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Electrical characteristics of $Li_2MM`_3O_8$, (M=Mg, Zn; M`=Ti, Sn)

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Oxides with general formula $Li_2MM`_3O_8$ (M = Mg, Zn; M`= Ti, Sn) have been synthesized and characterized by X-ray powder diffraction and scanning electron microscopy. The dielectric properties of $Li_2ZnSn_3O_8$ and $Li_2MgSn_3O_8$ phases with an ordered double hexagonal type structure are reported for the first time, and compared with those of $Li_2ZnTi_3O_8$ and $Li_2MgTi_3O_8$ which have ordered spinel type structures.

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1. Introduction

The intense research on materials with potential applications as gas sensors, moisture detectors, materials for electronics, catalysts, electrode materials for different types of battery, etc. has yielded numerous complex metal oxide phases. Among them, titanium and tin containing mixed oxides stand out, since they crystallize in many different structure types and exhibit interesting physical and chemical properties [1-7]. For example, pure SnO_2 is an n-type semiconductor [8,9], mixed oxides in the system Sn-Zr-Ti-O are dielectrics [10], while SnO_2 doped with lithium is a transparent conductor [11].

Recently, some new phases with the general formula $Li_2M(II)Sn_3O_8$, (M=Zn, Mg, Co, Fe, Mn) have been synthesized, and their crystal structure has been defined [12,13]. The phases represent interesting cation ordering in the double hexagonal type structure, not known previously, but similar to the ordering in some spinel type phases.

In the present work the dielectric properties of $Li_2ZnSn_3O_8$ and $Li_2MgSn_3O_8$ phases with ordered double hexagonal type structures are reported for the first time, and compared with those of $Li_2ZnTi_3O_8$ and $Li_2MgTi_3O_8$ which have ordered spinel type structures.

2. Experimental

Samples with composition $Li_2MM'_3O_8$, where M= Mg, Zn; M'=Ti, Sn, were synthesized by a solid state reaction between appropriate initial compounds. Li_2CO_3, MgO, TiO_2 and ZnO of analytical grade purity were used. SnO_2 with a high specific surface area and enhanced reactivity was prepared by dissolving metallic tin of 99.999% purity (United Min. and Chem. Corp.) in dilute nitric acid. Stannic acid was precipitated from the clear solution upon boiling. The precipitate was washed continuously until a neutral reaction was obtained, and then heated at 400 ^oC for 3 h. Compounds were obtained by mixing and grinding stoichiometric amounts of the initial compounds in an agate mortar. Prior to mixing, Li_2CO_3 was heated at 300 ^oC for 2h, while MgO and ZnO were heated at 800 ^oC for 2h. The homogenized powders were pressed into cylindrical pellets (12 mm diameter and 5 mm high) at 430 Mpa, and were subjected to thermal treatment. All samples were heated in air for 3h at 1000 ^oC. After intermediate homogenization and peletization the samples were subjected to a second heat treatment for 6h at 1000 ^oC.

The initial compounds and the synthesis procedure were controlled by X-ray powder diffraction. XRD spectra were recorded at room temperature with a computer controlled DRON-3 powder diffractometer with Cu-K_α radiation and scintillation registration. Data were collected in the 2θ range from 5^o to 105^o, with a step of 0.02^o and counting time of 1 s/step.

Scanning electron microscopy was performed on a Phillips 515 SEM.

The impedance measurements were performed at room temperature using a HP4274A multi-frequency LCR-meter, at frequencies in the range 10kHz -100 kHz. Measurements were performed on cylindrical pellets without metal contacts. Experimental data were analyzed in terms of the complex formalism for the impedance: $\{Z\} = Re\{Z\} - jIm\{Z\}$

The capacitance of the samples was measured using a Bounton Electronics 76A automatic capacitance bridge at a 1MHz test signal frequency.

3. Results and discussion

Powder XRD spectra of the investigated compounds are presented in Fig. 1. $Li_2MgTi_3O_8$ and $Li_2ZnTi_3O_8$

crystallize in a cation ordered spinel structure, cubic S.G. $P4_332$, with lattice parameters 8.3774(9) Å and 8.3710(2) Å respectively [14,15]. The structure consists of a cubic close packed array of oxygen layers stacked along the <111> direction in a sequence (ABCABC), in which cations occupy 1/8 of the tetrahedral and 1/2 of the octahedral interstices. Half of the lithium ions, together with the divalent metal ions, occupy the tetrahedral - 8c position. The remaining lithium ions occupy the octahedral - 4b position and the titanium ions occupy the octahedral - 12d cation position – Fig. 2(a,b). $Li_2MgSn_3O_8$ and $Li_2ZnSn_3O_8$ crystallize in an ordered double hexagonal type structure, orthorhombic S.G. $Cmc2_1$, with lattice parameters a=18.2594(3) Å, b=10.5496(2) Å, c=9.8353(1) Å and a=18.2048(8) Å, b=10.5098(5) Å, c=9.87158(7) Å respectively [12,13]. The structure can be described as a hexagonal close packed array of oxygen layers stacked along the <c> direction in a sequence (ABCB). Cations occupy 1/8 of the tetrahedral and 1/2 of the octahedral interstices – Fig. 2(c,d).

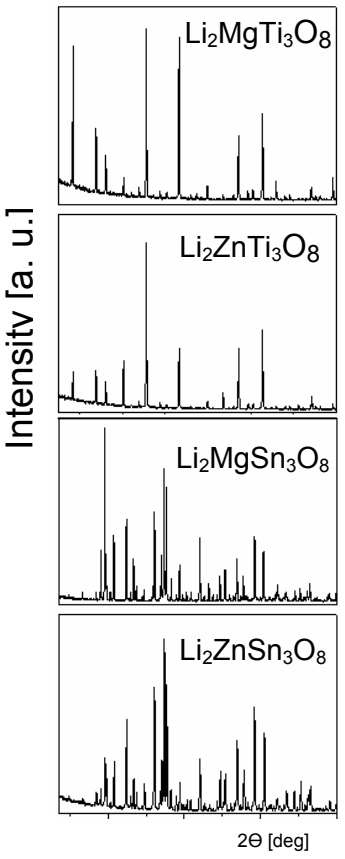

Fig. 1. X-Ray powder diffraction patterns of the phases with general composition $Li_2MM`_3O_8$ (M = Mg, Zn; M`= Ti, Sn).

In fact, both structures are built of identical cation layers: one containing three cations with octahedral coordination Kagomé layer - [Oc_3], and the other with two cations in tetrahedral and one in octahedral coordination - [T_2Oc]. The only difference comes from the oxygen layer sequence, and results in the displacement of one of the [T_2Oc] layers with respect to the previous [Oc_3] layer. The double hexagonal structure is more compact then the spinel one, which has been shown by comparison of the molar volume of compounds crystallizing in both structure types [12]. This affects the cation interactions between two adjacent cation layers.

Scanning electron photographs of the four compounds are shown in Fig. 3. It can be seen that all samples consist of two types of particle – large particles with approximate size 30 μm and small ones with a size about 0.1-0.3 μm. Magnesium and zinc containing samples are clearly distinguished by the particle morphology. The larger particles in the magnesium containing samples have irregular shapes - Fig. 3a. The smaller particles show well-defined edges and their size is non-uniform - Fig. 3b,c. In contrast, in zinc containing samples the larger particles have a rectangular form – Fig. 3d, while the smaller ones are globular but with a more uniform size - Fig. 3e,f. The dielectric constants of four samples are presented in Table 1.

Table 1. Dielectric constants of the phases with general formula $Li_2MM'_3O_8$, where M= Mg, Zn; M'=Ti, Sn, obtained by two different methods.

Phase composition	$\varepsilon_{(LCR)}$	$\varepsilon_{(RC)}$
$Li_2ZnSn_3O_8$	7.8	6.02
$Li_2ZnTi_3O_8$	14.3	15.36
$Li_2MgSn_3O_8$	9.8	9.75
$Li_2MgTi_3O_8$	16.9	11.02

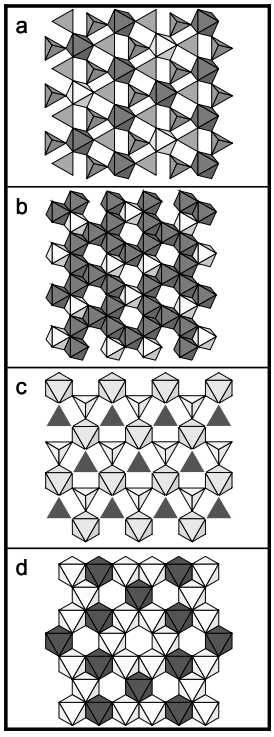

Fig. 2. Polyhedral presentations of the cation layers in the crystal structure of $Li_2MM`_3O_8$(M = Mg, Zn; M`= Ti, Sn). a – [T_2O] layer of the spinel type structure, b – [Oc_3] layer of the spinel type structure, c – [T_2O] layer of the double-hexagonal type structure, d – [Oc_3] layer of the double-hexagonal type structure.

For all samples, the impedance modulus $|Z|$ and the angle between the impedance vector and its real component were measured. The angles measured were all in the range 89-89.5° which is typical for materials with small dielectric losses.

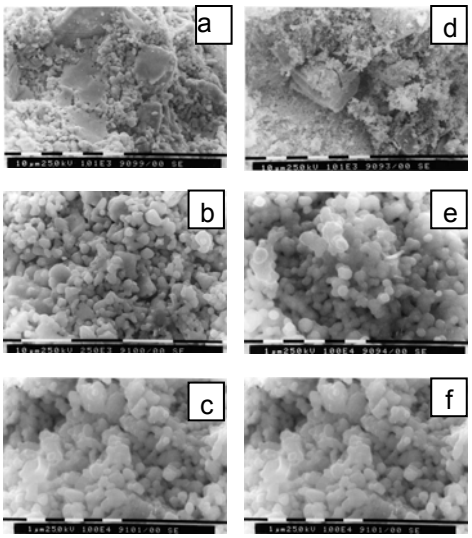

Fig. 3. Scanning electron photographs of the polycrystalline samples. General view: (a, d) of Li2MgSn$_3$O$_8$ and Li$_2$ZnSn$_3$O$_8$ respectively. Small particles: (b) - Li$_2$MgSn$_3$O$_8$; (c)- Li$_2$MgTi$_3$O$_8$; (e) – Li$_2$ZnSn$_3$O$_8$; (f) – Li$_2$MgSn$_3$O$_8$.

The complex impedance of this scheme is given by the equation:

$$\{Z\} = \frac{R}{1 + j\omega RC} \tag{1}$$

The corresponding complex conductivity is:

$$\{Y\} = \frac{1}{R} + j\omega C \tag{2}$$

where, $\omega = 2\pi f$, with f – the frequency, R- the resistance, C – the capacitance and $j^2 = -1$.

The values of the dielectric constants were calculated by using the equation:

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 S} \tag{3}$$

where d is the thickness of the sample, S is the contact surface and ε_o is the vacuum dielectric constant.

The observed differences in the ε values, obtained through the two methods, can be due to the accuracy of the measurements in the two cases Since the measured values lie in the upper range of the LCR-meter used (20 MΩ), the error in the corresponding values of ε is relatively high. More accurate values were obtained by capacitance measurements performed using a capacitance bridge at 1 MHz.

The dielectric constants measured for the new mixed oxide phases were comparable to the dielectric constants of the individual oxides from the literature: $\varepsilon_{r\ (ZnO)}$ = 4–8.5 [16], $\varepsilon_{r\ (TiO2)}$ = 140–260 [17], $\varepsilon_{r\ (SnO2)}$ = 9.6–13.5 [18], $\varepsilon_{r\ (MgO)}$ = 9.7 [19], showing that the presence of lithium does not reduce the conductivity of the mixed oxides.

The results obtained show that phases with double hexagonal type structures have lower dielectric constants than those with the spinel type structure. It is also worth mentioning that within each structure type, the magnesium containing samples have higher values of the dielectric constant than the zinc containing ones.

4. Conclusions

The difference between double hexagonal and spinel type structures originates from the difference in the oxygen layer sequences, which affect the type and the coordination number of the near neighbour cations. The interactions between cations from two adjacent layers contribute to the crystal binding energy and electronic structure of the phase [20] and therefore to the electrical properties of the material.

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