$CaTiO_3$-BASED CERAMICS: MICROSTRUCTURAL DEVELOPMENT AND DIELECTRIC PROPERTIES [†]

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[†] This paper is dedicated to the memory of Professor Dr. Drago Kolar

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Abstract

Ceramics based on $CaTiO_3$–$NdAlO_3$ solid solutions were synthesized in order to study their dielectric microwave properties. Microstructural analysis was performed with scanning electron microscopy (SEM) and transmission electron microscopy (TEM) using different analytical methods such as energy-dispersive X-ray spectroscopy (EDXS). It was observed that the heating conditions during sintering and subsequent cooling strongly affect the microstructural development of the $CaTiO_3$–$NdAlO_3$-based ceramics. Various types and concentrations of structural defects were identified, for example, dislocations, twins and/or antiphase boundaries. All such defects resulted in a degradation of the dielectric microwave properties, in particular the quality factor Q. The dielectric properties of $CaTiO_3$–$NdAlO_3$-based ceramics can be improved by an appropriate thermal treatment. Some of the microwave dielectric properties can also be improved by using iso- or alio-valent dopants.

Introduction

Commercial wireless communication applications emerged in the late 1970s, evolved in the 1980s, and are expanding rapidly through the 1990s. Numerous systems are rapidly filling the 400 MHz – 20 GHz band. At the start of the last decade cellular telephone (400 MHz – 1GHz), Television Receive Only (TVRO, 2 – 5GHz), Direct Broadcasting (DBS, 11 – 13GHz), and especially satellite communications become deployed worldwide. Today, the most important applications are wireless cable; high definition and interactive TV; collision avoidance; global positioning; cellular satellite; and personal communication systems (PCS) of many types. Among several factors, industrial growth has been spurred by the development of special ceramics and their commercialization as high-volume, low-cost products. These materials are easily integrated into rf/microwave circuits. They function as frequency filters, capacitors, inductors, and signal-distributing elements.

Microwave dielectric ceramics for wireless and global communications must exhibit low dielectric losses (high Q-values), high relative permittivities (ε'_r) and temperature-stable dielectric properties. There is a constant demand for electronic devices with improved properties that will enable further miniaturization and increase the reliability of microwave components. Although several manufacturers may produce similar components for the same application, there are subtle differences in circuit design, construction and packaging. Since the frequency drift of a device is a consequence of the overall thermal expansion of its unique combination of construction materials, each design requires a slightly different τ_f for temperature compensation. To fulfil the requirements for further miniaturization of the components, today's materials with $\varepsilon'_r < 35$ and $Qxf_r \sim 50.000$ need to be replaced by materials with higher relative permittivity values ($\varepsilon'_r > 45$) which maintain high quality factors ($Qxf_r \sim 45.000$). It has already been demonstrated that ceramics based on $La_{2/3}TiO_3$–$LaAlO_3$ solid solutions can fulfil some of these demands.[1]

Another promising example are ceramics based on $CaTiO_3$–$NdAlO_3$ solid solutions.[2,3] $CaTiO_3$ is an orthorhombic perovskite with $\varepsilon'_r \sim 170$, $Qxf_r \sim 3.500$ and a high positive temperature coefficient of resonant frequency τ_f ($\tau_f = +\ 800$ ppm/K).[4,5] At 1300 °C it undergoes a high-temperature phase transition to form a cubic structure. $NdAlO_3$ is a rhombohedral perovskite with $\varepsilon'_r \sim 22$, $Qxf_r \sim 58.000$ and a negative temperature coefficient of resonant frequency ($\tau_f = -\ 33$ ppm/K).[6] Therefore, depending on the chemical composition of the $CaTiO_3$–$NdAlO_3$ solid solution, relative permittivities (ε'_r) higher than 45 can be obtained accompanied by high quality factors ($Qxf_r > 40.000$) and a temperature-stable coefficient of resonant frequency τ_f. However, the resulting dielectric microwave properties depend strongly on the firing conditions, especially on the sintering temperature and the cooling rate, indicating the possibility that the structural development during sintering and cooling plays a key role.

In the present work, results on the microstructural characterization of $CaTiO_3$–$NdAlO_3$-based ceramics are reported. Such ceramics show very promising dielectric properties in the microwave frequency range, which can be improved by iso- and/or alio-valent doping.

Experimental

Samples were synthesized by a solid-state-reaction method. Starting powders $CaCO_3$ (Johnson Matthey 99,99%), TiO_2 (Johnson Matthey >99 %), Nd_2O_3 (Johnson Matthey 99,99%) and Al_2O_3 (Johnson Matthey 99,99%) were mixed in alcohol, dried, pressed into pellets and calcined with intermediate crushing for 40 hours in the temperature range 1350 ^{0}C to 1450 ^{0}C until equilibrium was achieved. For the purpose of microwave-property measurements and microstructural analysis, calcined powders were isostatically pressed into discs and sintered at temperatures between 1350 ^{0}C and 1500 ^{0}C for 10 hours.

The progress of the reaction was monitored by X-ray diffraction analyses (XRD) with a Philips PW 1710 X-ray powder diffractometer using CuK_α radiation. Microstructural analyses of the samples were performed with a JEOL JXA-840A scanning electron microscope (SEM) equipped with a Tracor-Northern energy-dispersive X-ray spectrometer (EDXS) and with a JEOL JEM-2000FX transmission electron microscope (TEM) with attached Link AN 10000 EDXS system.

The microwave dielectric properties were measured by a Network Analyzer (HP, Model HP 8719C, Santa Rosa, CA). We applied the closed resonant-cavity method using $TE_{01\delta}$ mode. In order to determine the unloaded Q-value, the reflection coefficients (S_{11}) were analysed as proposed by Kajfez and Hwan.[7] The permittivity was calculated using the variation improvement of the Itoh-Rudokas model.[8] Systematic errors in the microwave property measurements was minimized by the use of an improved approach to the measurements, described elsewhere.[9] The temperature coefficient of the resonant frequency τ_f were measured in the temperature range from 20 to 60 ^{o}C.

Results and discussion

The typical microstructure of a ceramic with a composition 70 mol % $CaTiO_3$–30 mol % $NdAlO_3$ after sintering at 1450 ^{0}C for 10 hours is shown in Fig. 1. The microstructure is dense, with an average grain size of approximately 10 µm.

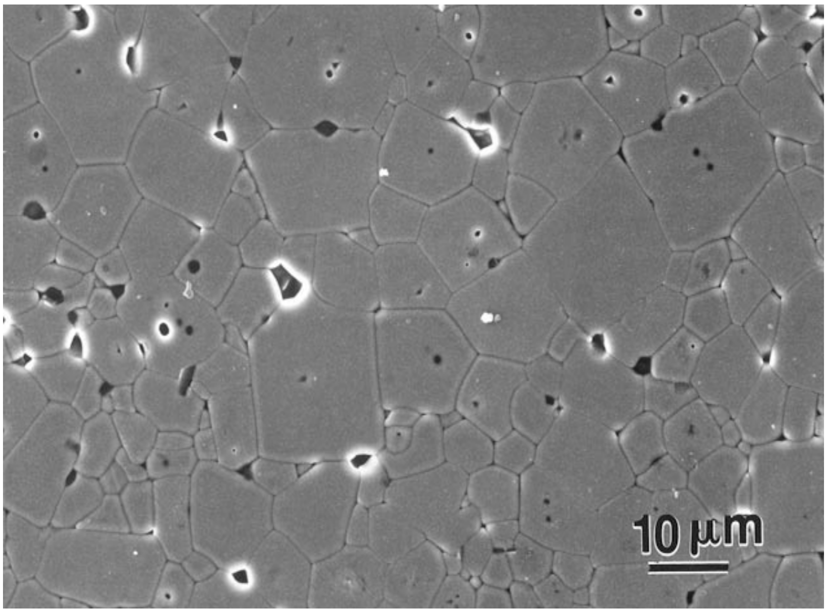

Fig. 1: Microstructure of 70 mol % $CaTiO_3$–30 mol. % $NdAlO_3$-based ceramics after sintering at 1450 °C for 10 hours (cooling rate 5 °C/minute).

In Fig. 2 a TEM micrograph of an area near the grain boundary (GB) in a $CaTiO_3$-$NdAlO_3$ sample is shown. The grains are composed of many smaller, irregularly shaped domains (D). Besides domains, planar loop-forming features were observed inside the grains (Fig. 3a and 3b). Due to their characteristic shape, and based on bright-field (BF) – dark-field (DF) experiments (two-beam case condition), and the contrast and symmetry of the fringes, we determined that these planar defects (boundaries) are of the π type, so we were able to conclude that they are antiphase boundaries (APB).

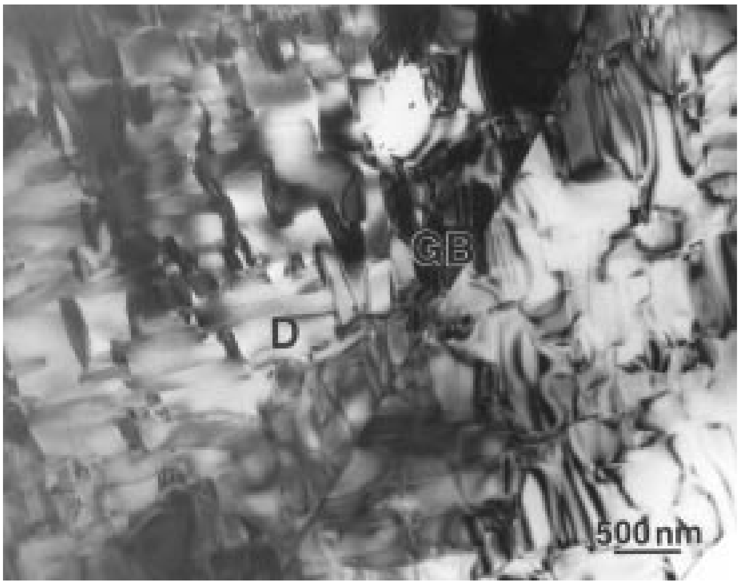

Fig 2: TEM mircographs of a $CaTiO_3$-$NdAlO_3$ sample: area near the grain boundary (GB) showing the presence of domains (D).

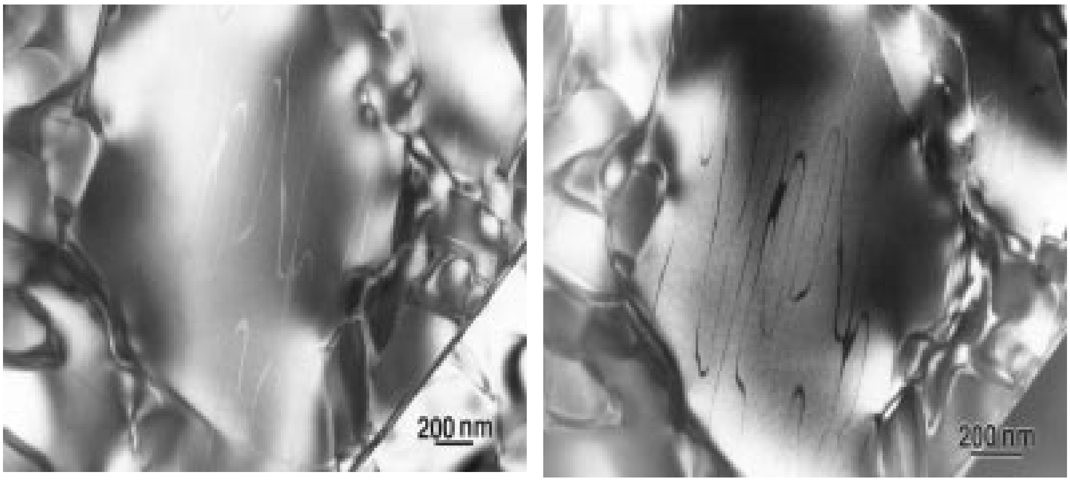

Fig. 3: TEM micrographs of antiphase boundaries in a $CaTiO_3$-$NdAlO_3$ sample: a.) bright-field, b.) dark-field. Note symmetrical contrast in BF and inversely symmetrical contrast of fringes in CDF, characteristic of APB boundaries.

The microwave dielectric property measurements on the samples (Table I.) revealed a high degree of correlation between the dielectric properties and the chemical composition of the $CaTiO_3$–$NdAlO_3$ based ceramics.

Table I.: Microwave dielectric properties of $CaTiO_3$–$NdAlO_3$-based ceramics vs. chemical composition.

CT - NA (mol%)	**Calcination (°C/h)**	**Sintering (oC/h)**	**ε'_r**	**Qxfr (GHz)**	**τ_f (ppm/K)**
73 – 27	1250/10 + 1350/10	1450/10	44,99	31.047	-15
71 – 29	1400/10 + 1400/10	1450/10	45,11	38.439	+ 6
70 – 30	1250/10 + 1350/10	1450/10	43,73	34.813	+ 14
67 –33	1350/10 + 1400/10	1450/10	41,98	42.921	+45
60 - 40	1250/10 + 1350/10	1450/10	37,18	40.776	+114

The results shown in Table I. clearly indicate a decrease of relative permittivity ε'_r with an increased concentration of $NdAlO_3$ in solid solution. At the same time the Qxf_r-value and temperature coefficient of resonant frequency τ_f gradually increases with increasing amounts of $NdAlO_3$.

The dielectric properties of $CaTiO_3$–$NdAlO_3$-based ceramics can be improved by an appropriate thermal treatment. However, it was found that the cooling rate shows a much stronger influence on the resulting microwave dielectric properties of the ceramics (especially on the Q-value) than the heating rate (Table II.).

Table II.: Microwave dielectric properties of 70 mol% $CaTiO_3$-30 mol % $NdAlO_3$ based ceramics vs. cooling rate (T_S = 1450 ℃/12 hours.

Ts (℃) ***Cooling rate***	***1450 °/10h*** ***0.5 °/min***	***1450 °/10h*** ***5 °/min***	***1450 °/10h*** ***50 °/min***
ε'_r	45	43	43
Qxf_r	44.000	38.000	33.000
τ_f (ppm/K)	+3	+3	+3

A variety of suitable dopants can be used to improve the microwave dielectric properties of $CaTiO_3$–$NdAlO_3$-based ceramics (Table III.).

Table III.: Possible dopants for the improvement of the microwave dielectric properties of $CaTiO_3$–$NdAlO_3$-based ceramics.

Element	***Coord. No.***	***Ionic Radius (Å)***	***Ionic Polarizability (Å^3)***
Ca^{2+}	12	1.34	3.16
Ba^{2+}	12	1.61	6.40
Sr^{2+}	12	1.44	4.24
Mg^{2+}	8	0.89	1.32
Nd^{3+}	12	1.27	5.01
Sm^{3+}	12	1.24	4.74
La^{3+}	12	1.36	6.07
Ti^{4+}	6	0.605	2.93
Al^{3+}	6	0.535	0.79
Ga^{3+}	6	0.620	1.50

Due to their high ionic polarizability we performed a set of experiments in which Nd^{3+} was substituted with Sm^{3+} and La^{3+} (in fact $NdAlO_3$ was substituted with $LaAlO_3$ or $SmAlO_3$). Microstructural analysis confirmed the formation of monophase ceramics during sintering at 1450°C for 12 hours with a significant amount of closed porosity (Fig. 4a). Densification can be improved by inhibiting grain growth during sintering which was achieved by either increasing the concentration of $LaAlO_3$ or by substituting 1 at % Sr^{2+} for Ca^{2+} (Fig. 4b).

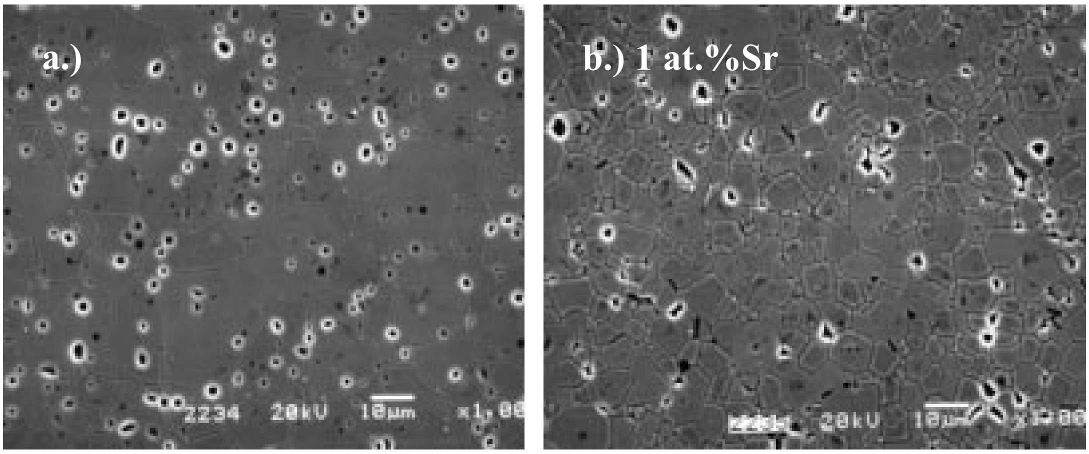

Fig. 4: Microstructure of 70 mol % $CaTiO_3$–30 mol % $LaAlO_3$-based ceramics after sintering at 1450 °C for 12 hours (cooling rate 5 °C/minute).

Measurements of the microwave dielectric properties revealed that both, Sm^{3+} and La^{3+} increases the relative permittivity ε'_r of ceramics. The temperature coefficient of resonant frequency τ_f reached a value close to zero for compositions 69 mol % $CaTiO_3$–31 mol % $SmAlO_3$ and 66 mol % $CaTiO_3$–34 mol % $LaAlO_3$. However, only the addition of $SmAlO_3$ also improved Qxf_r-value (Table IV.).

Table IV.: Microwave dielectric properties of $CaTiO_3$–$LaAlO_3$ and $CaTiO_3$–$SmAlO_3$ ceramics sintered at 1450 °C for 12 hours.

Composition (mol %)	ε'_r	Qxf_r **(GHz)**	τ_f **(ppm/K)**
$CaTiO_3$ –$SmAlO_3$			
75/25	51	31.000	+31
70/30	45	42.000	+1
65/35	41	42.000	-18
$CaTiO_3$ –$LaAlO_3$			
	47	36.000	+13
	44	30.000	-3
	41	33.000	-17

Ga^{3+} seems to be a very suitable replacement for Al^{3+}. Ga^{3+} possesses a much higher ionic polarizability than Al^{3+}, the ionic radii are very similar for both (0.535 Å for Al^{3+} and 0.620 Å for Ga^{3+}) and both have a coordination number of 6. However, microstructural analysis showed the development of a nonhomogenous microstructure after sintering the $CaTiO_3$-$NdGaO_3$ ceramics for 12 hours at 1450 °C (Fig. 5).

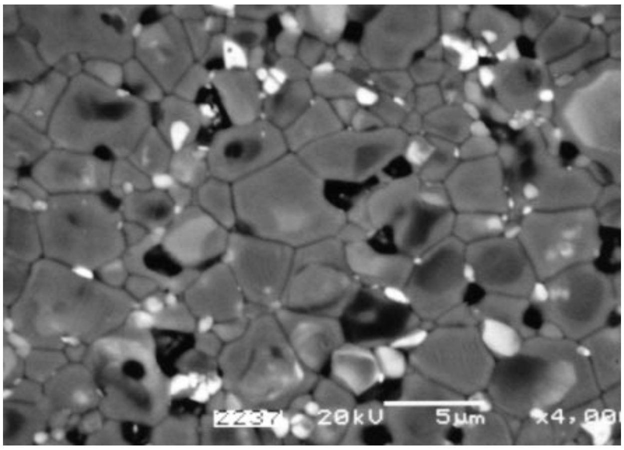

Fig. 5: Microstructure of 70 mol % $CaTiO_3$–30 mol % $NdGaO_3$-based ceramics after sintering at 1450 °C for 12 hours (cooling rate 5 °C/minute): nonhomogenous microstructure with $LaGaO_3$-based precipitates, formation of core-shell structure in solid-solution grains.

Formation of a multiphase microstructure in the $CaTiO_3$–$NdGaO_3$-based ceramics did not affect relative permittivity and τ_f significantly, but in general decreased the Qxf_r value (Table V.).

Table V.: Microwave dielectric properties of $CaTiO_3$–$NdGaO_3$ ceramics, sintered at 1450 °C for 12 hours.

Composition (mol.%)	ε'_r	Qxf_r **(GHz)**	τ_f **(ppm/K)**
$CaTiO_3$ –$NdGaO_3$			
70/30	49	32.000	+35
65/35	45	38.000	+1
60/40	44	30.000	-18
$CaTiO_3$ –$LaGaO_3$			
70/30	52	27.000	+40
65/35	48	32.000	+2
60/40	45	34.000	-20
$CaTiO_3$ –$SmGaO_3$			
70/30	51	18.000	+41
65/35	45	34.000	+1
60/40	42	35.000	-11

Partial substitution of Ba^{2+}, Sr^{2+} and Mg^{2+} for Ca^{2+} in $CaTiO_3$ strongly inhibited grain growth during sintering. Very high relative permittivities were achieved when 10 mol% Ca^{2+} was replaced with Sr^{2+} ($\varepsilon'_r > 62$). When Mg^{2+} was used a spinel-based second phase formed during heat treatment causing nonhomogenous microstructural development and thus worsening the microwave dielectric properties (Fig. 6).

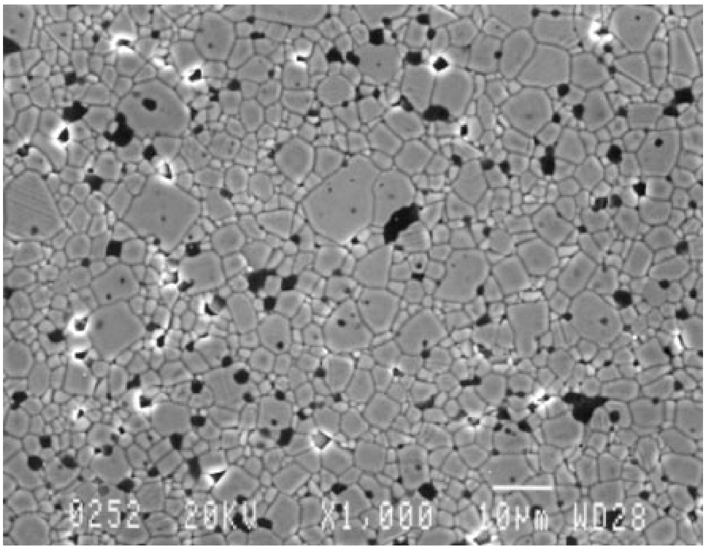

Fig. 6: Microstructure of 70 mol % ($Ca_{0.9}Mg_{0.1}$)TiO_3–30 mol % $SmAlO_3$-based ceramics after sintering at 1450 °C for 12 hours (cooling rate 5 °C/minute): nonhomogenous microstructure with spinel-based precipitates.

Conclusions

Ceramics based on $CaTiO_3$-$NdAlO_3$ solid solutions show very promising microwave dielectric properties: ε'_r higher than 45, $Qxf_r > 40.000$ and a temperature-stable coefficient of resonant frequency τ_f. These properties can be significantly improved by iso-valent doping and by processing parameters such as cooling rate. Microstructural analyses confirmed the presence of various types of defects in such ceramics which strongly influence the resulting microwave properties. Depending on the sintering temperature and cooling rate, dislocations, twins and antiphase boundaries were found. The concentration of the defects is high, which leads us to the conclusion that the resulting dielectric microwave properties of such ceramics can be even further improved by a proper thermal treatment resulting in a decrease in the concentration of the identified microstructural defects.

Experimental

Samples were synthesized by a solid-state-reaction method. Starting powders $CaCO_3$ (Johnson Matthey 99.99%), TiO_2 (Johnson Matthey >99 %), Nd_2O_3 (Johnson Matthey 99.99%) and Al_2O_3 (Johnson Matthey 99.99%) were mixed in alcohol, dried, pressed into pellets and calcined with intermediate crushing for 40 hours in the temperature range 1350 °C to 1450 °C until equilibrium was achieved. For the purpose of microwave-property measurements and microstructural analysis, calcined powders were isostatically pressed into discs and sintered at temperatures between 1350 °C and 1500 °C for 10 hours.

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Povzetek

Razvoj novih aplikacij za brezžične komunikacijske sisteme narekuje intenzivne raziskave takšnih keramičnih materialov, ki jih odlikujejo izboljšane dielektrične lastnosti v mikrovalovnem frekvenčnem območju (> 500 MHz). V delu poročamo o raziskavah dopiranih keramičnih trdnih raztopin na osnovi $CaTiO_3$ – $NdAlO_3$. Značilno za navedeni binarni sistem je, da osnovni komponenti med tvorita trdno raztopino v celotnem koncentracijskem intervalu. Z višanjem vsebnosti $NdAlO_3$ v trdni raztopini se temperatutni koeficient resonančne frekvenceτ_f znižuje ter pri sestavi 70 mol.% $CaTiO_3$ – 30 mol.% $NdAlO_3$ doseže vrednost $\tau_f = 0$. Relativna dielektričnost ε'_r je višja od 43, faktor kvalitete Q pa preseže vrednost (Qxf_r >34.000). Z izovalentnim dopiranjem takšne keramike njene mikrovalovne dielektrične lastnosti še izboljšamo. Tako delna zamenjava Nd^{3+} in/ali Al^{3+} z La^{3+}, Sm^{3+} in Ga^{3+} povzroči zvišanje relativne dielektričnosti ε'_r ,vpliva pa tudi na faktor kvalitete Q. Na faktor kvalitete Q pomembno vpliva tudi režim termične obdelave keramike, še posebno faza hlajenja po sintranju. Med termično obdelavo keramike namreč v njej nastaja vrsta strukturnih napak (dislokacije, dvojčki in antifazne meje), ki odločilno vplivajo na rezultirajoče mikrovalovne dielektrične lastnosti.