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Rational Sol-Gel-Based Synthesis Design and Magnetic and Dielectric Properties Study of Selected Nanocrystalline Double and Triple Perovskites

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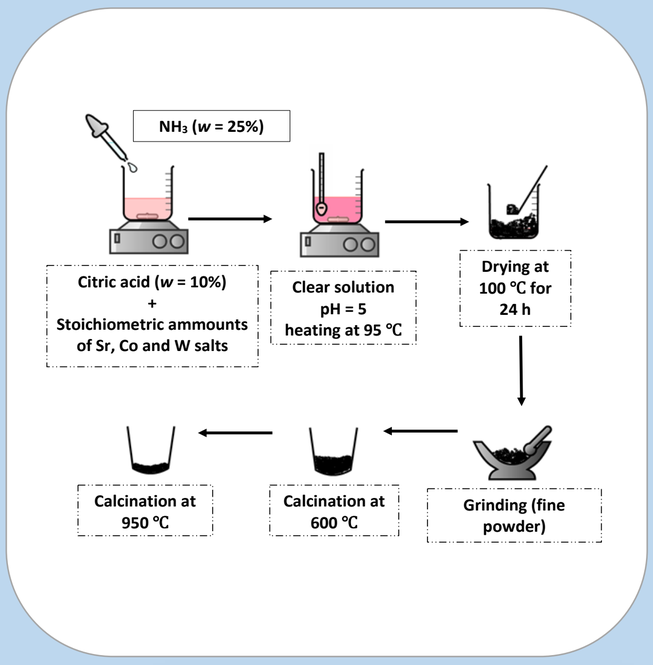
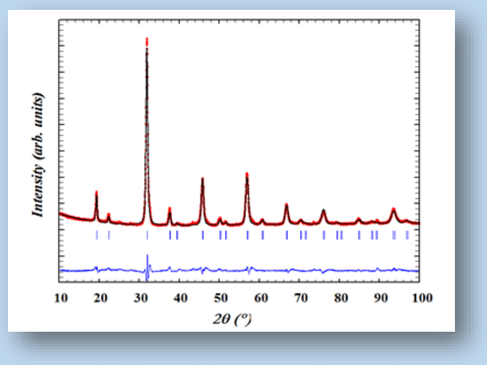
INTRODUCTION

Polar perovskite materials have attracted extensive attention due to the coexistence of magnetic ground state and semiconductor band gap within the same material. Mostly the structure and magnetic properties have been investigated for these compounds with lack of knowledge in the dielectric part. In this work, our goal is to clarify magnetic and dielectric properties and to investigate the effects that occur due to size reduction to nanoscale. For the first time, we give a detailed explanation of dielectric and magnetic properties of investigated complex perovskites and show effects of size reduction on the magnetic properties.

EXPERIMENTAL



RESULTS AND DISCUSSION



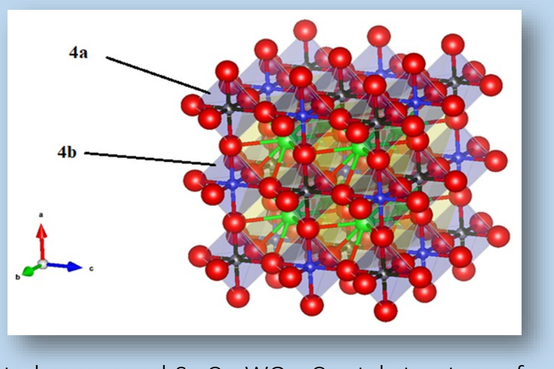


Figure 1. Rietveld output plot of the investigated compound $Sr_3Co_2WO_9$. Crystal structure of $Sr_3Co_2WO_9$ showing Sr atoms (light green), Co1 atoms (blue), Co2 atoms (dark olive), W1 atoms (grey) and O1 atoms (red).

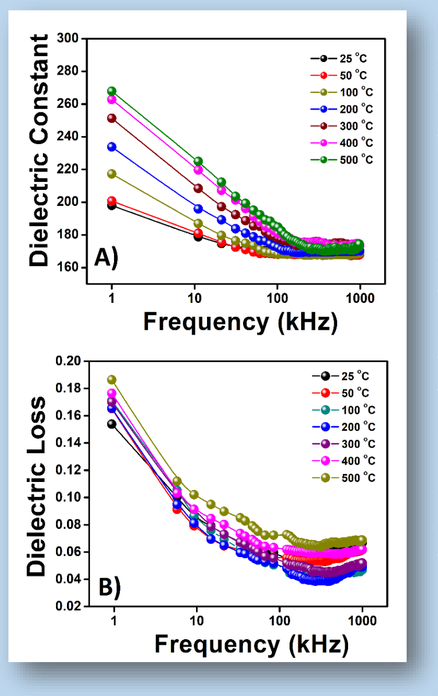


Figure 2. The dependence of A) dielectric constant and B) dielectric loss on frequency of the $Sr_3Co_2WO_9$ pellet sintered at 1250 °C at selected temperatures. The Maxwell-Wagner model suggests in the high frequency area the well conducting grains are dominant while low conducting grain boundaries are present in the low frequency area. In this material, the mechanism of electron hopping occurs between Co^{3+} ions being situated at two different octahedral crystallographic sites (4a and 4b). Electrons need to pass through the well conducting grains and the poorly conducting grain boundaries. Since grain boundaries generate high resistance, the electrons get accumulated leading to an enhanced space charge polarization.

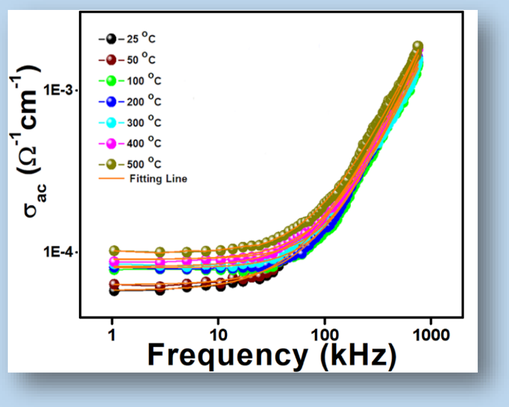


Figure 3. Dependence of AC conductivity on frequency at various temperatures. The solid line corresponds to fitting using the Jonscher law.

Table 1. Fitting parameters of polarizability *A* and dimensionless factor *n* extracted from AC conductivity curves for various temperatures. Parameter *n*>1 suggests involvement of localized hopping without the species leaving the neighborhood.

Temperature (°C)	*A*	*n*
25	2.759×10^{-7}	1.860
50	1.614×10^{-7}	1.954
100	3.923×10^{-8}	2.291
200	4.397×10^{-8}	2.259
300	4.866×10^{-8}	2.023
400	4.806×10^{-8}	2.070
500	4.832×10^{-8}	1.916

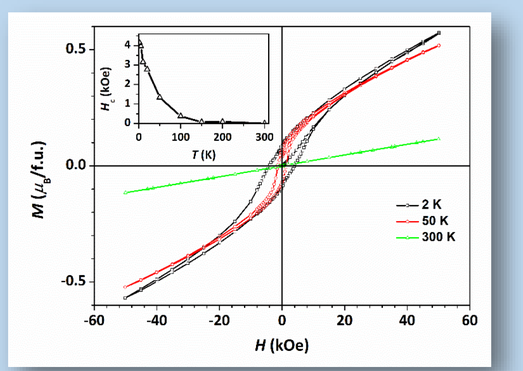


Figure 4. Isothermal magnetization at 2 K, 50 K, and 300 K. Inset: coercive magnetic field as function of temperature. Considering two Co^{3+} ions per formula unit and, as calculated from the susceptibility measurements and obtained effective magnetic moment, only 40 % of them being in a HS state with *S*=2, the saturation magnetization should be of the order of $2{\cdot}0.4{\cdot}gS\mu_B \approx 3.2\mu_B$ per formula unit. The measured remanent magnetization of 0.09 μ_B/f.u. at 2 K is much smaller, which is in accordance with the proposed ferrimagnetic ordering of magnetic moments.

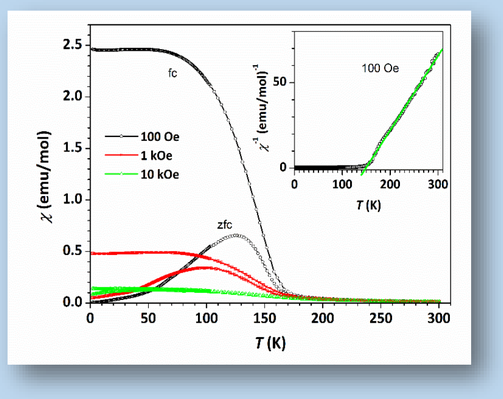


Figure 5. The susceptibility χ as a function of temperature measured in different magnetic fields. Inset: inverse FC susceptibility measured in 100 Oe and Curie-Weiss fit (full green line).
The inverse susceptibility (inset in **Figure 5** is linear above the transition temperature which enable us to fit the data with the Curie-Weiss law $\chi(T) = C/(T-\vartheta)$. The obtained parameters are the Curie constant C = 2.3 emu K/mol, and the Curie-Weiss temperature ϑ = 146 K.

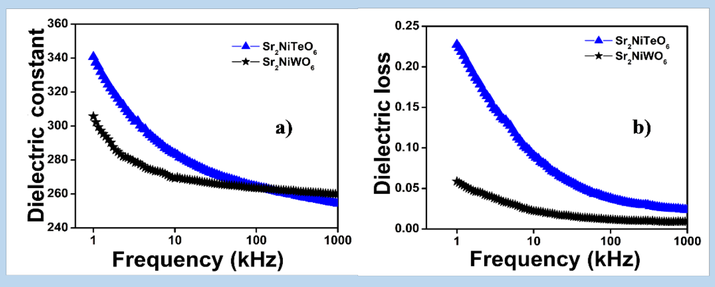


Figure 6. (a) Dielectric constant and (b) dielectric loss of Sr_2NiWO_6 and Sr_2NiTeO_6 ceramic at room temperature.

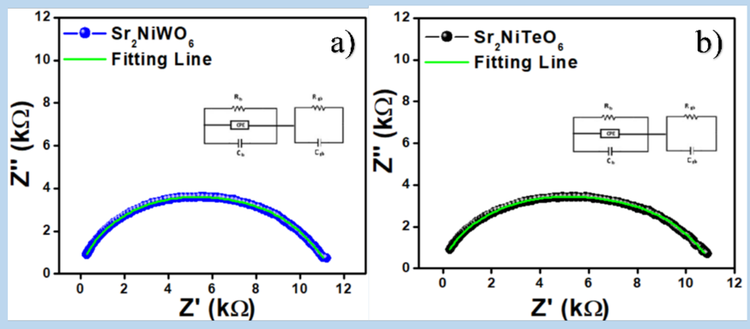


Figure 7. Nyquist plot of (a) Sr_2NiWO_6 and (b) Sr_2NiTeO_6 ceramics at room temperature. In the inset, the equivalent electrical circuits are displayed.

CONCLUSIONS

The triple perovskite $Sr_3Co_2WO_9$ has been synthesized in the nanocrystalline form with an average crystallite size of 23 nm using a modified aqueous citrate sol-gel method. The crystal structure of $Sr_3Co_2WO_9$ is cubic at the room temperature, space group *Fm*-3*m* with lattice parameter *a*= 7.9073(6) Å. The detected hysteresis loops reveal ferrimagnetic ordering with Curie temperature of 144 K. The measured effective magnetic moment of 3 μ_B is close to the expected value for rarely observed intermediate spin *S* = 1 but can also be explained as a combination of HS (40 %) Co^{3+} and LS (60 %). Semiconducting nature was confirmed by AC conductivity measurements, which is between 10^{-5} and 10^{-4} Ω^{-1} cm^{-1}. The frequency dependent dielectric constant was explained by employing the Maxwell-Wagner model. The frequency dependent AC conductivity follows the universal Jonscher's power law. This material could be a good candidate for implementation as a constituent for devices where its semiconducting properties would be spin controlled. Double perovskites with Sr_2NiMO_6 (M = Te, W) structure type have been similarly synthesized. The reaction yielded phase pure nanocrystalline powders of two compounds Sr_2NiWO_6 (SNWO) and Sr_2NiTeO_6 (SNTO). According to the Rietveld refinement of powder X-ray diffraction data at room temperature Sr_2NiWO_6 is tetragonal (*I*4/*m*) and Sr_2NiTeO_6 is monoclinic (*C*12/*m*1) with average crystallite sizes of 49 and 77 nm, respectively. Both SNTO and SNWO possess high values of dielectric constants (341 and 308, respectively) with low dielectric loss (0.06 for SNWO) at frequency of 1 kHz. The Nyquist plot for both samples confirms the non-Debye type of relaxation behavior and the dominance of shorter-range movement of charge carriers. Magnetic studies of both compounds revealed antiferromagnetic behavior with T_N being 57 K for SNWO and 35 K for SNTO.