INFLUENCE OF CATION SUBSTITUTION ON THE SUPERCONDUCTING, MAGNETIC AND DIELECTRIC PROPERTIES IN PEROVSKITES

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by

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Dedicated

to

my Grand father

CERTIFICATE

This is to certify that the thesis entitled, "**Influence of cation substitution on the superconducting, magnetic and dielectric properties in perovskites**", being submitted by **Mr. Sarojalochan Samal**, to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. Sarojalochan Samal has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or full, to any other university or institute for award of any degree or diploma.

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ABSTRACT

Perovskites are of immense research interest because of their simple structure and their tolerance to a large variety of cations which leads to tailor the properties of the compounds. Studies have been focused on understanding the effect of substitution on the crystal structure and their correlation with different physical properties. In this thesis an attempt has been made to understand effect of cation substitution in superconductors, magnetic and dielectric materials. Apart from this, synthesis of new ordered perovskites has also been carried out and investigated their properties.

Chapter 1 gives a brief overview of the structure of perovskite and ordered perovskites and their electrical, magnetic and multiferroic properties. Structure property relationship in superconductors, especially on high temperature cuprate superconductors has been discussed. The influence of cation disorder on the superconducting transition temperature has also been discussed. In addition to this dielectric and microwave dielectric properties of perovskite oxides has been presented. Synthetic methodologies and a brief description of various characterization techniques that have been employed to study the synthesized materials have been reviewed. The motivation for carrying out the research work has been summarized.

Chapter 2 discusses the synthesis, characterization and superconducting properties of three series of compounds related to 1113-type of compound. The effect of cation disorder, introduced by substituting isovalent cation with smaller ionic radii, on Tc has been studied. $Ln_{1.2}Ba_{1.2}Ca_{0.6}Cu_3O_{7+\delta}$ (Ln = La, Nd, Sm), $La_{1.2-x}Nd_xBa_{1.2}Ca_{0.6}Cu_3O_{7+\delta}$ and $La_{1.2-x}Nd_xBa_{1.4}Ca_{0.4}Cu_3O_{7+\delta}$ compounds were synthesized by solid state route. Rietveld

refinement studies of X-ray data was carried out on $La_{1.2}Ba_{1.2}Ca_{0.6}Cu_3O_{7+\delta}$, $Nd_{1.2}Ba_{1.2}Ca_{0.6}Cu_3O_{7+\delta}$ and $Sm_{1.2}Ba_{1.2}Ca_{0.6}Cu_3O_y$ to understand the distribution of cations in the *Ln* and Ba sites of the tetragonal 1113-type structure. Detailed resistivity study has been carried out on all the compounds and it was observed a decrease in superconducting transition temperature (T_c) with increase in Nd content in the solid solutions. Careful analysis on the structural refinement and the variation in the transition temperature on the solid solutions revealed a correlation of Nd cation distribution at 1*d* and 2*h* site with the decrease in T_c. The results show the disorder at 2h site has a more pronounced effect on the superconducting transition temperature than the disorder at 1*d*-site. It is also shown that above a critical concentration of Nd, there is rapid decrease in T_c which is related to the maximum capacity of *Ln* ion at the 1*d*-site.

In Chapter 3 we present the synthesis of multiferroic oxides related to hexagonal $YMnO_3$ and studied their properties. In this chapter we have varied both A and B-site cation with different electronegativities and studied their effect on the magnetic and dielectric properties. For the first time we have extended the solubility range of iron in hexagonal $YMnO_3$ upto x = 0.3 ($YMn_{1-x}Fe_xO_3$) by the citrate gel method. We observed an interesting variation of lattice parameters with iron content in $RMn_{1-x}Fe_xO_3$ (R = Y, Yb; x = 0.0, 0.1, 0.2, 0.3). The *a* lattice parameter decreases with x, whereas the *c* lattice parameter increases. The increase in c lattice parameter has been attributed to the increase in electron population of d_z^2 orbital (high spin Fe^{3+} ion) in a trigonal bipyramidal crystal field. The analogous Ytterbium compounds ($YbMn_{1-x}Fe_xO_3$; $x \leq 0.3$) showing multiferroic behavior have also been synthesized. The *c*/*a* ratio increases with Fe substitution. Magnetic ordering is observed from the low temperature neutron diffraction study. The compounds were found to be antiferromagnetic and the ordering temperature T_N increased from 82 K for pure $YbMnO_3$ to 95 K for $YbMn_{0.7}Fe_{0.3}O_3$. Variable temperature dielectric measurements (15-110 K) show an anomaly in the dielectric constant at temperatures close to the antiferromagnetic ordering temperature for all the compositions, showing a unique correlation between the magnetic and electric field. The increase in the ordering temperature in $YbMn_{1-x}Fe_xO_3$ is explained on the basis of increase in covalence character of Mn/Fe-O-Mn/Fe bond with iron doping. We have also studied the rare earth substitution in $Yb_{1-x}A_xMnO_3$ (A = Ca, Sr).

Chapter 4 discusses the microwave dielectric properties of some new oxides in the La/Ba-Zn/Ti-O system with the perovskite structure. Suitable cation substitution at A- and B- site of the perovskite has been carried out to optimize the dielectric properties. $(Ba_{1/3}Ln_{2/3})(Zn_{1/3}Ti_{2/3})O_3$ (*Ln* = La, Pr and Nd), $(Ba_{(1+x)/3}La_{(2-x)/3})(Zn_{1/3}Ti_{(2-x)/3}Nb_{x/3})O_3$ (x =0.5, 0.75, 1.0, 1.25) and $(Ba_{1/3}La_{2/3})(Zn_{1/3-x}Mg_xTi_{2/3})O_3$ have been synthesized by solid state reactions and are found to crystallize in the cubic structure (space group $Pm\bar{3}m$). Rietveld refinement of powder X-ray diffraction data has been carried out for structural characterization. The lattice parameter and the grain size increases with Nb substitution. Compositions like $(Ba_{1/3}La_{2/3})(Zn_{1/3}Ti_{2/3})O_3$ and $(Ba_{2/3}La_{1/3})(Zn_{1/3}Ti_{1/3}Nb_{1/3})O_3$ show a dielectric constant (ε_r) of 33 at 6.67 GHz and 45 at 6.09 GHz and a quality factor ($Q.f$) of 21000 and 6552 GHz respectively. The temperature coefficient of resonant frequency (τ_f) shows a large and systematic decrease with a change of sign (from positive to negative) with increase in Nb content and hence zero τ_f could be obtained by choosing the appropriate ratio of two compositions.

In Chapter 5 we have discussed the synthesis and properties of new double perovskites of the type $LaBaNi_{1-x}Co_xTaO_6$, $LaBaNi_{1-x}Cu_xTaO_6$ and $LaBa_{1-x}Pb_xCoTaO_6$. The nickel-cobalt system forms complete solid solution whereas $LaBaNi_{1-x}Cu_xTaO_6$ and $LaBa_{1-x}Pb_xCoTaO_6$ form solid solutions till x = 0.4 and 0.2 respectively. Both solid state and flux method have been employed for the synthesis of above compounds. The compounds crystallize in the tetragonal space group, *I4/m*. These oxides have been characterized by powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), energy dispersive X- ray spectroscopy (EDX). The dielectric properties have been studied for $LaBaNi_{1-x}Co_xTaO_6$ (both air-annealed and Ar-annealed). The air annealed samples show very high dielectric constant and high dielectric loss at low frequency (< 100 kHz) whereas the argon annealed samples show comparatively low dielectric constant and low loss. Surface oxidation of Co (II) in air annealed samples may lead to high loss. The magnetic studies (10K-300K at 0.5T) show long range antiferromagnetic ordering for $LaBaNi_{1-x}Co_xTaO_6$ and $LaBa_{1-x}Pb_xCoTaO_6$ series of compounds and the ordering temperature (T_N) in $LaBaNi_{1-x}Co_xTaO_6$ gradually decreases with increase in Co doping. In case of $LaBaNi_{1-x}Cu_xTaO_6$ antiferromagnetic ordering is observed till x = 0.2 while the x = 0.4 composition shows a parasitic ferromagnetic behavior.

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