

Preparation and Dielectric Spectroscopy Characterization of A_2MnMoO_6 ($A = Ca, Sr$ and Ba) Double Perovskites

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The aim of this work is to study the behavior of the perovskite-type complex oxides A_2MnMoO_6 obtained by the citrate combustion synthesis method. We have prepared our samples of nanosized perovskite-type complex oxides A_2MnMoO_6 ($A = Ca, Sr$ and Ba) by citrate combustion method. The starting materials were $CaCO_3, SrCO_3, BaCO_3$ (treated with HNO_3 to form active nitrates) $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, Mn powder and citric acid in stoichiometric ratio. The precursors were presintered and sintered at different temperatures. The obtained powders were firstly characterised by infrared spectrophotometry. The infrared spectra have revealed several novel aspects of the structure. The position of bands indicates that all nanosized materials are polymetallic oxides exhibiting perovskite-type structure. The complex impedance properties have also been determined and they are discussed in relationship with the composition of the samples.

Keywords: double perovskites, sol-gel preparation, X-ray diffraction, SEM, Electrical properties

In the last years, a high interest is focused on perovskite-type compounds which show a large variety of interesting functional properties (as ferro/piezo/pyro-electricity, magnetic order, colossal magnetoresistance, superconductivity etc.) due to their compositional and structural diversity [1 - 4]. As a result, many compounds that belong to this group have been synthesized. The general formula of perovskites is ABO_3 , where A and B might be almost any metal or semimetal from the periodic table [2]. One of the major characteristic of perovskites is the possibility for multiple substitutions at the position of the cations. As a result, there are large groups of compounds with different cations in A position ($A'_x A''_{1-x} BO_3$); with different cations in B position ($AB'_x B''_{1-x} O_3$); and with substitution in both cation position ($A'_x A''_{1-x} B'_x B''_{1-x} O_3$) [2]. The perovskite structure is characterized by octahedral coordinated polyhedrons (formed by oxygen anions located at the corners of the octahedra) around the B-cations, while the B-cations are positioned in the centers. The octahedral polyhedrons are linked by their corners, forming a three-dimensional framework of octahedral chains. Inside the cavities of this framework, the A-cations are situated (with twelve ions coordination). The ideal perovskite structure generated has a cubic system with space group $Pm\bar{3}m$. However, a large number of perovskites exhibit deviations from the ideal cubic structure, mainly, because of the octahedrons tilting, but still retaining their connectivity. The perovskite compounds are found in all seven crystallographic systems [3 - 5] and their unit cell is compatible with many types of substitutions, leading to a large range of structural, electric and magnetic properties.

If in the unit cell of a perovskite structure exist two cations ordered on the B site this is becoming a unit cell of

a double perovskite structure as in $AB_{0.5x} B'_{0.5-0.5x} O_3$, which corresponds to the wellknown formula $A_2 B'_x B''_{1-x} O_6$.

Due to the technological importance substantial research efforts have also been devoted to understand the electronic and magnetic properties of the double-perovskite compounds containing magnetic ions in B positions.

The magnetic and electronic characteristics of double perovskites make them very interesting to be still investigated and to determine their functional properties in relationship with the preparation method, composition and microstructures. In particular, the compositions $A_2 B Mo O_6$, where B = Fe, Mn, Cr are magnetic ions are currently investigated for their potentiality as magnetoresistive systems and thermoelectrics [6]. Their electrical properties are also highly interesting: $Sr_2 Fe Mo O_6$ is a low-field magnetoresistive material at room temperature, with a half-metallic character [5], $Sr_2 Mn Mo O_6$ shows insulating property as it contains no Mo 4d electrons responsible for metallic conductivity, while $Ca_2 Mn Mo O_6$ was reported as being metallic in the high temperature region and insulating in the low temperature region [6, 7]. Various synthesis approaches were used in producing double perovskites, from solid state reaction to wet chemistry methods [8] and the functional properties are influenced by the preparation method, purity and crystalline phases.

The solid state preparation method was used for producing polycrystalline $A_2 Mn Mo O_6$ with A = Ba and Sr in a recent study [9], in which the crystallographic and magnetic data are reported. In the present paper, we report the investigation of a series of $A_2 Mn Mo O_6$ ($A = Ca, Sr$ and Ba) double perovskite ceramics synthesized by sol-gel combustion method. The phase formation, microstructures and electrical characterization at room temperature by impedance spectroscopy method are presented.

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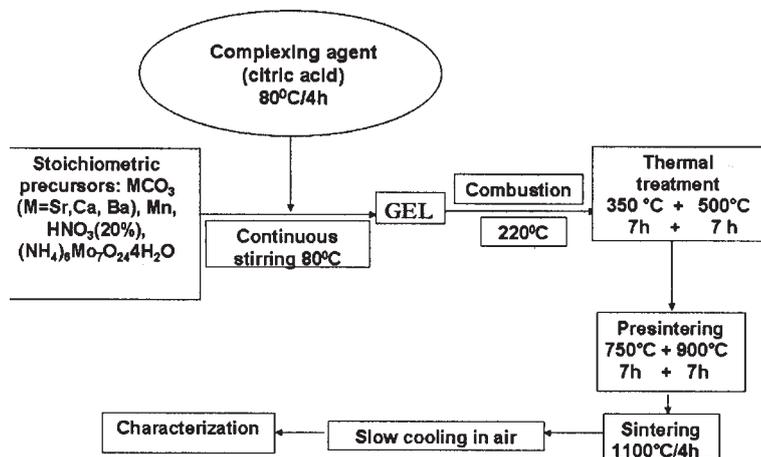


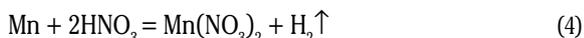
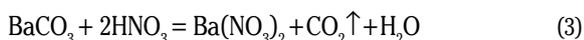
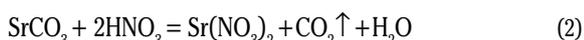
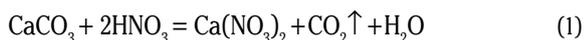
Fig. 1. Flowchart of the powders preparation

Sample preparation and experimental details

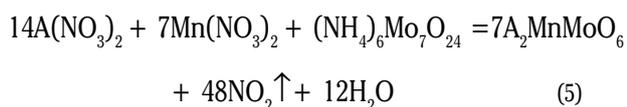
All the reagents were of analytical purity and provided by Sigma Aldrich Company.

The raw materials CaCO_3 , SrCO_3 , BaCO_3 , Mn powder were passed in solution by HNO_3 (20%), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ was dissolved in deionized water and citric acid was added in solid state. The synthesis procedure of the powders is described in the flowchart shown in figure 1 and is similar to one described in the references [11, 12].

The solubilization reactions for the starting compounds are as follows:



The overall reactions between cations resulting in the polymetallic oxides phase formation are most likely described by the following equation:



where A = Ca, Sr, Ba

The starting solutions of cations were mixed and heated up to 80°C with stirring, then the stoichiometric amount of citric acid was added (molar ratio citric acid: polymetallic oxides = 4: 1). The resulting mixtures were kept under stirring during 4 h at 80°C. After concentrating the solution by slow evaporation at 80 - 90°C, the obtained gel was dried in air up to 220°C, until the autocombustion took place. After the combustion process the thermal treatment was carried out in air at 350°C/7h and 500°C/7h. The samples were slowly cooled, then ground, pressed at 150 kPa into pellets of 10mm diameter and 2 mm thickness and presintered in air with a heating rate of 10°C/min at 750°C/7h and 900°C/7h. The samples were again slowly cooled, then re-ground, pressed and sintered in air, with a heating rate of 5°C/min at 1100°C for 4 h. After sintering the ceramic pellets were superficially polished to remove the surface layers.

The disappearance of nitrate and carbonate phases and the phase formation of the double perovskite A_2MnMoO_6 (A = Ca, Sr, and Ba) was monitored by using a Fourier transform infrared (FTIR) spectra, recorded in the range 4000 - 400 cm^{-1} with 2 cm^{-1} resolution on a Jasco 660 plus FTIR spectrophotometer using the KBr pellet technique.

Room-temperature X-ray diffraction measurements for investigating the formation of the perovskites phases in the prepared powders and in the sintered pellets were performed with a SHIMADZU XRD 6000 diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), with a scan step of 0.02° and a counting time of 1 s/step, for 2θ ranging between 20 and 80°.

HITACHI S2600N and VEGA/TESCAN scanning electron microscopes where used to analyze the ceramic microstructure of samples.

The dielectric measurements at room temperature in the low frequency range 10 - 10⁶ Hz were performed on a parallel-plate configuration of the sintered ceramic disks by using a Solartron 1260A Impedance/Gain-Phase Analyzer.

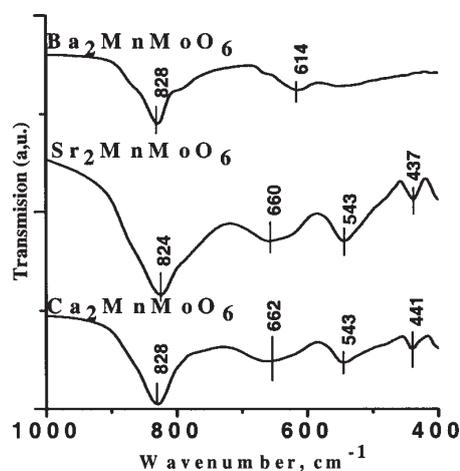


Fig. 2. FTIR spectra recorded for A_2MnMoO_6 (A = Ca, Sr and Ba) powders

Results and discussions

The perovskite phase formation was monitored by the FT infrared experiments and XRD investigations. Figure 2 shows IR spectra of the A_2MnMoO_6 (A = Ca, Sr and Ba) powders after calcination step in the spectral wavenumber range 1000 - 400 cm^{-1} of wavenumber.

The FTIR spectra of the perovskite structure have three characteristic absorption bands between 850 - 400 cm^{-1} , respective to composition and these are usually used to identify the perovskite phase formation [13]. The IR spectra of the compounds A_2MnMoO_6 (A = Ca, Sr and Ba) investigated in the present study (fig. 2) allow to detect two bands for A = Ba and four bands for A = Ca, Sr. These

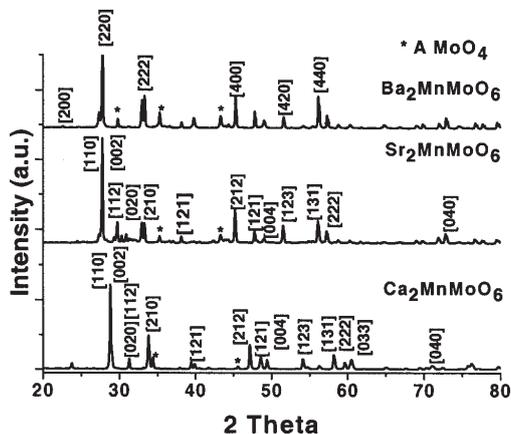


Fig. 3. Room-temperature XRD patterns for the A_2MnMoO_6 ($A = Ca, Sr$ and Ba) powders

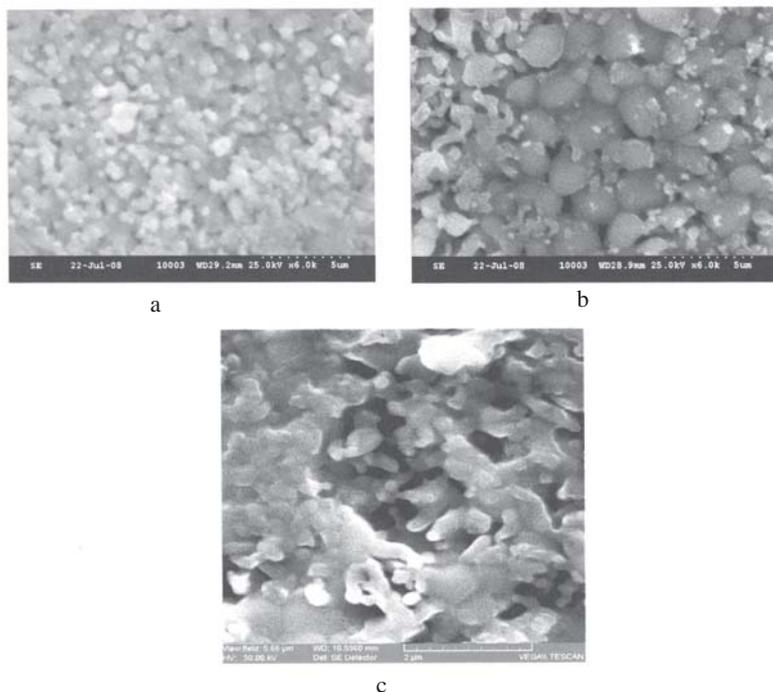


Fig.4. The SEM images of the A_2MnMoO_6 ceramics: a) $A = Ca$, b) $A = Sr$ and c) $A = Ba$

bands are: one in the high-wavenumber range ($\sim 800 \text{ cm}^{-1}$) associated to the symmetric stretching vibration of perovskite octahedral, two at $\sim 660 \text{ cm}^{-1}$ and 550 cm^{-1} assigned to the antisymmetric stretching mode of the MoO_6 -octahedra, due to the higher charge of this cation. The bands around 440 cm^{-1} appear due to deformational modes of the MoO_6 polyhedra. For all the compounds with $A = Ca, Sr$ and Ba , the presence of these bands confirm the formation of perovskite phase.

Figure 3 shows the XRD patterns obtained for A_2MnMoO_6 ($A = Ca, Sr$ and Ba) powders showing the predominant double - perovskite phase. The observed peaks can be fitted space group $Fm\bar{3}m$ for A_2MnMoO_6 ($A = Ba$) and of the space group $P21/n$ for A_2MnMoO_6 ($A = Ca$ and Sr) [10].

The size of cation A seems to be relevant to the structural distortions. In our case the tolerance factor increases with the size of cation A : with increasing of the ionic radius in the serie $r_{Ca^{2+}} < r_{Sr^{2+}} < r_{Ba^{2+}}$, the tolerance factor increases from $t = 0.9064$ (for compound with Ca) at $t = 0.9584$ (for compound with Sr) and at $t = 1.0160$ (for compound with Ba).

The SEM images of the A_2MnMoO_6 ($A = Ca, Sr$ and Ba) ceramic after the sintering step are presented in figure 4.

Dense and homogeneous microstructure, consisting of small grains with sizes of $0.5 - 0.6 \mu\text{m}$ was observed for the Ca_2MnMoO_6 ceramic (fig. 4a).

A more porous and heterogeneous microstructure with a bimodal grain size distribution, consisting of larger grains

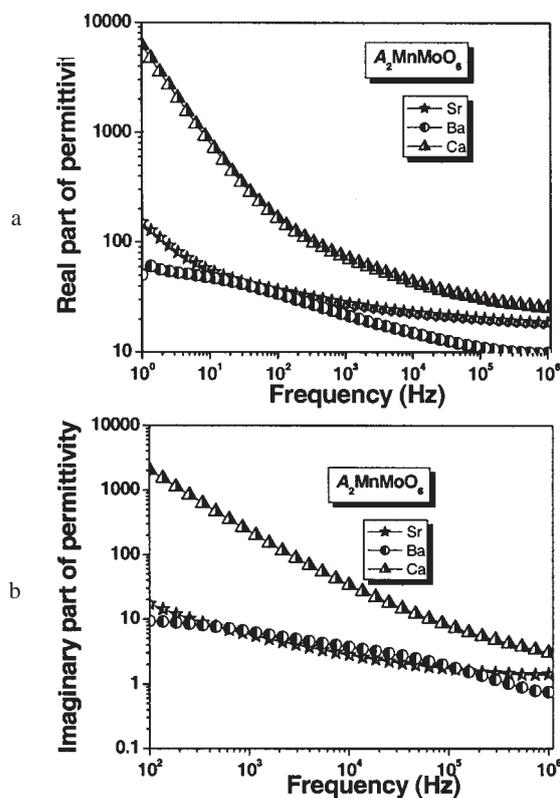


Fig.5. Comparative dielectric properties vs. frequency of the A_2MnMoO_6 ($A = Sr, Ba, Ca$) ceramics: a) real part of the permittivity, b) imaginary part of the permittivity, c) tangent loss and d) complex impedance plot

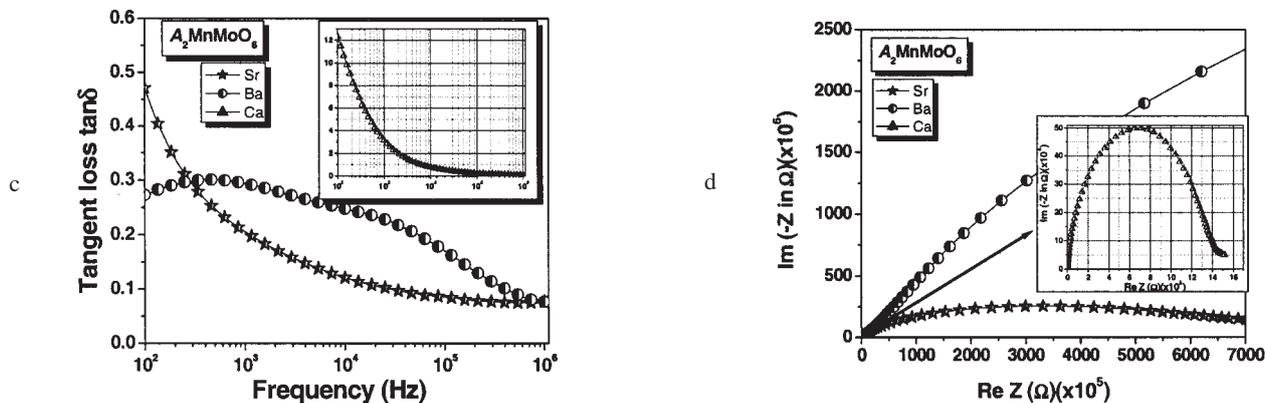


Fig.5. Comparative dielectric properties vs. frequency of the A_2MnMoO_6 ($A = Sr, Ba, Ca$) ceramics: a) real part of the permittivity, b) imaginary part of the permittivity, c) tangent loss and d) complex impedance plot

(of 2.5–3 μm) with well-defined boundaries which coexist with smaller (submicron) ones, was noticed for the Sr_2MnMoO_6 ceramic (fig. 4b).

The worst densified and, therefore, the most porous microstructure is the one observed for Ba_2MnMoO_6 ceramic, indicating an early stage of the sintering process of this sample (fig. 4c). This heterogeneous and fine-grained microstructure presents also a tendency to a bimodal grain size distribution and consists of grains of $\sim 0.1 - 0.6 \mu m$ and a significant amount of intergranular porosity.

The complex impedance data of the A_2MnMoO_6 ceramics sintered at $1100^\circ C/4h$ prepared by the gel combustion method are comparatively shown in the figures 5a - 5d. The dielectric properties at room temperature were measured as a function of frequency in the range of 10 Hz to 1MHz.

All the ceramics show a relaxation at low-frequency (Maxwell - Wagner type), characterized by high values of real part of permittivity (of ~ 100 for Sr and Ba composition and ~ 10000 for Ca sample) and by tangent losses with values below 0.5 for $A = Sr$ and Ba ceramics and ~ 12 for Ca sample indicating a conducting behaviour (figs. 5a and 5c). In perovskites, an important contribution to high losses is attributed to the oxygen vacancies, usually present in such systems. The losses also are strongly diminishing with increasing frequency and they reduce below unity for $f = 10^6$ Hz.

The impedance spectra of the ceramic samples are characterized by several semicircular arcs (fig. 5d), the most evident being the case of the Ca composition ceramic (inset of fig. 5d). The presence of more than one component in the complex impedance plots demonstrated that the ceramic samples present some degree of local electrical inhomogeneities.

Conclusions

We have performed a detailed analysis of the structural, microstructures and electrical characterization of the double perovskite A_2MnMoO_6 ($A = Ca, Sr$ and Ba). Nanosized double perovskite-type complex oxides of A_2MnMoO_6 ($A = Ca, Sr$ and Ba) were prepared by another method than that found in literature. Some advantages of the sol-gel combustion method used for obtaining A_2MnMoO_6 powders are: low temperature, short time of the synthesis, low cost materials, a good homogeneity of

the powders, which demonstrated to be useful in order to obtain a good lattice arrangement.

It can be notice that while Ba_2MnMoO_6 compound is cubic, A_2MnMoO_6 ($A = Ca$ and Sr) compounds are strongly distorted forming a monoclinic system. All the ceramics show a relaxation at low-frequency (Maxwell - Wagner type). The impedance spectra of the ceramic samples are characterized by more semicircular arcs, the most evident being for Ca composition ceramic. This might be explained on the base of ionic radii variation ($r_{Ca^{2+}} < r_{Sr^{2+}} < r_{Ba^{2+}}$). A smaller ionic radius will determine a higher number of anionic vacancy. Also, Ca^{2+} has a higher polarizing action on the water molecules, due to his smaller ionic radius.

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