



Modified amorphous layered titanates as precursor materials to produce heterostructured nanopowders and ceramic nanocomposites



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ABSTRACT

This report is concentrated upon manufacturing some new kinds of electroceramics based on synthesis of layered potassium polytitanate nanoparticles, following chemical treatment of these particles in aqueous solutions containing transition metal ions (Me^{n+}), and thermal treatment of the obtained amorphous precursor materials at the temperatures which allow producing the final ceramic material characterized with desired functional properties. It was shown that the final ceramics consisted of $MeTiO_3$, hollandite-like $K(Ti,Me)_8O_{16.5}$ crystals and some admixtures of Me or Me_xO_y and $K_2Ti_6O_{13}$, depending on chemical composition of powdered precursor. It was recognized that the ceramic materials obtained in the system investigated were characterized with nonlinear electric properties which could be regulated by the type of precursor material and its chemical composition.

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1. Introduction

Nowadays the materials which have a superstructure are of the most interesting in both fundamental and applied research due to some special properties related to appearance of additional structural (supramolecular) effects. Bulky pillared compounds, multilayered thin films, membranes or supports, hybrid organic–inorganic nanocomposites, interstratified material and high surface area catalysts present some applications of such materials [1–7]. Because of their nanometer-size dispersion, the nanocomposite compounds exhibit markedly improved properties when compared with the pure substances as well as conventional composites. Layered nanomaterials, due to their unique structure consisting of platy nanosheets, represent an interesting opportunity to develop superstructural materials with intentional and controllable functionalities. Synthetic layered double hydroxides (LDH), some natural silicates and aluminasilicates, architectures based on metal complexes as well as different synthetic layered titanates, niobates and zirconates could be considered among the layered materials applied as precursors to produce interesting functional materials. The chemical composition and morphology of such materials can be modified by three main techniques which allow producing different heterostructured nanocomposites based on the well-known “host–guest” technique, which includes

intercalation, restaking or pillaring [8]. These strategies are common in the synthesis of nanopowders considering as final products. However, there are few attempts to investigate structural and functional features of the materials obtained by sintering the compacts based on heterostructured nanopowders, which are considered as raw materials (precursors). On the other hand, alkali titanates are widely applied layered nanomaterials due to their relatively low cost and simple synthesis methods [9–12]. Taking into account the fact that titanate based heterostructured nanopowders exert a lot of specific optical, catalytic, electric, and magnetic properties [2,13–15], studying possible usage of such materials as precursors for manufacturing different functional ceramic materials is of high interest.

This work presents the results related to the synthesis of electroceramics based on heterostructured titanates obtained by the host–guest technique using the nanoscale platy potassium polytitanate (PPT) powder as a “host” material.

2. Experimental

The potassium polytitanate applied in this research was synthesized in accordance with our previous work [16] by the treatment of powdered TiO_2 (anatase, Aldrich 99%+, average size of particles ca. 7 μm) in the molten mixture of KNO_3 and KOH in the alumina crucible using an electric furnace at 500 °C for 2 h. The TiO_2 : KOH : KNO_3 weight ratio was 1:1:8. The synthesized potassium polytitanate was carefully washed with distilled water three times (2 dm³ of H_2O per 100 g of the product for each washing), filtrated (Whatman paper no. 40) and dried at 50 °C in the oven to obtain the parent PPT powder characterized with the TiO_2/K_2O molar ratio equal to 4.1.

The synthesized particles morphology was investigated by TEM (JEOL JEM-1011 operated with accelerating voltage of 80 kV). The chemical composition of the PPT was investigated by Philips XL30ESEM equipped with EDS EDAX Pegasus analyzer, operated with accelerating voltage of 20 kV. The phase composition of the all

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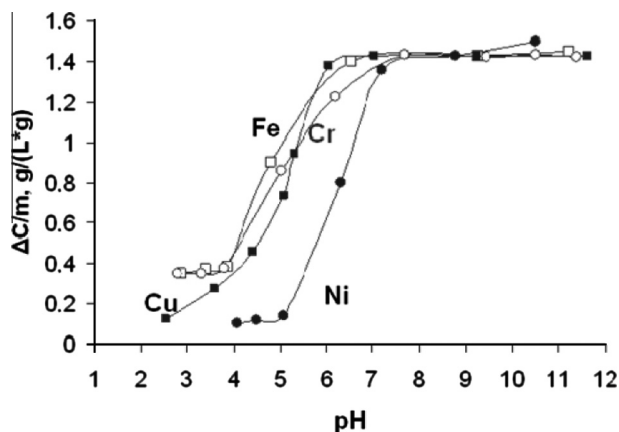


Fig. 1. Influence of the pH value on a change the metal concentration in the aqueous solutions of different metal sulfates (ΔC , normalized value).

applied or produced substances was investigated using XRD analysis (Philips X'Pert-MPD) and identified with the ICDD/2002 standard database. The thermal behavior of the synthesized powders was analyzed with DSC NETZSCH STA 449C equipment.

To synthesize heterostructured precursors, the ultrasonically treated aqueous dispersion of the PPT powder was mixed with aqueous solutions of different transition metal salts (sulfates, 10^{-3} mol/dm³), stirred for 4 h, filtrated using paper Wathman-42 and further dried at 40 °C. The treatment was made at different pH values which were regulated by adding the H₂SO₄ or KOH aqueous solution. The concentration of the transition metals in the solutions was controlled by ICP spectrometer Profile Plus. The obtained products were separated by centrifugation and investigated by SEM, TEM and XRD methods.

In order to obtain the ceramic specimens, the heterostructured powders produced at different pH values of aqueous solutions were compressed in the stainless steel mold (80 MPa); the obtained discs (diameter of 8 mm, thickness of 3.5–3.8 mm) were thermally treated for 2 h in the electric furnace (Thermoline 2500) at 850 °C (the temperature found to support sintering processes in all the systems investigated). Electrical properties of the ceramics were investigated at room temperature by means of complex impedance spectroscopy, in the 10 Hz–2 MHz frequency range with the signal amplitude varying in the range of 10–50 mV, using a Z2000 and Solartron-1260 impedance analyzers controlled by a personal computer.

3. Results and discussion

A mechanism of interaction processes between transition metal ions and PPT particles dispersed in the aqueous solution depends on pH value. The preliminary experiments, performed to specify the character of the processes taking place in the aqueous solutions of transition metal sulfates at different pH values, regulated by KOH and H₂SO₄ admixtures, indicated (Fig. 1) that for all the studied solutions at pH higher than a critical value (5–7 for different salts) all the Me ions participated in the sedimentation of Me(OH)_y/Me_xO_y particles. At pH values lower than a critical value (pH = 3.5–5.0) the Me cations only participated in the ion-exchange processes. Furthermore, there is an intermediate range of pH values where both these processes take place. The chemical composition

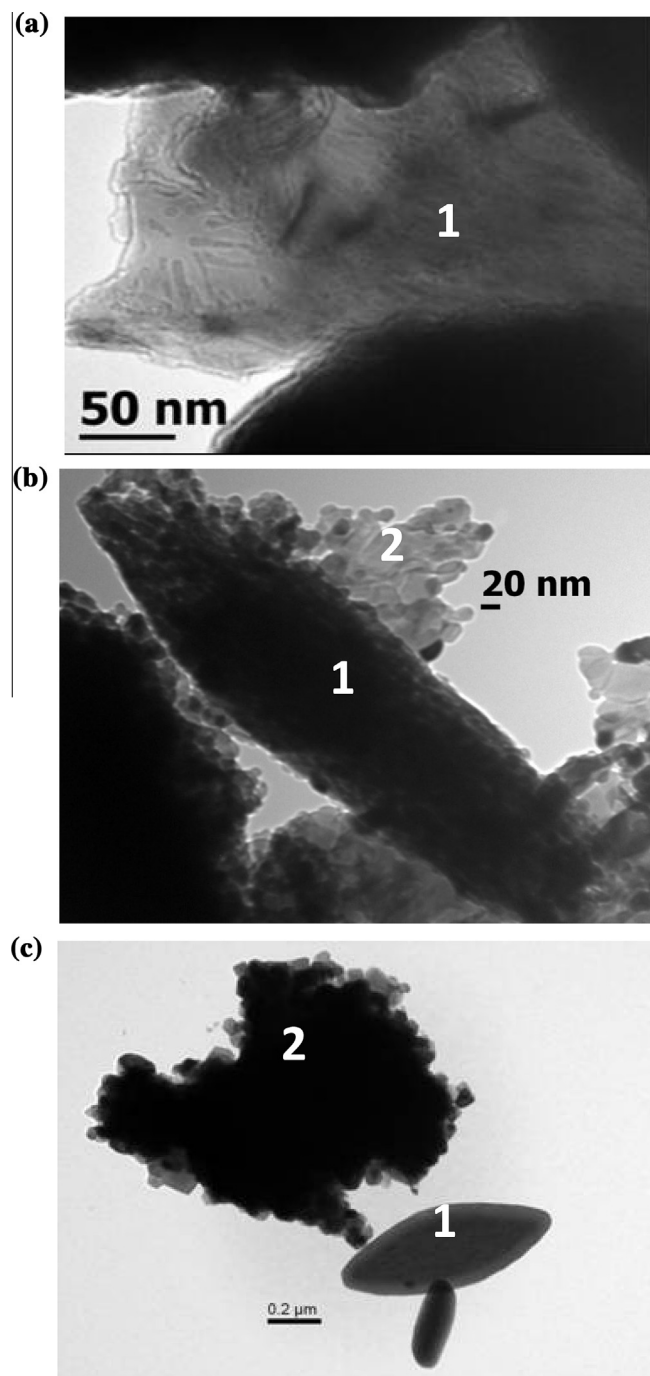


Fig. 2. TEM photographs of the powders obtained as a result of the interaction of Ni ions with aqueous dispersion of the PPT powder at pH = 4.6 (a), 6.8 (b) and 8.8 (c). 1-PPT particles, 2-Ni clusters, 3-NiO/Ni(OH)₂ particles.

Table 1

Chemical composition of the product obtained by the treatment of PPT powders with aqueous solutions of different metal sulfates at different pH values.

Me (salt)	pH < pH(critical)			pH ~ pH(critical)			pH > pH(critical)			
	K ₂ O	TiO ₂	Me _x O _y	K ₂ O	TiO ₂	Me _x O _y	K ₂ O	TiO ₂	TiO	Me _x O _y
Ni	2.6	94.5	2.9	5.6	86.6	7.8	10.3	74.4		13.3
Co	n.d.	n.d.	n.d.	6.2	87.2	6.6	n.d.	n.d.		n.d.
Cu	1.6	92.9	5.5	5.2	84.8	10.9	9.4	74.3		15.8
Zn	n.d.	n.d.	n.d.	4.5	76.4	19.1	n.d.	n.d.		n.d.
Cr	1.6	95.2	3.2	8.6	86.6	4.8	10.9	76.3		12.8
Fe(II)	0.8	90.4	8.8	5.0	85.8	9.2	12.0	73.8		14.2

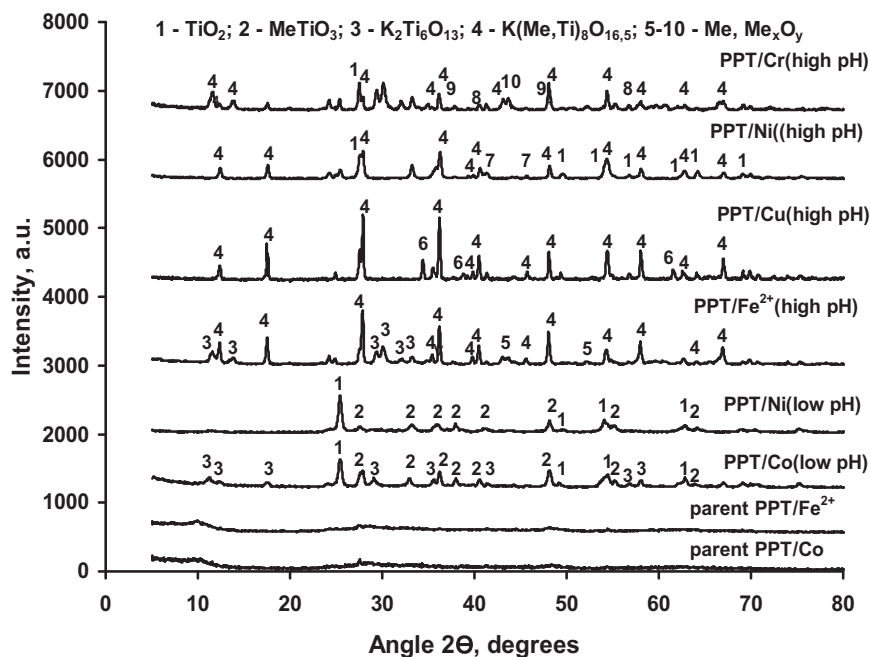


Fig. 3. XRD patterns of the compacts based on parent potassium polytitanate powders obtained in different conditions (pH value) and the ceramic products obtained by their thermal treatment (sintering) at 850 °C.

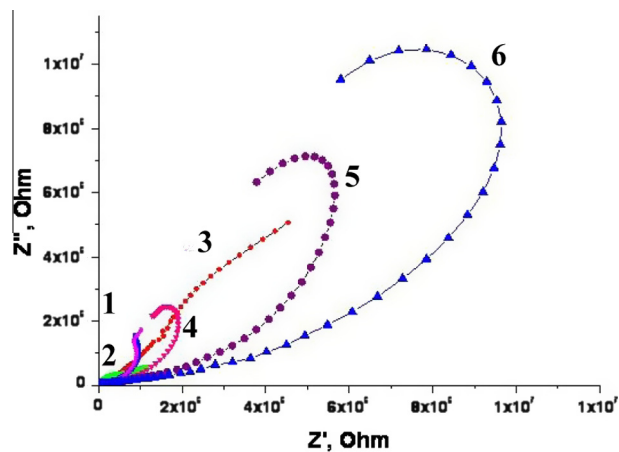


Fig. 4. Cole–Cole electric impedance plots obtained for the ceramic materials produced in the system of PPT/Fe with different $\text{MeTiO}_3/\text{K}(\text{Ti,Me})_8\text{O}_{16.5}$ ratio (increased contents of the hollandite-like crystalline phase, covers 1–6 accordingly, promote increased nonlinearity of the electric properties). Z' and Z'' – real and imaginary parts of complex impedance, respectively.

of the powders obtained in the dispersions containing the same quantity of Me-sulfate (10^{-3} mol/dm³) and the parent PPT powder is different (Table 1) and depends on pH value. Decreased pH promotes increased [Me] in the intercalated form and reduced [K], whereas the powders obtained at high pH values are characterized with a presence of Me almost only in the metal oxide/hydroxide form.

The powders produced at different pH values, even with a use of the same salt, have different structural features (Fig. 2). The product obtained at low pH is presented with PPT particles intercalated by Me ions. It is important that any part of these cations is restored to the atomic state and forms clusters in the flat channels of the PPT particles (Fig. 2a). The products obtained at intermediate pH values consist of platy PPT particles partially intercalated with

Me ions and decorated with $\text{Me}_x\text{O}_y/\text{Me}(\text{OH})_y$ nanoparticles (Fig. 2b), whereas the powders produced at high pH values can be considered as mixtures of separated PPT and $\text{Me}_x\text{O}_y/\text{Me}(\text{OH})_y$ particles (Fig. 2c). All of the products obtained as a result of such treatment are quasi-amorphous (Fig. 3).

The DSC results have shown that the powders produced by the treatment of PPT particles in the aqueous solutions of different transition metal salts lose adsorbed water in the range of 100–400 °C and crystallize at 600–820 °C. Typical XRD patterns of the products obtained after crystallization are reported in Fig. 3. It is possible to note that the powders obtained after the thermal treatment are characterized with a presence of several phases; however, there is a main crystalline phase, depending on the $\text{Me}_x\text{O}_y/\text{TiO}_2$ ratio and [K₂O] in the precursor material. In the ceramic materials based on the precursors produced at high pH, the crystalline structures are presented by different combinations of perovskite-like metal titanates (MeTiO_3) and hollandite-like crystals, which could be considered as $\text{K}(\text{Ti,Me})_8\text{O}_{16.5}$ solid solutions (ICDD card 47-0690). In the ceramics based on precursors which were produced at intermediate values of pH, the main crystalline phase is only presented by hollandite-like crystals $\text{K}(\text{Ti,Me})_8\text{O}_{16.5}$ (Me = Fe, Co, Ni, Cr and Cu), where Me atoms occupy some Ti positions. Whereas, the structure of ceramic materials, which were produced using the precursors produced at low pH, consists mainly of TiO_2 (anatase) crystals. However, all the ceramic materials obtained also contain relatively small inclusions of Me_xO_y and/or Me crystals. The contents of these inclusions as well as $\text{MeTiO}_3/\text{K}(\text{Ti,Me})_8\text{O}_{16.5}$ ratio depend on chemical composition of parent powders and can be regulated by conditions used in the precursor material synthesis.

The ceramics based on PPT/Me precursor materials is characterized with very interesting and anomalous behavior of the electric properties which strongly depend on the chemical composition and the structure of a precursor. The main interest is related to the ceramics based on heterostructured precursors produced at intermediate pH values. This group of materials was characterized with anomalous nonlinear electric properties. The impedance

spectra of such ceramic materials have shown that an exchange of the Me cation as well as regulation of $[\text{Me}_x\text{O}_y]$ and $[\text{K}_2\text{O}]$ in the precursor allowed obtaining the final ceramic materials with regulated nonlinearity of the electric properties depending the temperature of sintering (Fig. 4). The mechanism of this phenomenon has to be investigated carefully; however, it is clear that such character of the electric impedance could be applied in the design of nonlinear transducers used in different electric circuits.

4. Conclusions

The methodology to synthesize intercalated, heterostructured or mixed nanopowders based on amorphous potassium polytitanate modified by treatment in aqueous solutions containing the salts of transition metals (Ni, Co, Cu, Cr and Fe) was developed. It was recognized that the structure and chemical composition as well as morphology of the synthesized nanopowders could be regulated by pH values established in aqueous dispersions during the treatment.

It was shown that the heterostructured powders obtained at $\text{pH} = 5\text{--}7$ could be applied as precursors to produce functional ceramic materials characterized with nonlinear electric properties and consisted of MeTiO_3 , hollandite-like $\text{K}(\text{Ti,Me})_8\text{O}_{16.5}$ crystals and some admixtures of Me or Me_xO_y and TiO_2 or $\text{K}_2\text{Ti}_6\text{O}_{13}$, depending the chemical composition of parent powders.

Acknowledgments

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