PHYSICS AND CHEMISTRY OF SOLID STATE
V. 25, No. 3 (2024) pp. 540-545

Section: Chemistry

DOI: 10.15330/pcss.25.3.540-545

Vasyl Stefanyk Precarpathian National University

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 25, № 3 (2024) С. 540-545

Хімічні науки

UDC: 546.185

ISSN 1729-4428 (Print)
ISSN 2309-8589 (Online)

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Synthesis and Ionic Conductivity of Glass ceramics with General Composition $(2\text{-}x)Na_2O : xM^I{}_2O : 3CoO : 2P_2O_5$ (x = 0 or 0.05, M^I – Li, K)

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Glass ceramic samples with general composition: $(2\text{-}x)Na_2O : xM^I{}_2O : 3CoO : 2P_2O_5$ (x = 0 or 0.05, M^I – Li, K) were synthesized by melt method with subsequent annealing of homogeneous glass at a temperature of 650 °C. According to powder X-ray diffraction data, monophase phosphates with the general composition $Na_{4-x}M^I{}_xCo_3(PO_4)_2P_2O_7$ which belong to the orthorhombic system (space group *Pn2₁a*) were obtained. The calculated cell parameters of prepared phosphates correlate with the size of the substituted alkali metal atom. The FTIR spectroscopy data confirm the presence of two anion types (PO_4 and P_2O_7) in the structure of crystalline phosphates. The ionic conductivity properties of the synthesized samples were investigated using impedance spectroscopy method. Analisys of results showed an increase of specific conductivity at the partial substitution of sodium atoms (0.1 Na → 0.1 Li) in an initial structure $Na_4Co_3(PO_4)_2P_2O_7$. The obtained results can be in future used in the preparation of solid electrolytes for sodium-ion batteries based on substituted glass ceramics with the composition $Na_{4-x}M^I{}_xCo_3(PO_4)_2P_2O_7$ with improved ion-conducting characteristics.

Keywords: complex phosphates, glass ceramics, ion conductivity, FTIR spectroscopy.

Received 19 January 2024; Accepted 25 August 2024.

Introduction

Complex phosphates of alkali metal and bi- or three valent metals have attracted much attention in Na-ion batteries, because of their structural and thermal stability. For example, cathodes based on orthophosphates ($NaM^{II}PO_4$, M^{II} – Fe, Co, Mn [1-5] and $Na_3V_2(PO_4)_3$ [6-7]), pyrophosphates $Na_xMP_2O_7$ (M - V, Fe, Mn, Co, Ni [8-9]) and mixed anionic compounds $Na_4M_3(PO_4)_2P_2O_7$ (M – Fe, Mn, Co, Ni) [10-12], as well as solid electrolytes of different composition [13-16] are perspective materials.

Known mixed anionic $Na_4M_3(PO_4)_2P_2O_7$ phosphates are isostructural and belong to orthorhombic system (space group $Pn2_1a$). Their 3D-frameworks composed of $[M_3P_2O_{13}]_n$ layers built up from edge- and corner-shared MO_6-octahedra and PO_4-tetrahedra [17-18]. The $[M_3P_2O_{13}]_n$ layers are interconnected by diphosphate P_2O_7 groups along *a*-direction. As result the extensive tunnel network creates (along crystallographic directions [100], [010] and [001]) where Na atoms located [17-18]. The results in [19] showed that Na ions tend to diffuse across 3D migration pathways with a low activation barrier of 0.20 - 0.24 eV. Simulation of the process of sodium removal from the $Na_4Co_3(PO_4)_2(P_2O_7)$ structure (battery charging) showed the sequence of sodium extraction from different positions of Na2, Na1 and Na4, which is accompanied by the oxidation of Co^{2+} to Co^{3+} (one third for each Na atom) and the formation of phases $Na_3Co_3(PO_4)_2(P_2O_7)$ and $Na_2Co_3(PO_4)_2(P_2O_7)$ [11]. The sol-gel [20-23] and solid state [24-29] methods are the most commonly used synthesis techniques for preparation of mixed anionic phosphates $Na_4M_3(PO_4)_2P_2O_7$. The obtained results indicate the influence of the synthesis method on the properties of the obtained material [20-29].

The aim of this work was to study the effect of partial substitution of sodium atoms for bigger or smaller potassium or lithium atoms for system with the general composition $(2\text{-}x)Na_2O : xM^I{}_2O : 3CoO : 2P_2O_5$ (x = 0 or 0.05, M^I – Li, K) on formation of phases and ion-conducting properties of glass-ceramic.

I. Materials and methods

The melt synthesis method was used for preparation of glass ceramic with the general composition: (2-*x*)Na_2O : *x*$M^I{}_2O$: 3CoO : $2P_2O_5$ (*x* = 0 or 0.05, M^I – Li, K). The method of the experiment provided for obtaining melts with the necessary ratio of elements and further annealing homogeneous systems for crystallization of phosphates. Thoroughly ground initial components: $NaPO_3$, CoO, Li_2CO_3 and K_2CO_3 (all were an analytical grade) were melted at a temperature of 1000°C for 2 hours for homogenization. The resulting melts were quickly cooled by pouring them onto a copper sheet. The obtained glasses were heated to 650 °C for 2 hours and kept in isothermal conditions for 2 hours. As result the glass ceramics with different elemental compositions were obtained. The phase composition of the obtained samples was determined using the powder X-ray diffraction method. The patterns were recorded using a Shimadzu XRD-6000 powder diffractometer (graphite monochromator; 2θ method of continuous scanning at a speed of 1°/min; 2θ = 5.0 - 70.0°). The anionic composition of the samples was confirmed using the FTIR spectroscopy method. Infrared spectra were recorded using a PerkinElmer Spectrum BX spectrometer for samples pressed into tablets with KBr in the range of 400 - 4000 cm^{-1}.

Investigation of electro-physical characteristics of synthesized glass ceramic samples was carried out by the impedance spectroscopy method [30-32]. Samples for measurement were prepared in the form of cylindrical tablets (Ø = 11 mm and h = 1.7 - 2 mm) by cold pressing of thoroughly ground powder. Electrical contact of the samples with the measuring circuit was carried out using platinum electrodes with a diameter of 8 mm. The characteristics were investigated at temperature range from 25 °C to 530 °C and the frequency interval ν = 1 - 107 Hz. The electrical impedance module |Z| and the shift angle φ between the sinusoidal probing voltage (amplitude 50 mV) and the current in the circuit were experimentally determined. These data were used for calculation of values of the real (Z'(ν)) and imaginary (Z''(ν)) impedance components as well as real component of electrical conductivity (σ'(ν)), dielectric permittivity (ε'(ν)), imaginary component of dielectric modulus (M''(ν)) using the formula given in [32].

II. Experimental results

XRD patterns of prepared glass ceramics are showed in Fig. 1. According to powder X-ray diffraction data for sample with initial composition $2Na_2O$: 3CoO : $2P_2O_5$ the crystalline phosphate $Na_4Co_3(PO_4)_2P_2O_7$ (PDF2 # 01-089-0579), that belongs to orthorhombic system (space group *Pn*2_1*a*) was obtained (Fig. 1,a). General view of patterns for samples with composition 1.95Na_2O:
0.05$M^I{}_2O$: 3CoO : $2P_2O_5$ (M^I – Li, K) in respect of positions and intensity of reflexes is similar to corresponding for $Na_4Co_3(PO_4)_2P_2O_7$ and is absent of impurity phases (Fig. 1,b, c). These facts indicate the partial substitution of sodium atoms and formation of single phasic phosphates $Na_{4-x}M^I{}_xCo_3(PO_4)_2P_2O_7$ (M^I – Li, K). The calculated cell parameters for prepared $Na_4Co_3(PO_4)_2P_2O_7$ (*a* = 18.046(8)Å, *b* = 6.519(6) Å, *c* = 10.516(8) Å) are close to corresponding data reported in [10], while insignificant change for Li - (*a*= 18.043(4)Å, *b* = 6.512(6) Å, *c* = 10.508(7) Å) and K - (*a* = 18.081(4) Å, *b* = 6.523(1) Å, *c* = 10.517(3) Å) containing phosphates additional confirmed the realization of partial substitution (0.1Na → 0.1M^I) in an initial structure $Na_4Co_3(PO_4)_2P_2O_7$.

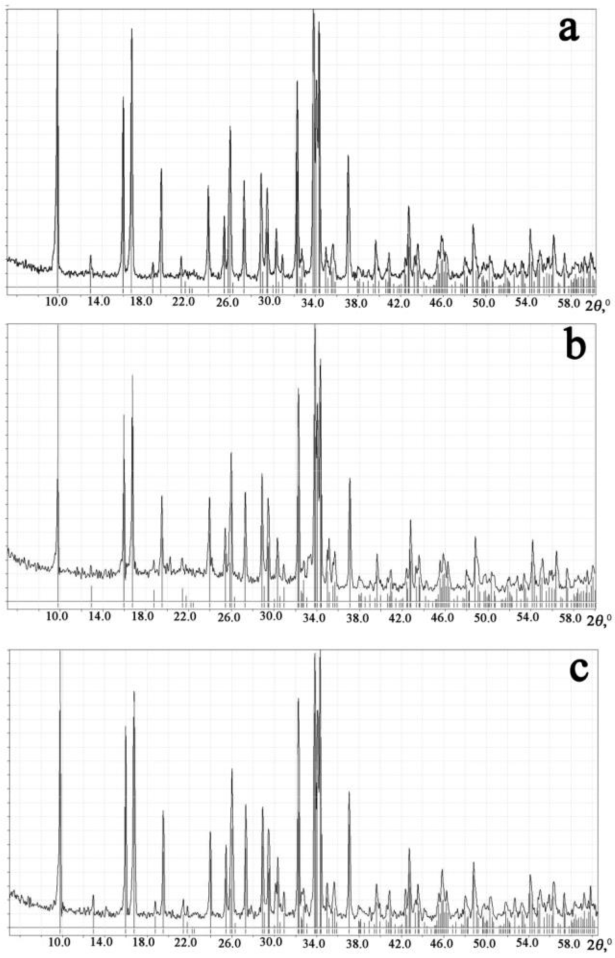

Fig. 1. XRD patterns of glass ceramics with general composition (2-*x*)Na_2O : *x*$M^I{}_2O$: 3CoO : $2P_2O_5$, *x* = 0 (*a*) or 0.05, M^I – Li (*b*) and K (*c*) annealed at temperature 650°C. Indexing was done with respect to data for $Na_4Co_3(PO_4)_2P_2O_7$ (PDF2 # 01-089-0579).

FTIR spectra for synthesized glass ceramics consist of the characteristic isolated PO_4 and P_2O_7 bands (Fig. 2). Vibrations of PO_4 group include symmetric and asymmetric stretching ν(P-O) and bending δ(O-P-O) modes. Vibrations of P_2O_7 are assembly of vibrations of PO_3 group and P-O-P bridges. The overlap of certain modes complicates the precise interpretation of spectra for synthesized samples (Fig. 2). The frequency range of 990 - 1200 cm^{-1} includes asymmetric stretching vibration ν(P-O) in PO_3 and PO_4-groups, while corresponding symmetric stretching vibrations contribute to the 890 -

990 cm^{-1} region. The bands, in the lowest frequency range of 500 - 680 cm^{-1} have been assigned to the bending O-P-O vibrational modes (δ(O-P-O)). Mode at 732 cm^{-1} belonging to symmetric bringes (P-O-P) bonds in P_2O_7.

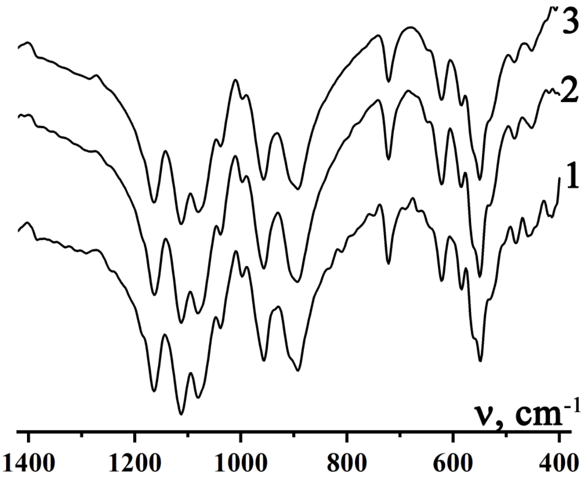

Fig. 2. FTIR-spectra for prepared glass ceramics in the system with general composition (2-*x*)Na_2O : *x*$M^I{}_2O$: 3CoO : $2P_2O_5$, *x* = 0 (curve 1) or 0.05; M^I – Li (curve 2) and K (curve 3)).

Fig. 3,a shows a typical impedance dependence of the imaginary component Z"(ν) on the real component Z'(ν) (Nyquist curve) for a glass-ceramic with the composition $Na_4Co_3(PO_4)_2P_2O_7$. Three sections which describe the characteristics of sample can be distinguished on the curve. The low-frequency region (1 - 10 Hz) corresponds to the processes on the contact between the electrode and sample surface. The significant slope of the curve in this region is explained by the strong blocking effect of the platinum electrode on transport ions. The character of the curve in the area of intermediate frequencies describes a strongly deformed semicircle and is associated with strongly disordered regions at the point of microcrystallites contact. The high-frequency part of the curve in the form of a small semicircle describes the processes in the volume of microcrystallites. A detailed analysis of this section was carried out to describe the electrophysical properties of the materials without taken into account the influence of electrode and intercrystalline effects. The intersection of the curve with the ordinate axis (the axis of the active impedance component) coincides with the active electrical resistance of glass-ceramic with the composition $Na_4Co_3(PO_4)_2P_2O_7$, which is equal to $8.85 \cdot 10^5$ Om.

The analysis of the frequency dependences of the impedance imaginary components and dielectric modulus (Fig. 3,b) and the real components of electrical conductivity and dielectric constant (Fig. 3,c) showed an increase of the of the imaginary impedance values Z"exp(ν) and a significant slope of the frequency dependence of the dielectric permittivity ε'(ν) (Fig. 3,c) at frequencies lower than 5 Hz. Such character of curves is associated with the polarization of the electrode. The maximum at 100 Hz on frequency dependence of the impedance imaginary components corresponds to the processes on the boundaries between the microcrystallites of the sample. This frequency value corresponds to the maximum on the large semicircle shown in Fig. 3,a. In the frequency range from $2 \cdot 10^4$ Hz to 10^5 Hz, a bend with a maximum of $3.6 \cdot 10^4$ Hz (Fig. 3,b) is observed, which coincides with the maxima of the small semicircle on the Nyquist curve (Fig. 3,a) and is caused by the own characteristics of microcrystalline component of the

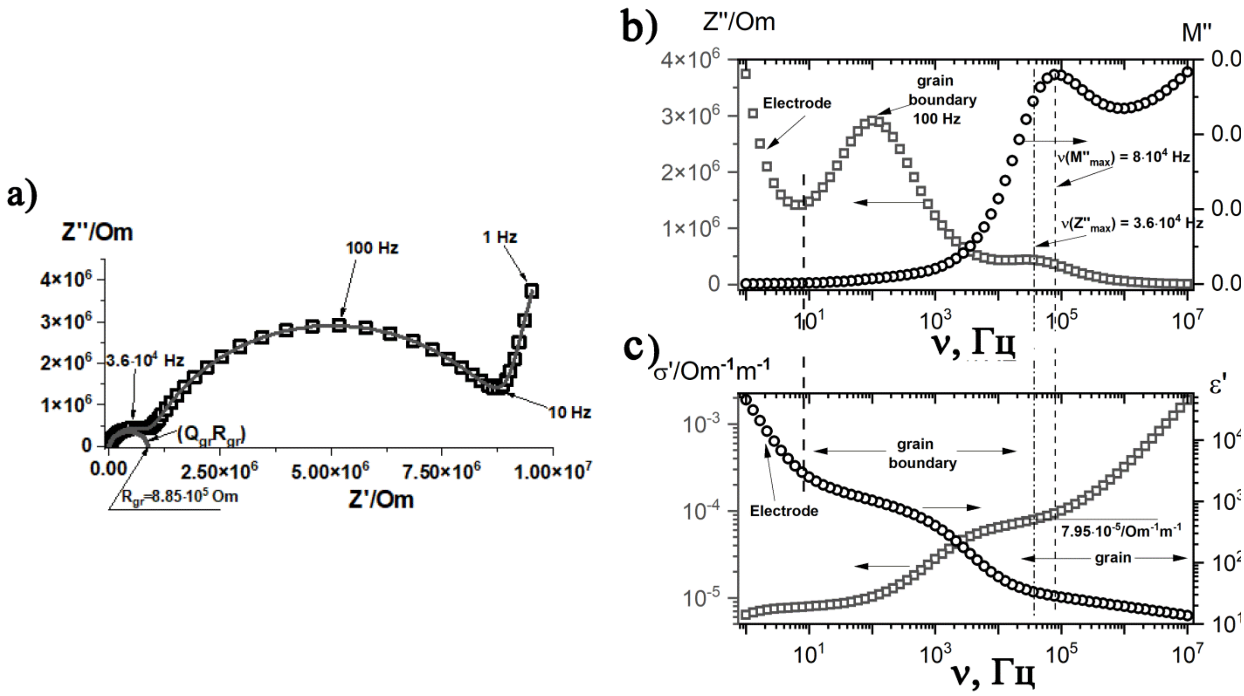

Fig. 3. Complex impedance (Nyquist curve) at a temperature of 230°C – (a), frequency dependences (Bode curves) of imaginary components of impedance Z"(ν) and dielectric modulus M"(ν) – (b), real components of electrical conductivity σ '(ν) and dielectric constant ε'(ν) – (c) for a glass ceramic with composition $Na_4Co_3(PO_4)_2P_2O_7$.

sample.

On the curve of the frequency dependence of imaginary component of the dielectric modulus M"(ν) in the region of high frequencies, a maximum at $8\cdot10^4$ Hz is directly related with electrical processes in the volume of the microcrystalline structure. This result allows to determine of the specific electrical conductivities of prepared materials using the values of active resistances R_{gr}. It was established that for a glass ceramic with composition $Na_4Co_3(PO_4)_2P_2O_7$ at a temperature of 230 °C, the specific electrical conductivity σ_{dc} equal to $6.9\cdot10^{-5}$ $Om^{-1}m^{-1}$.

A similar analysis was carried out for glass ceramics with composition 1.95Na_2O : 0.05M^I_2O : 3CoO : 2P_2O_5, M^I – Li and K and the values of specific electrical conductivities in the temperature range from 25°C to 530 °C were calculated. The obtained results are shown in Fig. 4 in Arrhenius coordinates. The analysis of the obtained results showed that the partial substitution of sodium atoms by smaller lithium atoms leads to an increase of the specific conductivity (Fig. 4, curve 2) for a glass ceramic with the composition 1.95 Na_2O : 0.05Li^I_2O : 3CoO : 2P_2O_5, while the addition of potassium cations reduces the ionic conductivity (Fig. 4, curve 3).

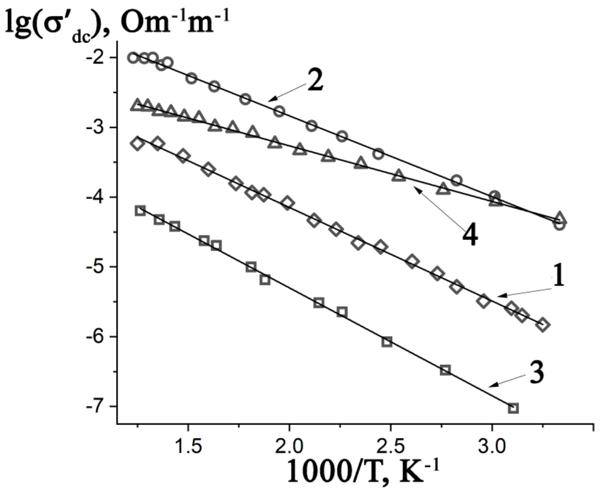

Fig. 4. Arrhenius plot of conductivity for prepared glass ceramic with the initial composition (2-*x*)Na_2O : *x*M^I_2O : 3CoO : 2P_2O_5, *x* = 0 (curve 1) or 0.05 for M^I – Li (curves 2 and 4) and K (curve 3) annealed at temperature of 650°C (curves 1-3) and initial samples (curve 4).

It was found that for a glass ceramic with a general composition $Na_{4-x}M^I_xCo_3(PO_4)_2P_2O_7$ (M^I – Li, K) at a temperature of 230°C, the specific electrical conductivity σ_{dc} equals to $1.5\cdot10^{-3}$ $Om^{-1}m^{-1}$ – for Li and $5.1.\cdot10^{-6}$ $Om^{-1}m^{-1}$ – for K-containing sample.

A comparison of the characteristics for Li-containing sample obtained after homogenization of the initial components at a temperature of 1000 °C with further its freezing and the corresponding sample annealed at 650 °C, that according to XRD result is single phase $Na_{3.9}Li_{0.1}Co_3(PO_4)_2P_2O_7$, showed that the annealing sample at 650°C contributes to its crystallization with an increase of the specific conductivity of the material to $1.5\cdot10^{-3}$ $Om^{-1}m^{-1}$, comparing with initial sample ($\sigma_{dc} = 5.5\cdot10^{-4}$ $Om^{-1}m^{-1}$ (Fig. 4, curves 2 and 4).

The activation energy (E_a) values of the specific electrical conductivity for the synthesized glass ceramics were calculated using the temperature dependence of the specific electrical conductivity (Fig. 4). It was established that the partial substitution of sodium atoms by lithium atoms almost did not effect on the value of E_a ($Na_4Co_3(PO_4)_2P_2O_7$ – 0.28eB, $Na_{3.9}Li_{0.1}Co_3(PO_4)_2P_2O_7$ – 0.27 eV), while substitution by potassium atoms leads to an increase in E_a to 0.31 eV for $Na_{3.9}K_{0.1}Co_3(PO_4)_2P_2O_7$. It should be noted that the value of the activation energy for the lithium-containing sample obtained after initial components homogenization at a temperature of 1000 °C and with further its freezing is 0.16 eV, which is slightly lower than for the corresponding sample annealed at 650 °C. Thus, results indicate that annealing of glass ceramic allows to obtain the materials with higher specific conductivity.

Conclusions

Glass ceramics with general composition (2-*x*)Na_2O : *x*M^I_2O : 3CoO : 2P_2O_5 (*x* = 0 or 0.05, M^I – Li and K) were obtained by melt synthesis method. Further annealing of homogeneous systems at a temperature of 650 °C led to the crystallization of monophase phosphates with composition $Na_{4-x}M^I_xCo_3(PO_4)_2P_2O_7$ belonging to the orthorhombic system (space group *Pn*2$_1$*a*). The calculated cell parameters for obtained phosphates indicate the partial substitution of sodium atoms by potassium or lithium atoms. The presence of PO_4 and P_2O_7 anion types was confirmed by FTIR spectroscopy. It is shown that the introduction of lithium atoms into the composition of glass-ceramics contributes to an increase in specific conductivity without a significant effect on the value of the activation energy.

Aknowledgements

The authors thank the Ministry of Education and Science of Ukraine for financial support (project 0122U001959).

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Синтез та іонна провідність склокерамік загального складу (2-*x*)Na_2O : *x*$M^I{}_2O$: 3CoO : 2P_2O_5 (*x* = 0 чи 0.05, M^I – Li, K)

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Склокерамічні зразки загального складу (2-*x*) Na_2O : *x*$M^I{}_2O$: 3CoO : 2P_2O_5 (*x* = 0 чи 0,.05, M^I – Li, K) синтезовані методом розплавного синтезу з подальшим відпалом гомогенного скла при температурі 650 °C. Згідно даних порошкової рентгенографії одержано монофазні фосфати загального складу $Na_{4-x}M^I{}_xCo_3(PO_4)_2P_2O_7$, що належать до орторомбічної сингонії (пр. гр. *Pn*2_1*a*), а розраховані параметри їх комірок корелюють із розмірами заміщуючого атому лужного металу. Результати ІЧ-спектроскопії підтверджують присутність двох типів аніонів (PO_4 та P_2O_7) у складі кристалічних фосфатів. Дослідження іонної провідності синтезованих зразків методом імпедансної спектроскопії виявило підвищення питомої провідності при частковому заміщенні атомів натрію (0,1 Na → 0,1 Li) у вихідній структурі $Na_4Co_3(PO_4)_2P_2O_7$. Одержані результати в подальшому можуть бути використані при одержанні твердих електролітів для натрій-іонних батарей на основі заміщених склокерамік складу $Na_{4-x}M^I{}_xCo_3(PO_4)_2P_2O_7$ з покращеними іонпровідними характеристиками.

Ключові слова: складні фосфати, склокераміка, іонна провідність, ІЧ-спектроскопія.