

## Synthesis and electrical properties of the ceramic materials based on $K_xMn_yR_zTi_{8-y-z}O_{16}$ ( $R = Al, Cr, Fe$ ) hollandite-like solid solutions

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**Abstract:** The potassium polytitanates (PPT) modified in the aqueous solutions containing the mixtures of water soluble salts of  $Mn^{2+}$  and trivalent metals ( $R^{3+} = Fe^{3+}, Cr^{3+}$  or  $Al^{3+}$ ) are used as intermediates to produce ceramic sinters consisting of hollandite-like solid solutions corresponding to the chemical composition of  $K_{1.3\pm0.1}Mn_{1.5\pm0.1}R_{0.2}Ti_{6.3\pm0.1}O_{16}$ . It has been shown that an introduction of various trivalent metals into the salt compositions used to obtain Mn-containing powdered potassium polytitanate (PPT-Mn/ $R^{3+}$ ) makes it possible to produce single-phase ceramics based on the resulting products by sintering. The resulting ceramic materials are characterized with a colossal dielectric constant at low frequencies and *ac*-conductivity varied in a wide range of values depending  $R^{3+}$ . The mechanism of relaxation processes occurring in the resulting ceramic materials and the prospects for their application are considered. The ceramics based on PPT-Mn/Cr intermediates are characterized by relatively high *ac*-conductivity ( $10^{-7.5} \text{ Sm}\cdot\text{cm}^{-1}$ ) and permittivity ( $10^8$  at  $10^{-2} \text{ Hz}$ ), and can be used in manufacturing of BLC electrode materials, whereas, the ceramics produced with the PPT-Mn/Fe intermediate and characterized by relatively low *ac*-conductivity ( $10^{-9.2} \text{ Sm/cm}$ ) and high permittivity ( $10^{7.3}$  at  $10^{-2} \text{ Hz}$ ) can be used as a dielectric material in manufacturing of ceramic capacitors.

**Keywords:** intermediates; crystallization; hollandite-like solid solutions; functional ceramics; electrical properties.

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## Синтез и электрические свойства керамических материалов на основе голландитоподобных твердых растворов $K_xMn_yR_zTi_{8-y-z}O_{16}$ ( $R = Al, Cr, Fe$ )

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**Аннотация:** Полититанаты калия (ППТ), модифицированные в водных растворах, содержащих смеси водорастворимых солей  $Mn^{2+}$  и трехвалентных металлов ( $R^{3+} = Fe^{3+}, Cr^{3+}$  или  $Al^{3+}$ ), используются в качестве полупродуктов для получения керамических агломератов, состоящих из голландитоподобных твердых растворов, соответствующих химическому составу  $K_{1.3\pm0.1}Mn_{1.5\pm0.1}R_{0.2}Ti_{6.3\pm0.1}O_{16}$ . Показано, что введение различных трехвалентных металлов в солевые композиции, используемые для получения Mn-содержащего порошкообразного полититаната калия (ППТ-Mn/ $R^{3+}$ ), позволяет получать однофазную керамику на основе полученных продуктов методом спекания. Полученные керамические материалы характеризуются колоссальной диэлектрической проницаемостью на низких частотах и проводимостью на переменном токе, варьирующейся в широком диапазоне значений в зависимости от типа  $R^{3+}$ . Рассмотрен механизм релаксационных процессов, происходящих в полученных керамических материалах, и перспективы их применения. Керамика на основе

полупродуктов ППТ-Mn/Cr характеризуется относительно высокими значениями электропроводности ( $10^{-7.5}$  См/см) и диэлектрической проницаемости ( $10^8$  при  $10^{-2}$  Гц) и может быть использована в производстве BLC-электродных материалов, тогда как керамика, полученная с использованием интермедиата ППТ-Mn/Fe и характеризующаяся относительно низкой электропроводностью ( $10^{-9.2}$  См/см) и высокой диэлектрической проницаемостью ( $10^{7.3}$  при  $10^{-2}$  Гц) может быть использована в качестве диэлектрического материала при производстве керамических конденсаторов.

**Ключевые слова:** интермедиаты; кристаллизация; голландитоподобные твердые растворы; функциональная керамики; электрические свойства.

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## 1. Introduction

Modern electronics needs new functional materials characterized by regulated electric properties and various combinations of functionalities. Such materials can be used in manufacturing of electric capacitors, storage devices, thermistors, electric filters, etc. [1–3]. Among them, the materials exhibiting a colossal dielectric constant (CDC,  $\epsilon > 10^3$ ) are of great interest for producing high-density charge storage devices (memory drives) including boundary layer capacitors (BLC) and multilayer ceramic capacitors (MLCC).

Ferroelectrics with perovskite-like structure ( $BaTiO_3$ ,  $PbTiO_3$ ,  $PbZrO_3$ , etc.) currently form the basis of most ceramics demonstrating CDC values, but only within a narrow temperature range close to  $T_c$ . The best known non-ferroelectric CDC materials ( $CaCu_3Ti_4O_{12}$ ,  $Ba(Fe_{0.5}Nb_{0.5})O_3$ , and NiO based ceramics) possess excellent dielectric properties ( $\epsilon \sim 10^5$ ) [4, 5]. Nevertheless, creating materials characterized by higher dielectric constant values, regulated frequency dependence of permittivity and lower temperature of sintering remains a significant problem.

In this regard, the hollandite-like solid solutions could open up new ways in the design and production of advanced non-ferroelectric ceramic materials. Some solid solutions, synthesized in the system of  $K_2O-M_xO_y-TiO_2$  ( $M = Ni, Cu, Co, Cr, Fe$ ) [6–8], have shown  $\epsilon = 10^3-10^6$  ( $f = 0.01$  Hz) at  $(23 \pm 2)^\circ C$ . The  $K_xM_yTi_{8-y}O_{16}$  hollandite-like ceramics based on the amorphous potassium polytitanates (PPT) modified in aqueous solutions of some transition metal salts [6] feature submicro-sized crystals facilitating the production of layered ceramics. This experimental technique enables relatively simple and fast production of the hollandite-like materials compared to other traditional time-consuming experimental methods, such as multistage molten salt

and solid state synthesis [9], as well as a more complex sol-gel technique [8].

However, the hollandite-like solid solution based on modified potassium polytitanates, as well as those produced by other methods [6–9], are significantly contaminated with secondary crystalline phases ( $TiO_2$ ,  $MeTiO_3$ ,  $Me_2O_3$ ).

The goal of this research is to justify a method of producing mono-phase hollandite-like ceramics characterized by enhanced CDC values. This can be achieved by using the potassium polytitanate intermediates modified in the aqueous solutions containing the combinations of divalent ( $Mn^{2+}$ ) and trivalent ( $R^{3+}$ ) metals.

## 2. Materials and Methods

### 2.1. Materials and preparing methods

The parent potassium polytitanate powder (PPT) was synthesized at  $500^\circ C$  by the molten salt method described in [10]. The PPT-based intermediates were produced by treating the parent PPT in the aqueous solutions containing the mixtures of sulfates of  $Mn^{2+}$  and trivalent metals ( $Al^{3+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$ ). The  $[Mn]/[R]$  molar ratio ( $n$ ) in the mixed aqueous solutions was selected as  $n = 2 : 1$  to align with the stoichiometry of layered double hydroxides (LDH) incrusting the PPT flakes by corresponding nanoscale LDH particles [11].

Given that such mixed salt solutions are characterized by complicated physicochemical processes accompanied with hydrolysis, sedimentation of certain products and complexation [12–14], depending on pH and nature of the used salts, the prepared solutions (0.01 M for each salt,  $pH = 6.4 \pm 0.2$ ) were soaked for 6 hours to obtain chemically stable systems. Further, the solutions were filtered with the Whatman No 40 filters to separate the sediments (metal hydroxides), and used to modify PPT particles. Finally, the PPT powder was

introduced into the resulting aqueous solution (1 g per 100 mL) and stirred for 4 hours [6, 7].

The resulting precipitate was washed with distilled water until reaching a pH = 8.5 and dried at 50 °C for 4 hours. The final products were marked as PPT-Mn/R<sup>3+</sup> (R = Al, Cr, Fe).

The powdered intermediates were compacted at 200 MPa to produce the discs of 12 mm in diameter and (2.0 ± 0.1) mm in thickness, and then sintered at 900 °C for 2 hours to produce the ceramic specimens.

## 2.2. Testing methods

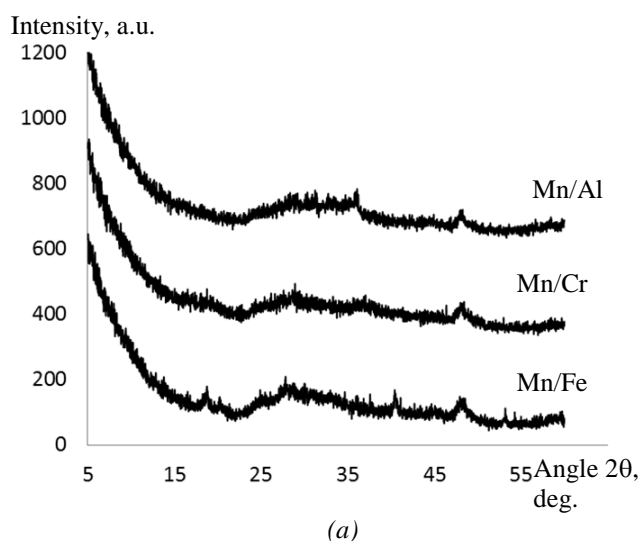
The resulting ceramics were investigated using a scanning electron microscope (SEM) Aspex EXplorer (acceleration voltage of 15 kV) and X-ray ARL X'TRA diffractometer (CuK $\alpha$  source,  $\lambda$  = 0.15406 nm, 40 kV). The chemical composition was determined through the wavelength dispersive X-ray fluorescence analysis (Spectroscan MAX-GV).

To evaluate the electrical properties, the bases of the produced ceramic discs were coated with silver-palladium adhesive (K13 trade mark), and the obtained specimens were investigated using the impedance spectroscopy analyzer Novocontrol Alpha AN at (23 ± 2) °C. The mechanical strength of the discs was measured in accordance with ASTM C1424-15.

The porosity of the ceramic sinters was calculated using a ratio of the real and apparent densities, determined by the picnometric method (Russian Standard 24409-80).

## 3. Results and Discussion

The XRD patterns of the obtained ceramic materials are presented in Fig. 1. All the materials can be classified as K<sub>x</sub>Mn<sub>y</sub>R<sub>z</sub>Ti<sub>8-y-z</sub>O<sub>16</sub> solid solutions.



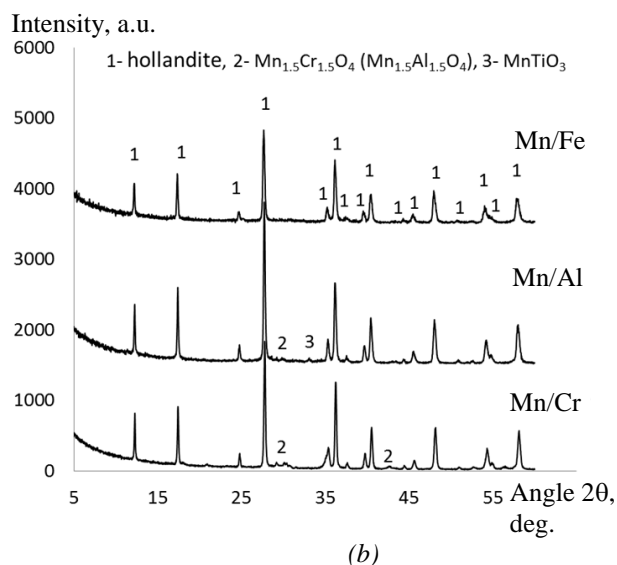
Their structure corresponds to the hollandite-like phases, specifically KMnTi<sub>3</sub>O<sub>8</sub> (54-1183) or K<sub>1.46</sub>Ti<sub>7.2</sub>Fe<sub>0.8</sub>O<sub>16</sub> (5-60) (JCPDS-ICDD-2009 base of data).

It can be inferred that during the thermal treatment the R<sup>3+</sup> additives stabilize structure of the titanate polyanions, as represented in the PPT, and inhibit crystallization of perovskite-like MnTiO<sub>3</sub>, which intensively forms in the PPT-Mn based intermediates [7].

The chemical composition of the obtained ceramics (Table 1) allows us to classify the obtained substances as K<sub>1.3</sub>Mn<sub>1.5</sub>Al<sub>0.2</sub>Ti<sub>6.2</sub>O<sub>16</sub>, K<sub>1.4</sub>Mn<sub>1.4</sub>Cr<sub>0.2</sub>Ti<sub>6.4</sub>O<sub>16</sub> and K<sub>1.3</sub>Mn<sub>1.6</sub>Fe<sub>0.2</sub>Ti<sub>6.2</sub>O<sub>16</sub> hollandite-like solid solutions with similar structure and composition. This formula corresponds to the general stoichiometry K<sub>x</sub>Me<sup>3+</sup><sub>y</sub>Ti<sub>8-y</sub>O<sub>16</sub> ( $x \approx y$ ), which is traditionally recognized in the literature for such substances and indicates the presence of manganese in the Mn<sup>3+</sup> state, similar to the hollandite-like solid solutions based on PPT-Mn intermediates [7].

The secondary phases observed in the sinters correspond to MnTiO<sub>3</sub> (PPT-Mn/Al precursor) and spinel-like Mn<sub>1.5</sub>Cr<sub>1.5</sub>O<sub>4</sub> (Mn<sub>1.5</sub>Al<sub>1.5</sub>O<sub>4</sub>); however, the total content of these phases in all the investigated systems is less than 3 %, allowing to consider them as traces.

The chemical compositions of all the intermediates (PPT-Mn/R), as well as the ceramic powders obtained by their thermal treatment, are very close and facilitate the formation of the same crystalline phase (a hollandite-like solid solution K<sub>1.3±0.1</sub>Mn<sub>1.5±0.1</sub>R<sub>0.2</sub>Ti<sub>6.3±0.1</sub>O<sub>16</sub>) at high temperatures.



**Fig. 1.** XRD patterns of the PPT-Mn/R<sup>3+</sup> precursors (a) and ceramic sinters based thereon (b)

**Table 1.** Chemical composition (X-ray fluorescence analysis data), compressive strength (CS), porosity (P), electric conductivity ( $\sigma_{dc}$ ) and electric resistance of the equivalent circuit (R) of the obtained ceramic materials (Me = Fe, Cr or Al)

Precursor material	Content, at. % ( $\pm 0,1$ )					CS, MPa	P, %	$\sigma_{dc}^*$ , $\times 10^8$ $\text{Sm}\cdot\text{cm}^{-1}$	$R^*$ , M $\Omega$
	K	Mn	Me	Ti	O				
PPT-Mn/Al	5.2	6.1	0.8	24.6	63.3	$145 \pm 10$	$4 \pm 1$	0.90	0.67
PPT-Mn/Cr	5.0	6.0	0.8	25.1	63.0	$123 \pm 12$	$7 \pm 2$	0.42	1.40
PPT-Mn/Fe	5.1	6.3	0.8	24.5	63.2	$111 \pm 18$	$9 \pm 2$	0.91	1.11

\* calculated from the impedance spectra.

To explain this phenomenon we have to take into account that in accordance with the X-ray fluorescence and XRD analysis data, the separated sediments obtained after soaking the mixed aqueous solutions consist of amorphous hydroxides of metals (Fe, Cr, Al) characterized by low critical values of pH ( $\text{pH}_{\text{cryt}} = 2.0$ ; 5.6 and 4.8, respectively [12–14]). These critical pH values are lower than  $\text{pH} = 6.4$  obtained in the parent mixed aqueous solutions. Consequently, soaking these solutions leads to a removal of the main part of Fe, Cr and Al with sediments, whereas most of Mn ( $\text{pH}_{\text{cryt}} = 8$  [12]) remains in the solutions. We can also assume that the remaining Fe, Cr or Al in the parent solution forms any hydroxo-anion aqua-complexes with Mn containing ions ( $\text{Mn}^{2+}$ , and  $\text{MnOH}^+$ ) found in the solution at  $\text{pH} = 6.4$  [13–16]. Most likely, the nature of such complexation is similar for various  $\text{R}^{3+}$  containing ions [16]. As a result, the initial molar ratio of  $[\text{Mn}]/[\text{R}] \approx 2$  was transformed to  $[\text{Mn}]/[\text{R}] \approx 7$  in all investigated parent aqueous solutions, and this phenomenon was confirmed across 5 experimental series for each combination of salts. Therefore, the PPT-Mn/R products obtained by PPT treatment in the mixed aqueous solutions were considered as stable intermediates to produce ceramics based thereon.

The resulting ceramic bodies have a dense structure (Fig. 2a) significantly low porosity and high compressive strength (Table 1).

The impedance spectra of the ceramic sinters are presented in Fig. 2b. The impedance spectra observed in the low-frequency region represent the angle close to 45° with the  $Z'$  axis (high contribution of the diffusion process). At the same time, the shape of the Cole-Cole plots (semicircles) at high frequencies indicates that volume processes related to conductivity, taking place in these conditions, predominantly influence the impedance. The electrical resistance ( $R$ ) and dc-conductivity of the

corresponding equivalent circuits can be determined from the  $Z'' = f(Z')$  dependence (Fig. 2b) [17].

Using the measured  $Z'$  and  $Z''$  values, the following characteristics were calculated: complex specific conductivity  $\sigma^*$ ,  $ac$  – and  $dc$  conductivities, the real  $\varepsilon'$  and imaginary  $\varepsilon''$  components of the dielectric constant

$$\varepsilon^* = \varepsilon'(\omega) - i\varepsilon''(\omega) = -i \frac{1}{\varepsilon_0 \omega s} \frac{1}{Z^*} ;$$

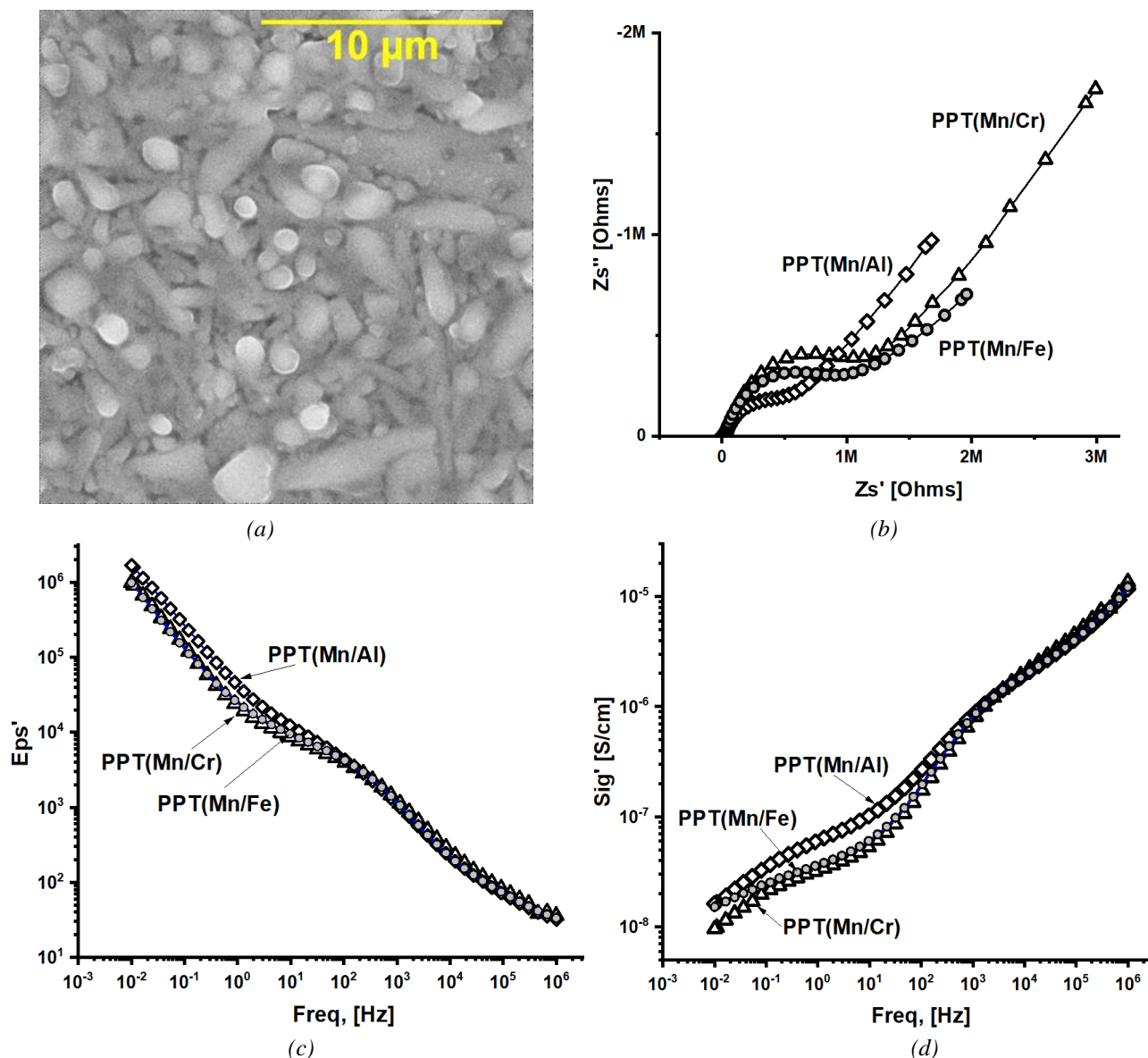
$$\sigma^* = \frac{1}{Z^*} \frac{1}{s} ,$$

where  $s$  is the electrode area and  $\omega$  is the angular frequency.

The resistance corresponding to ionic conductivity was calculated by extrapolating the high-frequency region of the hodograph (Fig. 2b) to the axis of real resistances ( $R$ ). Conductivity  $\sigma$  (ionic component or volumetric conductivity) was calculated using the relation  $\sigma = d/(R \cdot s)$ , where  $d$  is the thickness of the ceramic sample (disk),  $R$  is the resistance found by extrapolation. The electronic component of conductivity (low-frequency conductivity measured at a frequency of  $10^{-2}$  Hz) was determined from Fig. 2d as an extrapolation of the frequency dependences of conductivity on the  $\log(\sigma_{ac})$  axis, i.e. determination of conductivity at a frequency of  $10^{-2}$  Hz.

A simple shape of the semicircles in the Cole-Cole plots and relatively high values of the electric resistance determined by extrapolating the high-frequency arc to intersect the axis of real resistances indicate that the transport of electric charge carriers along boundaries of the crystals ( $2e^- + 1/2\text{O}_2 = \text{O}^{2-}$ ) reveals principal contribution in the conductivity [18].

Thus, the intermediates based on the PPT-Mn/R system have allowed for the production of mono-phase ceramic dielectrics through sintering, whereas the PPT-Mn intermediates only facilitated the



**Fig. 2.** Typical fracture surface of the ceramic sinter (PPT-Mn/Cr) (a), Cole-Cole plots of the impedance data (b) and frequency dependences of permittivity (c) and conductivity (d) for the sinters based on various PPT-Mn/ $R^{3+}$  intermediates

formation of ceramic composites, characterized by the presence of various secondary crystalline phases, lower permittivity and higher conductivity [7]. The permittivity of the obtained ceramics has extremely high values (Fig. 2c) and monotonically decreases with increased frequencies. The origin of high dielectric constant in the obtained non-ferroelectric systems at the room temperature can be attributed to both intrinsic and extrinsic relaxation processes (such as grain boundary, electrode interface) [19, 20]. The sources of conductivity and relaxation mechanisms in these materials can be discussed in terms of defect structures. A movement of the charged point defects ( $Ti^{3+}$ , typical for the hollandite-like structures [9]), free charge carriers ( $e^-$ ,  $K^+$ ) and oxygen vacancies as well as accumulation of charge carriers at the grain

boundaries enhances the dielectric constant in these materials. Transition metals with various oxidation states (Mn, Fe, Cr) can also act as charged point defects and facilitate hopping conductivity. Nevertheless, it is interesting that the hollandite-like solid solutions of all the investigated compositions are characterized by very similar values of permittivity and conductivity in a wide range of frequencies in spite of different kinds of  $R^{3+}$  metal used as a dopant.

The findings indicate that the mono-phase PPT-Mn/Fe based ceramic materials are promising for the MLCC manufacturing due to their higher permittivity and lower conductivity compare to previously investigated hollandite-like materials based on simple PPT-Me intermediates [6–8].

#### 4. Conclusion

1. The obtained results indicate that the potassium polytitanates modified in the stabilized aqueous solutions containing the mixtures of water soluble salts of Mn and trivalent metals ( $R$ ), such as Fe, Cr or Al, can be used as intermediates to produce mono-phase ceramic sinters consisting of hollandite-like solid solutions (purity of 99+) corresponding to the formula of  $K_{1.3\pm0.1}Mn_{1.5\pm0.1}R_{0.2}Ti_{6.3\pm0.1}O_{16}$ .

2. The sintered ceramics produced through this method have a colossal dielectric constant ( $10^6$ – $10^8$ ) at low frequencies and relatively low  $ac$ -conductivity varying in the range of  $10^{-7.5}$ – $10^{-9.2}$  depending on the  $R^{3+}$  type.

3. The ceramic materials based on PPT-Mn/ $R$  intermediates can be used in manufacturing of hybrid (electrostatic-electrochemical) electrode materials and could be advantageous in manufacturing high-density charge storage devices, such as ceramic capacitors.

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#### 6. Conflict of interests

The authors declare no conflict of interest.

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