Temperature compensated microwave dielectrics based on lithium containing titanates

A.G. Belous*, O.V. Ovchar

V.I.Vernadskii Institute of General and Inorganic Chemistry of UAS, 32/34 Palladin Avenue, Kyiv-142, 03680, Ukraine

Abstract

Ceramic materials in the system $Ln_{2/3-x}^{3+}Li_{3x}^{1+}TiO_3$ (Ln = rare earth element), which are known to exhibit lithium ion conductivity, were examined over wide frequency and temperature ranges with regard to their conductivity (σ) and dielectric properties (ε and tg δ). In the microwave range both positive temperature coefficient of dielectric constant (τ_ε) and dielectric loss magnitude in lithium containing materials $Ln_{2/3-x}Li_{3x}TiO_3$ can be ascribed to the presence of lithium-ion conductivity. The substitution of rare-earth ions with smaller ionic radii for larger La ions suppresses both the cation conductivity and dielectric losses. In this case Li ions do not participate in conductivity but contribute noticeably to the relaxation. The latter results in the positive τ_ε and relatively low tg δ. Using the system $Ln_{2/3-x}Li_{3x}TiO_3$ as an example it has been shown that the materials with the mobile lithium cation sublattice can be used for the volume temperature compensation of microwave (MW) dielectrics with the negative τ_ε.
© 2003 Elsevier Ltd. All rights reserved.

Keywords: Dielectric properties; Functional applications; Perovskites; Sintering; X-ray methods

1. Introduction

When developing modern communication equipment operating in microwave region the miniaturization of the component base still remains an important engineering problem. This requires the utilization of temperature stable dielectric materials with low values of dielectric loss tangent (tg δ). The value of dielectric constant (ε) in these materials determines the effective size of microwave components. Microwave dielectrics can be developed in several different ways, for example on the basis of single phase compositions and by forming multiphase materials.[1] Single phase microwave dielectrics are generally developed on the basis of solid solutions, for example $Ba(Zn,Mg)_{1/2}(Nb,Ta)_{2/3}O_3$,[2] $Ba_{6-X}Ln_{8+2/3X}Ti_{18}O_{54}$,[3,4] $(La,Ca)(Ti,Al)O_3$,[5] or by using aliovalent substitution in one of the crystal sublattices.[6] At the same time, microwave dielectrics based on multiphase compositions can be developed by producing gradient (composite) materials,[7,8] and by using volume temperature compensation.[9]

There is a great number of well known high-Q paraelectrics (e.g. TiO_2, $CaTiO_3$, $SrTiO_3$) distinguished by large negative temperature coefficient of dielectric constant (τ_ε).

The materials with $\tau_\varepsilon > 0$ and low tg δ include single-domain crystals of ferroelectrics, e.g. $LiNbO_3$ and $LiTaO_3$. The positive sign of τ_ε in these materials is ascribed to the presence of high-temperature phase transitions. The values of dielectric constant in these materials are relatively low resulting in the dimensions of MW components. Earlier, it has been shown [8] that high dielectric constant (about 100 at room temperature) together with low MW losses could be also observed in antiferroelectrics which may be therefore utilized as the dielectrics with $\tau_\varepsilon > 0$. However, the number of reported dielectrics with high ε, $\tau_\varepsilon > 0$, and low tg δ in MW frequency range is relatively poor.

Recently, the authors of Ref. 10 developed new temperature stable MW dielectrics based on the solid solutions which involve lithium containing phase ($Ln_{1/2}Li_{1/2}TiO_3$) as the end member with the positive temperature coefficient of dielectric constant ($\tau_\varepsilon > 0$). However, the data related to the dielectric properties of these phases are not yet enough to explain the nature of the positive sign of τ_ε.

It should be noted that the phases $Ln_{1/2}Li_{1/2}TiO_3$ belong to the wider family of complex oxides $Ln_{2/3-x}M_{3x}TiO_3$ (Ln is rare-earth element, and M is alkali metal) which are of a great scientific and engineering interest. The specialty of these oxides consists in the fact that atoms M partially substitute Ln.[11,12] In the

case when $M = Na$, K the compounds with the perovskite structure are formed. They are characterized by high MW permittivity (about 100) and $\tau_\varepsilon < 0$.[13] In the case when A sites in the perovskite ABO_3 are occupied by only small-size lithium ions the lattice does not meet the steric requirements to the perovskite, and as a consequence, the perovskite structure is not formed. However, one may expect that when cation sublattice contains both small lithium ions, which can move easily down the structural channels, and large lanthanum ions, which meet all geometric requirements to the perovskite, the perovskite structure may be formed. In this case the resulting products may display high cation conductivity of the lithium ions. This approach was first utilized by us in the materials $La_{2/3-x}Li_{3x}TiO_3$[14,15] and $La_{2/3-x}Li_{3x}Nb_2O_6$[16] which are the cation conductors, and due to this reason are characterized by high dielectric loss in the MW range. However, it is possible to expect that the dielectric loss in the compounds $Ln_{2/3-x}Li_{3x}TiO_3$ may be decreased by decreasing the cation conductivity. One of the possible ways to do this is by decreasing the ionic radii of rare-earth elements used in place of larger-size La ions in the compounds $Ln_{2/3-x}Li_{3x}TiO_3$.

Therefore, the target of this work was the investigation of electrophysical properties of lithium containing phases $(Ln_{1/2}Li_{1/2}TiO_3)$ as well as the solid solutions based on them over the wide temperature and frequency ranges in order to clarify physical nature of temperature stabilization of dielectric constant.

2. Experimental procedure

Polycrystalline samples, prepared by conventional ceramic technique, have been examined. Extra pure and reagent grade oxides and carbonates were used as starting reagents. The starting reagents were initially mixed and ball-milled in agate bowls in acetone for 4 h. The mixed blend was then dried and the powders were calcined at 1000–1100 °C in air. When producing the ceramics based on solid solutions the end members were initially calcined, and then mixed in a proper ratio to obtain the composition required. Produced under the pressure of 500 kg/cm^2 green pellets were then sintered at 1300–1400 °C for 2 h in air. The phase composition and lattice parameters of the materials were analyzed by powder X-ray diffraction (XRD) using a "DRON 4" diffractometer and Cu K_α radiation. Temperature and frequency behavior of the conductivity (σ), dielectric constant, and dielectric loss tangent were measured by means of bridge circuits and Q-meters at lower frequencies (10^2–10^7 Hz). Temperature behaviour of the dielectric properties of the materials synthesized were measured by coaxial line method at the frequencies of about 10^9 Hz, and by dielectric resonator method at

frequencies of about 10^{10} Hz. Submillimeter-wave (SMM) measurements were carried out using a backward-wave tube, by measuring the optical-path length and the absorption (α) in a parallel-plate sample coated with a quarter-wavelength anti-reflecting coating.

3. Results and discussion

In order to examine the formation of solid solutions in the system $(1-x)Sm_{1/2}Li_{1/2}TiO_3$–$xSm_{1/2}Na_{1/2}TiO_3$ the phase composition of sintered materials has been investigated. It should be noted that lithium containing compounds $La_{1/2}Li_{1/2}TiO_3$ and $Nd_{1/2}Li_{1/2}TiO_3$ are either hexagonal or tetragonal perovskites.[12] It is also known that $Sm_{1/2}Li_{1/2}TiO_3$ is the structural analogue of lanthanum and neodymium containing compounds. On the other hand $La_{1/2}Na_{1/2}TiO_3$ is the tetragonal perovskite.[15] The analysis of X-ray powder diffraction patterns of the materials $(1-x)Sm_{1/2}Li_{1/2}TiO_3$–$xSm_{1/2}Na_{1/2}TiO_3$ revealed presence of no secondary phases but the matrix phase with the tetragonal perovskite structure (Fig. 1). This denotes the variation in electrophysical properties within the system investigated is exceptionally due to the change in sodium concentration.

Fig. 2 demonstrates the measurement results of the dielectric parameters (ε and tg δ) of the materials $Sm_{1/2}Li_{1/2}TiO_3$ and $Sm_{1/2}Na_{1/2}TiO_3$ collected at 10^9 Hz. In sodium containing samples $Sm_{1/2}Na_{1/2}TiO_3$ a decrease in the dielectric constant is observed whereas the dielectric loss are of the order of 10^{-3}, and slightly increase with the temperature. It is interesting to note that in the case of lithium containing compound $Sm_{1/2}Li_{1/2}TiO_3$ an increase in the dielectric constant is observed within the entire temperature range of 20–600 °C ($\tau_\varepsilon > 0$). The dielectric loss of $Sm_{1/2}Li_{1/2}TiO_3$ are an order of magnitude higher than those of sodium containing analogue $Sm_{1/2}Na_{1/2}TiO_3$.
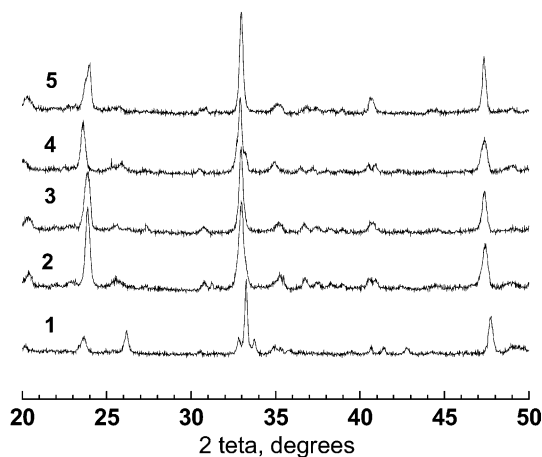

Fig. 1. X-ray powder diffraction patterns of sintered materials of the system $(1-x)Sm_{1/2}Li_{1/2}TiO_3$–$xSm_{1/2}Na_{1/2}TiO_3$; $1-x=0$; $2-x=0.4$; $3-x=0.6$; $4-x=0.7$; $5-x=1.0$.

Temperature dependency of the conductivity (σ) in $Sm_{1/2}Li_{1/2}TiO_3$ ceramics is shown in Fig. 3 supplemented with data for the related materials $La_{1/2}Li_{1/2}TiO_3$ and $Nd_{1/2}Li_{1/2}TiO_3$. In accordance with the results of Refs. 12 and 13 the compounds $La_{1/2}Li_{1/2}TiO_3$ and $Nd_{1/2}Li_{1/2}TiO_3$ are Li-conducting solid state electrolytes. In the titanates $La_{1/2}Li_{1/2}TiO_3$ and $Nd_{1/2}Li_{1/2}TiO_3$ the charge transport is mainly concerned with the structural channels formed by oxygen octahedra. Diminishing their effective size by substituting Nd for La with the largest ionic radii results in the ten-fold decrease in the conductivity of $Nd_{1/2}Li_{1/2}TiO_3$ compared with $La_{1/2}Li_{1/2}TiO_3$ (Fig. 3).

Both the character and the magnitude of the conductivity (σ) in $Sm_{1/2}Li_{1/2}TiO_3$ examined in this work, assign this compound to be lithium-ion conductor like $La_{1/2}Li_{1/2}TiO_3$ and $Nd_{1/2}Li_{1/2}TiO_3$. However,

$Sm_{1/2}Li_{1/2}TiO_3$ represents Li-ion conductivity only at high temperatures (Fig. 3). Fig. 3 shows that in the compound $Ln_{1/2}Li_{1/2}TiO_3$ the conductivity decreases when changing rare-earth element from La to Sm while the activation energy increases linearly depending on the ionic radii of Ln (Fig. 4).

In the microwave region superionic conductors $La_{1/2}Li_{1/2}TiO_3$, $Nd_{1/2}Li_{1/2}TiO_3$, and $Sm_{1/2}Li_{1/2}TiO_3$ exhibit positive temperature coefficient τ_ε which retains its polarity up to submillimeter wavelength (Fig. 5). This is due to the relaxation of small lithium ions within the cavities of structural channels formed by oxygen octahedra, which makes an additional contribution to the permittivity with increasing temperature. In the ceramics with the composition $La_{2/3-x}Li_{3x}TiO_3$ dielectric loss, which is in proportion to the cationic conductivity, is too high to allow the utilization of $La_{2/3-x}Li_{3x}TiO_3$ in
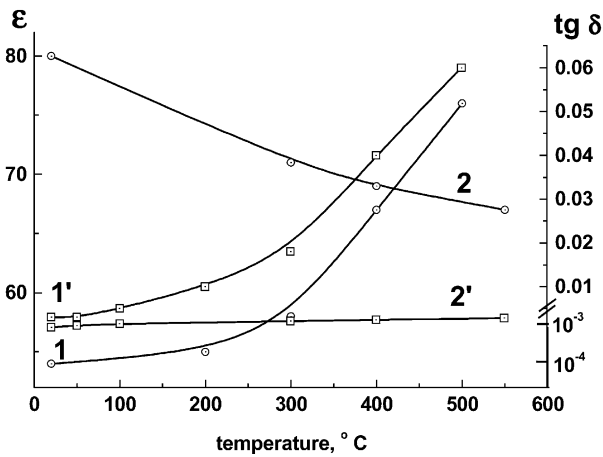

Fig. 2. Temperature dependencies of dielectric constant (ε) and dielectric loss tangent (tg δ) of the materials $Sm_{1/2}Li_{1/2}TiO_3$ (1, 1′) and $Sm_{1/2}Na_{1/2}TiO_3$ (2, 2′) at 10^9 Hz.
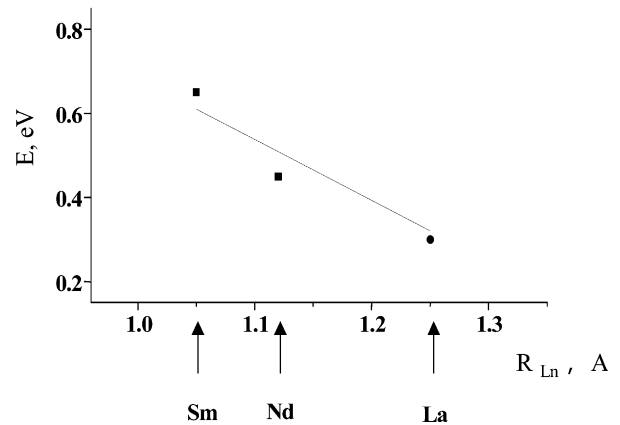

Fig. 4. Variation of the activation energy in the compounds $Ln_{1/2}Li_{1/2}TiO_3$ (where Ln is La, Nd, Sm) against ionic radii of rare-earth element.

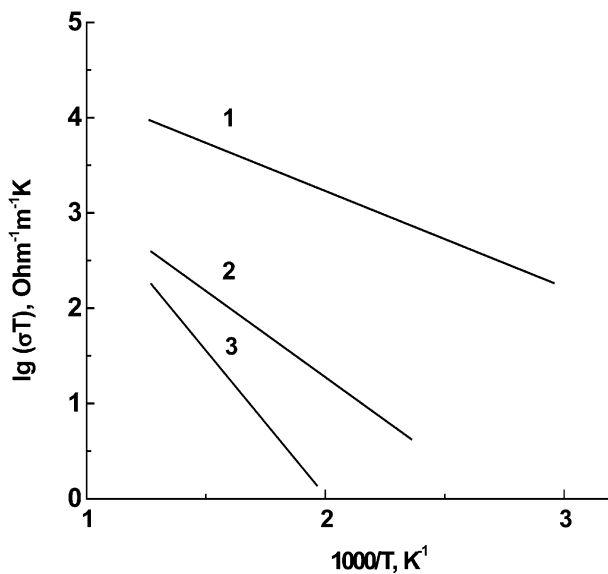Fig. 3. Electrical conductivity $\sigma(T)$ of the ceramics $La_{1/2}Li_{1/2}TiO_3$ (1), $Nd_{1/2}Li_{1/2}TiO_3$ (2), and $Sm_{1/2}Li_{1/2}TiO_3$ (3).
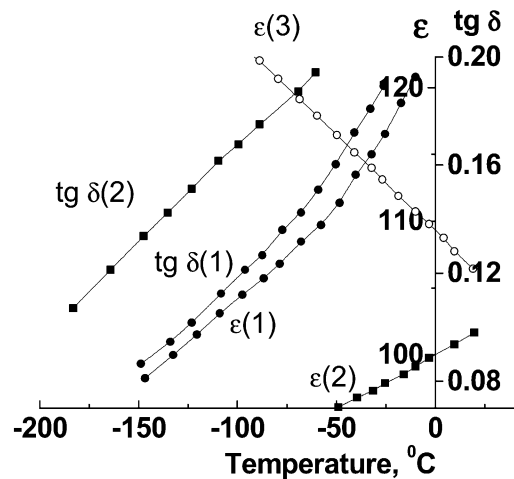

Fig. 5. Temperature dependencies of dielectric constant (ε) and dielectric loss tangent (tg δ) in the compounds $La_{1/2}Li_{1/2}TiO_3$—ε (1), tg δ (1); $La_{1/2}Li_{1/4}Na_{1/4}TiO_3$—$\varepsilon$ (2), tg δ (2); $La_{1/2}Na_{1/2}TiO_3$—ε (3), measured at 134 GHz.

Table 1
Dielectric properties in the system $x\mathrm{Sm_{1/2}Li_{1/2}TiO_3}$–$(1-x)\mathrm{Sm_{1/2}Na_{1/2}TiO_3}$ at 10 GHz

x	ε	τ_ε, ppm/°C (20–100 °C)	Q (10 GHz)
0	80	−520	1300
0.30	95	−240	100
0.50	90	−140	150
0.55	85	−80	200
0.58	80	−5	200
0.60	75	+60	200
1.0	52	+560	100

the microwave range. However, by reducing the size of both the conducting channels and crystallographic cavities containing lithium ions by means of isovalent substitution of small rare-earth ions, e.g. Nd or Sm ions, for larger La ions, it is possible to meet the conditions which would restrict lithium ion relaxation (to relatively small-size cavities) and would not allow the movement of lithium ions throughout the crystal structure. In this case the positive temperature coefficient of permittivity is accompanied by relatively low dielectric loss. This makes it possible to obtain solid solutions exhibiting both high permittivity and temperature stability in the microwave range together with acceptable MW dielectric loss. These ceramics can be produced, for instance, on the basis of lithium-containing and sodium-containing rare-earth titanates with perovskite structure, which differ by contrasting behaviour of the dielectric constant against the temperature.

Unlike lithium-containing titanates $\mathrm{Ln_{1/2}Li_{1/2}TiO_3}$ sodium and potassium- containing titanates display negative τ_ε which is characteristic of linear dielectrics.[11] As a consequence, the dielectric properties of the solid solutions $x\mathrm{Sm_{1/2}Li_{1/2}TiO_3}$–$(1-x)\mathrm{Sm_{1/2}Na_{1/2}TiO_3}$ were examined with the view of producing temperature stable dielectric constant in the material. Measurement results, which are in good agreement with the data of Ref. 10 are presented in Table 1. These data give evidence for the possibility of producing materials with close to zero τ_ε at $x = 0.57$–0.59.

4. Conclusions

Lithium-containing phases ($\mathrm{Ln_{1/2}Li_{1/2}TiO_3}$) with the perovskite structure are characterized by cation conductivity of lithium ions. The characteristic feature of the phases $\mathrm{Ln_{1/2}Li_{1/2}TiO_3}$ is the relaxation of lithium ions over wide frequency ranges (including MW and SMM), that is not generally observed in dielectrics. When forming a mobile sublattice with controllable size of conducting structural channels, it is possible to produce materials which would exhibit high dielectric constant, positive sign of τ_ε, and relatively low dielectric loss. These materials could be utilized for temperature stable MW dielectrics.

References

1. Belous, A. G., Physicochemical aspects of the development of MW Dielectrics and their use. *J. Eur. Ceram. Soc.*, 2001, **21**, 2717–2722.

2. Nomura, S., Toyoma, K. and Kaneta, K., Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ ceramics with temperature-stable high dielectric constant and low microwave loss. *Jap. J. Appl. Phys.*, 1982, **10**(21), 624–626.

3. Ohsato, H., Kato, H., Mizuta, M., Nishigaki, S. and Okuda, T., Microwave dielectric properties of the Ba$_{6-3x}$(Sm$_{1-Y}$R$_Y$)$_{8+2x}$Ti$_{18}$O$_{54}$ (R = Nd and La) solid solutions with zero temperature coefficient of the resonant frequency. *Jap. J. Appl. Phys.*, 1997, **9B**(34), 5413–5417.

4. Belous, A., Ovchar, O., Valant, M., Suvorov, D. and Kolar, D., The effect of partial isovalent substitution in the A-sublattice on MW properties of materials based on Ba$_{6-x}$Ln$_{8+2x/3}$Ti$_{18}$O$_{54}$ solid solutions. *J. Eur. Ceram. Soc.*, 2001, **21**, 2723–2730.

5. Lymar', T. F., Maydukova, T. P., Mudrolubova, L. P. and Prohvatilov, V. G., Formation of solid solutions in the system LaAlO$_3$–CaTiO$_3$, and their electrical properties. *Izvestija Akademii Nauk, ser. Neorgan. Mater.*, 1969, **5**(10), 1773–1775 (in Russian).

6. Belous, A. G., Physicochemical aspects of the development of new functional materials based on heterosubstituted titanates of rare-earth elements with the perovskite structure. *Theoretical and Experimental Chemistry.*, 1998, **6**(34), 331–346 (in Russian).

7. Plourde, I. K., Temperature stable microwave dielectric resonators utilising ferroelectrics. *IEEE, GMTT. Int. Microwave Symp., Colorado*, 1973, 202–204.

8. Belous, A. G., Politova, Y. D., Venevtsev, Y. N., Tsykalov, V. G. and Poplavko, Y. M., Lead-cobalt tellurate as a material for microwave dielectric resonators. *In Russian, Elektronnaya Tekhnika, Ser. Elektronika SVCh.*, 1981, **7**(331), 45–46.

9. Gornikov, Yu.I., Makarova, Z.Ya., Belous, A. G., Gavrilova, L. G., Paskov, V. M. and Chalyi, V. P., The effect of zinc oxide additions on the phase composition and dielectric properties of barium tetratitanate. *Sov. Prog. Chem.*, 1984, **12**(50), 1243–1245.

10. Takahashi, H., Baba, Y., Ezaki, K., Okamoto, Y., Shibato, K., Kuroki, K. and Nakano, S., Dielectric characteristics of (A$^{1+}_{1/2}$A$^{3+}_{1/2}$)TiO$_3$ ceramics at microwave frequencies. *Jpn. J. Appl. Phys*, 1991, **30**(9B), 2339–2342.

11. Belous, A. G., Novitskaya, G. N. and Polianetskaya, S. V., The investigation of the oxides Ln$_{2/3-x}$M$_{3x}$TiO$_3$ (Ln- Gd-Lu; M- Li, Na, K). *Izv. Akad. Nauk SSSR, ser. Neorgan. Mater.*, 1987, **8**(23), 1330–1332 (in Russian).

12. Belous, A. G., Novitskaya, G. N., Polianetskaya, S. V. and Gornikov, Y. I., Crystal-chemical and electro-physical characteristics of complex oxides Ln$_{2/3-x}$M$_{3x}$TiO$_3$. *Zhurn. Neorg. Khimii*, 1987, **2**(32), 283–286 (in Russian).

13. Belous, A. G., Novitskaya, G. N., Polianetskaya, S. V. and Gornikov, Y. I., Investigation of complex oxides of the composition La$_{2/3-x}$Li$_{3x}$TiO$_3$. *Izv. Akad. Nauk SSSR, ser. Neorgan. Mater.*, 1987, **3**(23), 470–472 (in Russian).

14. Belous, A. G., Butko, V. I., Novitskaya, X., Polianetskaya, S. V., Homenko, B. S. and Poplavko, Y. M., Electrical conductivity of the perovskites. *Ukr. Phys. Journal*, 1986, **31**(4), 576–581 (in Russian).

15. Belous, A. G., Gavrilova, L. G., Polianetskaya, S. V., Makarova, Z. Y. and Chalyi, V. P., Stabilisation of perovskite structure in lanthanum titanate. *Ukr. Khim. Zh.*, 1984, **50**(5), 460–461 (in Russian).

16. Belous, A. G., Novosadova, E. B., Diduh, I. R., Pashkova, E. V. and Homenko, B. S., Process of the Formation of cation conductivity in complex perovskite-like niobates. *Ionic Melts and Solid Electrolytes*, 1989, **4**, 68–73 (in Russian).