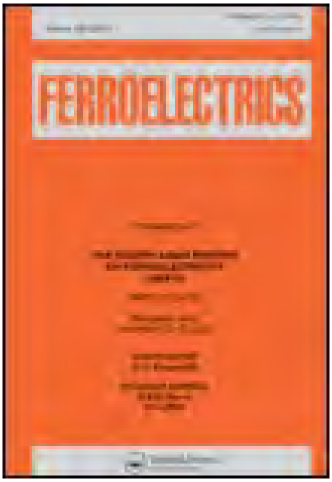

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Pb-Induced Temperature Stabilization of High Dielectric Constant in Barium Neodymium Titanates

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Dielectric properties of Pb-substituted titanates $(Ba_{1-a}Pb_a)_{6-x}Nd_{8+2x/3}Ti_{18}O_{54}$ were investigated at various x values. The results showed the formation of temperature stable dielectrics over the wide range of Pb concentrations. It has been found that the effect of Pb substitution on dielectric properties of sintered ceramics intensifies with a higher x while the solid solubility limit of Pb^{2+} ions decreases. Non-linear variation of dielectric characteristics against the lead concentration was shown to be due to the location of Pb^{2+} ions in different crystallographic sites in the unit cell. New MW materials, differed by Pb content, with temperature stable and controllable dielectric constant of 80–100 have been developed.

Keywords: rare-earth titanates; microwave dielectrics; dielectric constant

1. INTRODUCTION

Barium-lanthanide titanates with general formula $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ are known to be formed in the system BaO-Ln_2O_3-TiO_2.[1-3] The lowest dielectric loss in MW range is observed in the ceramics in case Ln= Nd, Sm.[1, 2, 8-10] However, temperature stability of dielectric constant should be generally improved in these materials towards the values of $\tau_f = \pm 10$ ppm/K while the values of dielectric constant and Q-factor should remain high. From the one hand the literature reported that admixtures of Bi_2O_3 and PbO allow the reduction (improvement) of τ_f in barium- neodymium titanates, [4-6] from the other hand the increase in dielectric constant was shown when lowering x in the system $Ba_{6-x}Nd_{8+2x/3}Ti_{18}O_{54}$.[10] Therefore, the study of dielectric characteristics of the materials, when partially substituting Pb^{2+} for Ba^{2+}, seems to be rational at lower x ($x \leq 1.5$).

2. EXPERIMENTAL PROCEDURE

The samples were produced by conventional ceramic technique, high-purity $BaCO_3$, Nd_2O_3, $PbTiO_3$, TiO_2 were utilized as the starting reagents. The phase composition and lattice parameters of the materials were identified by means of X-ray diffraction patterns collected by "DRON 4-UM" when using Cu K_a radiation. Electro-physical characteristics of ceramic samples were measured by dielectric resonator method at the frequencies of about 10 GHz.

3. RESEARCH RESULTS AND DISCUSSION

The phase composition of the materials was examined at $x = 0, 0.75, 1.5$. The results of X-ray diffraction analysis denote a single- phase composition of lead-containing materials of the system within the range of y varying from 0 to 0.4 for $x = 0$, from 0 to 0.6 - for $x = 0.75$, and from 0 to 0.7 for $x = 0$. Beyond the single-phase region the secondary phase, which was identified as $Nd_4Ti_9O_{24}$, was detected in all cases.

The measurement results of temperature coefficient of resonant frequency (τ_f), dielectric constant (ε), and Q-factor (Q) as a function of lead concentration in the system $(Ba_{1-y}Pb_y)_{6-x}Nd_{8+2x/3}Ti_{18}O_{54}$ are represented in Figures 1,2, and 3 respectively. Figure 1 shows a monotonic decrease in τ_f (curves 1-3) with the growth of lead concentration, τ_f meeting zero values in all cases. The concentration regions may be separated on the plots τ_f (y) in accordance with the different rate of change in τ_f (Fig.1). The regions with different slope degree, like those observed on the plots of τ_f (y), may also be separated on the plots of dielectric constant *vs.* lead concentration $\varepsilon(y)$ (Figure 2).

When measuring microwave Q-factor in the systems $(Ba_{1-y}Pb_y)_{5.25}Nd_{8.5}Ti_{18}O_{54}$ ($x = 0.75$) and $(Ba_{1-y}Pb_y)_6Nd_8Ti_{18}O_{54}$ ($x = 0$) the maximums of Q were revealed at $y \approx 0.2$ and at $y \approx 0.35$ respectively while the maximum of Q was not observed in the system $(Ba_{1-y}Pb_y)_{4.5}Nd_9Ti_{18}O_{54}$ ($x = 1.5$) (Figure 3),.

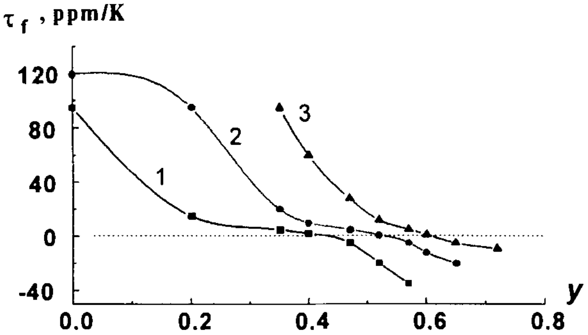

FIGURE 1 Temperature coefficient of resonant frequency of the materials as a function of lead content in the system $(Ba_{1-y}Pb_y)_{6-x}Nd_{8+2x/3}Ti_{18}O_{54}$ measured at 10 GHz. 1- $x = 1.5$; 2- $x = 0.75$; 3- $x = 0$.

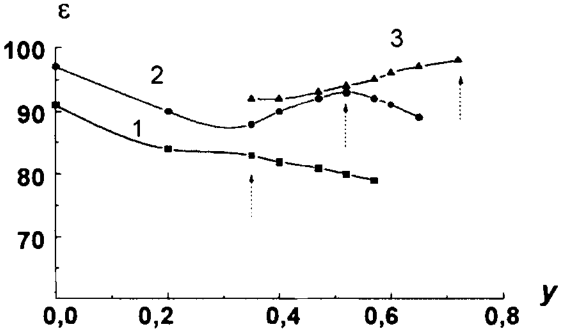

FIGURE 2 Dielectric constant of the materials as a function of lead content in the system $(Ba_{1-y}Pb_y)_{6-x}Nd_{8+2x/3}Ti_{18}O_{54}$ measured at 10 GHz. 1- $x = 1.5$; 2- $x = 0.75$; 3- $x = 0$.

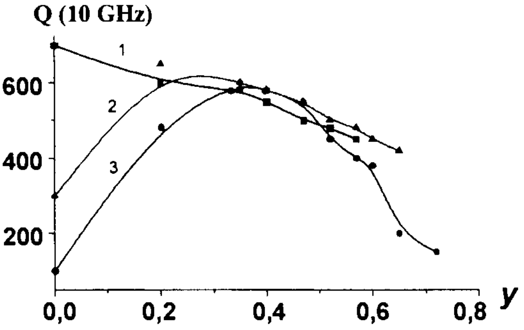

FIGURE 3 Q-factor of the materials as a function of lead content in the system $(Ba_{1-y}Pb_y)_{6-x}Nd_{8+2x/3}Ti_{18}O_{54}$ measured at 10 GHz.
1- x = 1.5; 2- x = 0.75; 3- x = 0.

The crystal structure of solid solutions $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ consists of infinite columns which are formed by oxygen octahedra linked to each other like in tetragonal tungsten bronzes.[3, 8,9] There are tri-, tetra-, and pentagonal channels formed in the cavities between oxygen octahedra. The cations of sublattice A (Ba^{2+} and Ln^{3+}) are located in tetra-, and pentagonal channels; there are 10 tetragonal sites while there are only 4 pentagonal sites in the unit cell. The tetragonal sites may be occupied by both Ba^{2+} and Ln^{3+} ions while all pentagonal sites are occupied by larger Ba^{2+} ions, so when x varies from 0 to 0.2 the structural formula may be presented as $[Ln_{8+2x/3}Ba_{2-x}V_{x/3}][Ba_4]Ti_{18}O_{54}$, where V represents structural vacancies. In the first square brackets the cations located in tetragonal sites in perovskite blocks are shown, the cations located in pentagonal sites are in the second square brackets. When examining the composition $Ba_{3.5}PbNd_9Ti_{18}O_{54}$, which corresponds to the system $(Ba_{1-y}Pb_y)_{6-x}Nd_{8+2x/3}Ti_{18}O_{54}$ at $x = 1.5$ and $y = 0.22$,[6] it has been found that Pb^{2+} ions are not randomly distributed at all crystallographic sites but fill up only tetragonal sites.[7]

3.1 System $(Ba_{1-y}Pb_y)_6Nd_8Ti_{18}O_{54}$ ($x = 0$)

Referring to previous researches,[7-9] at low lead concentration the structural formula of the system $(Ba_{1-y}Pb_y)_6Nd_8Ti_{18}O_{54}$ may be presented as $[Nd_8Ba_{2-6y}Pb_{6y}][Ba_4]Ti_{18}O_{54}$. At lead concentration corresponding to $y = 0.33$ all empty tetragonal sites in perovskite blocks are completely occupied, so the structural formula becomes $[Nd_8Pb_2][Ba_4]Ti_{18}O_{54}$. At larger lead concentrations ($0.3 \leq y \leq 0.7$), when the yield still remains single-phase, the amount of Pb^{2+} ions is in excess of the empty tetragonal sites in perovskite blocks. Therefore, one can assume that lead ions substitute also barium ions located in pentagonal sites. In this case the ion distribution over the unit cell may be presented as follows: $[Nd_8Pb_2][Ba_{6-6y}Pb_{6y-2}]Ti_{18}O_{54}$. Q-factor meets maximum values with the increase in lead concentration (Figure 3, curve 3). At low lead concentration ($0 \leq y \leq 0.33$), when lead replaces barium in tetragonal sites, Q-factor increases with the increase in y. This phenomenon is probably due to the reduction of internal strain in the crystalline lattice. The influence of internal strain on Q-factor has been researched: Q-factor decreases with the increase in the internal strain.[8-10]

In the given case, when Ba^{2+} ions, which reside in tetragonal sites together with the ions Nd^{3+}, are substituted by Pb^{2+} ions with smaller ionic radii, in accordance with the data obtained in References 8-10, the internal strain decreases and, as a consequence, Q-factor increases over the y range of 0 to 0.33. Maximum Q-factor values are attained at $y \approx 0.3$ (Figure3, curve 3). The further increase in the lead concentration ($0.3 \leq y$) results in a lowering Q-factor. This might be explained by the fact that at high lead concentrations lead ions substitute also those barium ions which were previously located in pentagonal sites, resulting also in additional internal strains. This agrees well with the conclusions presented in References 8-10.

3.2 System $(Ba_{1-y}Pb_y)_{5.25}Nd_{8.5}Ti_{18}O_{54}$ ($x = 0.75$)

Referring to previous researches,[7-9] at low lead concentration in the system $(Ba_{1-y}Pb_y)_{5.25}Nd_{8.5}Ti_{18}O_{54}$ - when lead ions substitute barium ions in tetragonal sites - the structural formula may be presented as $[Nd_{8.5}Ba_{1.25-5.25y}Pb_{5.25y}V_{0.25}][Ba_4]Ti_{18}O_{54}$. At lead concentration corresponding to $y = 0.24$ all tetragonal barium sites are completely occupied by lead ions, so the structural formula is $[Nd_{8.5}Pb_{1.25}V_{0.25}][Ba_4]Ti_{18}O_{54}$. Within the range of $0 \leq y \leq 0.24$ Q-factor increases in the system with the rise in y, culminating in maximum values at $y \approx 0.25$ (Fig.3, curve 2). The increase in Q-factor of the materials in the system $(Ba_{1-y}Pb_y)_{5.25}Nd_{8.5}Ti_{18}O_{54}$, when y varies from 0 to 0.24, is connected with the decrease in internal strain of crystalline lattice.[8-10]

Within the confines of $0.24 \leq y \leq 0.6$, when the yield still remains single-phase, the amount of Pb^{2+} ions is in excess of the empty tetragonal sites in perovskite blocks. Therefore, one can assume that when $0.24 \leq y$ lead ions substitute also barium ions located in pentagonal sites. When partially substituted for barium ions, lead ions embed initially tetragonal sites in perovskite blocks.[7] At $y = 0.24$ there are structural vacancies in tetragonal sites: $[Nd_{8.5}Pb_{1.25}V_{0.25}][Ba_4]Ti_{18}O_{54}$. As a consequence, at lead concentrations corresponding to $0.24 \leq y \leq 0.28$ lead ions embed into empty sites in perovskite blocks simultaneously forming the vacancies in pentagonal sites in accordance with the scheme: $[Nd_{8.5}Pb_{5.25y}V_{1.5-5.25y}][Ba_{5.25-5.25y}V_{5.25y-1.25}]Ti_{18}O_{54}$. Q-factor decreases in this case due to the decrease in total amount of the vacancies in tetragonal sites and, eventually, due to the increase in internal strain of crystalline lattice.[8-10] At the lead concentrations corresponding to $y \geq 0.28$, when all empty tetragonal sites are completely occupied, the structural formula is $[Nd_{8.5}Pb_{1.5}][Ba_{5.25-5.25y}Pb_{5.25y-1.5}V_{0.25}]\ Ti_{18}O_{54}$.

Q-factor of the materials still decreases also within the confines of $0.3 \leq y \leq 0.6$ (Figure 3, curve 2). This may be connected with the rise in internal strain due to the substitution of lead ions for barium ions which were located previously in pentagonal sites; this agrees well also with the conclusions of References 8-10.

3.3 System $(Ba_{1-y}Pb_y)_{4.5}Nd_9Ti_{18}O_{54}$ ($x = 1.5$)

The materials of the system are single-phase at y varying from 0 to 0.4, which agrees with the data of Reference 6.

At low lead concentration in the system $(Ba_{1-y}Pb_y)_{4.5}Nd_9Ti_{18}O_{54}$ -when lead ions substitute barium ions in tetragonal sites- the structural formula may be presented as $[Nd_9Ba_{0.5-4.5y}Pb_{4.5y}V_{0.5}][Ba_4]Ti_{18}O_{54}$ ($0 \leq y \leq 0.11$). Within the confines of $0.11 \leq y \leq 0.4$, when the yield still remains single-phase, the amount of Pb^{2+} ions is in excess of the empty tetragonal sites in perovskite blocks and, as a consequence, one can assume that when $0.11 \leq y$ lead ions replace barium ions located in pentagonal sites. When partially substituted for barium ions, lead ions embed initially into tetragonal sites in perovskite blocks.[7] When $0.11 \leq y \leq 0.22$ lead ions embed into empty tetragonal sites forming the vacancies in pentagonal sites in accordance with the structural formula $[Nd_9Pb_{4.5y}V_{1.0-4.5y}][Ba_{4.5-4.5y}V_{4.5y-0.5}]Ti_{18}O_{54}$. At $y = 0.22$, when all tetragonal sites are completely occupied, the composition is $Ba_{3.5}PbNd_9Ti_{18}O_{54}$ which corresponds to that studied previously in Reference 7. On the strength of the above reasoning for the systems $(Ba_{1-y}Pb_y)_{5.25}Nd_{8.5}Ti_{18}O_{54}$ ($x = 0.75$) and $(Ba_{1-y}Pb_y)_6Nd_8Ti_{18}O_{54}$ ($x = 0$), as well as on the strength of X-ray data denoting the formation of single-phase materials, one can assume that, at high lead concentrations ($0.22 \le y$), lead ions occupy also pentagonal sites, so the structural formula becomes as follows: $[Nd_9Pb]$ $[Ba_{4.5-4.5y}Pb_{4.5y-1}V_{0.5}]Ti_{18}O_{54}$ ($0.22 \le y \le 0.4$). Referring to the cases when $x = 0$ and $x = 0.75$, as soon as all barium ions resided in tetragonal sites are completely substituted by lead ions, Q-factor attains maximum values. At $x = 1.5$ the composition meets the above requirement at $y = 0.11$; however, maximum Q-factor is not observed on the plot of $Q(y)$. The internal strain is lowest at $x = 1.5$ amongst all the materials $Ba_{6-x}Nd_{8+2x/3}Ti_{18}O_{54}$,[8-10] that is probably why lead substitution for barium results only in the decrease in Q-factor value, and the maximum of Q is not observed (Figure 3, curve 3).

The temperature coefficient of resonant frequency meets zero values in all studied systems: $(Ba_{1-y}Pb_y)_6Nd_8Ti_{18}O_{54}$ (x=0), $(Ba_{1-y}Pb_y)_{5.25}Nd_{8.5}Ti_{18}O_{54}$ (x=0.75), and $(Ba_{1-y}Pb_y)_{4.5}Nd_9Ti_{18}O_{54}$ (x=1.5). The lower x is, the higher is the lead concentration which corresponds to zero τ_f.

At the concentration regions corresponding to the complete substitution of barium ions resided in tetragonal sites the inflections are also observed on the plots of τ_f against lead concentration (Figure1, curves 1-3). The temperature coefficient of resonant frequency decreases monotonically in all the materials. It should be noted that, when examining the system $(Ba_{1-z}Pb_z)_{4.5}Nd_9Ti_{18}O_{54}$ in Reference 6, the value of τ_f met the minimum when lead concentration increased [6] while at this research the minimum was not observed. This difference between the data obtained and the previous data [6] may be related to the processing peculiarities as well as to the eventual lead evaporation when sintering the ceramics by previous researchers at higher temperatures.

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