and Vysochanskii Yu.** The characterization of two dimensional electrostrictive $CuInP_2S_6$ materials for transducers. Materials Science Forum. 2006. Vol. 514-516. P. 230-234.
13. **Cordero F., Craciun F., Franco A. and Galassi C.** Ageing and memory in PLZT above the polar freezing temperature. Ferroelectrics. 2005. Vol. 319. P. 19–26.
14. **Kircher O. and Bohmer R.** Aging, rejuvenation, and memory phenomena in a lead-based relaxor ferroelectric. Eur. Phys. J. 2002. Vol. B26. P. 329-338.

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xLMT – (1-x)BT keramikų su x = 0,025, 0,05, 0,075, 0,1 ultragarso, pjezoelektrinių ir dielektrinių savybių tyrimai

Reziumė

Pristatomi ultragarsiniai, dielektriniai ir pjezoelektriniai bešvinių keramikų sistemos (1-x) $BaTiO_3$-x$La(Mg_{1/2}Ti_{1/2})O_3$ (BT-LMT) tyrimai. Medžiagose, kurių x=0,025, 0,05, 0,075 ir 0,1, stebimi 3 faziniai virsmai, o žemų temperatūrų fazėje – pjezoelektrinis efektas. Be to, pastebėtos ultragarso greičio ir slopinimo anomalijos fazinių virsmų aplinkoje. Iš ultragarso greičio ir slopinimo temperatūrinių priklausomybių matavimų nustatyta, kad šias anomalijas sąlygoja faziniai virsmai. Parodyta, kad kambario temperatūroje paveikus išoriniu elektriniu lauku, pjezoelektrinį efektą šiose keramikose sąlygoja elektrostrikcija.

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