Structural, Electrical and Magnetic Characterization of the Double Perovskites $Sr_2Cr_{(1+x)}W_{(1-x)}O_6$

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We report on the preparation and characterization of the double perovskite compounds $Sr_2Cr_{1+x}W_{1-x}O_6$ (x = 0 ÷ 0.5) with a Curie temperature near 300 K. We have prepared our samples by solid state reaction. The mixtures were calcined at 950°C for 20 h in a 5%H_2/N_2 gas mixture and then pressed into pellet and sintered at 1100-1580°C in a 5%H_2/N_2 gas mixture. The samples were characterized by X-ray diffraction, electronic microscopy (SEM), transport and magnetic measurements. The diffraction patterns were indexed on a cubic Fm3m lattice of the double perovskite structure. Electron microscopy show that the samples have grain size between 0.1 and 0.2 μm. Transport properties for all samples shows an increase of the resistivity with decreasing temperature. The compounds are ferrimagnetics and the magnetoresistance regularly increases as temperature diminishes. Our results show that Sr_2CrWO_6 is an interesting candidate for room temperature magnetoelectronic materials.

Keywords: solid-state synthesis, double perovskite, X-ray diffraction, SEM, magnetoresistance

Double perovskites with formula $A_2BB'O_6$, where A represents an alkaline earth, B and B' are metal transition magnetic and nonmagnetic ions and O is the oxygen, have been known for many years but recently the study of these materials has increased due to the various technological application [1, 3, 4].

In 1998 there were reported considerable magneto-resistance behavior and a high magnetic transition temperature in a Sr_2FeMoO_6 compound [12]. Since then many other compounds have been proposed changing the metallic-magnetic ions on the B and B' site or partially replacing the divalent alkaline earth ions on the A site by trivalent rare earth ions such as La for the purpose of obtaining these amazing properties.

In order to observe low field magnetoresistive effects in other compounds the series $Sr_2CrB'O_6$ has recently been studied [5, 6]. The compound Sr_2CrReO_6 presented the highest Curie temperature known with T_C = 635 K, increasing importantly the T_C reported for the Sr_2FeMoO_6 material [2].

In the particular case of the Sr_2CrWO_6 thin film samples have been made which revealed ferrimagnetisms, with T_C up to 458 K [7]. The major difference between Fe based and Cr based-double perovskites oxides is that in the Cr compound there can be no valence compensation between the Cr and the Mo, W ions since Cr can only be in the 3+ state (d^3).

In this study we present the synthesis and structural, magnetic and transport properties of the double perovskite $Sr_2Cr_{1+x}W_{1-x}O_6$. We investigated this material as a possible candidate for room temperature magnetoelectronic devices.

Experimental part

Polycrystalline samples $Sr_2Cr_{1+x}W_{1-x}O_6$ (x = 0 ÷ 0.5) were prepared from stoichiometric mixtures of $SrCO_3$, Cr_2O_3 and WO_3 with a high purity. These powders were thoroughly mixed and were first fired at 950°C for 20h in 5%H_2/N_2 gas mixture. The obtained powders were mixed again in an agate mortar and pressed into pellets and heated at temperatures from 1100 to 1580°C for 12 h in a 5%H_2/N_2 gas mixture. Sr_2CrWO_6 powder was sintering at 1600 and 1650°C to reduce the amount of parasitic phases such a $SrWO_4$ as found by X-ray analysis. It is observed that the samples fired at 1600 and 1650°C are nearly phase pure, however the 1650°C sample is partially molten.

X-ray diffraction measurements at room temperature used to investigate the purity of the perovskite phase and data were recorded from a flat plat sample on a Bruker D8-diffractometer using monochromated $Cu_{k\alpha}$ radiation. Rietveld refinement on the X-ray powder diffraction data were performed using the program FULLPROF and GSAS [8, 9]. Scanning electron microscopy were carried out using a LEO-260 electron microscope with EDX and detector Si-Li Noran to analyze the ceramics microstructure and to check the chemical composition of the ceramic samples. Field and zero field cooled magnetizations were measured on a Quantum Design SQUID magnetometer. The sample sizes were 100-200μg and were packed into teflon tape packet. Hysteresis loop were measured at 5 K between magnetic field of –5.5 T and +5.5 T. Electrical resistivity was measured at temperatures with a standard method using silver epoxy contact for the ceramic samples.

Results and discussions

The polycrystalline samples $Sr_2Cr_{1+x}W_{1-x}O_6$ (x = 0 ÷ 0.5) were characterized by X-ray powder diffractometer to detect parasitic phases in our case the insulating compound $SrWO_4$. Interestingly even in samples containing $SrWO_4$ no chromium containing parasitic phases could be detected (the most simple explanation for this observation is the high vapor pressure of Cr_2O_3 resulting in a loss of chromium).

The figure 1a displays the observed XRD patterns for Sr_2CrWO_6 sintered at 1580°C, 1600°C and 1650°C. It is observed that an increase of the sintering temperature the impurity phase diminishes. The figure 1b presented XRD patterns for $Sr_2Cr_{1+x}W_{1-x}O_6$ (x = 0.1 ÷ 0.5) sintered at 1580°C and we observed that increasing the degree of substitution, the impurity phase diminishes and for x = 0.4 disappeared. For all compounds we used the FULLPROF and GSAS for the Rietveld refinements in order to obtained

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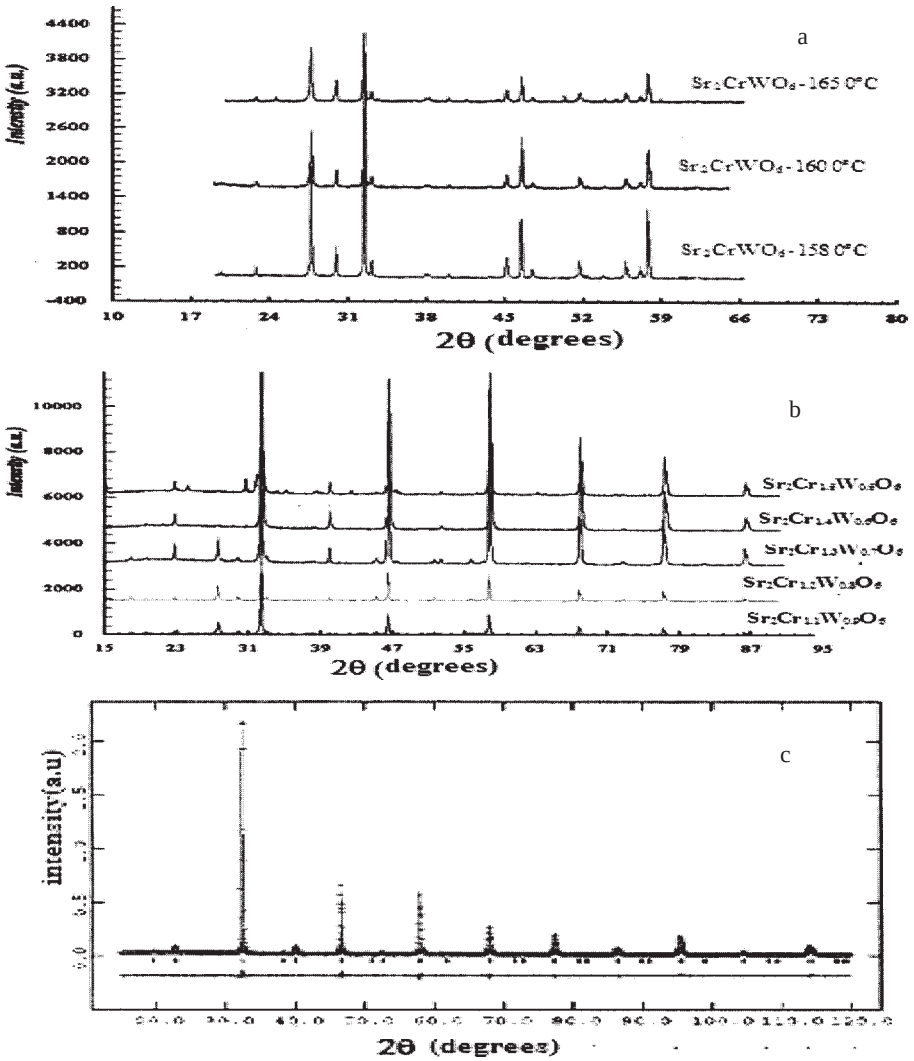

Fig.1.(a) X-ray diffraction patterns for Sr_2CrWO_6 sintered at 1580°C, 1600°C and 1650°C; (b) X-ray diffraction patterns for: $Sr_2Cr_{1+x}W_{1-x}O_6$ sintered at 1580°C; (c) Observed (crosses) and calculated (full line) patterns for $Sr_2Cr_{1+x}W_{1-x}O_6$ with x = 0.4. Positions for the Bragg reflections are marked by verticals bars.

Table 1
ATOMIC POSITIONS AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (U_{iso}) for $Sr_2Cr_{1+x}W_{1-x}O_6$, WITH , x = 0.4

Atom	Mult.	Frac	x	y	z	U_{iso}(Å^2)
Sr	8	1.000	0.250	0.250	0.250	0.0241
Cr	4	0.7583	0.000	0.000	0.000	0.0112
W	4	0.2243	0.000	0.000	0.000	0.0112
Cr	4	0.6733	0.500	0.500	0.500	0.0178
W	4	0.3273	0.500	0.500	0.500	0.0178
O	24	0.975	0.252	0.500	0.000	0.0166
a = 7.797 Å, Fm3m						
R_B = 7.8%, R_P = 6.7%						

information on the crystal structure. All the observed peaks can be fitted with the reflection condition of the space group Fm3m.

The possibility of anti-site disordering due to some W sites being occupied by Cr atoms and vice versa was taken into account. The atomic parameters derived from typical refinements for the $Sr_2Cr_{1+x}W_{1-x}O_6$ with x = 0.4 are given in table 1. In a second stage atoms and occupancies have been refined on the basis of data from the literature [10]. The cationic nature in mixed occupied positions has been validated by the stoechiometry and the values of thermal parameters. The final atomic positions, isotropic temperature factors and the R final value are reported in table 1. The final R values are comforting the pertinence of the proposed models.

The morphologies of the all sample sintered were observed using a Scanning Electron Microscope (SEM). Figure 2a shows SEM microstructures of the Sr_2CrWO_6 sintered at 1580°C and we observed the presence of a impurity phase $SrWO_4$. Figure 2b shows the SEM microstructures of the sample $Sr_2Cr_{1+x}W_{1-x}O_6$ sintered at 1580°C with x = 0.4. As the values of x increase the size of particles become more homogeneous and the simple with x = 0.4 is pure with small particle with good cristalinity and have grain size between 1 and 5μm. Therefore, the analysis SEM confirms the results witch we obtained by X-ray analysis.

For Sr_2CrWO_6 with the electronic configuration $Cr^{3+}(3d^3)$–$W^{5+}(5d^1)$ the theoretical effective magnetic moment (spin only) $2\mu_B$/f.u. For our compound sintered at 1580°C we found magnetic moment $0.36\mu_B$/f.u. The origin of this difference with the theoretical magnetization can be found in the anti-site B cation disorder implying that some W^{5+} cations occupy the positions of Cr^{3+} cations and vice versa. The plots of magnetization against temperature for Sr_2CrWO_6 are also given in the upset of figure 3.

It is observed that for all compounds the magnetization decrease with increasing temperature and all compounds are ferrimagnetics. We note that T_c = 300 K for the 1580°C sample is well below the value of 453 K reported earlier [8]. This difference is most likely caused by disorder on the Cr/W position or by oxygen deficiency.

Figure 4 shows the temperature dependence on the resistivity for the $Sr_2Cr_{1+x}W_{1-x}O_6$ with x = 0.4. All the samples

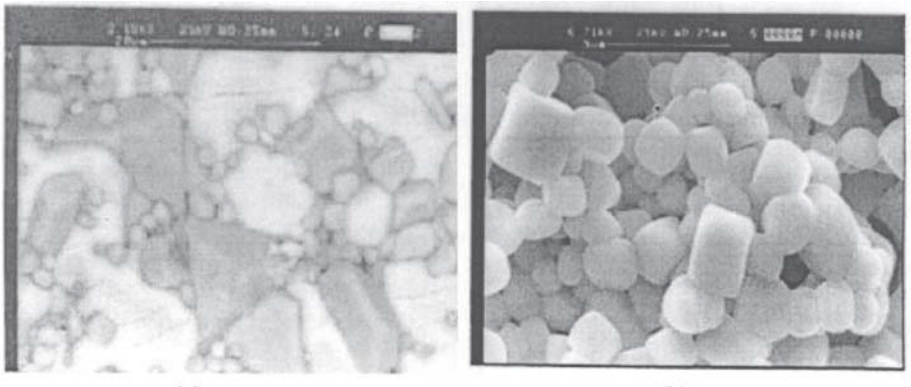

Fig.2.(a) SEM image of the ceramic sample obtained by solid state reaction route for Sr_2CrWO_6 sintered at 1580°C (b) SEM image of the ceramic sample obtained by solid state reaction route for $Sr_2Cr_{1+x}W_{1-x}O_6$, with x = 0.4, sintered at 1580°C

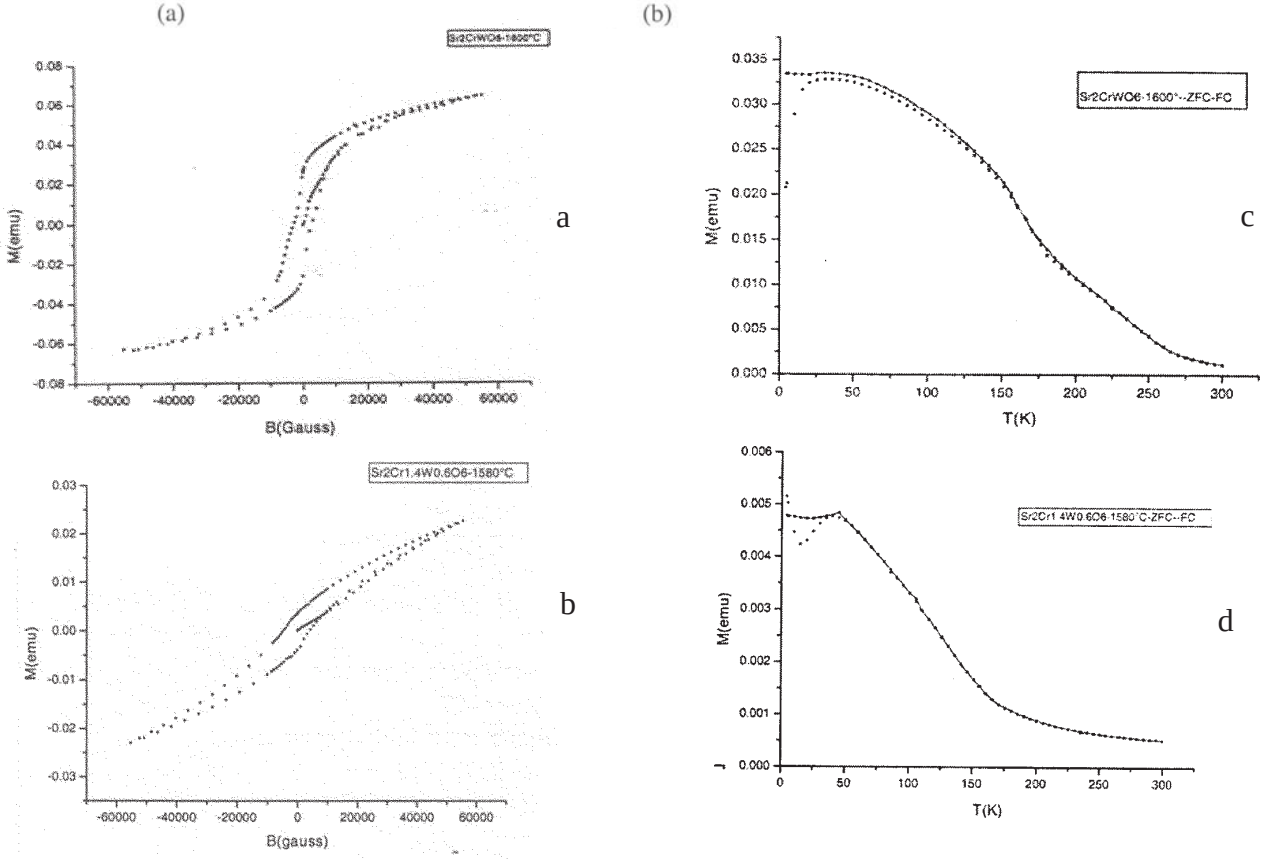

Fig.3.(a) Magnetizations vs. field (T = 5 K) for the Sr_2CrWO_6, sintered at 1600°C
(b) Magnetizations vs. field (T = 5 K) for the $Sr_2Cr_{1+x}W_{1-x}O_6$ with x = 0.4 sintered at 1580°C;
(c) Variation of magnetoresistance with temperature for the Sr_2CrWO_6 sintered at 1600°C;
(d) Variation of magnetoresistance with temperature for the $Sr_2Cr_{1+x}W_{1-x}O_6$, x = 0.4 sintered at 1580°C

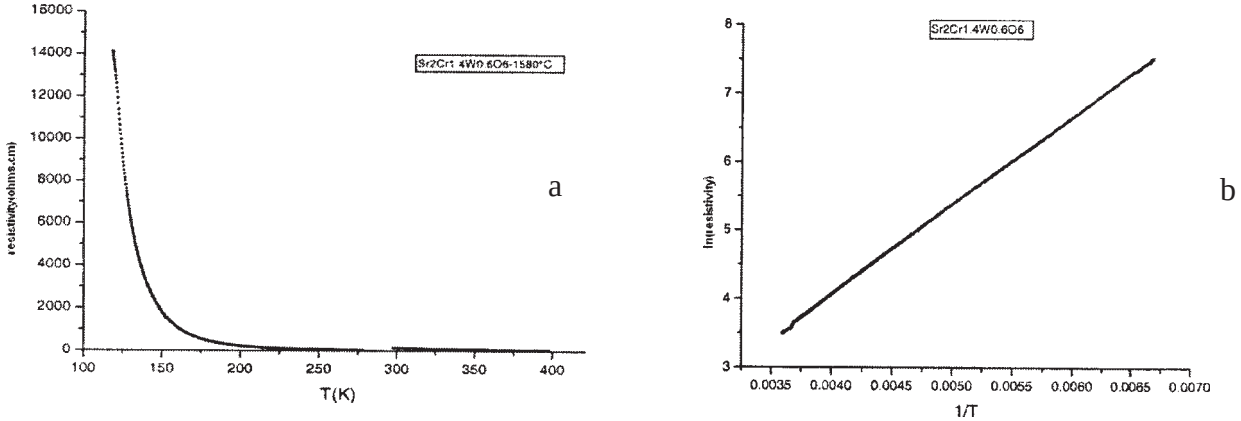

Fig.4.(a)Variation of the resistivity with temperature for $Sr_2Cr_{1+x}W_{1-x}O_6$, x = 0.4 sintered at 1580°C
(b)Variation of the ln(resistivity) with temperature for $Sr_2Cr_{1+x}W_{1-x}O_6$, with x = 0.4 sintered at 1580°C

show an increase of the resistivity with decreasing temperature and show an isolator like behavior.

Conclusions

We obtained a new series of double perovskites $Sr_2Cr_{1+x}W_{1-x}O_6$ (x = 0 ÷ 0.5) by a solid state reaction defined in the cubic structure with S. G. - *Fm3m*, behaving as

isolators having T_C of about 300 K. Comparing Sr_2CrWO_6 double perovskite with other perovskite materials suggest that this material is an interesting candidate for application in magnetoelectronics due to its high Curie temperature and low resistivity

References

1.GARCIA-LANDA, B., RITTER, C., IBARRA, M. R., BLASCO, J., ALGARABEL, P. A., MAHENDERON R., GARCIA, J., Solid State Commun.,110, 1999, p. 435

2.KOBAYASHI-K, I., KIMURA, T., SAEADA, H., TEKURA, K., TOKURA, Y., Structure Nature, 395, 1998, p. 677

3.CHIOARU, L.C., JITARU, I., BICHER, M., MATEI, V., MIHAI, O., Rev. Chim., (Bucharest), **60**, nr.3, 2009, p.283

4.BURZO, E., BALASZ, I., ALBU, M., Rev. Chim. (Bucharest), **59**, no.11, 2008, p.1205

5.PHILIPP, J. B., MAJEWSKI, P., ALFF, L., ERB, A., GROSS, R., GRAF, T., BRANDT, M. S., SIMON, J., WALTHER, T., MADER, W., TOPWAL, D., SARMA, D. D., Phys. Rev. B, 68, 2003, p. 144431.

6.PHILIPP, J. B., REISINGER, D., SCHONECKE, M., MARX, A., ALFF, L., GROSS, R., Appl. Phys. Lett., 79, 2001, p. 3654

7.RETUERTO, M., ALONSO, J. A., GARCIA-HERNANDEZ, M., MARTINEZ-LOPE, M., J. Solid State Communications, 139, 2006, p.19.

8.PHILIPP, J. B., REISINGER, D., SCHONECKE, M., OPEL, M., MARX, A., ERB, A., ALFF, L., GROSS, R., J. Appl. Phys. 93, 2003, p. 6853 .

9.KATO, H., OKUDA, T., OKIMOTO, Y., TOMIODE, Y., TAKENOYA, Y., OHKUBO, A., KAWASAKI, M., TOKURA, Y., Appl. Phys. Lett., **81,** 2002, p. 328 .

10.LINDEN, J., YAMAMOTO, T., NAKAMURA, J., KARPPINEN, M., YAMAUCHI, H., Applied Physics Letters, 78, nr. 18, 2001, p. 2736

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