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Structural Changes in the Perovskitic Compounds Series

$\text{Sr}_2\text{Mg}_{1-x}\text{M}^{\text{II}}_x\text{MoO}_6$

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Abstract. Two series of perovskite type compounds ($\text{Sr}_2\text{Mg}_{1-x}\text{Zn}_x\text{MoO}_6$ and $\text{Sr}_2\text{Mg}_{1-x}\text{Ni}_x\text{MoO}_6$) are characterized from the structural point of view. The synthesis conditions are briefly described. The cation distribution of the two series compounds were determined by X-ray diffraction.

The synthesis of $\text{A}_2\text{BB}'\text{O}_6$ perovskites ($\text{A}=\text{Sr}$; $\text{B}=\text{W}$, Mo ; $\text{B}'=\text{Ni}$, Co , Zn) allowed to obtain compounds with a tetragonal structure, a and b parameters taking values between 5.561 and 5.596 Å and c between 7.886 and 7.978 Å [1, 2]. Palamaru *et al* [3, 4] obtained $\text{Sr}_2\text{MgMoO}_6$ starting from the following materials SrMoO_4 , $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{Mg}(\text{OH})_2$ and $\text{Sr}(\text{NO}_3)_2$. The perovskite has a nearly cubic structure ($a=b=7.879$, $c=7.928$ Å). We meant to synthesize by similar methods, $\text{Sr}_2\text{Mg}_{1-x}\text{M}^{\text{II}}_x\text{MoO}_6$ type oxides ($\text{M}^{\text{II}}=\text{Ni}$, Zn), for their potential to be used as supports for HTSC.

Table 1. Cation distribution of the system $\text{Sr}_2\text{Mg}_x\text{Zn}_{1-x}\text{MoO}_6$ (I - W type site; II - Ni type site [5])

Composition	$I_{220+202}$	$I_{311+113}$	I_{222}	$I_{400+004}$	Observations
$\text{Sr}_2(\text{Mg})_I(\text{Mo})_{\text{II}}\text{O}_6^*$	100	9.8	10.1	35.7	Calculated intensities
$\text{Sr}_2\text{MgMoO}_6^{**}$	100	8.3	15.6	36.5	Observed intensities
$\text{Sr}_2(\text{Mg}_{0.25}\text{Zn}_{0.25}\text{Mo}_{0.5})_I(\text{Mg}_{0.5}\text{Mo}_{0.5})_{\text{II}}\text{O}_6^*$	100	0.9	12.2	36.7	Calculated intensities
$\text{Sr}_2\text{Mg}_{0.75}\text{Zn}_{0.25}\text{MoO}_6^{**}$	100	0.0	10.0	38.7	Observed intensities
$\text{Sr}_2(\text{Mg}_{0.5}\text{Zn}_{0.5})_I(\text{Mg}_{0.5}\text{Mo}_{0.5})_{\text{II}}\text{O}_6^*$	100	0.7	5.6	32.4	Calculated intensities
$\text{Sr}_2\text{Mg}_{0.5}\text{Zn}_{0.5}\text{MoO}_6^{**}$	100	3.7	7.4	42.2	Observed intensities
$\text{Sr}_2(\text{Mg}_{0.25}\text{Zn}_{0.75})_I(\text{Mg}_{0.25}\text{Mo}_{0.75})_{\text{II}}\text{O}_6^*$	100	1.0	12.3	35.0	Calculated intensities
$\text{Sr}_2\text{Mg}_{0.25}\text{Zn}_{0.75}\text{MoO}_6^{**}$	100	2.3	9.2	39.2	Observed intensities
$\text{Sr}_2(\text{Zn}_{0.5}\text{Mo}_{0.5})_I(\text{Zn}_{0.5}\text{Mo}_{0.5})_{\text{II}}\text{O}_6^*$	100	0.7	5.6	32.4	Calculated intensities
$\text{Sr}_2\text{ZnMoO}_6^{**}$	100	0.0	5.9	37.0	Observed intensities

* :Calculated cation distribution ; ** : Nominal composition

The samples were obtained by the ceramic method using as starting materials high purity SrMoO_4 , $\text{Sr}(\text{NO}_3)_2$, MgO , NiO and ZnO . The pre sintering was performed in air at 700°C and 850°C/1-1.5h, depending the M^{II} cation type. The samples were ground for 10h, pressed into pellets and heated in air at 1150 and 1250°C for 3-5h. The crude, presintered and sintered samples were characterized chemically, metallographically and by X-ray diffraction. The theoretical intensities of the diffraction peaks were calculated using equation (1), and the cation distribution was tested using equation (2), [6]. For lower annealing temperatures an intermediate compound was evidenced. For these samples, the lower the MgO concentration the lower the intermediate compound concentration. The samples annealed at 1150°C contain a mixture of $\text{Sr}_2\text{Mg}_{1-x}\text{M}^{\text{II}}_x\text{MoO}_6$ (the outstanding phase) and $(\text{Mg}, \text{M}^{\text{II}})\text{O}$. The phases were identified using ASTM file cards 15-601 and 4-835. Higher annealing temperatures (1280°C in air) led to the decomposition of the main phase with the appearance of SrMoO_4 . X-ray measurements allowed the determination of the most probable cation distribution both for the system $\text{Sr}_2\text{Mg}_x\text{Zn}_{1-x}\text{MoO}_6$ (Table 1) and for the system $\text{Sr}_2\text{Mg}_x\text{Ni}_{1-x}\text{MoO}_6$ (Table 2). In the system $\text{Sr}_2\text{Mg}_x\text{Zn}_{1-x}\text{MoO}_6$ the magnesium cations are

disposed both on the middle of the edges and in the center of the unit cell, and on the corners and on the center of the unit cell faces, excepting the sample that contains only magnesium. In this case the magnesium seems to be placed on the corners and on the center of the unit cell faces.

Fig.1. The proposed structure for $\text{Sr}_2\text{MgMoO}_6$
(1) W type sites; (2) Ni types sites [5]; (3) Sr;
(4) O. $\text{W} \rightarrow \text{Mo}$ (Mg, Ni, Zn); $\text{Ni} \rightarrow \text{Mg}$ (Ni, Mo, Zn).

$$I_{hkl} = kp|F(hkl)|^2 A \frac{1 + \cos^2 2\theta}{\cos^2 \theta \sin \theta} \exp\left(-2B\left(\frac{\sin \theta}{\lambda}\right)^2\right) = kR_{hkl} \quad (1)$$

$$\sum_{h, k, l} \left| \frac{R_{hkl, \text{exp}} - R_{hkl, \text{calc}}}{R_{hkl, \text{calc}}} \right| = \min \quad (2)$$

The zinc cations are generally placed on the W type sites, excepting for the $\text{Sr}_2\text{ZnMoO}_6$ sample where they are placed on Ni type sites [5]. The cation distribution for $\text{Sr}_2\text{MgMoO}_6$ is in agreement with those obtained in our previous paper [3, 4]. Analyzing the theoretical data for the cation distribution, in the system $\text{Sr}_2\text{Mg}_x\text{Ni}_{1-x}\text{MoO}_6$, one can be noticed that the magnesium ions are placed both on the Ni and W sites in the Sr_2NiWO_6 compound. There is no a preferential ordering neither for magnesium nor for nickel ions, may be because their ionic radii are almost identical. The cation ordering is influenced both by the temperature and by the chemical composition.

Because the W type sites[5] corresponding to the octahedral places have a smaller volume than that of the Ni type sites, the Mg/Ni energy of interaction with the oxygen ions is stronger in the first case than in the second.

Table 2. Cation distribution of the system $\text{Sr}_2\text{Mg}_x\text{Ni}_{1-x}\text{MoO}_6$ (I - W type site; II - Ni type site [5])

Composition	I_{111}	$I_{220+202}$	$I_{311+113}$	I_{222}	$I_{400+004}$	Observations
$\text{Sr}_2(\text{Mg}_{0.2}\text{Ni}_{0.8})\text{I}(\text{Mo})\text{II}\text{O}_6^*$	4.5	100	2.5	4.7	33.3	Calculated intensities
$\text{Sr}_2\text{Mg}_{0.2}\text{Ni}_{0.8}\text{MoO}_6^{**}$	24.4	100	6.7	11.7	28.9	Observed intensities
$\text{Sr}_2(\text{Mo})\text{I}(\text{Mg}_{0.4}\text{Ni}_{0.6})\text{II}\text{O}_6^*$	8.0	100	4.3	6.3	34.1	Calculated intensities
$\text{Sr}_2\text{MoMg}_{0.4}\text{Ni}_{0.6}\text{O}_6^{**}$	24.4	100	6.7	11.7	35.5	Observed intensities
$\text{Sr}_2(\text{Mo})\text{I}(\text{Mg}_{0.6}\text{Ni}_{0.4})\text{II}\text{O}_6^*$	13.1	100	6.9	8.2	34.9	Calculated intensities
$\text{Sr}_2\text{Mg}_{0.6}\text{Ni}_{0.4}\text{MoO}_6^{**}$	21.1	100	7.5	12.8	39.2	Observed intensities
$\text{Sr}_2(\text{Mg}_{0.8}\text{Ni}_{0.2})\text{I}(\text{Mo})\text{II}\text{O}_6^*$	1.3	100	1.0	16.8	38.1	Calculated intensities
$\text{Sr}_2\text{Mg}_{0.8}\text{Ni}_{0.2}\text{MoO}_6^{**}$	10.7	100	3.2	8.3	36.9	Observed intensities
$\text{Sr}_2(\text{Mo})\text{I}(\text{Mg})\text{II}\text{O}_6^*$	29.1	100	15.2	13.5	-	Calculated intensities
$\text{Sr}_2\text{MgMoO}_6^{**}$	45.6	100	9.2	13.6	-	Observed intensities

*: Calculated cation distribution; **: Nominal composition

A clear difference between the $\text{Sr}_2\text{Mg}_x\text{Zn}_{1-x}\text{MoO}_6$ and $\text{Sr}_2\text{Mg}_x\text{Ni}_{1-x}\text{MoO}_6$ type compounds could be observed: the zinc ions are placed on both type sites only in $\text{Sr}_2\text{ZnMoO}_6$, in all the remaining compounds of the corresponding series being placed in W sites. The zinc ions had preference for W type sites whose volume is smaller than that corresponding to Ni type sites. The nickel ions are randomly placed both on W type and Ni type sites.

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