Preparation by Citrate Combustion and Characterization of Complex Oxides $Ca_{2-x}La_xMnMoO_6$

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The aim of this work is to understand the behaviour of the perovskite-type complex oxides $Ca_{2-x}La_xMnMoO_6$ obtained by the combustion synthesis method. We have prepared our samples of nanosized perovskite-type complex oxides $Ca_{2-x}La_xMnMoO_6$ (x=0.75; 0.9; 1.0) by combustion method. The starting materials were $CaCO_3$, La_2O_3, $(NH_4)_6Mo_7O_{24}4H_2O$, Mn powder and citric acid in stoichiometric ratio. The precursors were pre-sintered and sintered at different temperatures. The obtained powders were firstly characterized by infrared spectrophotometry. The infrared spectra have revealed several novel aspects of the structure. The position of bands are attributed around 800 cm^{-1} and in the ranges of 670 - 590 cm^{-1}, 445 - 431 cm^{-1}, respectively: the results indicate that all nanosized materials have perovskite-type structure complex oxides. The complex impedance properties have also been determined and they are discussed in relationship with their compositions. The $Ca_{2-x}La_xMnMoO_6$ double perovskites are interesting systems for important potential applications.

Keywords: perovskites, sol-gel preparation, X-ray techniques, electrical properties

The research for $A_2BB'O_6$ type double perovskites (where A is an alkaline-earth or rare-earth ion, and B and B' are different transition metal cations) is due to the possible technological applications of these materials in many devices [1, 2, 3]. The studies of the crystal structures of the $ALaMnMoO_6$ (A = Sr, Ba) double perovskites show that the Sr compound is monoclinic with space group $P2_1/n$ (Glazer $a^-a^-c^+$) tilting and an undistorted double perovskite structure –pseudocubic- (space group *Fm3m)* for $BaLaMnMoO_6$ [4]. The XRD pattern of almost pure powder sample $BaLaMnMoO_6$ indicated an ordered Mn and Mo cations [5]. The $CaLaMnMoO_6$ double perovskite was studied by powder neutron diffraction and the results are: monoclinic structure with *P21/n* space group (Glazer $a^+b^-b^-$) tilting and the values of the parameters of the unit cell: a = 5.56961(9), b = 5.71514(9), c = 7.9358(1)Å and β = 90.043(1)°. Compared to $ALaMnMoO_6$ (A = Sr, Ba), $CaLaMnMoO_6$ has the largest octahedral distortion, as calculated from the structural data [6]. In this paper, synthesis, characterization and dielectric properties of $Ca_{2-x}La_xMnMoO_6$ are reported.

Experimental procedure

Sample preparation

For the preparation by sol-gel combustion method, high-purity starting materials as $CaCO_3$ (Sigma Aldrich), La_2O_3 (Merck), Mn (Sigma Aldrich) were dissolved in HNO_3 (20%) and $(NH_4)_6Mo_7O_{24}4H_2O$ (Sigma Aldrich) was dissolved in deionized water. The precursor solutions were mixed and after that heated and stirred. The right amount of citric acid (Sigma Aldrich) is added as chelating agent (citric acid: mixed oxide = 4:1) at 70°C and the resulting mixture was stirred for 20 min. A slightly yellow gel was obtained after concentrating the solution by slow evaporation at 80°C - 90°C. The gel was then dried in air up to 300 ± 3°C and after the combustion process the pre-sintering thermal treatment was carried out in air at 350°C, 500°C and 750 ± 3°C with 7 h plateau. The samples were slowly cooled, then ground, shaped by uniaxial pressing at 150 kPa into pellets of 10mm diameter and 2mm thickness and sintered in air with a heating rate of 10°C/min at 900°C for 7 h. The samples were slowly cooled, then re-ground, pressed with radial gradient into pellets of 10 mm diameter and 2 mm thickness and sintered in air, with a heating rate of 5°C/min at 1100°C for 4 h.

Sample characterization

IR spectra were obtained using a JASCO 660 PLUS spectrophotometer with wave number range 4000 – 400 cm^{-1} used to complete the structure studies. The samples were mixed with KBr in the mass ratio 0.04:1, and then compacted into pellets with a thickness of 0.5 - 0.75 mm and a diameter of 13 mm under a pressure of 0.3 GPa in atmospheric air.

X-ray diffraction measurements at room temperature, used to investigate the purity of the perovskite phase corresponding to the $Ca_{2-x}La_xMnMoO_6$ powders were performed with a SHIMADZU XRD 6000 diffractometer using Ni-filtered $Cu_{K\alpha}$ radiation (λ = 1.5418 Å), with a scan step of 0.02° and a counting time of 1 s/step, for $2\theta \in (20 – 80)°$.

The impedance spectroscopy measurements were performed on parallel-plate configuration of the sintered ceramic disks by using a dielectric holder with guard ring. The complex impedance in the frequency domain of 20 ÷ 210^6 Hz at room temperature was determined by using an impedance bridge type Agilent E4980A.

Results and discussion

IR spectra of the powder samples of $Ca_{2-x}La_xMnMoO_6$ are shown in function of La content in the figure 1 in the 1000 – 400 cm^{-1} range of wavenumber.

The formation of the perovskite phase was watched by the FT infrared method and then this was characterized by XRD method.

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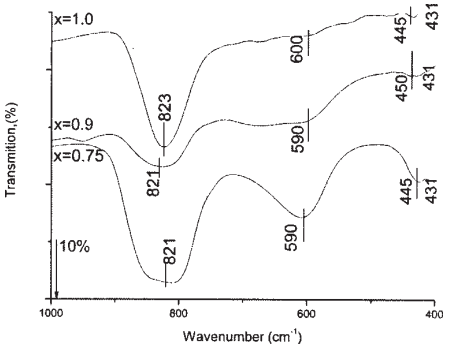

Fig. 1. FT-IR spectra for the $Ca_{2-x}La_xMnMoO_6$ powders

It has been reported that the IR spectra of the perovskite structure have three absorption bands, in most cases, regardless of stoichiometry and structure [7].

The figure 1 clearly shows that there are three absorption bands for $Ca_{2-x}La_xMnMoO_6$ between 850 - 400 cm^{-1}, one at high-wavenumber range (around 800 cm^{-1}), one at 600 cm^{-1} and one at lower range of wavenumber (around 430 cm^{-1}). The band centered at about 656 cm^{-1} can be assigned to the antisymmetric stretching mode of the MoO_6-octahedra, due to the higher charge of this cation. Another interesting point raised by the spectra is the presence of one band at around 822 cm^{-1}, which can be assigned to the symmetric stretching vibration of these octahedra. The bands around 430 cm^{-1} appear due to deformational modes of the MoO_6 polyhedra. The position of these bands suggests relatively long Mo-O bonds [8, 9] and the Mo-O stretching vibration in MoO_4^{2-} tetrahedrons appears at 742 - 901 cm^{-1} [10]. By increasing x (substitution content of calcium with lanthanum) a low displacement of bands into at high-wavenumber range was observed, because of the larger lanthanum size than calcium size.

The X-ray diffraction patterns of $Ca_{2-x}La_xMnMoO_6$ powders prepared by the sol-gel combustion method above are presented in figure 2.

Although the increased intensity of the diffraction peaks specific to the perovskite $Ca_{2-x}La_xMnMoO_6$ phase seems to indicate a higher crystallinity degree for the powder with x = 0.75. The powders synthesized by the sol-gel combustion method and annealed at the same temperature are crystallized showing the predominant double - perovskite phase characterized by a main peak at around 32° and others peaks at 2 theta around 28°, 32 °, 34°, 39°, 45°, 57°. The XRD patterns was indexed using Carine 3.1 program.

The room temperature X-ray diffraction patterns of the sintered ceramics at 1100°C show single phase compositions for all the samples, with well-developed diffraction peaks. Starting from monoclinic space group, P21/n indicated in the literature we have calculated with SPuDS program some unit cell parameters.

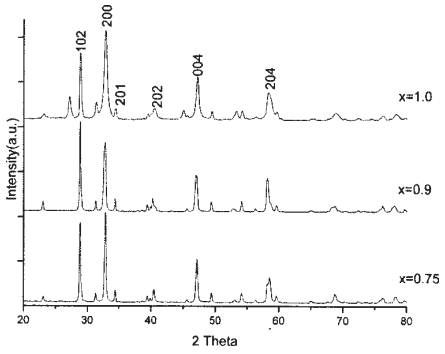

Fig. 2. Room-temperature XRD patterns for the $Ca_{2-x}La_xMnMoO_6$ powders

Complex impedance characterisation

The complex impedance data of the $Ca_{2-x}La_xMnMoO_6$ ceramics prepared by the sol-gel combustion method are comparatively shown in the figure 3 (a-c).

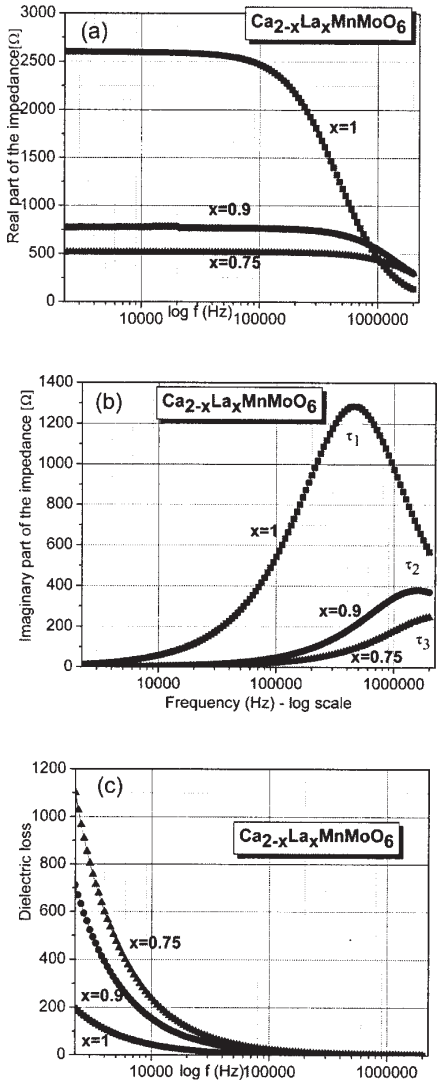

Fig. 3. Comparative impedance properties vs. frequency of the $Ca_{2-x}La_xMnMoO_6$ ceramics with x = 1, 0.90 and 0.75: 3a - Real part of the impedance, 3b - Imaginary part of the impedance, 3c - Tangent loss

Sample		Atom	x	y	z	Occupancy
a (Å)	5.5426	Ca	0.5235	0.5673	0.2483	0.50
b (Å)	5.7824	La	0.5235	0.5673	0.2483	0.50
c (Å)	7.9959	Mn	0.0000	0.5000	0.0000	1.00
u.c. volume, *V* (Å^3)	256.26	Mo	0.5000	0.0000	0.0000	1.00
ß	90.0376	O	0.2126	0.1879	-0.0525	
Tolerance factor	0.9010	O	0.3175	0.7157	-0.0525	
		O	0.3951	0.0191	0.2355	

Table 1
LATTICE CONSTANTS (a, b, c), THE VOLUME OF THE UNIT CELL, CALCULATED TOLERANCE FACTOR OF $CaLaMnMoO_6$ COMPOUND, ATOMIC POSITIONS AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS FOR $CaLaMnMoO_6$

All the compositions have not a dielectric character. They present a typical Debye relaxation characterized by a reduction of the real part (fig. 3a) of the impedance and a pronounced maximum of the imaginary part (fig. 3b).

The data allowed to accurately determine the Debye relaxation time for each composition, (with the exception of x = 0.75, for which is out of the available frequency range): $\tau_1 = 2.22x10^{-6}$s, $\tau_2 = 6.7x10^{-7}$s and $\tau_3 < 5x10^{-7}$s for the compositions of x = 1, 0.9, and 0.75, respectively. The dipolar relaxation character is determined by the presence of unit dipoles associated to the crystallographic distortion (non-centrosymmetric symmetry) of the double-perovskite unit cell of the $Ca_{2-x}La_xMnMoO_6$ compound. The shift of the relaxation time towards higher values with higher x indicates that an increasing rigidity of the dipolar reorientation movement during the application of the alternative ac-electric field takes place when more La ions are substituting the Ca-positions. This might be related to the fact that the La-O bonds are stronger than the Ca-O ones, according to the ionic potential calculations (Z^2/r=6.61 for La-O and 2.98 for the Ca-O bond in SI units, where Z is the ionic charge and r is the ionic radius in Å). No other dipolar phenomena are observed in the measurement frequency range (flat real part of the impedance below hundreds of kHz).

At a careful observation of the dielectric loss data (fig. 3 c), it is observed that the ac-conductivity is increasing with reducing the La addition, causing higher losses, particulary at low frequencies ($tg\delta$ = 200, 700 and 1100 for x = 1, 0.90 and 0.75, respectively). The ceramics become dielectric ($tg\delta<1$) only at very high frequencies: f > 0.5MHz, for x = 1, f > 1.5MHz for x = 0.90 and at f > 2MHz for x = 0.75. Being active at small frequencies (Hz range), the contributions to the losses are most probably associated with slow electric species, i.e. with space charge phenomena (Maxwell-Wagner polarization mechanism) [11].

In perovskites, one important contribution to such losses is attributed to the oxygen vacancies, usually present in such systems.

However, in the case of $Ca_{2-x}La_xMnMoO_6$, other important contributions can be additionally produced by local dielectric inhomogeneities, giving rise to bonded uncompensated electrical charges within the sample volume. For example, by considering a fixed oxidation state of the Mn^{2+} ion, an occupancy of 100%Mo^{5+} for x = 1, of 90%Mo^{5+} - 10% Mo^{6+} for x = 0.90 and of 75%Mo^{5+} - 25% Mo^{6+} can explain our results. In addition, the Mn ion itself can have different oxidation states, this complicating even more the volumic space charge into the ceramic samples, mainly at smaller x. In conclusion, most probably a higher electrical inhomogeneity (space charge) within the volume sample is obtained as small is x. By applying ac-fields, these slow charges are giving contributions mainly at low frequencies, as observed in our data (fig. 3 c).

Conclusions

Nanosized double perovskite-type complex oxides of $Ca_{2-x}La_xMnMoO_6$ (x = 0. 75; 0. 9; 1. 0) were prepared by another method than that found it in literature.

Some advantages of the sol-gel combustion method used for obtaining $Ca_{2-x}La_xMnMoO_6$ powders are: the low temperature, short time of the synthesis, low cost materials, a good homogenity of the powders, which demonstrated to be useful in order to obtain a good lattice arrangement. The impedance spectroscopy investigation shows the presence of typical Debye relaxation and space charge phenomena at low frequencies. An increasing rigidity of the dipolar movement during the application of the ac-electric field takes place when more La ions substitute the Ca positions.

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