



QUALITATIVE UNDERSTANDING OF MULTIFERROIC BEHAVIOR OF MN-BASED SYSTEM AND SYNTHESIS OF ROD-LIKE NANOSTRUCTURE OF $TbMnO_3$

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Abstract- In the present project work, to understand the role of A and B atoms of ABO_3 perovskite in multiferroic behavior, forty multiferroics are systematically reviewed on the basis of parameters like electronegativity, ionic radii, bond covalence and tolerance factor. The correlation of tolerance factor with Neel temperature and Curie Temperature of Mn-based orthorhombic perovskite multiferroics are studied. The nature of A-O chemical bonding and its influence on multiferroic behaviour is discussed. In the second part of this project the multiferroic $TbMnO_3$ was successfully prepared and characterized by XRD and SEM. The XRD shows the amorphous nature of as-synthesized $TbMnO_3$, after calcinations at 800°C the crystalline orthorhombic structure is formed. The SEM images confirm the rod-like morphology $TbMnO_3$ having diameter in range of 40-60 nm and length is in range of μm .

Keywords- Multiferroic, $TbMnO_3$, Bond covalence

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Introduction

Multiferroics are materials that exhibit coexistence of ferromagnetic, ferroelectric or ferroelastic. They display the phenomenon of controlling electrical polarization by the application of an external magnetic field. They have great possibility for application in multifunctional devices. Magnetolectrics multiferroics have recently attracted a lot of interest due to these exceptional properties. Unlike in conventional ferroelectrics in the manganite perovskite such as $TbMnO_3$ and $DyMnO_3$, ferroelectricity arises from of peculiar coupling of the lattice to a spiral ordering of Mn spin. A strong anisotropic dependence of the spontaneous electric polarization on the direction of magnetic field is found which can be related to the spiral ordering of the magnetic moments. Orthorhombic $TbMnO_3$ is multiferroic material which upon cooling show successive phase transition related to antiferromagnetic ordering at $T_N \sim 41K$ and ferroelectric ordering at $T_C \sim 23K$ respectively, while $DyMnO_3$ have antiferromagnetic ordering at 30 K and ferroelectric ordering at $T_C = 18 K$. [1-10]

Generally, it is observed that changing of A or B element in ABO_3 multiferroic, vary the ferromagnetic and ferroelectric phase transi-

tion temperature. To understand multiferroic behavior it is very essential to recognize the role of A and B. In the present project work, more than forty perovskite (ABO_3) multiferroics are reviewed. The role of parameters like ionic radii, electronegativity and nature of chemical bonding (A-O and B-O) of A and B elements are tried to correlate with Curie and Neel temperature of the system. [10-17]

Tolerance Factor and Nature of Chemical Bonding

The ionic radii and electronegativity is used to calculate the tolerance factor and bond covalence. The tolerance gives the knowledge of compactness of unit cell. Bond covalence helps us to understand the atomic interaction in the molecular level.

The bond covalence is calculated by using formula Covalence (A-

$$O) = \exp [-1/4(X_O - X_A)] \dots \dots \dots (i)$$

Where,

X_O - Electronegativity of O-atom,

X_A - Electronegativity of A-atom,

X_B - Electronegativity of B-atom.

The tolerance factor is calculated by using formula,

$$\text{Tolerance factor} = 1/\sqrt{2} [(R_A + R_O) / (R_B + R_O)] \dots \text{(ii)}$$

where,

R_A - Ionic radius of A-atom,

R_B - Ionic radius of B-atom,

R_O - ionic radius of o-atom.

Tolerance factor of almost forty Mn-base multiferroics are calculated and are found to be less than 1.

The tolerance factors versus Neel temperature and Curie temperature plot of some Mn-based perovskite multiferroic is shown in Fig 1. It point out that tolerance factor is directly related with temperatures. It clearly indicates that ionic size of A (in present case B is constant) playing important role in magnetic and electric ordering, which are responsible for the magnetic and electric phase transition.

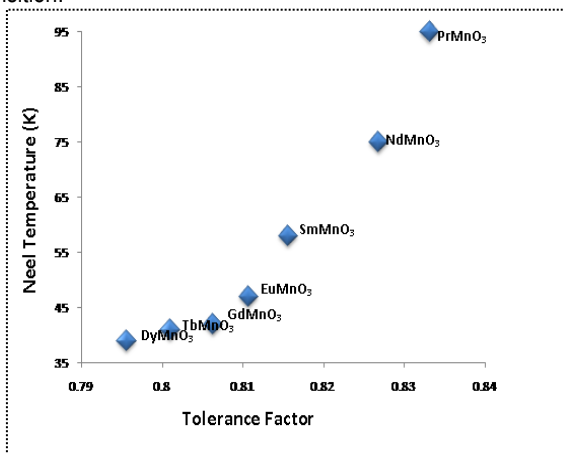


Fig. 1- Tolerance factor versus Neel Temperature of Mn-based perovskite multiferroic.

The covalence of A-O and B-O bonds of the perovskite system are calculated by using Pauli's electronegativity equation (i). It is found that bonds covalence of A-O lies in between 0.55 to 0.7, while for B-O, it is in between 0.62 to 0.665. It clearly indicates that both the bonds are partial covalent and partial ionic.

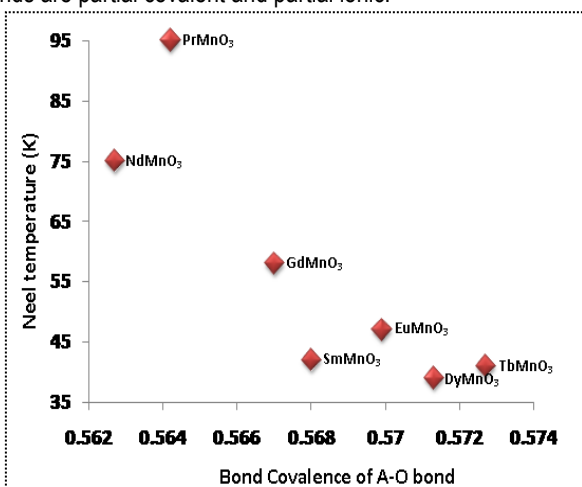


Fig. 2- Bond covalence of B-O bond versus Neel Temperature of Mn-based perovskite multiferroic.

Covalence for B-O bond is observed to be in average 65 % and A-O bond is in average 70%. It means in B-O bonds 60% of charge is shared between B and O atoms and 40% charge shifted towards O. Same can be explained for A-O bond also. Oxygen electron cloud is commonly share with A and B type of atoms in the structure. Change in A or B position due to temperature sensitive structural phase transition, changes sharing of electron cloud between A-O and B-O. Its gives rise to change of covalence of A-O and B-O bond.

The position of B is shifted slightly from the centre position, which is responsible for charge imbalance at B site in the molecular level as a consequence of phase transition. Variation of Neel temperature with bond covalence (Fig 2) exhibits that Neel temperature is inversely related with bond covalence. It can be interpreted as electron sharing between A and O affect on spiral ordering of Mn spin which is responsible for successive phase transition upon cooling in Mn-based orthorhombic perovskite multiferroic. The systematic study to comprehensive understanding this behavior is under investigation.

Experimental

TbMnO₃ particles are prepared by taking stoichiometric (1:1) amounts of 0.05 M solutions of TbCl₃.6H₂O (99.9%, Aldrich) and MnCl₂.4H₂O (AR, Fishers), in double distilled water, were mixed and stirred for 2 hour. For synthesis, we followed two different routes to study the effect of precipitation conditions on samples properties. In first route, 0.05 M solution of KOH (GR, Merck) was added to this solution of the mixed salts, under vigorous stirring, leading to a dark brown color solution. After 17 hours, magnetic stirring at room temperature, the colloidal solutions was filtered and washed with water. After drying at room temperature, these samples were calcined (heat treated in air, at atmospheric pressure) at 800°C for 90 minutes. The powder is used for further characterization. XRD and SEM are shown.

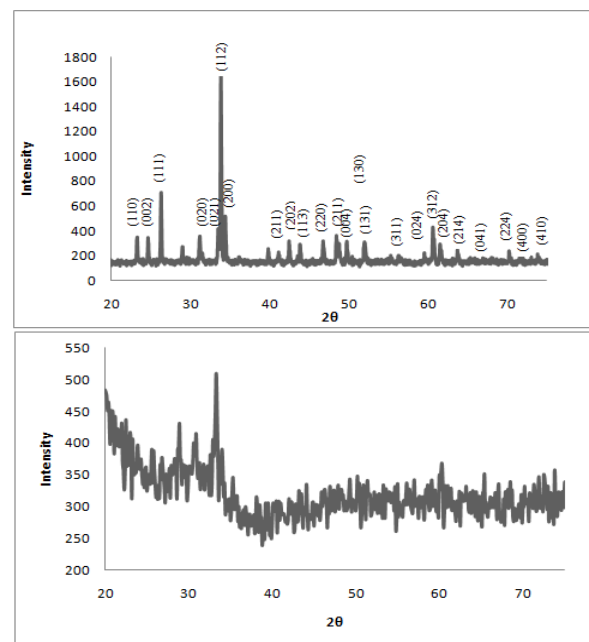


Fig. 3- XRD patterns of TbMnO₃

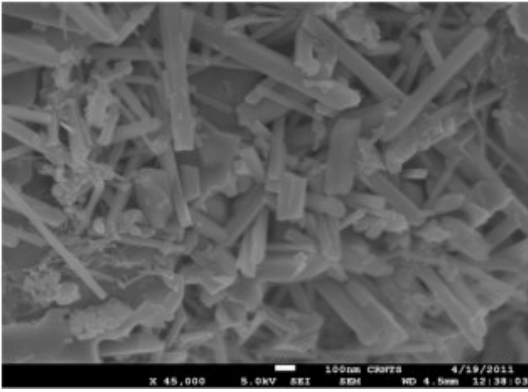


Fig. 4- SEM image of TbMnO₃- nanorods

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