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Influence of doping additives and fluxes on the electrical properties of ceramic materials based on hollandite-like solid solutions in the K_2O-MnO-Al_2O_3-Cr_2O_3-TiO_2 system

© Nikolay V. Gorshkov[a], Alexey R. Tsyaganov[a], Andrey V. Durakov[a], Alexey A. Makarov[a], Alexander V. Gorokhovsky[a]✉

[a] *Yuri Gagarin State Technical University of Saratov, 77, Polytekhnicheskaya St., Saratov, 410054, Russian Federation*

✉ algo54@mail.ru

Abstract. Intermediates to produce ceramic powders were synthesized using amorphous potassium polytitanate ($K_2O{\cdot}4TiO_2{\cdot}xH_2O$, PPT) modified in aqueous solutions of mixtures of manganese and aluminum sulfates, taken in a 2 : 1 molar ratio, and manganese, aluminum, and chromium sulfates, taken in a 2 : 1/2 : 1/2 molar ratio. It was shown that heat treatment of these intermediates enables the synthesis of single-phase powders of hollandite-like solid solutions $K_{1.70}Mn_{1.66}Al_{0.81}Ti_{5.52}O_{16}$ and $K_{1.76}Mn_{1.60}Al_{0.39}Cr_{0.45}Ti_{5.48}O_{16}$, respectively. Ceramic dielectrics were fabricated using compacted powders of the obtained products, which were sintered at 1080 °C/3 h. The electrical properties of the ceramic specimens produced were investigated by impedance spectroscopy methods. It was shown that partial replacement of Al with Cr in the intermediate composition increases the permittivity (from 820 to 1580) and reduces dielectric loss (tg(δ), from 0.89 to 0.22). Moreover, some justified doping additives (Nb_2O_5, 0.5 %; Nd_2O_3, 0.3 %; LiF, 0.8 %) and a flux (zinc borate, 2%) allow for a further increase in dielectric constant (up to 57,800 ± 600), decrease of tg(δ) (down to 0.084 ± 0.02) and significantly increase the temperature stability of permittivity for the obtained ceramics in the temperature range from –55 to +125 °C up to the level corresponding to a X7T category of dielectrics.

Keywords: titanates; hollandite-like solid solutions; ceramics; synthesis; permittivity; dielectric losses.

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Влияние допирующих добавок на электрофизические свойства керамики на основе голландитоподобных твердых растворов системы K_2O-MnO-Al_2O_3-Cr_2O_3-TiO_2

© Н. В. Горшков[a], А. Р. Цыганов[a], А. В. Дураков[a], А. А. Макаров[a], А. В. Гороховский[a]✉

[a] *Саратовский государственный технический университет имени Гагарина Ю.А., ул. Политехническая, 77, Саратов, 410054, Российская Федерация*

✉ algo54@mail.ru

Аннотация. На основе аморфного полититаната калия ($K_2O{\cdot}4TiO_2{\cdot}xH_2O$, ПТК), модифицированного в водных растворах смеси сульфата марганца и сульфата алюминия, взятых в мольном соотношении 2 : 1, а также смеси сульфатов марганца, алюминия и хрома, взятых в мольном соотношении 2 : 1/2 : 1/2, синтезированы интермедиаты для получения керамических порошков. Показано, что термическая обработка этих интермедиатов при 850 °C/2 ч позволяет получить монофазные порошки голландитоподобных твердых растворов состава $K_{1,70}Mn_{1,66}Al_{0,81}Ti_{5,52}O_{16}$ и $K_{1,76}Mn_{1,60}Al_{0,39}Cr_{0,45}Ti_{5,48}O_{16}$ соответственно. На основе компактированных порошков полученных продуктов изготовлены керамические диэлектрики, спеченные при 1080 °C/3 ч.

Электрические свойства полученных образцов исследованы методами импедансной спектроскопии. Показано, что частичная замена Al на Cr в составе интермедиата увеличивает диэлектрическую проницаемость (от 820 до 1580) и снижает диэлектрические потери (от 0,89 до 0,22) на рабочей частоте 1 кГц. При этом введение обоснованной комбинации допантов (Nb_2O_5, 0,5 %; Nd_2O_3, 0,3 %; LiF, 0,8 %) и флюсообразующей добавки (борат цинка, 2 %) позволяет добиться существенного увеличения диэлектрической проницаемости (до 57800 ± 600) и снижения диэлектрических потерь (tg(δ), до $0{,}084 \pm 0{,}02$), а также увеличивает температурную стабильность диэлектрической проницаемости керамики в интервале от –55 до +125 °C до уровня требований к диэлектрикам категории X7T.

Ключевые слова: титанаты; голландитоподобные твердые растворы; керамика; синтез; диэлектрическая проницаемость, диэлектрические потери.

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1. Introduction

Developing electronic components requires searching for new types of functional ceramic materials that can expand product ranges, improve existing device performance, and reduce their size [1]. For ceramic capacitor structures, materials with an exceptionally high dielectric constant (CDC [2, 3]) are of the greatest interest. The most sought-after ceramic materials in the production of multilayer capacitor structures used in microelectronics correspond to the X7R category according to the international EIA-198-1 classification. These materials are characterized by a high dielectric constant and stability of this value over a wide temperature range with low dielectric losses [4, 5].

Our previous studies [6–8] have shown that hollandite-like solid solutions of the K_2O-Me_xO_y-TiO_2 system (where Me represents divalent and trivalent metals capable of isomorphously substituting titanium in the crystal structure of titanates) have good application prospects in this field. The high mobility of potassium ions in the solid solution structure results in the extremely high polarizability of these systems when an electric field is applied. This occurs because the ions can move with low energy costs through tunnels formed by paired titanium-oxygen octahedra in a 2×2 arrangement. Additionally, local inhomogeneities in the distribution of electron density arise from the substitution of titanium by transition metals. These factors result in an anomalously high dielectric constant [9–11]. Additionally, sintering of ceramics based on hollandite-like solid solutions of this system can be carried out at relatively low temperatures (1000–1100 °C), even without flux additives.

It was also noted that the difficulties associated with obtaining single-phase powders of hollandite-like solid solutions can be overcome by introducing both divalent and trivalent metal oxides into the K_2O-TiO_2 system simultaneously, for example, a combination of MnO-Me_2O_3 (where Me = Fe, Al, or Cr) [12]. However, ceramic materials obtained in this system based on potassium polytitanate ($K_2O{\cdot}4TiO_2{\cdot}xH_2O$), modified in aqueous solutions of mixtures of manganese sulfates and one of the listed trivalent metals, have sufficiently high dielectric permittivity values at the operating frequency of multilayer ceramic capacitors (1 kHz), and they are characterized by high dielectric losses ($\mathrm{tg}\,\delta > 1$), which creates problems for their use in industrial practice [7]. Traditional types of ceramic ferroelectrics with a perovskite structure can reduce dielectric losses by introducing doping additives and fluxes into their compositions [1, 4, 5]. However, this approach has not yet been used for dielectrics with a hollandite structure.

In this regard, the aim of this work was to investigate the possibility of increasing the dielectric permittivity and its temperature stability, as well as reducing dielectric losses in ceramics synthesized on the basis of potassium polytitanate, modified in aqueous solutions with a mixture of salts of one divalent (Mn^{2+}) and two trivalent (Al^{3+} and Cr^{3+}) metals. The objectives were to conduct a comparative study of the electrical properties using only Al^{3+} salts or an equimolar mixture of Al^{3+} and Cr^{3+} salts for modification, as well as to investigate the effect on the electrical properties of the synthesized ceramics of various combinations of doping additives and a standard flux (zinc borate).

2. Materials and Methods

2.1. Synthesis of hollandite-like solid solution powders

The synthesis of hollandite-like solid solutions was carried out using potassium polytitanate (PPT) powder grade 4 (TU 2146-021-96961827-2009) as an

intermediate, which had the chemical composition $K_2O{\cdot}4.1TiO_2{\cdot}2.1H_2O$. It was synthesized by reacting TiO_2, KOH, and KNO_3 in a 3 : 3 : 4 ratio at 500 °C for 2 h, and subsequently chemically modified in aqueous solutions of mixtures of manganese sulfates ($MnSO_4{\cdot}5H_2O$, Russian Standard 435-77), aluminum ($Al_2(SO_4)_3{\cdot}12H_2O$, Russian Standard 12966-85), and chromium ($Cr_2(SO_4)_3{\cdot}6H_2O$, Russian Standard 4472-78). Modification was carried out by adding PPT powder to aqueous solutions of mixtures of the above-mentioned salts. As a base for modification, 0.1 M solutions of mixtures of manganese and aluminum sulfates or manganese (Mn) sulfate and a mixture of trivalent metal sulfates (Al, Cr), taken in a molar ratio of 2 : 1, were used. Ceramics based on the intermediate obtained after modifying PPT in a solution of this composition were selected for the studies based on preliminary experiments, as they exhibited the highest dielectric constant values.

Two types of mixtures were prepared: 1) a mixture of manganese and aluminum sulfates, taken in amounts of 12.10 and 13.96 $g{\cdot}L^{-1}$, corresponding to a molar ratio of [manganese sulfate] : [aluminum sulfate] = 2 : 1; 2) a mixture of manganese, aluminum, and chromium sulfates in concentrations of 12.10, 6.98, and 6.25 $g{\cdot}L^{-1}$, respectively, corresponding to a molar ratio of $[MnSO_4] : [Al_2SO_4] : [Cr_2SO_4] = 2.0 : 0.5 : 0.5$.

The resulting solutions had the same molar concentration of metal ions (0.1 M), but contained, in the first case: 0.05 M manganese sulfate and 0.025 M aluminum sulfate; and in the second case: 0.05 M manganese sulfate, 0.0125 M aluminum sulfate, and 0.0125 M chromium sulfate. That is, both solutions used to modify the PPT had the same content of sulfates of divalent and trivalent metals (0.05 M and 0.25 M, respectively), but in the first case, the trivalent metal was aluminum, and in the second case, it was an equimolar mixture of aluminum and chromium. Given that the dissociation of trivalent metal sulfates from 1 mole of salt yields 2 moles of trivalent ions, the solutions used contained $[Mn^{2+}] : [R^{3+}]$ in a 1 : 1 ratio.

Modification of the PPT particles was carried out under constant stirring of the dispersion prepared at a ratio of 10 g of PPT powder to 200 mL of an aqueous salt solution at pH = 10 (in accordance with the recommendations in [7]). The pH value of the modifying solution was selected based on the fact that the optimal conditions for modification and obtaining a homogeneous distribution of transition metal oxide-hydroxide complexes forming on the surface of PPT particles correspond to the value of pH_{crit}, above which independent (without the participation of the PPT surface) sedimentation of the hydroxides of this metal begins. For single-component aqueous solutions of manganese salts, $pH_{crit} = 10$, and in the case of chromium salts, $pH_{crit} \sim 6$; however, according to the experimental data obtained, this value changes when salts of several metals are present in the solution. A detailed study of the behavior of such systems is planned for the future; in this work, a modification variant at pH = 10 was used, which showed the most stable result in modifying the chemical composition of the intermediate.

The homogenized dispersion was centrifuged after standing for 4 hours, the resulting product was washed with distilled water until SO_4^{2-} ions completely disappeared from the filtrate (tested using a $BaCl_2$ solution), dried at 50 °C (6 h), and used for the synthesis of a solid solution. The synthesis of the solid solution, in accordance with the recommendations of previous studies [7], was carried out by heat treatment at 850 °C for 2 h.

2.2. Production of ceramic samples

The resulting powder was used to prepare powder mixtures for the synthesis of ceramic disc samples. Two types of mixtures were used: 1) those containing only powders of hollandite-like solid solutions prepared from PPT/Mn, Al or PPT/Mn, Al, Cr intermediates; 2) containing mixtures of solid solution powder synthesized based on PPT/Mn, Al, Cr, as well as flux in the form of zinc borate grade H-207 (PRC) – 2 wt. %, and dopants: Nb_2O_5 – 0.5 wt. %, Nd_2O_3 – 0.3 wt. %, LiF – 0.8 wt. %. The selection of the flux and the combination of doping additives was carried out in accordance with the recommendations presented in the literature [13]. It was taken into account that upon the introduction of the Nb_2O_5 additive, niobium, as a representative of the 4*d* group of elements (*n*-type dopant), can occupy the titanium site and contribute to the formation of cation vacancies, as well as suppress the formation of oxygen vacancies on the dielectric surface, which should inhibit charge transport across grain boundaries and reduce dielectric losses [3, 14, 15]. Furthermore, it was hypothesized that the additional introduction of Li^+ and F^- ions in the form of LiF into the system would block cation and oxygen vacancies, respectively. At the same time, the addition of Nd_2O_3 would contribute to a reduction in the growth rate of solid solution crystal grains [16] and increase the dielectric

permittivity of the ceramic material [17]. Additionally, when Nd_2O_3 is introduced into the ceramic composition, a synergistic effect resulting from the co-doping effect may arise, positively influencing the electrical properties of the combination of two *p*-type dopants (Nd_2O_3 and Cr_2O_3, which is part of the PPT/Mn, Al, Cr intermediate), as well as the *n*-type dopant (Nb_2O_5) [16–18].

To test these hypotheses, which were formulated based on the trends observed in the literature for $BaTiO_3$-based ceramics, the aforementioned additives were introduced into the control samples in the following order: No. 2a – flux only; No. 2b – flux and Nb_2O_5; No. 2c – flux, Nb_2O_5, and Nd_2O_3; No. 2d – flux, Nb_2O_5, Nd_2O_3, and LiF; and No. 2e – Nb_2O_5, Nd_2O_3, and LiF without flux.

The process of preparing the ceramic mixture involved weighing out the appropriate components and grinding and homogenizing them together in a Pulverisette 6 ball mill (with a ZrO_2-based ceramic grinding set) for 30 min. Afterward, a 2 % solution of polyvinyl butyral (PVB grade P-1) in isopropyl alcohol was added to the resulting mixture at a ratio of 5 wt. % PVB to 95 wt. % of the powdered ceramic mixture (temporary binder), homogenized it by simple mixing, followed by drying in an air-circulating oven at 90 °C for 3 h. The dried ceramic mixture was ground manually using an agate mortar until a homogeneous consistency was achieved. The resulting powder was pressed at a pressure of 300 MPa in steel molds into tablets (discs) with a diameter of 12 mm and a thickness of (1.0 ± 0.1) mm.

The resulting tablets were sintered according to a temperature schedule that included: a temperature ramp at a rate of 180 °C·h^{-1} with intermediate holds at 400°C for 1 hour (dehydration and pyrolysis of the temporary polymer binder) and at 1000 °C for 2 h, as well as a final hold at a maximum temperature of 1080 °C for 3 h.

2.3. Study of the electrical properties of ceramics

The bases of the sintered tablets were ground, after which silver contact paste (grade K-13) was applied to them; the contacts were fired at a temperature of 690 °C in air for 1 hour. After cooling, the samples were examined using impedance spectroscopy with a Novocontrol impedance spectrometer in the 102–105 Hz range. The measurement accuracy of the dielectric loss tangent was 0.0001.

To verify the temperature stability of the dielectric properties of the synthesized ceramic samples, the capacitance of the resulting capacitor structures was measured using an MCE-15AM instrument at a measurement frequency of 1 kHz in the temperature range from –60 to +125 °C. The samples were cooled in a climatic chamber using liquid nitrogen to a temperature of –60 °C, after which the temperature and capacitance of the capacitor cell were measured simultaneously as the temperature was increased. Upon reaching room temperature, the heater was turned on, and measurements continued up to a temperature of +125 °C.

2.4. Investigation of the composition and structure of the samples

The phase composition of the ceramic materials was investigated using an ARL X'TRA X-ray diffractometer. Powders were obtained by grinding synthesized tablets, then grinding ceramic fragments to a particle size of d < 0.315 mm in a Pulverisette 6 ball mill with a ZrO_2-based ceramic grinding set for 30 minutes. An ASPEX Explorer scanning electron microscope equipped with an energy-dispersive X-ray spectrometer attachment was used to study the morphology of the ceramics and their chemical composition.

3. Results and Discussion

The elemental chemical composition of hollandite-like solid solutions synthesized based on PPT/Mn, Al and PPT/Mn, Al, Cr, according to X-ray fluorescence analysis, corresponds to the chemical formulas $K_{1.70}Mn_{1.66}Al_{0.81}Ti_{5.52}O_{16}$ and $K_{1.76}Mn_{1.60}Al_{0.39}Cr_{0.45}Ti_{5.48}O_{16}$, respectively. Thus, based on the molar ratio [Mn]/[Me^{3+}], the obtained solid solution compositions are similar.

Figure 1 shows electron micrographs of the polished surface of ceramic discs sintered using powders of hollandite-like solid solutions based on PPT/Mn,Al and PPT/Mn,Al,Cr intermediates.

In general, the structure of PPT/Mn, Al-based ceramics is similar to that of hollandite-like solid solution samples synthesized from other variants of PPT/Me intermediates [6, 7, 12]. However, the relatively large crystal grain size (20 μm and larger, Fig. 1*a*) is worth noting. At the same time, the PPT/Mn,Al,Cr-based ceramic has a very small (~1 μm) grain size (Fig. 1*d*). The introduction of dopants and flux does not change this effect but contributes to the formation of a more homogeneous grain boundary (Fig. 1*d* and 1*e*).

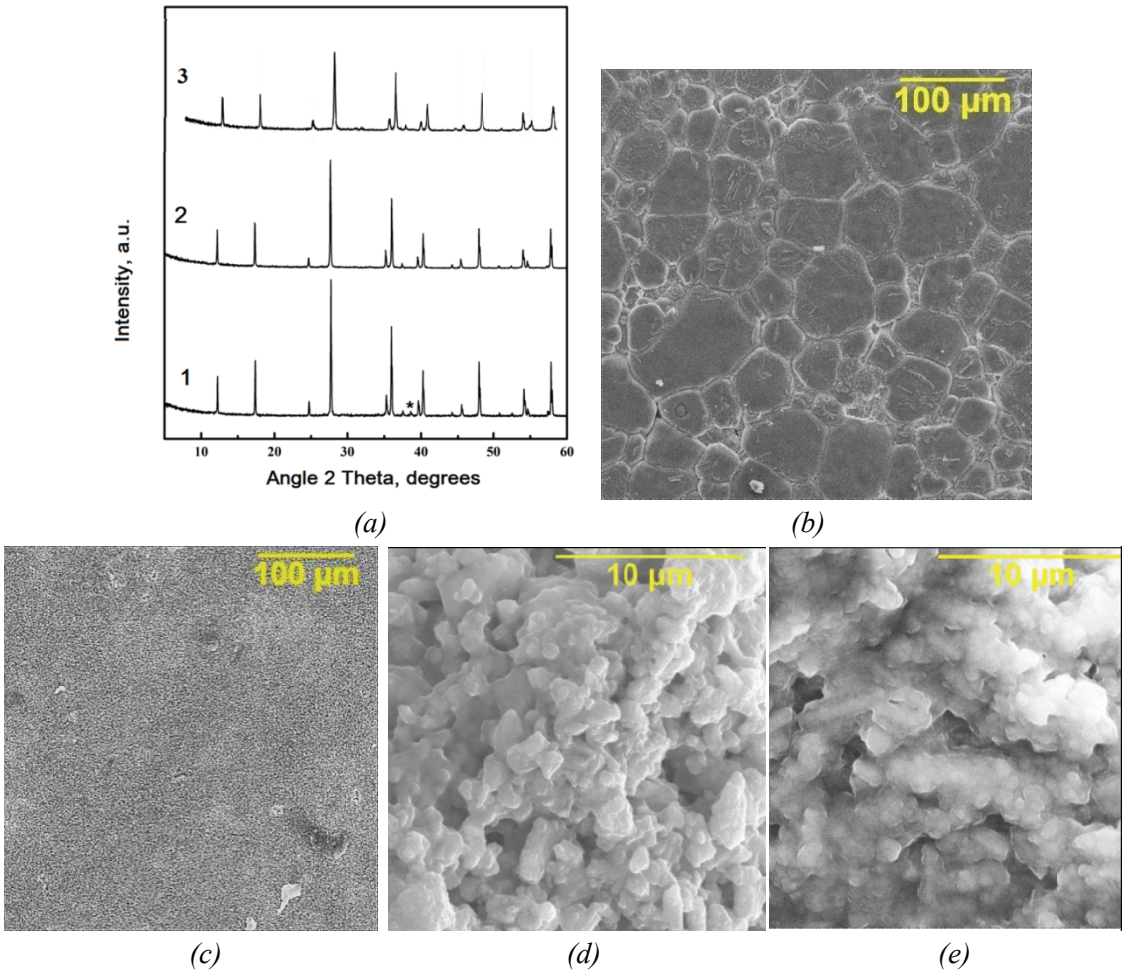

Fig. 1. X-ray diffractograms (*a*) of ceramics synthesized based on PPT/Mn, Al (*1*), PPT/Mn, Al, Cr without dopants and flux (*2*), and with a full set of dopants and flux (*3*); * – reflection corresponding to MnO_2; as well as electron micrographs of the structure of ceramic samples based on a solid solution obtained using PPT/Mn, Al (*b*), PPT/Mn, Al, Cr (*c*) and (*d*) powders: as well as PPT/Mn, Al, Cr with additions of Nb_2O_5, Nd_2O_3, LiF, and flux (*e*); (*b*) and (*c*) – polished surface; (*d*) and (*e*) – fracture

Thus, the presence of chromium in the composition of the PPT/Mn, Al, Cr intermediate inhibits the growth of solid solution crystal grains during the sintering of ceramic discs.

A comparison of the X-ray diffraction patterns of ceramic samples synthesized using PPT/Mn, Al and PPT/Mn, Al, Cr intermediate powders, Fig. 1*a*, shows that the simultaneous introduction of two trivalent metal oxides (Al and Cr) into the system also prevents the formation of secondary crystalline phases, although MnO_2 is present in the PPT/Mn, Al-based sample in an amount of less than 1 %.

Figure 2 shows the frequency dependence of the dielectric permittivity and dielectric loss for ceramic samples synthesized based on the PPT/Mn, Al and PPT/Mn, Al, Cr intermediates without the use of dopants or fluxes.

The results show that using a combination of Al and Cr salts to modify PPT, instead of Al alone, despite the approximately equal content of Al and Cr in the final product (solid solution), increases the dielectric permittivity of the ceramic at a frequency of 1 kHz (from 820 to 1580), and reduces its dielectric loss (tg δ decreases from 0.89 to 0.22). It is evident that chromium plays an active role in the formation of the intergranular boundaries of the ceramic, acting as a doping additive (by analogy with $BaTiO_3$-based ceramics [1, 4, 5, 16–18]). However, the electrical properties of the resulting material are still far from the characteristics typical of industrial samples of $BaTiO_3$-based capacitor ceramics (ε = 3000–4000, tg δ = 0.02–0.05 [19]).

In this regard, to improve the dielectric properties of the PPT/Mn, Al, Cr-based ceramic under study, doping additives and a flux were introduced into its composition. The results of the study of the obtained samples are presented in Fig. 3.

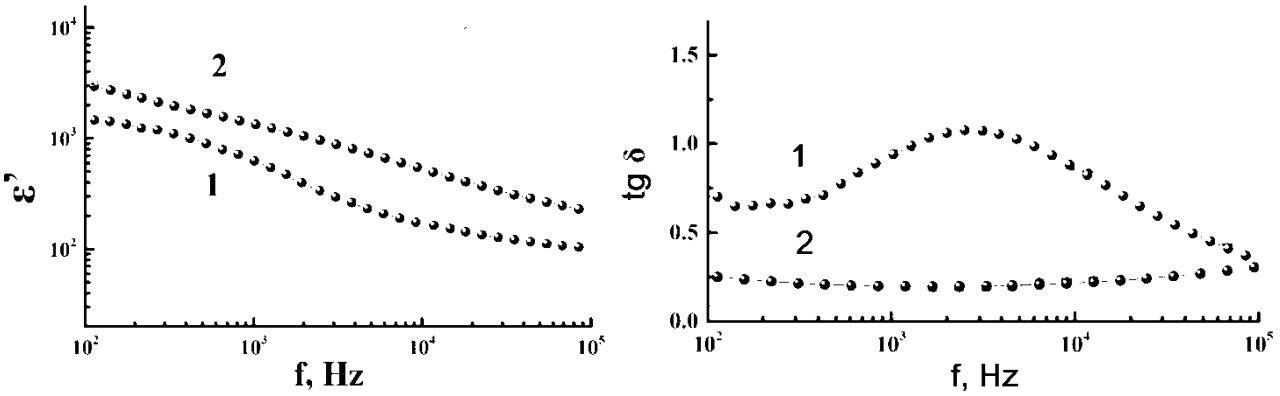

Fig. 2. Frequency dependencies of the dielectric permittivity (real part, ε′) and the tangent of the dielectric loss (tg δ), measured at room temperature for ceramic samples synthesized based on PPT/Mn, Al (*1*) and PPT/Mn, Al, Cr (*2*)

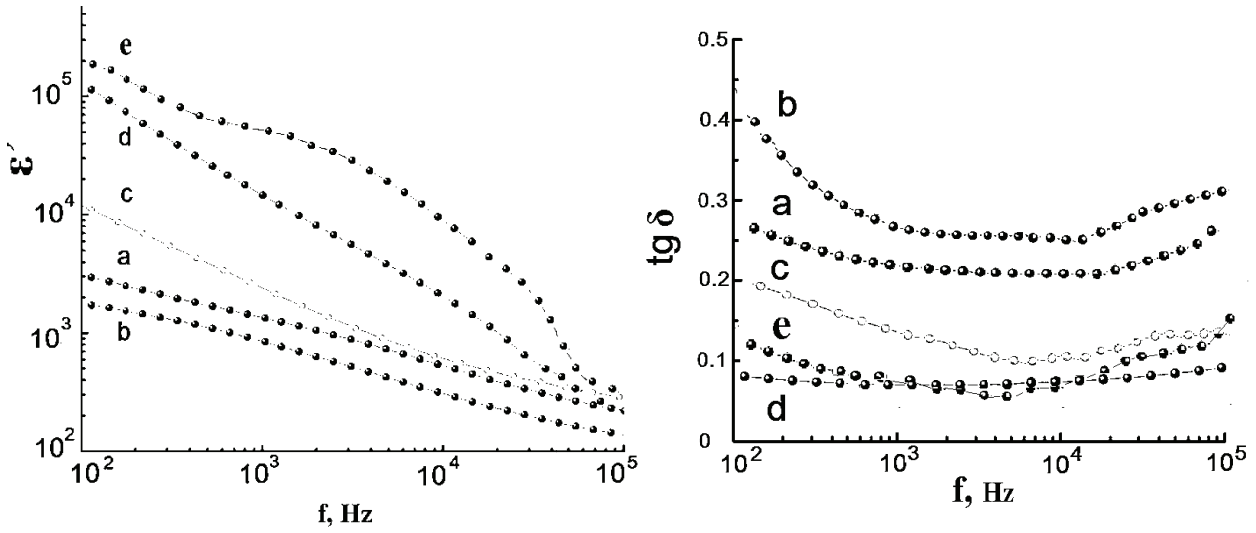

Fig. 3. Frequency dependencies of the dielectric permittivity (ε′) and the tangent of the loss angle (tgδ), measured at room temperature for ceramic samples synthesized based on the PPT/Mn, Al, Cr (*a*), with flux additive (*b*), with flux and Nb_2O_5 additives (*c*), with flux, Nb_2O_5, and Nd_2O_3 additives (*d*), and with flux, Nb_2O_5, Nd_2O_3, and LiF additives (*e*)

Analysis of the test results shows that the introduction of flux without doping additives slightly deteriorated the dielectric permittivity of the ceramics based on the studied hollandite-like solid solution. However, the combined introduction of flux and Nb_2O_5, flux and a combination of Nb_2O_5 and Nd_2O_3, as well as a combination of flux, Nb_2O_5, Nd_2O_3, and LiF led to a significant increase in the real part of the dielectric permittivity ε′ and a reduction in dielectric losses, most notably in the latter case (Fig. 3).

It should be noted that the ceramic samples tested at room temperature exhibit virtually identical electrical properties (ε, tg δ) within the margin of error, both in the presence and in the absence of flux. Nevertheless, the presence of flux is of fundamental importance, since when using an optimal combination of doping additives without introducing flux, the temperature stability of the dielectric permittivity (capacitance of the model capacitor) is lost. This fact is illustrated in Fig. 4.

In the presence of the melt formed during flux melting at sintering, it can be assumed that the doping additives are distributed more uniformly along the intergranular boundaries of the ceramic. This makes the ceramic's composition and properties more homogeneous and less susceptible to thermal effects.

Control measurements on six samples of ceramic discs made from a hollandite-like solid solution powder mixture based on the PPT/Mn, Al, Cr systems, as well as a zinc borate flux and a dopant complex (Nb_2O_5, Nd_2O_3, and LiF), showed that at an operating frequency of 1 kHz, the synthesized ceramic's dielectric permittivity is ε = (57,800 ± 600)

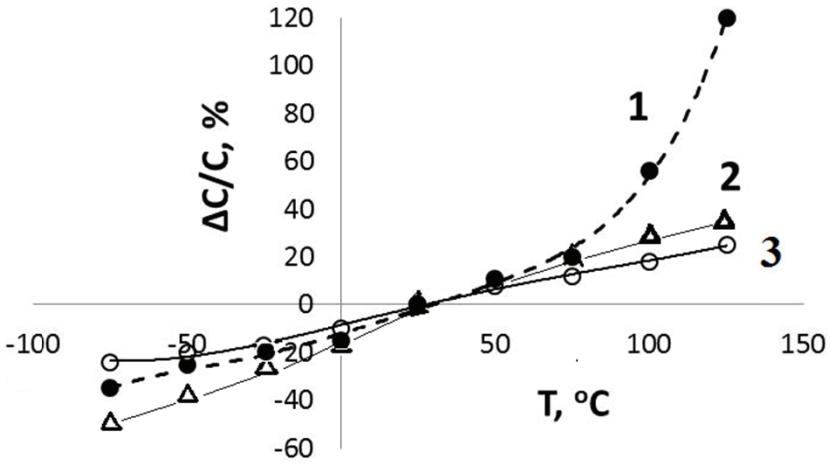

Fig. 4. Temperature stability of the capacitance of disc-shaped ceramic capacitor samples manufactured by sintering pressed blanks from a hollandite-like solid solution powder of PPT/Mn, Al, Cr (*1*), its mixture with dopants (*2*), as well as its mixture with dopants and flux (*3*)

and its dielectric loss is characterized by a tg(δ) value of (0.084 ± 0.002).

An important quantitative parameter that determines the potential for using ceramics in the production of ceramic capacitors is the relative change in dielectric constant across an operating temperature range of –55 to +125 °C.

Figure 4 shows how the capacitance of ceramic capacitors sintered from powders of the obtained hollandite-like solid solution of the K_2O-MnO-Al_2O_3-Cr_2O_3-TiO_2 system changes. The samples used contained: 1) no dopants or flux; 2) selected dopants with no flux; and 3) selected dopants with flux.

The results show that, for capacitors made from ceramic powder synthesized from a hollandite-like solid solution based on PPT/Mn, Al, Cr and containing no flux or doping additives, there is a significant deviation in the dielectric constant (capacitance) from the value measured at room temperature with changes in temperature, and this value exceeds the limits set by international standards, especially at temperatures above 70 °C (curve *1* in Fig. 4). However, if only a combination of doping additives is introduced into the ceramic composition without flux (curve *2* in Fig. 4), the dielectric constant stabilizes at high temperatures, but becomes unstable at sub-zero temperatures.

Concurrently, the incorporation of zinc borate (flux) and a combination of Nb_2O_5, Nd_2O_3, and LiF across the entire temperature range stipulated by international standards (from –55 to +125 °C) ensures adequate stability of the dielectric constant (+21 and –20 % of the value ascertained at room temperature).

The obtained results allow the synthesized ceramics based on a hollandite-like solid solution to be classified as category X7T, according to the EIA-198-1 international classification of capacitor materials. Within the temperature range of –55 to +125 °C, this category permits a capacitance deviation $\Delta C/C$ of +25 to –33 % of the value measured at room temperature. This class of materials is used in capacitor structures for smoothing, bypassing, connecting, and decoupling circuits in household appliances, control and power circuits, automotive electronics (ignition, diagnostic, and safety systems), and mobile communication devices and computers, where they are used for signal filtering, power stabilization, and improving microchip performance [20]. Additionally, the dielectric constant of ceramics based on hollandite-like solid solutions of the K_2O-MnO-Al_2O_3-Cr_2O_3-TiO_2 system is much higher than that of traditionally used $BaTiO_3$-based systems. This makes it possible to miniaturize multilayer ceramic capacitors (MLCCs) further, and MLCCs are important elements of electronic components [20].

The significant increase in the dielectric constant and temperature stabilization of ceramics synthesized using an intermediate containing a combination of MnO and two trivalent metals can be attributed to the accumulation of trivalent metals (Al and Cr) in the surface layer of the crystal during the crystallization of hollandite-like solid solutions [21]. These metals participate in forming the intergranular boundary structure. In this case, the mechanism by which Al and Cr participate in forming the intergranular boundary may differ.

Trivalent aluminum can form a dielectric layer (Al_2O_3) at the grain boundary of a hollandite-like solid solution. According to the generally accepted view, this increases the dielectric permittivity of the ceramic [3, 22]. This effect is known as the Maxwell-Wagner effect and is associated with different concentrations of charge carriers in contacting structures. Formation of an intergranular boundary between ferroelectric particles, which lack charge carriers, leads to their accumulation on the boundary in an electric field, causing an additional polarization effect.

At the same time, chromium (Cr), which is introduced into the composition of the intermediate, is a variable-valent metal. During heat treatment, it can assume various valence states ranging from +3 to +6. As a dopant that concentrates at the grain boundary, Cr can reduce dielectric losses and improve the temperature stability of the structure as well as the dielectric permittivity of the synthesized material [23, 24].

Further optimization of the dopant composition will reduce variation in the capacitance (dielectric permittivity) of ceramic materials based on solid solutions of the K_2O-MnO-Al_2O_3-Cr_2O_3-TiO_2 system, meeting the EIA-198-1 international standard for the highest X7R dielectric category (±15 % of the value measured at room temperature). It will also reduce dielectric loss from $tg(\delta) \approx 0.08$ at 1 kHz to less than 0.05.

4. Conclusion

Using potassium polytitanate, which is modified in an aqueous solution of a mixture of manganese, aluminum, and chromium sulfates (PPT/Mn, Al, and PPT/Mn, Al, Cr), as an intermediate allows for the production of single-phase powders of a hollandite-like solid solution of the K_2O-MnO-Al_2O_3-Cr_2O_3-TiO_2 system upon subsequent heat treatment. These powders can be used to make ceramic materials. In this context, chromium oxide in the structure of the resulting ceramic acts as a doping additive. It increases dielectric permittivity and reduces dielectric losses by decreasing the grain size of the ceramic material. It also presumably participates in forming intergranular boundaries.

Introducing a flux-forming additive (zinc borate, 2 %) into the ceramic composition does not positively affect the electrical properties of ceramics in the studied system. However, combining it with the doping additive Nb_2O_5, especially with a mixture of additives (Nb_2O_5, 0.5 %; Nd_2O_3, 0.3 %; and LiF, 0.8 %), significantly improves the electrical properties of ceramic samples. The dielectric permittivity increases from 1580 to (57,800 ± 600) at the operating frequency of 1 kHz and remains stable within the temperature range of –60 to +125 °C. The dielectric loss tangent decreases from 0.220 to (0.084 ± 0.02) due to the combined effect of the donor additive Nb_2O_5 and the acceptor additive Nd_2O_3, as well as the blocking of cation and oxygen vacancies at grain boundaries involving LiF.

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Настоящее исследование не получило внешнего финансирования.

6. Conflict of interests

The authors declare no conflict of interest.

Конфликт интересов

Авторы заявляют об отсутствии конфликта интересов.

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Information about the authors / Информация об авторах

Nikolay V. Gorshkov, Cand. Sc. (Eng.), Associate Professor, Yuri Gagarion State Technical University of Saratov (SSTU), Saratov, Russian Federation; ORCID 0000-0003-3248-3257; e-mail: gorshkov.sstu@gmail.com

Alexey R. Tsyganov, Cand. Sc. (Chem.), Associate Professor, SSTU, Saratov, Russian Federation; ORCID 0000-0002-5112-7939; e-mail: tsyganov.a.93@mail.ru

Горшков Николай Вячеславович, кандидат технических наук, доцент, Саратовский государственный технический университет имени Гагарина Ю. А. (СГТУ имени Гагарина Ю.А.), Саратов, Российская Федерация; ORCID 0000-0003-3248-3257; e-mail: gorshkov.sstu@gmail.com

Цыганов Алексей Русланович, кандидат химических наук, научный сотрудник, СГТУ имени Гагарина Ю.А., Саратов, Российская Федерация; ORCID 0000-0002-5112-7939; e-mail: tsyganov.a.93@mail.ru

Andrey V. Durakov, Postgraduate Student, SSTU, Saratov, Russian Federation; ORCID 0000-0003-1156-2028; e-mail: andrey.durakov@nanotec.pro

Alexey A. Makarov, Postgraduate Student, SSTU, Saratov, Russian Federation; ORCID 0009-0006-6650-1440; e-mail: aleksey.makw@gmail.com

Alexander V. Gorokhovsky, D. Sc. (Chem.), Professor, Head of the Department, SSTU, Saratov, Russian Federation; ORCID 0000-0002-4210-3169; e-mail: algo54@mail.ru

Дураков Андрей Владимирович, аспирант, СГТУ имени Гагарина Ю.А., Саратов, Российская Федерация; ORCID 0000-0003-1156-2028; e-mail: andrey.durakov@nanotec.pro

Макаров Алексей Алексеевич, аспирант, СГТУ имени Гагарина Ю.А., Саратов, Российская Федерация; ORCID 0009-0006-6650-1440; e-mail: aleksey.makw@mail.ru

Гороховский Александр Владиленович, доктор химических наук, профессор, заведующий кафедрой, СГТУ имени Гагарина Ю.А., Саратов, Российская Федерация; ORCID 0000-0002-4210-3169; e-mail: algo54@mail.ru

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