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Microwave dielectric properties of ceramics based on $CaTiO_3$–$LnMO_3$ System (Ln–La, Nd; M–Al, Ga)

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Abstract

Structural features and microwave dielectric properties of $LnMO_3$–$CaTiO_3$ samples (where Ln stands for La or Nd, M stands for Al or Ga) are studied. Solid solutions with the rhombic perovskite structure are shown to be formed with increasing molar concentration of $LnMO_3$ up to ~35% (for Ln–Nd, M–Al) or ~40% (for Ln–La, M–Ga). Further increase of the neodymium aluminate or lanthanum gallate molar content in the solid solution up to 70% leads to formation of solid solutions with the tetragonal perovskite structure. A family of promising ceramics for application in the microwave technology with dielectric permittivity lying within the range from 43 to 48, the dielectric permittivity temperature coefficient being near to zero, and heightened quality factor ($Q{\cdot}f \geqslant 40{,}000$ GHz) are obtained.

Keywords: Dielectric properties; Impurities; Milling; Sintering; Microwave ceramics; $(Ca,La,Nd)(Ti,Al,Ga)O_3$

1. Introduction

Ceramic materials based on calcium-titanate, lanthanoid aluminate solid solutions attract interest for applications at microwave frequencies because of their rather high dielectric permittivity ($\varepsilon \approx 40$–45) with small or vanishing dielectric permittivity temperature coefficient (τ_ϵ) and small enough dielectric losses within the wide temperature and frequency range.

Materials belonging to this system, known as ALTK ($CaTiO_3$–$LaAlO_3$), have been widely applied as dielectrics for high-frequency capacitors.[1,2] By synthesis of continuous families of perovskite solid solutions in this system it is possible to obtain a series of high-frequency ceramics for capacitors of various temperature stability classes from +33 ppm/°C to −750 ppm/°C with ε from 36 to 110. Nenasheva et al.[3,4] obtained microwave dielectrics based on ALTK with $\varepsilon = 40$–45 and τ_f from −10 to +10 ppm/°C with $Q{\cdot}f \geqslant 45\,000$ GHz for $\tau_f \approx 0$, $\varepsilon = 43$.

The basic process for synthesis of the ALTK materials was chemical coprecipitation from solutions of salts with subsequent sintering of the precipitate.[1,5] This technique ensures lowering of the solid solution forming temperature to ~1150 °C and gives $Q{\cdot}f$ up to 60,000 GHz, but it is rather expensive.

The aim of this work was to investigate the possibility of increasing the dielectric permittivity of these materials, keeping the quality factor high enough ($Q{\cdot}f$ no less than 40,000 GHz), τ_f near to zero and high linearity of the frequency shift Δf dependence within the wide temperature range. To minimize cost it is important that preparation of the parent powders is carried out via the traditional ceramic technique.

Solid solutions of the $x LnMO_3$–$(1-x)$ $CaTiO_3$ system are studied in this work (where Ln stands for La or/and Nd and M stands for Al or/and Ga) within the range of x from 0.1 to 0.7.

2. Preparation of samples

The parent powders were prepared via the conventional solid-phase synthesis technique from TiO_2, alumina, rare-earth, and gallium oxides and from calcium carbonate at temperatures of 1320–1400 °C (depending on a composition systems) for 4 h. After subsequent milling, samples in the form of dielectric resonators (DR) were prepared. They were sintered to high density

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at temperatures within the range 1450–1540 °C for 3 h in air.

The quality factor Q and τ_f were measured for test samples of the DRs at a frequency of 8 GHz within the temperature range −80 to +80 °C.

X-ray investigation of samples was carried out using the X-ray difractometer DRON-3 (Cu K_α, Ni-filter).

3. Results and discussion

Our study has shown that a family of solid solutions with the perovskite structure are formed within the concentration range up to $x=0.7$. The X-ray study results for samples of the system xNdAlO$_3$–(1−x) CaTiO$_3$ are presented in Table 1. All investigated samples were predominantly single-phase. The total impurity concentration in any sample does not exceed 3%. The rhombic perovskite is formed as the neodymium aluminate concentration increases up to 35 mol.%.

The unit cell volume decreases with increasing x. From $x=0.40$ up to $x=0.60$ the tetragonal perovskite is formed. The composition with $x=0.40$ still has some features of weak rhombic distortion. The pseudocubic perovskite is formed at $x=0.70$. The calculated unit cell volume steadily decreases with increasing x (see Table 1 and plot 1 in Fig. 1). Values of ε and of τ_ϵ are presented in Fig. 2 as function of the solid solution composition. It is seen that ε decreases and τ_ϵ increases up to +150 ppm/°C at $x=0.70$, as the neodymium aluminate content increases. The solid solution permittivity equals 43.5 at the concentration where the value of τ_ϵ is equal to zero (see Fig. 2).

Substitution of 50 at.% neodymium by lanthanum leads to an increase of the unit cell parameters and volume of the solid solutions (plot *2*, Fig. 1), but the permittivity and its temperature coefficient (Fig. 2, dashed line) do not change significantly from the first set of data.. The concentration range, where a transition from rhombic to tetragonal symmetry occurs, effectively coincides with the composition mentioned above (near x ≈0.4). At the same time, the quality factor of samples rises in the case of the (La$_{0.5}$Nd$_{0.5}$)AlO$_3$–CaTiO$_3$ solid solutions up to 40,000 GHz and reaches ∼60,000 GHz for $x=0.7$ (Fig. 3).

Taking into consideration the results obtained, we decided to study the formation of solid solutions and their microwave properties for the case of substitution of aluminum and neodymium by ions with a larger ionic radius, La^{3+} and Ga^{3+}, for instance. Results of the study of×LaGaO$_3$–(1−x)CaTiO$_3$ are presented in Table 2 and in Figs. 4–6.

Table 1
Results of X-ray study of xNdAlO$_3$–(1−x) CaTiO$_3$ samples for sintering temperature $T_{sin}=1540$ (3 h)

X	Symmetry	Lattice constant (Å)			Unit cell volume, Å^3
		a	b	c	
0	Rhombic	5381(1)	5440(2)	7643(4)	223.8
0.10	Rhombic	5364(2)	5403(2)	7675(4)	222.4
0.20	Rhombic	5362(2)	5401(2)	7650(3)	221.5
0.30	Rhombic	5354(2)	5376(2)	7656(4)	220.5
0.35	Rhombic	5348(2)	5369(2)	7667(4)	220.2
0.40	Tetragonal[a]	5380(1)		7595(4)	219.8
0.50	Tetragonal	5370(1)		7591(3)	218.9
0.60	Tetragonal	5361(1)		7577(4)	217.8
0.70	Pseudocubic	5784(1)			216.7

[a] Signs of rhombic distortion are present.

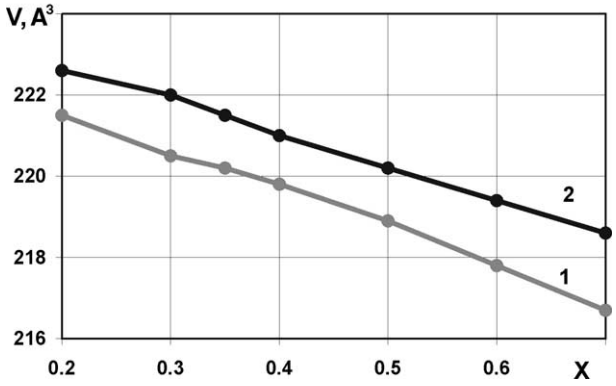

Fig. 1. The composition dependence of the unit cell volume V for samples of perovskite systems xNdAlO$_3$–(1−x) CaTiO$_3$ (1) and x(Nd$_{0.5}$La$_{0.5}$)AlO$_3$–(1−x) CaTiO$_3$ (2).

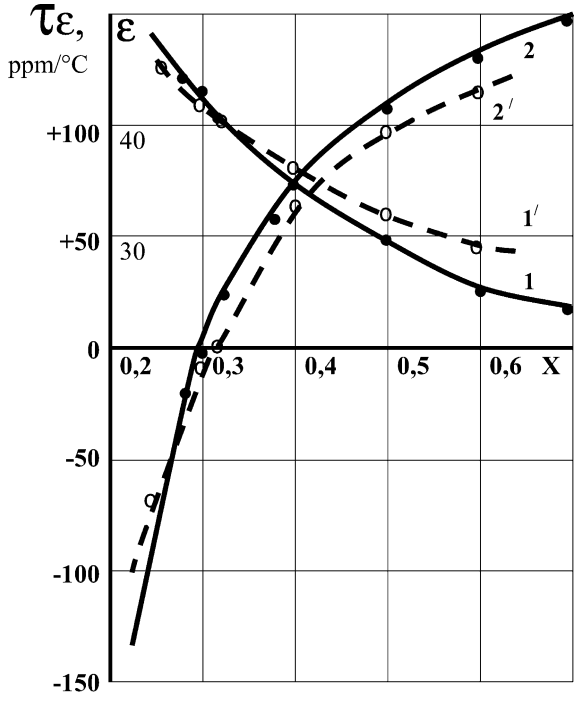

Fig. 2. The composition dependence of the dielectric permittivity ε(1, 1′) and its temperature coefficient τ_ϵ (2,2′) for samples of the systems x NdAlO$_3$–(1−x) CaTiO$_3$(1,2) and x(Nd$_{0.5}$La$_{0.5}$)AlO$_3$–(1−x) CaTiO$_3$(1′,2′).

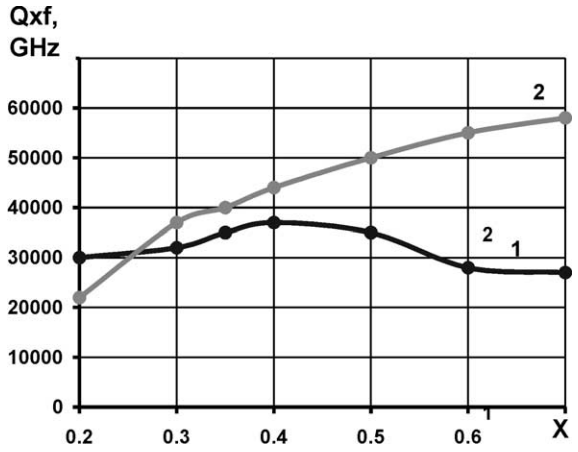

Fig. 3. Quality factor multiply frequency $Q \cdot f$ for samples of the systems xNdAlO$_3$–(1−x) CaTiO$_3$ (1) and x(Nd$_{0.5}$La$_{0.5}$)AlO$_3$–(1−x) CaTiO$_3$ (2).

Table 2
Results of X-ray study of xLaGaO$_3$–(1−x) CaTiO$_3$ samples for sintering temperature T_{sin} = 1540 (3 h)

X	Symmetry	Lattice constant (Å)			Unit cell volume (Å^3)
		a	*b*	*c*	
0	Rhombic	5381(2)	5440(3)	7643(4)	223.8
0.18	Rhombic	5399(2)	5444(2)	7708(5)	226.6
0.20	Rhombic	5409(3)	5457(3)	7686(6)	226.8
0.30	Rhombic	5434(3)	5464(3)	7696(5)	228.5
0.34	Rhombic	5438(3)	5468(4)	7703(4)	229.0
0.35	Rhombic	5439(2)	5467(3)	7704(5)	229.1
0.36	Rhombic	5445(3)	5467(3)	7708(6)	229.5
0.40	Rhombic	5445(3)	5466(3)	7721(4)	229.8
0.45[a]	Tetragonal	5463(1)		7726(3)	230.6
0.60	Tetragonal	5483(1)		7739(2)	232.7
0.70	Tetragonal	5485(1)		7762(3)	233.5

[a] Signs of rhombic distortion are present.

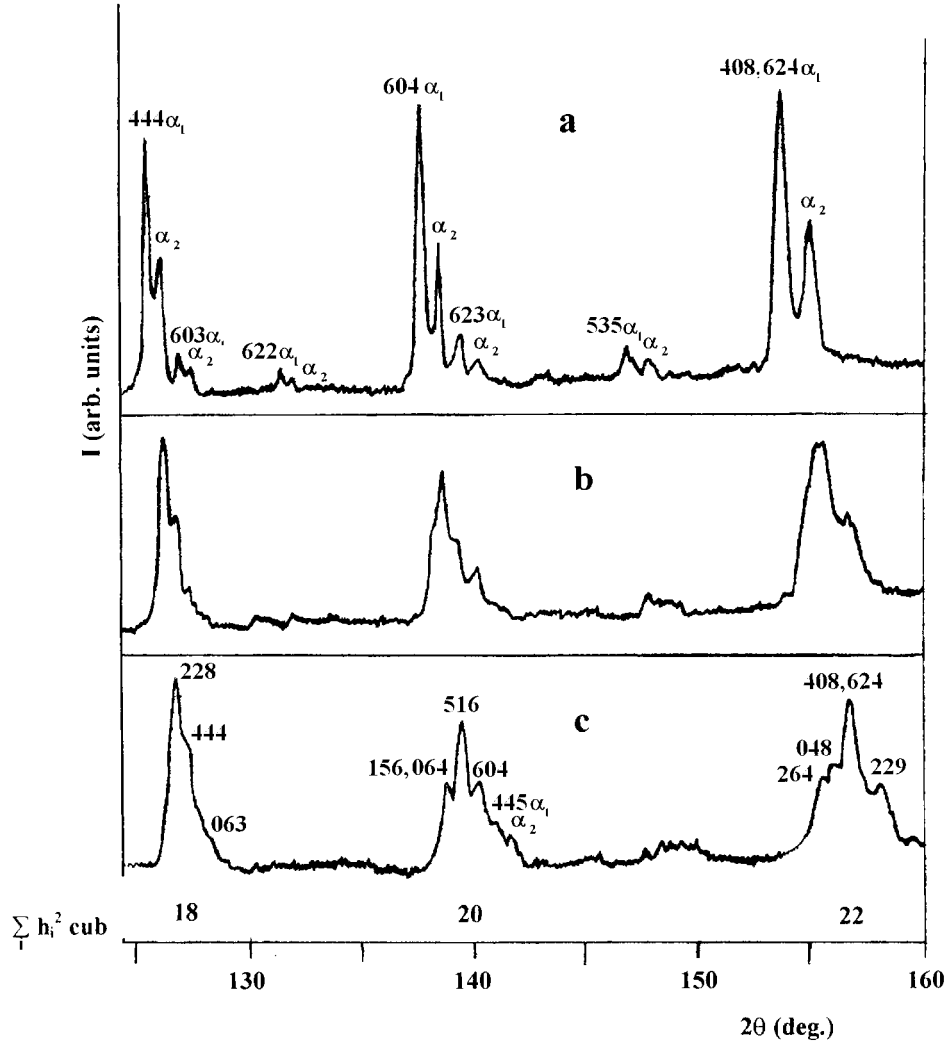

Fig. 4. Diffractogram features for samples of the system xLaGaO$_3$–(1−x) CaTiO$_3$ at x = 0.60 (a), x = 0.45 (b) and x = 0.36 (c).

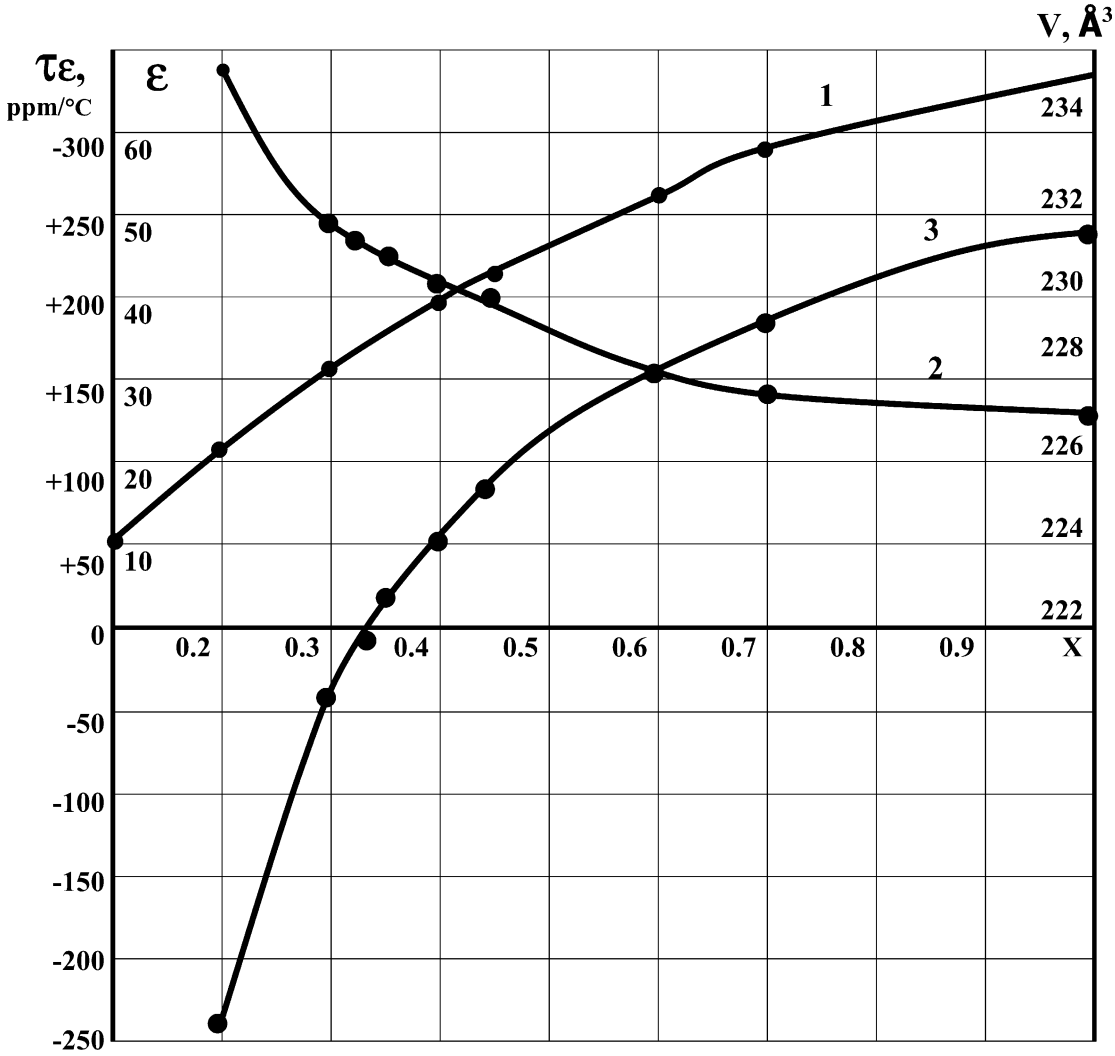

Fig. 5. The composition dependence of the unit cell volume V (1), dielectric permittivity ε (2) and its temperature coefficient τ_ϵ (3) for perovskite samples of the system xLaGaO$_3$–(1−x) CaTiO$_3$.

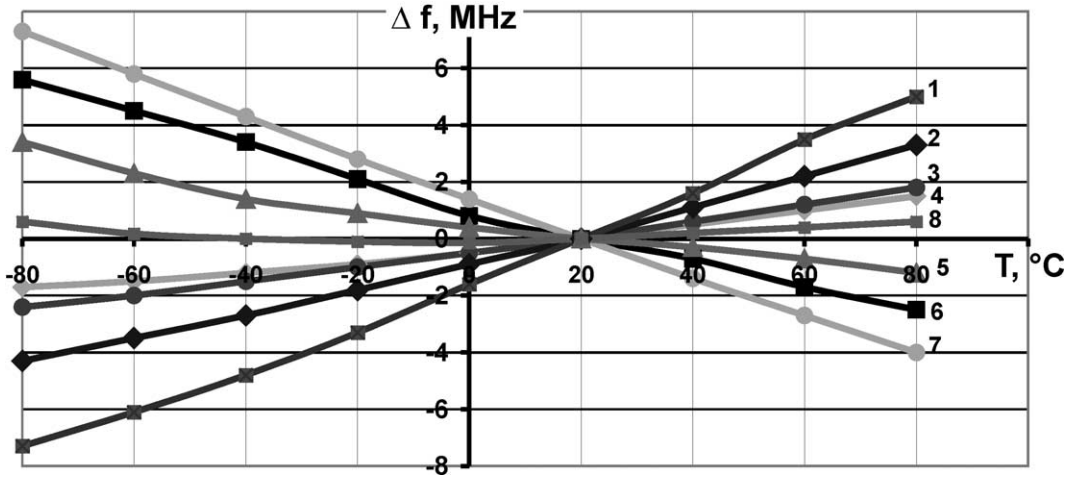

Fig. 6. The temperature dependence of the resonance frequency shift Δf for dielectric resonators (DR) based on solid solutions (La, Ca)(Ga, Ti)O$_3$, plots from 1 to 7 and (Nd, Ca)(Al,Ti)O$_3$, plot 8. (1) $\tau_f = +10.3$ ppm/°C, (2) $\tau_f = +7.9$ ppm/°C, (3) $\tau_f = +4.3$ ppm/°C, (4) $\tau_f = +3.5$ ppm/°C, (5) $\tau_f = -2.1$ ppm/°C, (6) $\tau_f = -5.9$ ppm/°C, (7) $\tau_f = -9.4$ ppm/°C, (8) $\tau_f = +1.4$ ppm/°C.

Table 3
X-ray data and microwave dielectric parameters of $LnMO_3$–$CaTiO_3$ (Ln–La, Nd ; M–Al, Ga) samples

No	Composition	Rhombic perovskite unit cell volume	ε	τ_f (ppm/°C)	$Q{\cdot}f$ (GHz)
1	$0.70CaTiO_3$–$0.30NdAlO_3$	220.5	43.5	−2.1	30,000
2	$0.70CaTiO_3$–$0.30(La_{0.5}Nd_{0.5})AlO_3$	221.9	41.5	+4.0	37,000
3	$0.70CaTiO_3$–$0.30LaGaO_3$	228.5	49.4	+21.5	29,000
4	$0.70CaTiO_3$–$0.30Nd(Ga_{0.5}Al_{0.5})O_3$	223.8	45.3	+11.5	38,000
5	$0.70CaTiO_3$–$0.30La(Ga_{0.5}Al_{0.5})O_3$	226.0	45.2	+13.4	40,000
6	$0.70CaTiO_3$–$0.30(La_{0.5}Nd_{0.5})(Ga_{0.5}Al_{0.5})O_3$	224.4	45.2	+9.3	43,000
7	$0.67CaTiO_3$–$0.33(La_{0.5}Nd_{0.5})GaO_3$	227.7	44.7	+6.3	41,000
8	$0.66CaTiO_3$–$0.34(La_{0.5}Nd_{0.5})GaO_3$	227.8	44.1	+0.7	43,000
9	$0.64CaTiO_3$–$0.36(La_{0.5}Nd_{0.5})GaO_3$	228.3	43.6	−9.7	43,000
10	$0.66CaTiO_3$–$0.34LaGaO_3$	229.0	47.5	+3.6	46,000
11	$0.64CaTiO_3$–$0.36LaGaO_3$	229.5	46.5	−2.9	48,000

An increase of gallium aluminate content in the solid solution up to $x=0.4$ leads to formation of the solid solution with the rhombic perovskite structure. Beginning from $x=0.45$ up to $x=0.70$, a family of solid solutions with the tetragonal perovskite structure is formed in all the investigated concentration range. Features of diffractograms for this system are depicted in Fig. 4. The composition with $x=0.45$ is seen to have some features of the rhombic perovskite. The unit cell volume (Fig. 5) rises almost linearly with increasing x. At the same time, a rise of the lanthanum gallate content leads to a decrease of ε and an increase of τ_ϵ. Samples of this system demonstrate large enough permittivity ($\varepsilon=46$–48) accompanied by rather small τ_ϵ. The quality factor of such compositions reaches 5500–6000 at the frequency $f\approx 8$ GHz.

A family of tentative compositions that are the most promising for microwave applications is presented in Table 3. All samples are solid solutions with the rhombic perovskite structure. As can be seen from the presented data, solid solutions based on the lanthanum gallate (samples 10 and 11) are the most promising due to their high ε, τ_ϵ near to zero, and maximal values of $Q{\cdot}f$.

Frequency shift curves Δf for DR samples of the studied compositions within the temperature range −80 to +80 °C are depicted in Fig. 6. It is seen that these compositions ensure that DR′s with τ_f from −10 to +10 ppm/°C can be obtained. Linearity of the frequency shifting $\Delta f/f_o$ with temperature (Fig. 7) is distinctly higher than for samples prepared from the ALTK[4] material.

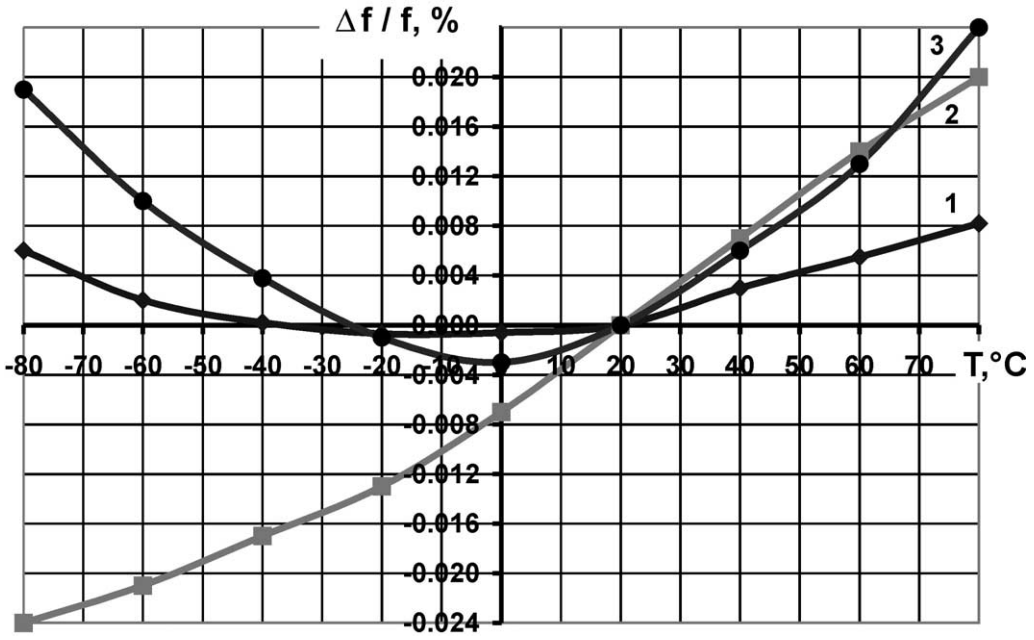

Fig. 7. The temperature dependence of ($\Delta f/f$) for the DR samples based on solid solutions (Nd, Ca)(Al, Ti)O_3, plot 1, (La, Ca)(Ga, Ti)O_3, plot 2 and (La, Ca) (Al, Ti)O_3 (ALTK), plot 3.

4. Conclusions

Features of the crystal structure and the microwave dielectric properties of x ($LnMO_3$)–(1−x) $CaTiO_3$ samples are reported. An increase of x up to the value $x=0.35$ (for $NdAlO_3$) and $x=0.40$ (for $LaGaO_3$) is shown to lead to formation of solid solution with the rhombic perovskite structure. Formation of solid solutions with the tetragonal perovskite structure is observed with increasing x up to $x=0.7$. Dielectrics with ε values lying within the range 43 – 48 with τ_ε near to zero are obtained in the concentration region near to the transition boundary. The maximal quality factor $Q\times f=46{,}000$ – 48,000 GHz was observed in samples containing about 35 mol.% of lanthanum gallate in the solid solution. The combined data indicates good prospects for the application of these dielectrics in microwave technology.

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