Investigation of Physical Properties in Some 3d Based Nano-crystalline Double Perovskite oxides Ln_2CoMnO_6 (Ln = Pr, Sm, Gd, Ho, Yb)

ABSTRACT

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Abstract

Keywords: *Double perovskites, nano-crystalline, structural study, magnetic properties, phase transition, spin-phonon coupling, dielectric properties.*

Transition metal oxides (TMOs) are the most fascinating class of compounds which exhibit many interesting properties. These compounds adopt variety of structural symmetry which plays a critical role in deciding their physical properties. The double perovskite structure has been studied in great detail and have shown potential application in technology. However, in recent times the interest of many researchers has shifted to 3*d* based double perovskites, since these compounds have shown exotic phenomena like, ferromagnetism, half metals, antiferromagnetic insulator, Mott instability, magneto-electricity, colossal magnetoresistance at high temperatures, magneto-dielectric phenomenon room temperature feroelectricity etc. Double Perovskites with 3*d* transition metal ions are of greater interest since, 3*d* elements have strong electronic correlation (*U*) however crystal field effect and Hunds coupling are competing with each other and decides the spin state of the ions (high/low). Double perovskites materials have recently attracted the attention of researchers due to its rich physics and potential for novel application. Double perovskite name is due to the unit cell which is twice that of perovskite. The general formula of double perovskite is $A_2BB'O_6$. Where A stand for an rare/alkali-earth metals and B, B′ are transition metal cations. Rock-salt like arrangement of corner sharing BO_6 and $B'O_6$ units in the crystal structure of double perovskites form a nice and symmetries structure. This structure is similar to that of perovskites with 12-coordinate A site and 6-coordinate B site but the unit cell is double of pervoskites due to which it is known as double perovskite. Ion at A site largely influences the physical properties of these compounds. A-site ion can be a lanthanides or rare-earth element. The 3*d* based double perovskites with rare-earth atom at A-site have shown potential for exotic physics. These complex compounds are often characterized by strong interplay of spin, orbital and charge degrees of freedom and are extremely sensitive to small perturbations. These materials offer a strong competition between ferromagnetic and antiferromagnetic order resulting from dominant exchange

interaction. These complex compounds offer wide range of technological applications and lead to intense research on 3*d* based double perovskites like Ln_2CoMnO_6 and Ln_2NiMnO_6 recently. While later Ln_2NiMnO_6 have been studied extensively due to multiferrioc properties where Ln_2CoMnO_6 have been given less attention.

In this thesis we have chosen Ln_2CoMnO_6 based compound to study their structural, magnetic, electric, dielectric properties. Ln_2CoMnO_6 have potential to show exotic properties. Efforts have been made to investigate these compounds in bulk or which however is not sufficient to comprehend these materials in detail. The materials have potential to show giant magnetocaloric effect, magnatoresistance, electrical properties, ferromagnetic strong insulating behaviour, dielectric properties, Griffith phase, spin-phonon coupling etc. In this thesis we make an effort to understand physcal properties of nano-crystalline Ln_2CoMnO_6 (Ln= Pr, Sm, Gd, Ho, Yb) and double perovskite. Here Co^{2+} ($d^7\ t_{2g}^5\ e_g^2$) and Mn^{4+} ($d^3\ t_{2g}^3\ e_g^0$) at B and B′ respectively gives rise to well-ordered structure. However Co^{2+}- Co^{2+} and Mn^{4+}- Mn^{4+} or Co^{3+} - Mn^{3+} placement of atoms on B, B′ gives disordered phase. The ordered phase crystallizes in monoclinic structure otherwise orthorhombic structure. In ordered structure the Co^{2+}-O-Mn^{4+} interacts via super exchange interaction and ferromagnetic ordering is expected.

We have synthesized Ln_2CoMnO_6 double perovskite in nano-crystalline form by using the sol-gel method and present a comprehensive detail study on the structural, magnetic and dielectric properties of several double perovskites Ln_2CoMnO_6, (Where Ln= Pr, Sm, Gd, Ho, Yb). In this study all samples shows perfect Co^{2+} and Mn^{4+} ordering in their unit cell. Our results reveal that magnetic properties strongly depend on Ln-size. Nano-crystalline sample shows magnetic phase transition with Curie temperature and their magnetic phase transition directly depend on Ln size larger the atomic radii the greater the magnetic phase transition temperature. Synthesis of nano-crystalline sample was done by sol-gel method. The structural characterization is done by X-ray diffraction technique. The structural analysis shows that the sample is in single phase and crystallizes in monoclinic structure. The particle size has been estimated with the help of scanning electron microscopy measurement. The magnetic properties have been studied using DC magnetization. All the samples show a PM-FM phase transition with the ordering of Co^{2+}/ Mn^{4+} sublattice. The ordering temperature decrease with decreasing Ln-ionic size. Further the Ln rare-earth atoms undergo magnetic interaction at low temperature and Ln-sublattice order exactly opposite to the Co/Mn sublattice giving rise to anti-ferromagnetic ordering. The appearance of Griffith phase is observed above FM transition in paramagnetic state. In some cases the detailed analysis of

magnetization data above T_c confirms the presence of Griffith singularity. We have also found that Pr_2CoMnO_6 undergoes PM-FM magnetic transition which is more like mean field type as revealed by critical analysis. We further studied the sample Pr_2CoMnO_6 for charge transport. The temperature[2] dependent resistivity shows the hopping of small polarons that gives the conduction mechanism. Ferromagnetic insulating magnites specially in perovskites have shown strong spin-phonon coupling. To observe this feature in double perovskite we have carried out temperature dependent Raman study. The Raman spectra, reveals that the materials shows strong spin-phonon coupling exhibited by deviation of phonon mode frequency from anharmonic behavior. Dielectric measurements have been performed for Ln_2CoMnO_6 (Ln= Sm, Gd, Ho, Yb) samples. The Ln_2CoMnO_6 compounds shows deviation from Debye model. The detailed investigation of impedance spectroscopy, electric modules and AC conductivity have also been presented for the samples.

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