Electrical properties of new organo-inorganic layered perovskites

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This paper deals with the synthesis of new halide complexes with the general formula $(choline)_2[Cu_y M_{1-y}X_4]$ (where $choline^+$- is quaternary ammonium ion of 2-amino-1-ethanol, $[(CH_3)_3N^+-(CH_2)_2-OH]$ and M = Sn; y= 0; 0.25; 0.50; X=Cl or I; M = Pb; y= 0; 0.25; 0.50; 0.75; X=I), $(choline)_2[Fe_yPb_{1-y}X_4]$ (y=0; 0.25; 0.50; X=Cl or y=0.50; X=I) and $(choline)_2[Cu_{0,50}Fe_{0,25}Pb_{0,25}I_4]$, having layered perovskite-like structure. The synthesized series of halide complexes have been characterized by elemental, spectral and thermal analysis, X-ray diffraction and electric conductivity measurements.

1. Introduction

A great variety of crystalline systems of perovskite type such as simple, double or triple pure and doped oxides are well characterized today (Fig. 1).

Crystalline organo-inorganic complex halides with layered perovskite-like structure represent one of the most studied hybrid materials in which the integration of both specific properties of organic and inorganic components is allowed at molecular scale.

The interest in synthesis and exhausted characterization of these hybrid materials is both theoretical and practical, this type of materials presenting many applications in various technologies in optoelectronic field such as: computerized optics, optic communications, dynamic image processing optic information and so on [1].

Organo-inorganic layered perovskites are formed by inorganic halides of a divalent metal (Cu, Ni, Co, Fe, Mn, Pd, Cd, Ge, Sn, Pb, Eu or Yb) intercalated with various organic cations like: monoammonium cations $(R - NH_3^+)$ as double layer, diammonium cations $(H_3N - R - NH_3^{2+})$ as single layer or two monoamonium cations $(R - NH_3^+)$ and A^+ (small organic or inorganic cation). Organo-inorganic hybrids with perovskite-like structure can be differently represented based on orientation type, organic and inorganic compounds and small organic or inorganic cation (Fig. 2).
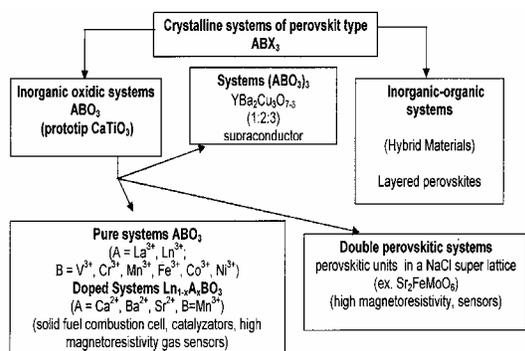

Fig. 1. Crystalline systems of perovskite type.

The inorganic halides layers are "perovskite" layers because they derive from three-dimensional perovskite structure AMX_3 by replacing a layer along a crystalline direction (< 100 > or < 110 >) from three-dimensional lattice.
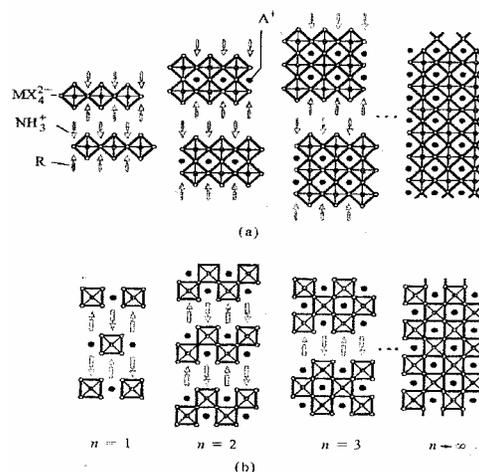
Fig. 2. Schematic representation of two layer perovskite families: (a) $[(R-NH_3)_2A_{n-1}]$ < 100 > oriented; (b) $[(R-NH_3)_2A_{n-1}M_nX_{3n+2}]$ < 110 > oriented, where n defines the thickness of the perovskite sheets (when n=∞ a tridimensional structure of ABX_3 perovskite is obtained) [2, 3].

The great stability of the layered perovskite hybrids and their tendency of auto-assembling in solid, liquid and vapor phases are consequences of specific chemical interactions between their components:

- covalent/ ionic bonds – which determine the formation of metal-halide corner-shared octahedral planes

- hydrogen/ionic bonds –between organic cations and inorganic lattice halides

- different weaker interactions (Van der Waals, π-π and so on) between organic R groups.

The nature of bonding between organic and inorganic components of hybrid perovskite structure suggests that inorganic scaffold could play an important role in organic component spatial structure and conformation. The organic cations could also have an important influence upon inorganic scaffold. There are some examples of organo-inorganic hybrid systems in which one component controls the structure and properties of the other component determines the hybrid material structural characteristics [4-7].

Considering the advantages of the layered organo-inorganic hybrid perovskites materials, as thermal stability, high electronic mobility and their various electrical properties (insulators, semiconductors), these types of materials could be used for optoelectronic devices fabrication and also as semiconducting channels in thin film field-effect transistors (TETs) fabrication [8].

This paper deals with the synthesis and characterization by elemental, spectral and thermal analysis, X-ray diffraction and electric conductivity measurements, a number of some layered perovskites obtained in the systems composed of divalent metal halides - choline halides – hydrogen halides.

2. Experimental part

In well-determined experimental conditions varying several parameters, like molar ratio of reactants, temperature (0^0C or room temperature), pH of reaction (HCl or HI) and inert atmosphere (Ar), have been synthesized a number of 20 metal complex halides of choline$^+$ X$^-$ (where choline$^+$- is quaternary ammonium ion of 2-amino-1-ethanol, $[(CH_3)_3N^+-(CH_2)_2-OH]$; X$^-$ - Cl,I) (Table 1).

Table 1. The studied systems and isolated compounds.

No.	Studied systems	Isolated compounds
1	$(1-y)MCl_2 – yCuCl_2 – HCl –$ choline chloride (M = Sn, Pb; y = 0,00; 0,25; 0,50)	1. $(choline)_2[SnCl_4]$ 2. $(choline)_2[PbCl_4]$ 3. $(choline)_2[Cu_{0,25}Sn_{0,75}Cl_4]$ 4. $(choline)_2[Cu_{0,50}Sn_{0,50}Cl_4]$ 5. $(choline)_2[Cu_{0,25}Pb_{0,75}Cl_4]$ 6. $(choline)_2[Cu_{0,50}Pb_{0,50}Cl_4]$
2	$(1-y)MI_2 – yCuI_2 – HI –$ choline iodide (M = Sn, Pb; y = 0,00; 0,25; 0,50; 0,75; 1,00)	7. $(choline)_2[CuI_4]$ 8. $(choline)_2[SnI_4]$ 9. $(choline)_2[PbI_4]$ 10. $(choline)_2[Cu_{0,25}Sn_{0,75}I_4]$ 11. $(choline)_2[Cu_{0,50}Sn_{0,50}I_4]$ 12. $(choline)_2[Cu_{0,75}Sn_{0,25}I_4]$ 13. $(choline)_2[Cu_{0,25}Pb_{0,75}I_4]$ 14. $(choline)_2[Cu_{0,50}Pb_{0,50}I_4]$ 15. $(choline)_2[Cu_{0,75}Pb_{0,25}I_4]$
3	$(1-y)PbCl_2 – yFeCl_2 – HCl –$ choline chloride (y = 0,25; 0,50; 1,00)	16. $(choline)_2[FeCl_4]$ 17. $(choline)_2[Fe_{0,25}Pb_{0,75}Cl_4]$ 18. $(choline)_2[Fe_{0,50}Pb_{0,50}Cl_4]$
4	$(1-2y)CuI_2 – yPbI_2 – yFeI_2 – HI –$ choline iodide (y = 0,25; 0,50)	19. $(choline)_2[Fe_{0,50}Pb_{0,50}I_4]$ 20. $(choline)_2[Cu_{0,50}Fe_{0,25}Pb_{0,25}I_4]$

Synthesis of complex halides

Complex chlorides, (choline)$_2$[Cu$_y$ M$_{1-y}$Cl$_4$] (choline$^+$-[(CH$_3$)$_3$N$^+$-(CH$_2$)$_2$-OH] ,M = Sn or Pb, y= 0; 0.25; 0.50) and *(choline)$_2$[Fe$_y$Pb$_{1-y}$ Cl$_4$] (y=0; 0.25;0.50)* have been synthesized in the reaction of the mixture CuCl$_2$/FeCl$_2$ and SnCl$_2$/PbCl$_2$ (molar ratio y:(1-y) where y = 0,00; 0,25; 0,50; 1,00) in conc. HCl with choline chloride, [HO–(CH$_2$)$_2$–(CH$_3$)$_3$N$^+$]Cl$^-$, (molar ratio Sn(II)/ Pb(II):choline =

1:4) in inert atmosphere. After one hour heating at 80^0C reaction mixtures have been cooled at 0^0C on ice bath. After 30 days, the obtained crystals were filtered out, washed with small amounts of water, ethylic alcohol and ethylic ether and dried over P$_4$O$_{10}$. The colors of the crystals were white for y = 0.00, yellow for y = 0.25; 0.50 and reddish-yellow for y = 1.00.

Complex iodides (choline)$_2$[Cu$_y$ M$_{1-y}$I$_4$] (choline$^+$-[(CH$_3$)$_3$N$^+$-(CH$_2$)$_2$-OH], M = Sn; y= 0; 0.25; 0.50; M =

Pb; y= 0; 0.25; 0.50; 0.75) and *(choline)$_2$[Fe$_{0.50}$Pb$_{0.50}$I$_4$]* have been synthesized in the reaction of the mixture CuSO$_4$•5H$_2$O/FeSO$_4$•7H$_2$O, SnCl$_2$•2H$_2$O/Pb(NO$_3$) (molar ratio y:(1-y) where y = 0,00; 0,25; 0,50; 0,75; 1,00) and KI (Sn(II)/Pb(II):K(I) = 1:4) in conc. HI with choline iodide, [HO–(CH$_2$)$_2$–(CH$_3$)$_3$N$^+$]I$^-$, (molar ration Sn(II)/Pb(II):choline = 1:4) in inert atmosphere. The obtained precipitated were filtered out and washed with large amounts of water and ethylic alcohol and dried and kept in vacuum desiccator. The colors of the powders were white, yellow, reddish, brown and grey.

Elemental analysis were performed by atomic absorption with a double beam Varian SpectraA240 FS spectrophotometer for Cu, Sn, Pb, detection using EA 1110, for elemental analysis of carbon and nitrogen, software EAGER 200 S/W. Iron was determined colorimetric and chlorine and iodine – gravimetrical

Electronic reflectance spectra were measured on room temperature using UV-VIS Jasco V560 spectrophotometer with MgO as the standard.

Infrared spectra have been recorded with Perkin-Elmer spectrophotometer with MgO as the standard.

Thermal analysis has been recorded with in air at 25-800ºC temperatures on Paulik-Paulik-Erdey apparatus with Al$_2$O$_3$ as the standard.

X-ray diffraction patterns have been recorded with Bruker AXS D8 ADVANCE type diffractometer.

Electric conductivity measurements *were performed as plates using four-point method in 25-400^{0}C temperature range.*

3. Results and discussion

The *electronic reflectance spectra* of the synthesized halide complexes have been recorded to establish metallic ions stereochemistry (Fig.4). The bands from UV range (≈ 270 nm) in all complexes spectra could be assigned to a metal-halide charge transfer transition.

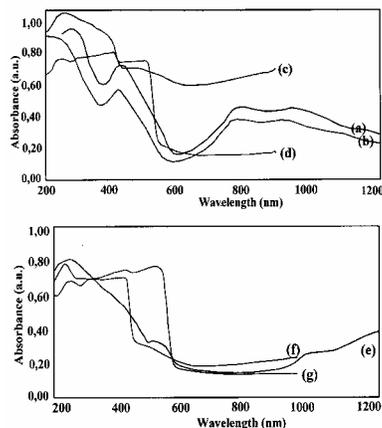Fig. 4. Electronic reflectance spectra of (a) (choline)$_2$[Cu$_{0.25}$Sn$_{0.75}$Cl$_4$]; (b) (choline)$_2$ [Cu$_{0.25}$Pb$_{0.75}$Cl$_4$]; (c) (choline)$_2$[Cu$_{0.25}$Sn$_{0.75}$ I$_4$]; (d) (choline)$_2$[Cu$_{0.25}$Pb$_{0.75}$ I$_4$]; (e) (choline)$_2$[Fe$_{0.5}$Pb$_{0.5}$ Cl$_4$]; (f) (choline)$_2$[Fe$_{0.5}$Pb$_{0.5}$I$_4$]; (g) (choline)$_2$[Cu$_{0.5}$Fe$_{0.25}$ Pb$_{0.25}$I$_4$].

The bands from visible domain presented in the complexes spectra are *d-d* bands corresponding to strongly tetragonal distorted octahedral configuration (D$_{4h}$ symmetry) [5]. In the spectra of iodide complexes, the characteristic metal-halide charge transfer bands are placed at higher wavelength in comparison with charge transfer bands from the spectra of complex chlorides due to the different position of halogen in electronegativity series (lower iodine electronegativity in comparison with chlorine) [9].

The *IR spectra* of all complex halides showed that the general structure of free choline is preserved in complexes. The characteristic frequencies of choline (frequencies of aliphatic ternary amine, primary alcohols, ethyl group) were found unchanged in the IR spectra of perovskite like complex halides. The lower intensity of these characteristic frequencies or their small shifts in infrared spectra of complex halides could be a result of organic layer shrinking in the presence of bulky complex halide anions. It can be concluded that choline salt is placed as monolayer between inorganic halide layers and the prepared compounds have small size due to choline small size.
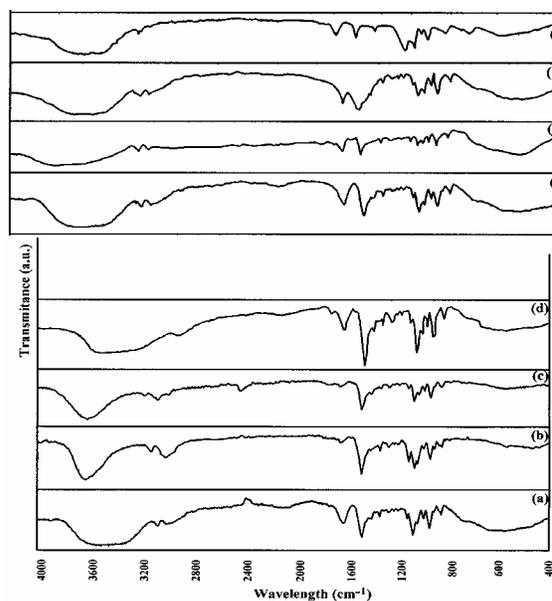
Fig. 5. IR Spectra of (a) choline chloride; (b) (choline)$_2$[Cu$_{0.5}$Sn$_{0.5}$Cl$_4$]; (c) (choline)$_2$[Cu$_{0.5}$ Pb$_{0.5}$Cl$_4$]; (d) (choline)$_2$[Fe$_{0.5}$ Pb$_{0.5}$Cl$_4$]; (f) choline iodide; (g) (choline)$_2$[SnI$_4$]; (h) (choline)$_2$[Cu$_{0.5}$Pb$_{0.75}$ I$_4$]; (i) (choline)$_2$[Cu$_{0.5}$Fe$_{0.25}$ Pb$_{0.75}$ I$_4$].

The study of thermogravimetric behavior of the synthesized compounds (Fig. 5.) showed that due to the presence of organic cation the thermal decomposition begins at relatively low temperature.
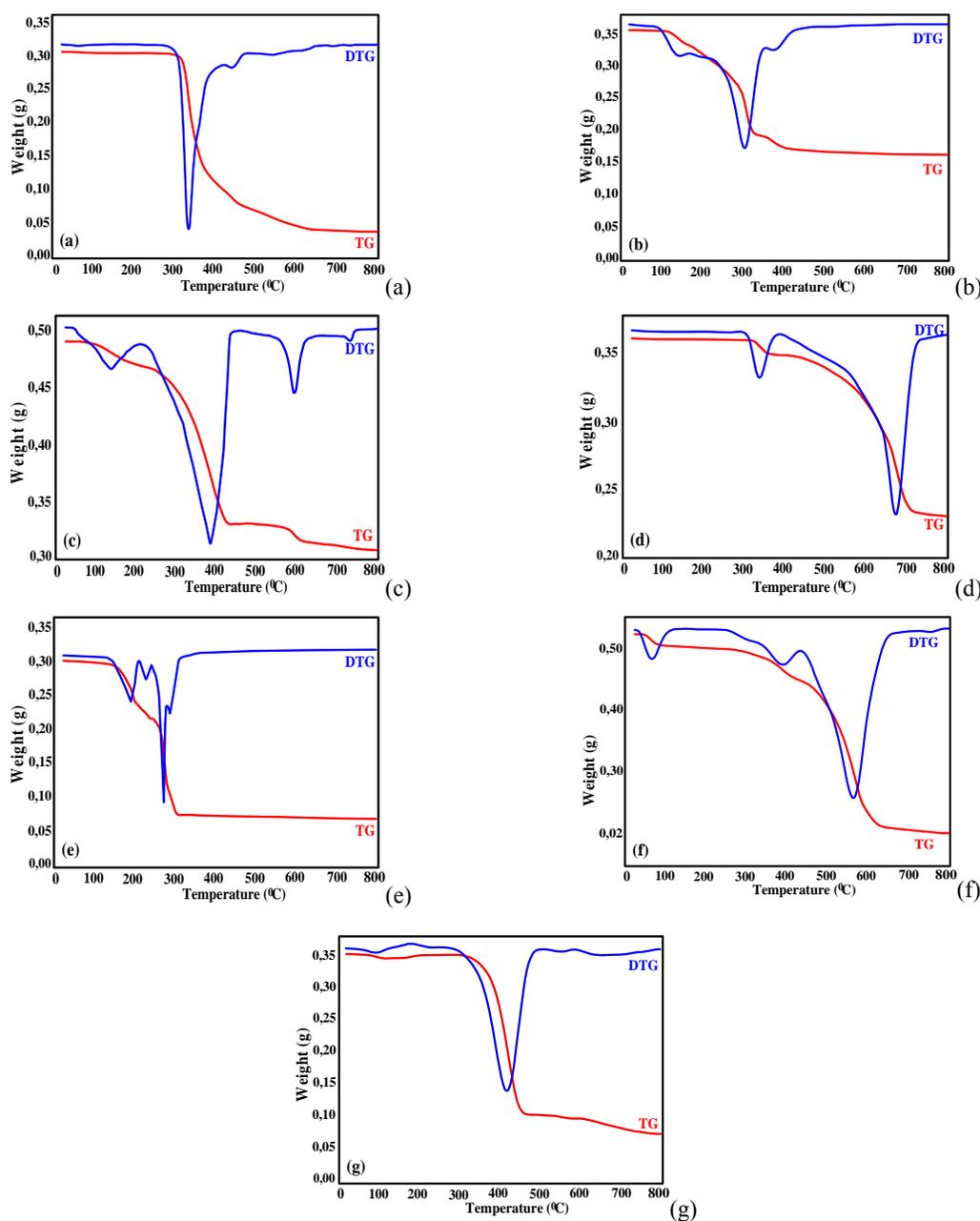
Fig. 6. The thermogravimetric data for compounds:
(choline)$_2$[Cu$_{0,50}$Sn$_{0,50}$Cl$_4$] (a), (choline)$_2$[Cu$_{0,25}$Pb$_{0,75}$Cl$_4$] (b), (choline)$_2$[Cu$_{0,50}$Sn$_{0,50}$I$_4$] (c); (choline)$_2$[Cu$_{0,25}$Pb$_{0,75}$I$_4$] (d),
(choline)$_2$[Fe$_{0,25}$Pb$_{0,75}$Cl$_4$] (e), (choline)$_2$[Fe$_{0,50}$Pb$_{0,50}$I$_4$] (f), (choline)$_2$[Cu$_{0,50}$Fe$_{0,25}$Pb$_{0,25}$I$_4$] (g).

Some of compounds present an endothermic effect around 80-150 ^{0}C, most probably due to order-disorder transition of the choline cation from organic layer. Choline decomposition and oxidation occur between 300 ^{0}C and 400 ^{0}C, followed by the decomposition and oxidation of inorganic anions at temperature over 400 ^{0}C and the metallic oxide lattices formation at temperatures between 550 ^{0}C and 650 ^{0}C. The weight loss for all halide complexes occurs between 250 and 650 ^{0}C and

corresponds to total decomposition of these. It can be observed that the total decomposition of chloride complexes appear at lower temperatures (350-400 ^{0}C) than that of iodide complexes (550 – 650 ^{0}C).

Fig. 7. presents the *XRD patterns* which prove that all synthesized complex halides present unique orthorhombic perovskite phase of K$_2$NiF$_4$.

The unit cell volumes of the complex compounds containing iodine are higher than unit cell volumes of

similar complex compounds containing chlorine (Table 2.). The unit cell volumes of Cu, Sn, and Pb iodides varies in the following order: $V(choline)_2[CuI_4]$ < $V(choline)_2[SnI_4]$ < $V(choline)_2[PbI_4]$.
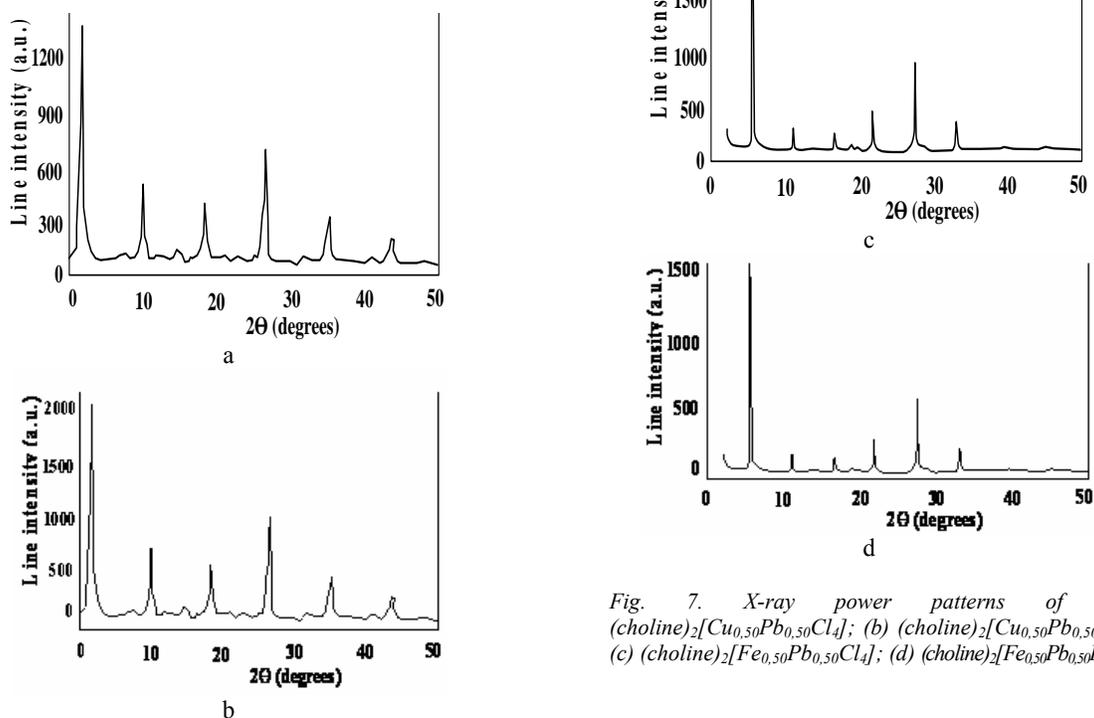
Fig. 7. X-ray power patterns of (a) $(choline)_2[Cu_{0.50}Pb_{0.50}Cl_4]$; (b) $(choline)_2[Cu_{0.50}Pb_{0.50}I_4]$; (c) $(choline)_2[Fe_{0.50}Pb_{0.50}Cl_4]$; (d) $(choline)_2[Fe_{0.50}Pb_{0.50}I_4]$.

Table 2. The parameters and unit cell volumes.

Isolated compound	Cell parameters (Å)			Cell volume (Å^3)
	a	b	c	
$(choline)_2[SnCl_4]$	3,882	3,896	12,953	195,91
$(choline)_2 [PbCl_4]$	4,002	3,994	13,018	208,08
$(choline)_2 [Cu_{0.25}Sn_{0.75}Cl_4]$	3,873	3,876	12,948	194,37
$(choline)_2[Cu_{0.50}Sn_{0.50}Cl_4]$	3,861	3,868	12,937	193,21
$(chline)_2[Cu_{0.25}Pb_{0.75}Cl_4]$	3,984	3,973	12,992	205,64
$(choline)_2[Cu_{0.50}Pb_{0.50}Cl_4]$	3,979	3,966	12,984	204,90
$(choline)_2[CuI_4]$	4,005	4,009	13,100	210,33
$(choline)_2[SnI_4]$	4,069	4,074	13,067	216,61
$(choline)_2[PbI_4]$	4,105	4,107	13,110	221,03
$(choline)_2[Cu_{0.25}Sn_{0.75}I_4]$	4,063	4,069	13,041	215,60
$(choline)_2[Cu_{0.50}Sn_{0.50}I_4]$	4,059	4,063	12,992	214,26
$(choline)_2[Cu_{0.75}Sn_{0.25}I_4]$	4,037	4,031	12,976	211,16
$(choline)_2[Cu_{0.25}Pb_{0.75}I_4]$	4,102	4,104	13,030	219,35
$(choline)_2[Cu_{0.50}Pb_{0.50}I_4]$	4,101	4,105	12,795	215,40
$(choline)_2[Cu_{0.75}Pb_{0.25}I_4]$	4,008	4,003	13,269	212,89
$(choline)_2[FeCl_4]$	3,946	3,958	13,003	203,08
$(choline)_2[Fe_{0.25}Pb_{0.75}Cl_4]$	3,987	3,992	13,012	207,10
$(choline)_2[Fe_{0.50}Pb_{0.50}Cl_4]$	3,974	3,982	13,010	205,88
$(choline)_2[Fe_{0.50}Pb_{0.50}I_4]$	4,007	4,100	13,181	216,55
$(choline)_2[Cu_{0.50}Fe_{0.25}Pb_{0.25}I_4]$	4,016	4,064	13,124	214,20

In the $(choline)_2[Cu_y M_{1-y}X_4]$ series, unit cell volumes decrease when y values increase due to the replacement of Sn^{2+} or Pb^{2+} ions with Cu^{2+}, an ion with smaller ionic radius. Also, by the substitution of Pb(II) in

(choline)$_2$[Fe$_y$Pb$_{1-y}$X$_4$] series with Fe(II), a smaller ion determines the decreasing of the unit cell values. The aspect of XRD diffraction patterns of the studied halide complexes sustains the fact that the distance between inorganic layers is not affected by metallic ions replacement; probably the length of organic layer is the main factor of the inter-layer distance. The confirmation of the possible application of the complex halides with layer perovskite-like structure as optoelectronic devices has been provided by investigations regarding the electrical properties of some of the prepared complex halides with a good thermal stability. By measuring their electric conductivities it has been observed that these compounds are insulator at room temperatures (Fig. 8). Transitions insulator-semiconductor is observed by raising the temperature; an electrical behavior of this type could be explained by growing mobility of charge carrier with raising temperature in a hopping mechanism. In addition, the electric conductivities of complex iodide are higher than those of chlorine complex. Moreover, according to the literature it was observed that the complex compounds containing Sn are better semiconductors than those Pb containing [10-14].
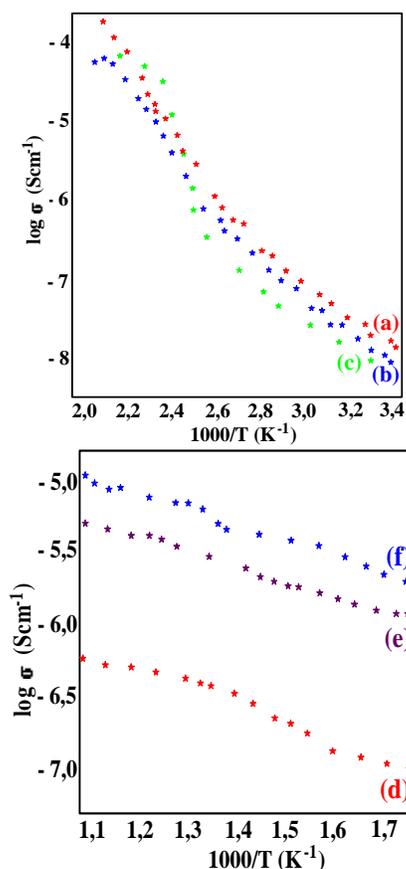

Fig. 8. Logarithmic diagram of electrical conductivities vs. 1000/T of (choline)$_2$[PbCl$_4$] (a), (choline)$_2$[Cu$_{0,25}$Pb$_{0,75}$Cl$_4$] (b), (choline)$_2$[Fe$_{0,50}$Pb$_{0,50}$Cl$_4$] (c), (choline)$_2$[PbI$_4$] (d), (choline)$_2$[Fe$_{0,50}$Pb$_{0,50}$I$_4$] (e), (choline)$_2$[Cu$_{0,50}$Fe$_{0,25}$Pb$_{0,25}$I$_4$] (f).

4. Conclusions

This paper presents the synthesis of 20 new layered preovskite compounds in a four systems in well-defined conditions. The synthesized complex halides are insulators at room temperatures, but the transition insulator-semiconductors are observed by raising the temperatures at 200-300 ^{0}C. Among the prepared compounds, iodide complex, (choline)$_2$[Cu$_{0.50}$Fe$_{0.25}$Pb$_{0.25}$I$_4$] and chloride complex, (choline)$_2$[PbCl$_4$] display the highest conductivity. Regarding the thermal stability, the electric conductivity these complexes remain unchanged until 625 ^{0}C. The advantages of optoelectronic uses of the synthesized and characterized layered perovskites lied on their high thermal stability and on their various electrical properties (insulators, semiconductors).

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