



Synthesis and Characterization of $\text{Ba}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ ($x=1.0, 1.2, 1.3$ and 1.4) double perovskites by ultrasound assisted wet chemical method

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Abstract: $\text{Ba}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ ($x = 1.0, 1.2, 1.3$ and 1.4) (BFMO) double perovskite was synthesized by sonochemical procedure at low preparation temperature (950°C) under Ar/H_2 atmosphere. X-ray diffraction studies revealed single phase with cubic crystal structure for all the samples. The average grain size of 118 nm and variation of porosity were analyzed using scanning electron microscopy (SEM). Confirmation of purity and presence of elements (Ba, Fe, Mo, and O) in BFMO compound are done by spectra analysis on Energy dispersive X-ray spectroscopy (EDS). Formation of BFMO double perovskite materials was confirmed by identifying absorption bands of Mo-O and Fe-O vibrations in range $400\text{--}1000\text{ cm}^{-1}$ from spectral analysis done on FTIR (Fourier transform infrared spectroscopy).

Keywords: Double perovskite, Sonochemical, Characterization.

I. Introduction

Double perovskite oxides of type $\text{Sr}_2\text{FeMoO}_6$ exhibited room temperature negative colossal magnetoresistance at low magnetic field [1]. This fundamental and technological signification of materials encouraged researchers worldwide to work on this research area [1-5]. General formula of Double perovskite oxides of type $\text{A}_2\text{BB}'\text{O}_6$, where A represents alkaline earth like Sr, Ca and Ba and B, B' are transition metals such as $\text{B} = \text{Fe}, \text{Cr}, \text{Mn}, \dots$ and $\text{B}' = \text{Mo}, \text{W}, \text{Re}, \dots$ [6-8]. These types of $\text{A}_2\text{BB}'\text{O}_6$ oxides possess a tetragonal structure with space group symmetry of $I4/mmm$ or cubic with space group symmetry of $Fm\bar{3}m$ or monoclinic with a space group symmetry of $P2_1/n$ depending on chemistry or doping [9-12]. Structure of A_2FeMoO_6 double perovskite consists of alternating MoO_6 and FeO_6 octahedra along the axis of the crystal, while the voids in between the octahedral are engaged by 'alkaline earth' cation [1, 15]. Below Curie temperature (T_c) double perovskite A_2FeMoO_6 exhibits metallic and ferrimagnetic properties. Magnetic structure and saturation magnetization (M_s) of $4\text{ }\mu\text{B}$ per formula unit of A_2FeMoO_6 double perovskite in the ferrimagnetic state is explained using antiferromagnetic coupling between the itinerant down spin $\text{Mo}^{+5}(4d^1)$ and the localized up spin $\text{Fe}^{3+}(3d^5)$ theoretically [16]. Saturation magnetization is found to deviate (lower side) as reported [1, 17], one of the reasons for M_s being lower is due to lattice site disorder between Mo and Fe ions [1, 18]. $\text{Sr}_2\text{FeMoO}_6$ and $\text{Ba}_2\text{FeMoO}_6$ compound exhibited saturation magnetization and Curie temperature of $3.45\text{ }\mu\text{B/f.u.}$ and $3.70\text{ }\mu\text{B/f.u.}$, $420\text{--}450\text{ K}$ and $320\text{--}340\text{ K}$, respectively [2, 13-16, 19-21]. $\text{Ba}_2\text{FeMoO}_6$ compound exhibited magnetoresistance (MR%) of 15 % (@330 K and 7T) [2], which is far better than one reported for $\text{Sr}_2\text{FeMoO}_6$ compound [1]. Results of improved magnetic properties encourage working on Ba contained double perovskite compared to Sr in A_2FeMoO_6 at A site. It is more of interest to study the Fe/Mo exchange in $\text{Ba}_2\text{FeMoO}_6$ for magnetic properties. Studies on Fe/Mo ordering, magnetic properties and MR% have been reported in compound $\text{Sr}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ at different compositions of x [22-26]. Most of the studies on Ba based A_2FeMoO_6 are done using solid state or sol-gel synthesis method. Many perovskites of type ABO_3 , have been investigated using sonochemical method [27-32] Therefore, the present investigation is done on $\text{Ba}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ ($x=1.0, 1.2, 1.3$ and 1.4) series using sonochemical method for Characterization. Further, these materials were also characterized by XRD, SEM, EDS and FTIR.

II. Experimental

Polycrystalline samples of $\text{Ba}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ ($x = 1.0, 1.2, 1.3$ and 1.4) were synthesized by sonochemical method. Exact proportional amounts of analytical grade chemicals such as $\text{Ba}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and H_2MoO_4 were added in a beaker of 200ml double distilled water and stirred on magnetic stirrer at room

temperature (RT) until clear solution is formed, to this Citric acid is added in 2:1 mole ratio (citric acid to metal ion), solution is again stirred for 10 mins to obtain clear solution. A highly intense Sonication of frequency 20 kHz was carried out with a horn made up of titanium at a temperature of 353K (Sonics- Vibra cell, USA) for about 20 mins. After Sonication, ammonia is added to the solution to adjust pH to ~ 7 . Solution is kept on a hot plate of a magnetic stirrer at 80°C and ethylene glycol is added in 1:1.2 ratio (metal ion to ethylene glycol). The resulting solution is kept in a hot air oven at 230 °C for 24hrs, the residue formed was collected and dried on Bunsen burner at 250°C for about 5 mins to obtain a required composition and further ground to get homogenous powder.

The resulting powders were taken into crucibles and made to undergo heat treatment at 400°C /6hr, 600°C/6hr and 800°C/6hr with intermittent grinding. The obtained powders were pressed into pellets of 1cm diameter and 2mm thickness using a die by applying 2 ton/m². The resulting pellets were sintered at 950°C for 6hrs. For reducing the Mo⁶⁺ to Mo⁵⁺ or loss of oxygen, the pellets were heated at 950°C in a stream mixture of 10% H₂/Ar gas for about 6hrs.

The final materials are subjected to X-ray diffraction (Philips PW-1830) studies to confirm the structure. SEM (Zeiss INCA) studies are done to confirm the grain size, EDS (Oxford INCA EDX) is carried out on all samples to check purity and elements present. FTIR (PerkinElmer spectrum two) spectra are used to analyze all samples to confirm perovskite formation.

III. Results and discussion

3.1. Crystal structures

Figure 1 shows the XRD profiles recorded at temperature 300 K of BFMO samples. It is noted from X-ray patterns that all BFMO samples were in single phase with cubic crystal structure having space group of $Fm\bar{3}m$ [10, 12, 16, 33, 34]. Lattice parameter 'a' and volume of unit cell 'V' were evaluated for all BFMO samples using (hkl) values (220), (222), (400), (420), (422) (440) and (620) with cubic structure for Ba₂Fe_xMo_{2-x}O₆ (x = 1.0, 1.2, 1.3 and 1.4) which are tabulated in **Table 1**. It was noticed from **Figure 2** that lattice parameter (a) and volume (V) were decreases with increase in composition (x), this trend is due to the replacement of Fe³⁺ with higher atomic radius(0.645Å) in Mo⁵⁺ of smaller atomic radius(0.61Å) and valence disproportion[35, 36], which obeys the Vegard's law [37]

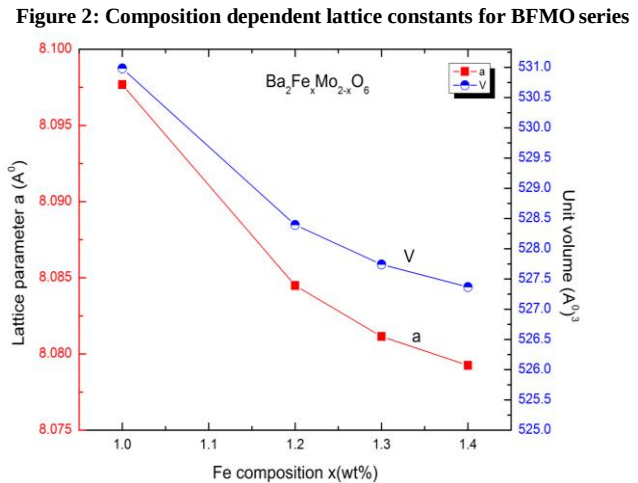
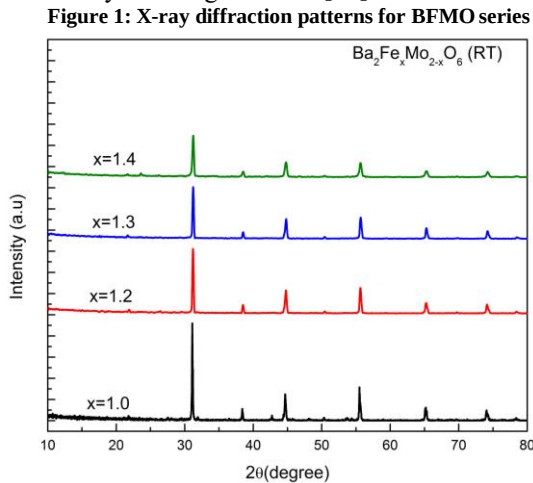


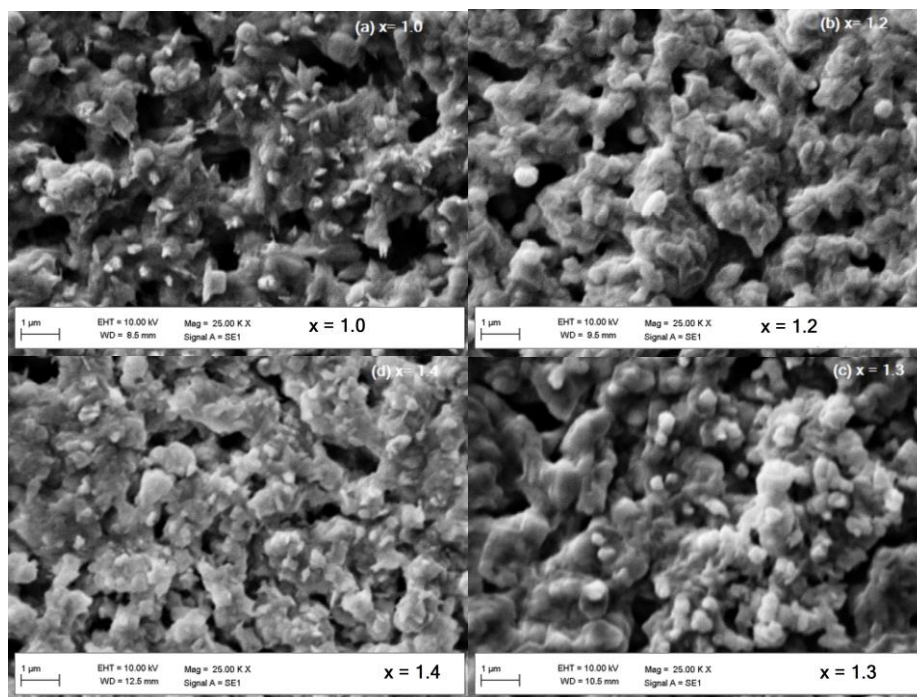
Table I Lattice parameters (a) and unit cell volume (V) of Ba₂Fe_xMo_{2-x}O₆ (x = 1.0, 1.2, 1.3, and 1.4)

Composition (x)	Space group	a (Å)	V (Å) ³
1.0	$Fm\bar{3}m$	8.0976	530.98
1.2	$Fm\bar{3}m$	8.0844	528.39
1.3	$Fm\bar{3}m$	8.0811	527.74
1.4	$Fm\bar{3}m$	8.0792	527.36

3.2. Scanning Electron Microscopy (SEM)

Scanning electron micrograph (SEM) pictures of sintered pellets Ba₂Fe_xMo_{2-x}O₆ (x = 1.0, 1.2, 1.3, and 1.4) were recorded as shown in **Figure 3(a-d)**. All initial particles are spherical in shape with visible grain shapes. It is observed from **Figure 3(a-d)** that grain sizes of particles were around 118 nm, which is due to lower preparation temperature (950°C).

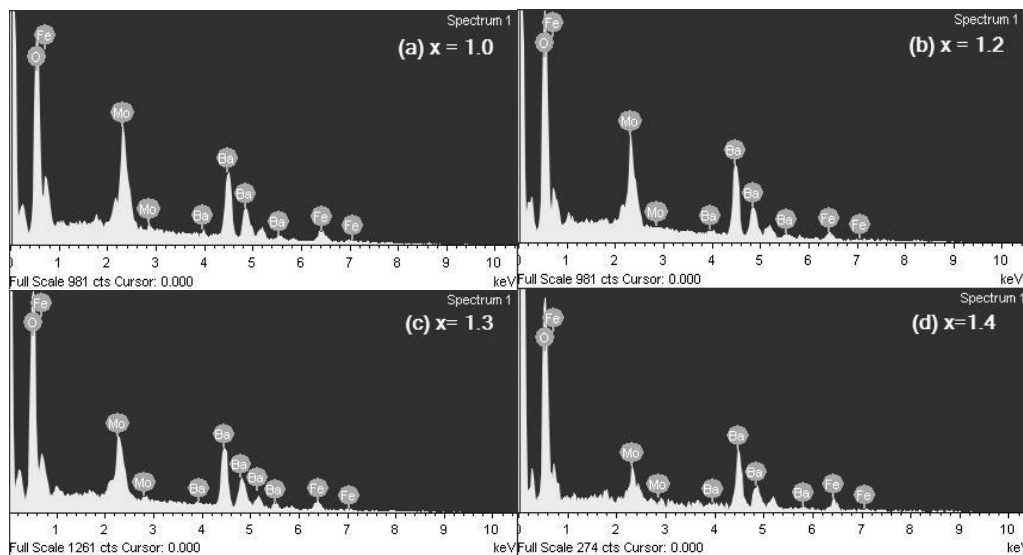
Figure 3(a-d): Scanning electron micrograph (SEM) pictures of BFMO series



3.3. Energy dispersive X-ray spectroscopy (EDS)

Elements energy dispersive X-ray spectrum that formed $\text{Ba}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ ($x = 1.0, 1.2, 1.3$, and 1.4) is presented in **Figure 4(a-d)**. Homogeneity, purity and existence of composition elements (Ba, Fe, Mo, and O) used in preparation were confirmed from EDS graphs.

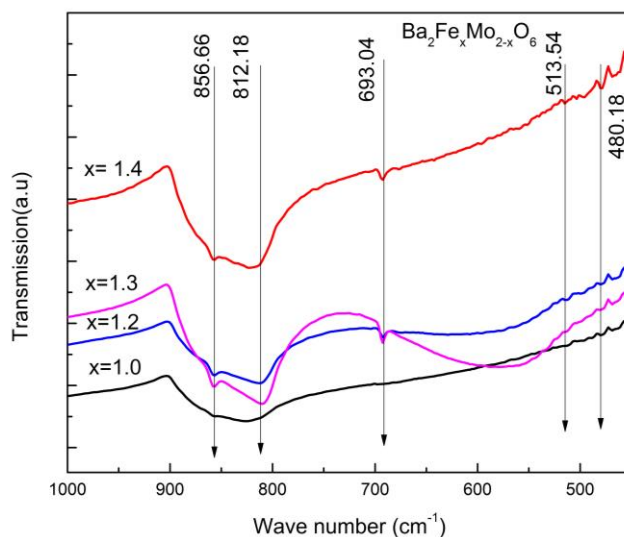
Figure 4(a-d): Elements energy dispersive X-ray spectrum of BFMO series



3.4. Fourier transform infrared spectroscopy (FTIR)

Figure 5 shows FTIR spectra of the BFMO samples in the spectral wave number range $1000\text{--}400\text{ cm}^{-1}$ at room temperature. For perovskite structure, FTIR spectra should have three characteristic absorption bands between $850\text{--}400\text{ cm}^{-1}$ with respective to composition these bands are used to confirm perovskite phase formation [38]. From the FTIR spectra of the BFMO samples investigated in the present study, required bands for Fe and Mo are detected. These bands are, one strong band in the high wavenumber range ($\sim 856\text{ cm}^{-1}$) associated to the Mo-O symmetric stretching mode of MoO_6 -octahedra, another band at $\sim 693\text{ cm}^{-1}$ assigned to the antisymmetric stretching mode of the MoO_6 -octahedra, due to the higher charge of this cation [39]. One weak absorption band at about 480 cm^{-1} is ascribed to Fe-O vibration absorption of FeO_6 -octahedra. **Figure 5** gives confirmation on perovskite formation by detection of Fe and Mo bands.

Figure 5: Fourier transform infrared (FTIR) spectra of BFMO series



IV. Conclusions

The authors studied, $\text{Ba}_2\text{Fe}_x\text{Mo}_{2-x}\text{O}_6$ ($x = 1.0, 1.2, 1.3$ and 1.4) double perovskites prepared by Sonochemical method and characterized samples using techniques such as X-ray Diffraction (XRD), Scanning electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDS) and Fourier transform infrared spectroscopy (FTIR). Cubic structure with space group $Fm\bar{3}m$ was confirmed from XRD, lattice parameters were found to decrease with increase in Fe composition(x). SEM revealed average grain size of BFMO as 118 nm. Homogeneity, purity and presence of preparation elements Ba, Fe, Mo and O were confirmed from EDS graphs. FTIR confirmed the formation of perovskite structure.

V. References

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