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New organo-inorganic layered perovskites in systems of trivalent metallic halides and ammonium quaternary salts of amino alcohols

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The layer perovskites of chol[$La_yBi_{1-y}X_4$] type (where X = Cl, I; y = 0.00; 0.25; 0.50; 0.75) and cholX = quaternary ammonium salt of 1, 2-aminoethanol, [$HO–(CH_2)_2–(CH_3)_3N]^+X$) have been synthesized and characterized by electronic and IR spectra, thermal analysis, X-ray diffraction pattern and electrical conductivity measurements. Some correlations between synthesis method and composition of the perovskite systems have been also made.

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Keywords: Layered perovskite, Quaternary ammonium salt, Amino alcohols

1. Introduction

The organo-inorganic perovskites are one of the most extensively studied crystalline families of hybrids, consisting of a wide range of inorganic anions, alternating with a variety of different organic cations. In addition to structural flexibility, interesting and potentially useful magnetic, electrical and optical properties arise in the perovskites as a result of the unusual structural and electronic properties.

The inorganic component of the layered perovskites is usually represented by complex halides (Cl^-, Br^-, I^-) of divalent (Cu, Ni, Co, Fe, Mn, Pd, Cd, Ge, Sn, Pb, Eu, Yb) or trivalent (Bi, Sb) metals, the charge difference for the last ones being accommodated by vacancies on the metal site [1-6].

The organic component is situated between the perovskite layers of inorganic complex halides (Fig. 1). It can be interposed as a monolayer of diammonium cations (($H_3N^+ – R – N^+H_3$)) or a double cation layer of monoammonium cations ($R – N^+H_3$).

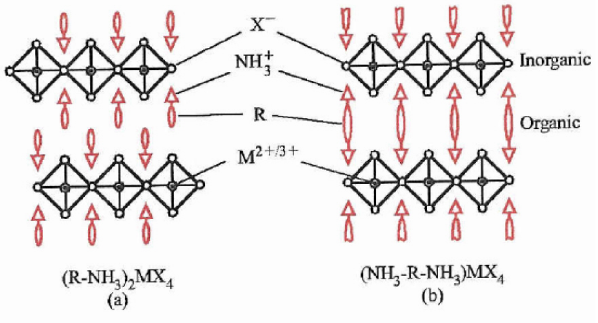

Fig. 1. Schematic representation of single-layer <100> oriented perovskites with organic cations of monoammonium ($R-NH_3^+$) (a) and diammonium ($^+NH_3-R-NH_3^+$) (b) type, [3].

The substantial stability of these organo-inorganic layered perovskite hybrids derives from their specific chemical interactions – from relatively weak Van der Waals interaction among the organic components, to hydrogen bonding interactions between the organic and inorganic components (as well as among the organic molecules), and stronger ionic and covalent interactions within the metal halide sheets.

This paper is a part of our study [7, 8] about the synthesis and characterization of new crystalline composites of layered perovskites obtained in the systems of metallic halides and ammonium quaternary salts of amino alcohols.

2. Experimental data

Synthesis of chol[$La_yBi_{1-y}Cl_4$] compounds

A mixture of $La(OH)_3$ and $4Bi(OH)_3·BiO(OH)$ with 1:0.6 (y = 0.25); 1:0.2 (y = 0.5); 1:0.07 (y = 0.75) molar ratios in conc. HCl was boiled for completely dissolving of insoluble products; choline chloride, [$OH(CH_2)_2-N^+(CH_3)_3]Cl^-$, (La(III):cholCl = 1:4) was then added. The mixture was heated about one hour at 60ºC and then mixture was cooled at 0ºC on an ice bath. The smallest crystals formed after 2-3 days were white. The crystals were filtered, washed first with ethylic alcohol and then with ethyl ether and dried in air.

Synthesis of chol[$La_yBi_{1-y}I_4$] compounds

At a mixture of $La(OH)_3$ and $4Bi(OH)_3·BiO(OH)$ with 1:0.6 (y = 0.25); 1:0.2 (y = 0.5); 1:0.07 (y = 0.75) molar ratios in HI was added choline iodide, [$OH(CH_2)_2-N^+(CH_3)_3]I^-$, La(III):cholI = 1:4). The smallest yellow brown crystals were filtered, washed with distilled water, ethanol and ethyl ether and dried in air.

Isolated compounds and elemental chemical analysis results are presented in Table 1.

Table 1. Isolated compounds and elemental chemical analysis results.

Compounds	Molecular weight (calculated)	Elemental chemical analysis, wt % (calculated/found)					
		La	Bi	Cl	I	C	N
chol[$BiCl_4$] (a)	455	-	45.93/ 43.75	31.21/ 30.23	-	13.19/ 12.65	3.08/ 2.80
chol[$La_{0,25}Bi_{0,75}Cl_4$] (b)	437.8	7.94/ 8.50	35.83/ 33.90	32.46/ 31.10	-	13.71/ 13.45	3.2/ 3.86
chol[$La_{0,50}Bi_{0,50}Cl_4$] (c)	420	16.55/ 17.88	24.88/ 23.37	33.81/ 31.83	-	14.29/ 14.70	3.33/ 2.75
chol[$La_{0,75}Bi_{0,25}Cl_4$] (d)	402.5	25.90/ 24.23	12.98/ 11.10	35.28/ 34.10	-	14.91/ 13.20	3.48/ 2.75
chol[BiI_4] (e)	821	-	25.46/ 23.76	-	61.88/ 60.24	7.31/ 7.76	1.70/ 1.50
chol[$La_{0,25}Bi_{0,75}I_4$] (f)	803.5	4.32/ 5.26	19.51/ 17.95	-	63.22/ 62.30	7.47/ 7.80	1.74/ 1.53
chol[$La_{0,50}Bi_{0,50}I_4$] (g)	786	8.84/ 9.50	13.30/ 14.56	-	64.63/ 65.10	7.63/ 7.45	1.78/ 1.25
chol[$La_{0,75}Bi_{0,25}I_4$] (h)	768.5	13.57/ 12.50	6.80/ 7.15	-	66.10/ 66.72	7.81/ 5.97	1.82/ 0.75

The *electronic spectra* have been recorded at room temperature using a UV-VIS Jasco V560 spectrophotometer.

The *IR spectra* were recorded with a Perkin-Elmer spectrophotometer using pressed KBr pellets technique.

TG-ATD analysis was performed in air, between 25-800ºC on a Paulik-Paulik-Erdey derivatograph (Al_2O_3 as standard material).

Electrical conductivity measurements of the pressed pellet samples have been carried out using four-probes method in the temperature range 300-725 K, at 25-50 K intervals.

3. Results and discussion

Electronic reflectance spectra of the complex chlorides and iodides are similar as position and shape of bands (Fig. 2).

The complex chlorides and iodides absorb only in the near-ultraviolet range. The bands observed in the spectra of these compounds are choline band (270 nm) and Bi-X charge-transfer (CT) bands (300-500 nm).

The slow shift of CT bands to higher wavelengths in the spectra of complex iodides compared with wavelengths in the spectra of complex chlorides can be assigned to the lower iodine electronegativity compared with that of chlorine.

The IR spectra (400-4000 cm^{-1}) of the complex chlorides and iodides, as well as the IR spectra of choline chloride and choline iodide are showed in figure 3.

The IR spectra of complex halides present the vibration frequencies of choline cation; the frequencies assignments to groups: $R_3N]^+Cl^-$ (1360, 1650, 3080 cm^{-1}), -CH_2-N^+ (1360, 1420 cm^{-1}), C-N (1140, 1260 cm^{-1}), C-OH (wide band in 3400-3600 cm^{-1} range and medium intensity bands in 1010-1060 cm^{-1} range) and $(CH_2)_2$ (880 cm^{-1}) are conserved in the spectra of all complex chlorides and iodides, as a proof of the choline structure conservation in these complexes. The low intensity of bands or certain slow shift of bands in the spectra complex iodides compared with those of choline iodide can be assign to a constriction of organic layer in the presence of bulky complex iodide anion, $[La_yBi_{1-y}I_4]^-$.

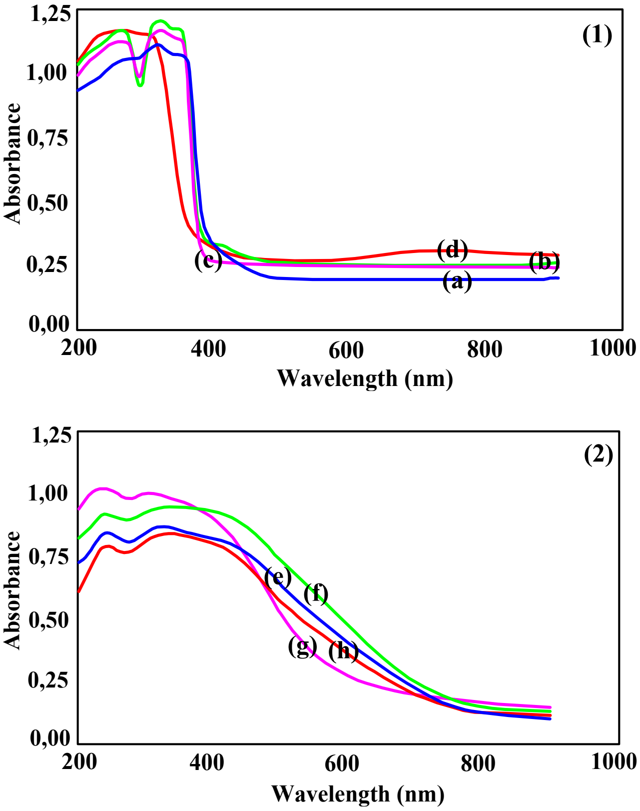

Fig. 2. Electronic reflectance spectra of the complex chlorides (1) and complex iodides (2).

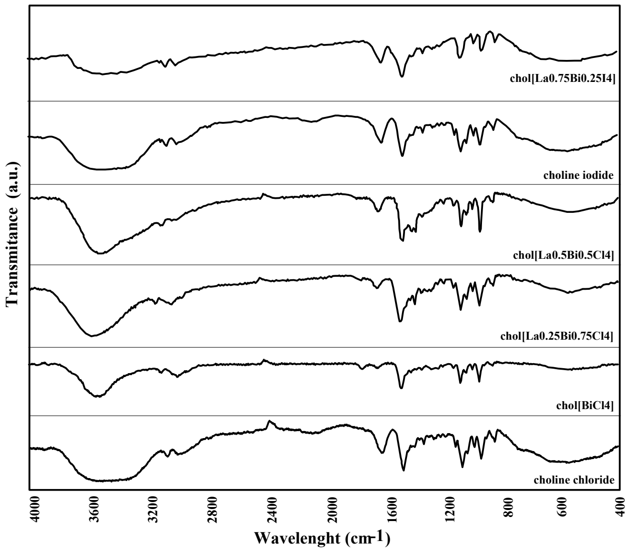

Fig. 3. IR spectra of the complex chlorides, complex iodides, choline chloride and choline iodide.

The Fig. 4 shows the data of *thermal analysis* (TG and DTG curves) for chol[$La_{0.5}Bi_{0.5}Cl_4$] and chol[$La_{0.5}Bi_{0.5}I_4$] compounds. The presence of organic cation in these compounds determines their decomposition at relatively low temperature (250 – 350ºC).

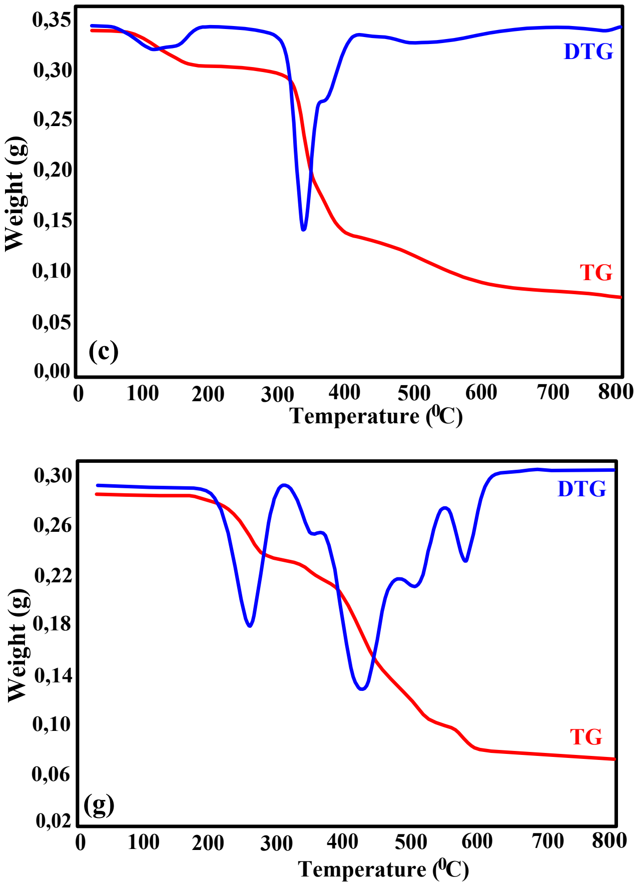

Fig. 4. Thermogravimetric data for chol[$La_{0.5}Bi_{0.5}Cl_4$] (c) chol[$La_{0.5}Bi_{0.5}I_4$] (g) compounds.

The endothermic effects observed for chol[$La_{0.5}Bi_{0.5}Cl_4$] compound can be assign as following: the slowly lose of weight at about 100-150ºC to the order-disorder transition of organic cation within the organic layer and choline melting and the drastic lose of weight at about 350ºC to the decomposition and burn of choline and inorganic component decomposition. The last effect (at about 600ºC) can be assign to the burn of products resulted from inorganic component decomposition followed by the formation of oxides lattices.

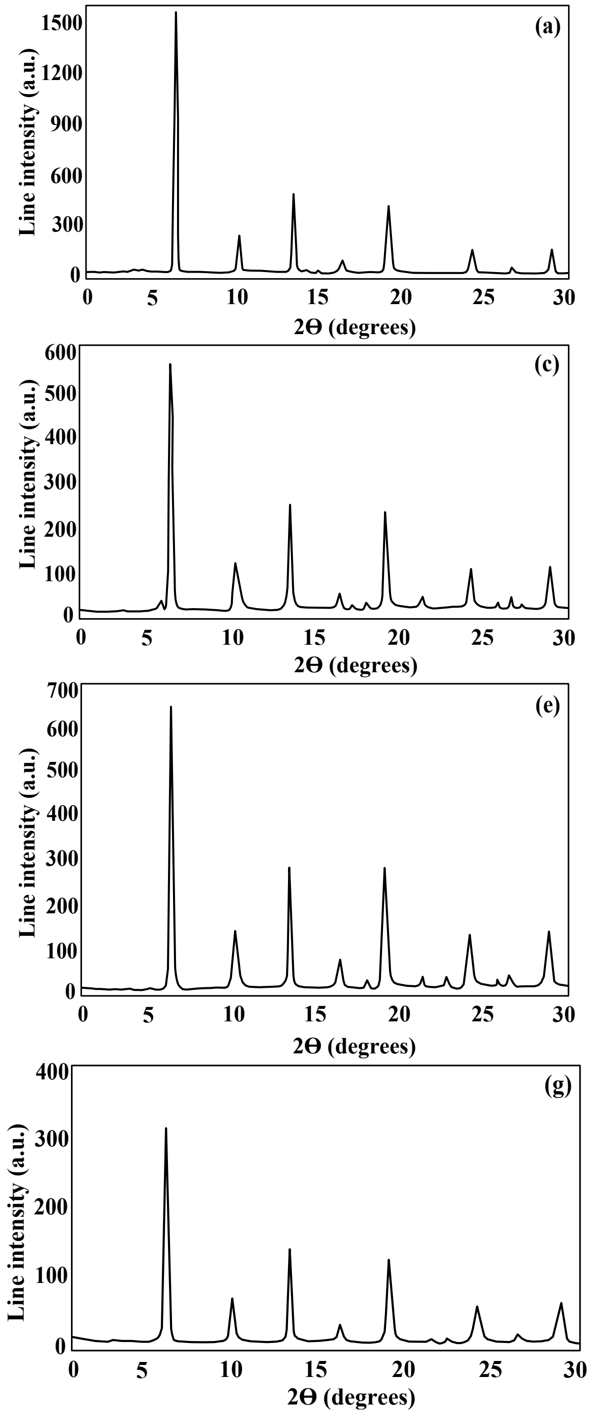

Fig. 5. X-ray power patterns of the compounds with chloride and iodide (a – chol[$BiCl_4$]; c – chol[$La_{0.5}Bi_{0.5}Cl_4$]; e – chol[BiI_4]; g – chol[$La_{0.5}Bi_{0.5}I_4$]).

Three endothermic effects are observed in the case of chol[$\mathrm{La_{0.5}Bi_{0.5}I_4}$] compound. These effects are associated with the slowly lose of weight at about 250ºC (choline melting), followed by a drastic lose of weight at about 400ºC (decomposition and burn of choline). The last thermic effect at about 550ºC is assigned to decomposition and burn of inorganic component and formation of oxides lattices.

The X-Ray diffraction data for synthetized chol[$\mathrm{La_yBi_{1-y}X_4}$] compounds (X = Cl, I; y = 0.00; 0.50) show that all samples are single phases with orthorhombic $\mathrm{K_2NiF_4}$ layered perovskite structure (International Centre for Diffraction Data – pdf number: 00-024-1326) (figure 5).

All parameters and the volumes of the unit cell are presented in Table 2.

Table 2. Parameters and unit cell volumes.

Complex halides	a [Å]	b [Å]	c [Å]	V [Å^3]
chol[$\mathrm{BiCl_4}$]	4.155	4.162	13.125	226.97
chol[$\mathrm{La_{0.25}Bi_{0.75}Cl_4}$]	4.080	4.105	13.105	219.49
chol[$\mathrm{La_{0.5}Bi_{0.5}Cl_4}$]	4.025	4.023	13.075	211.72
chol[$\mathrm{La_{0.75}Bi_{0.25}Cl_4}$]	4.002	3.997	13.024	208.33
chol[$\mathrm{BiI_4}$]	4.273	4.300	13.275	243.91
chol[$\mathrm{La_{0.25}Bi_{0.75}I_4}$]	4.260	4.255	13.245	240.08
chol[$\mathrm{La_{0.5}Bi_{0.5}I_4}$]	4.215	4.218	13.205	234.77
chol[$\mathrm{La_{0.75}Bi_{0.25}I_4}$]	4.188	4.1913	13.182	231.48

A relative decrease is observed in the unit cell volume with the increasing of lanthanum content due to the substitution of $\mathrm{Bi^{3+}}$ ion by the smaller $\mathrm{La^{3+}}$ ion ($r_{\mathrm{La}}{}^{3+}$ = 1.16 Å and $r_{\mathrm{Bi}}{}^{3+}$ = 1.20 Å) in the crystalline lattice. The unit cell volume of complex chlorides is smaller compared with the unit cell volume of complex iodides.

The interlayer distance between inorganic sheets is not affected by the substituted Bi ions since the length of organic layer is the main factor of the interlayer distance.

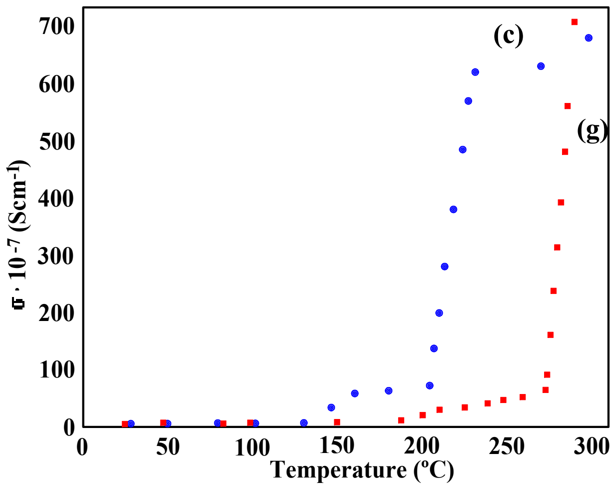

Fig. 6. Electrical conductivities of chol[$\mathrm{La_{0.5}Bi_{0.5}Cl_4}$] (c) and chol[$\mathrm{La_{0.5}Bi_{0.5}I_4}$] (g) compounds.

The electrical properties of chol[$\mathrm{La_yBi_{1-y}X_4}$] compounds *vs* temperature was also studied in this paper.

The electrical conductivities in air at room temperature of studied compounds (chol[$\mathrm{La_{0.5}Bi_{0.5}Cl_4}$], chol[$\mathrm{La_{0.5}Bi_{0.5}I_4}$]) have shown values characteristic for insulators. When increasing the temperature, the conductivities increase having typical semiconducting values (Fig. 6, Fig. 7). This electric behaviour corresponds to hopping mechanism of activated carriers.

The conductivity measurements were limited by temperature (250-350ºC), because after this temperature decomposition of compounds was observed.

A higher conductivity has been observed for iodide complex.

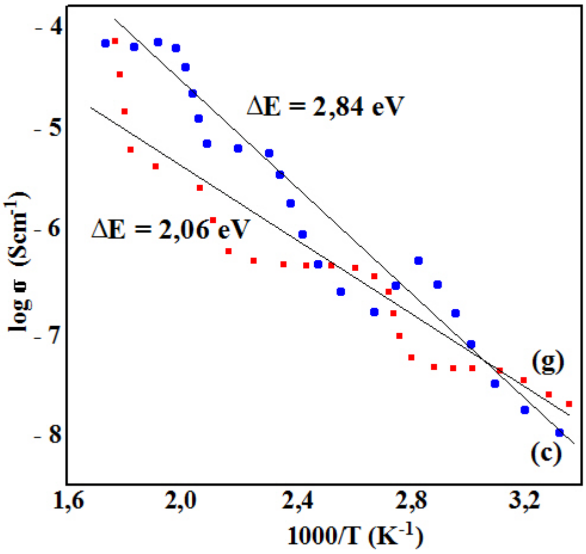

Fig. 7. Logarithmic diagram of electrical conductivities vs 1000/T of chol[$\mathrm{La_{0.5}Bi_{0.5}Cl_4}$] (c) and chol[$\mathrm{La_{0.5}Bi_{0.5}I_4}$] (g) compounds and activation energies

5. Conclusions

New crystalline composites, chol[$\mathrm{La_yBi_{1-y}X_4}$], of the layered perovskite type have been prepared in the systems y$\mathrm{La^{3+}}$ – (1-y)$\mathrm{Bi^{3+}}$ – HX – cholX (X = Cl, I, and chol = $\mathrm{(CH_3)_3N^+–(CH_2)_2–OH}$]). The isolated compounds have been characterized by electronic reflectance and FT-IR spectra, thermal analysis, XRD diffraction patterns, as well as electrical measurements.

The structure of the organic layers is conserved in all complex chlorides and iodides as IR spectra indicate.

The presence of organic cation in these compounds determines their decomposition at relatively low temperature (250 – 350ºC).

The unit cell volumes of chol[$\mathrm{La_yBi_{1-y}X_4}$] compounds decrease, with the increasing of $\mathrm{La^{3+}}$ content in the crystalline lattice.

The change from insulating behaviour to semiconducting one by the increasing of the temperature was observed. This electrical behaviour corresponds to the hopping mechanism of activated carriers.

Other new organic-inorganic layered perovskites can be obtained by the diversification of the organic and inorganic composition and some correlation between synthesis methods – composition of the perovskite system – structural properties and possible applications could be achieved.

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