

Structural and Magnetic Properties of Ca and Mg Co-substituted BiFeO₃ Samples

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Abstract—Bi_{0.8}Ca_{0.2-x}Mg_xFeO₃ (x=0.03~0.18) samples have been prepared by a sol-gel auto-combustion method. All the diffraction peaks show good crystal, and with the increase of Mg²⁺ ion concentration, the half high width of the diffraction peak become wider. Bi_{0.8}Ca_{0.14}Mg_{0.06}FeO₃ sample of crystallization is better under 600 °C. The magnetic of the sample receded with the increasing of temperature. With increase of x value, the grains increase and the reunion phenomenon intensified, this is because of the sample force between the particle surface enhancement.

Index Terms—BiFeO₃, Bismuth ferrite, sol-gel method, Structure, Magnetic properties.

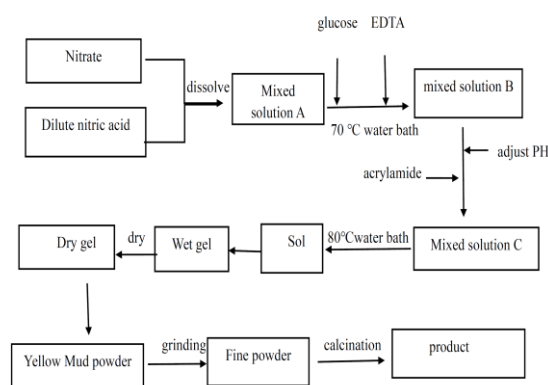


Fig.1. The process flow of experimental

I. INTRODUCTION

In recent years, Bismuth ferrite (BiFeO₃) has recently drawn much interest owing to its physical properties and technological applications^[1,2]. However, the presence of impurities such as Bi₂₅FeO₄₀ or Bi₂Fe₄O₉, the existence of Fe²⁺ ions, and volatilization of Bi³⁺ are limited its application^[3-4]. To improve the magnetic property of BiFeO₃^[5-7], a partial substitution of A-site cation in BiFeO₃ with rare earth ions (La³⁺, Sm³⁺, Y³⁺, Gd³⁺) or alkali earth ions (Sr²⁺, Ba²⁺, Ca²⁺, Mg²⁺) has been used^[8-12]. For example, Prachi Sharma *et al.*^[13] synthesized Bi_{1-x}La_xFe_{1-y}Mn_yO₃ and found dielectric constant decreases with the increase in frequency. Lin Peng-Ting *et al.*^[14] synthesized Bi_{1-x}La_xFeO₃ and study its multiferroic property. The ferromagnetic can be enhance in La-doped BiFeO₃. In this present work, we prepared Bi_{0.8}Ca_{0.2-x}Mg_xFeO₃ (x=0.03~0.18) samples by the sol-gel technique and the main aim is to study the structural, magnetic, FI-IR and morphology of Bi_{0.8}Ca_{0.2-x}Mg_xFeO₃ system.

II. EXPERIMENT SECTION AND SYNTHESIS

Polycrystalline Bi_{0.8}Ca_{0.2-x}Mg_xFeO₃ (x=0.03~0.18) were synthesized by the sol-gel method using Bi (NO₃)₃·5H₂O, Fe (NO₃)₃·9H₂O, Ca (NO₃)₂·6H₂O, Mg (NO₃)₂ as the starting materials and distilled water as a solvent. The methods of polyacrylamide sol-gel method synthetic Bi_{0.8}Ca_{0.2-x}Mg_xFeO₃ powder as shown in Fig.1. The XRD, SEM, MPMS and FT-IR were used to investigate the microstructure and magnetic properties of Bi_{0.8}Ca_{0.2-x}Mg_xFeO₃.

III. RESULTS AND DISCUSSION

Fig.2 shows XRD patterns of Bi_{0.8}Ca_{0.2-x}Mg_xFeO₃ powders calcined at 600 °C for 3h. As shown in Fig.2. (a), a small amount of impurity phase was observed when x≥0.15. All the diffraction peaks show good crystal with the increase of x value.

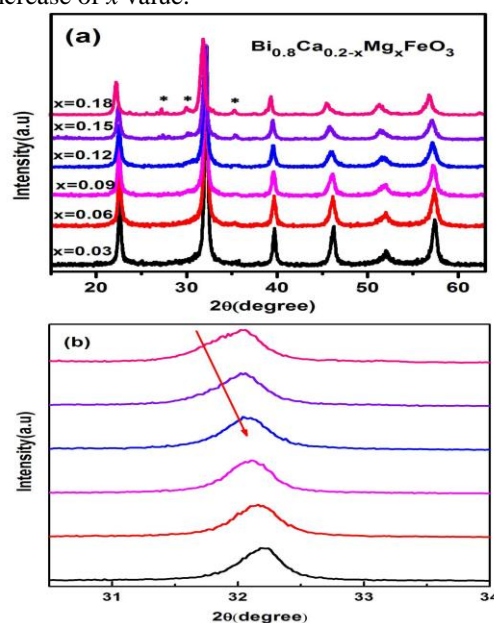


Fig.2. XRD patterns of Bi_{0.8}Ca_{0.2-x}Mg_xFeO₃ (x=0.03~0.18) powders calcined at 600 °C for 3 h.

From the Fig.2. (b), the diffraction peaks change to lower deviation with the increase of Mg^{2+} ion concentration. it is due to the different of the radius Ca^{2+} ($r=1.12\text{\AA}$) and Mg^{2+} ($r=0.72\text{\AA}$) which Lead to the change of the structure of samples^[15-16], and with the increase of Mg^{2+} ion concentration, the half high width of the diffraction peak become wider. According to the scherrer's equation^[17], more wider of the Peak, the smaller grains it can get ; more narrower of the peak, and the more bulky grain it can get. So with the increase of Mg^{2+} concentration in the solution, the generated $Bi_{0.8}Ca_{0.2-x}Mg_xFeO_3$ grain size is smaller, namely the role of Mg^{2+} ions doped with fine grains. There are none obvious impurity phase appear. And the diffraction peak first become sharp and then decline.

From the Fig.3, XRD patterns of $Bi_{0.8}Ca_{0.2-x}Mg_xFeO_3$ ($x=0.06$) powders calcined at different temperatures for 3 h. The diffraction peak is sharp crystal sample better, on the contrary, the poor crystallization. So samples of crystallization is better under $600\text{ }^\circ\text{C}$.

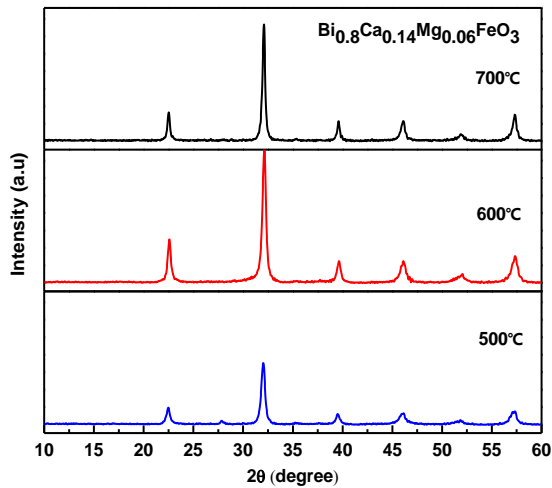


Fig.3. XRD patterns of $Bi_{0.8}Ca_{0.2-x}Mg_xFeO_3$ ($x=0.06$) calcined at different temperatures for 3 h.

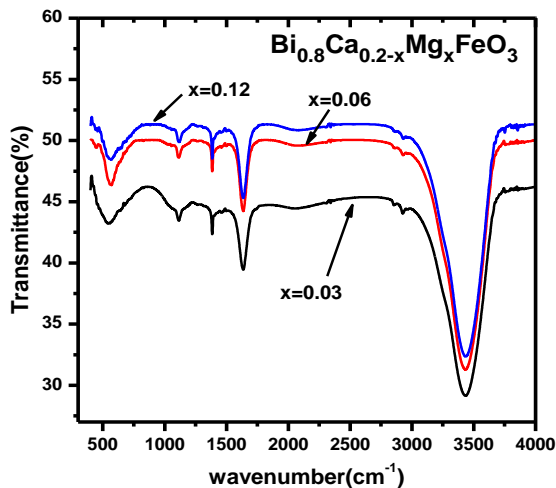


Fig.4. IR spectrum of $Bi_{0.8}Ca_{0.2-x}Mg_xFeO_3$ ($x=0.03, 0.06, 0.12$) powder calcined at $600\text{ }^\circ\text{C}$ for 3 h.

The infrared absorption spectra of different doping ratio as shown in Fig.4, when $x=0.03$, there appear

antisymmetric stretching vibration absorption at $450-1100\text{ (cm}^{-1}\text{)}$. With the increasing of x value, the antisymmetric stretching disappear. Strong characteristic absorption peak exists at 3450 cm^{-1} , This suggests that at the wave velocity complexing agent severe complexing with the metal cation^[18], and with the increase of x value, the characteristic peak enhance, This means that the complexation reaction more intense. As Jiang's conclusion that the changes of band near 500 cm^{-1} tell us crystal institutional change^[19].

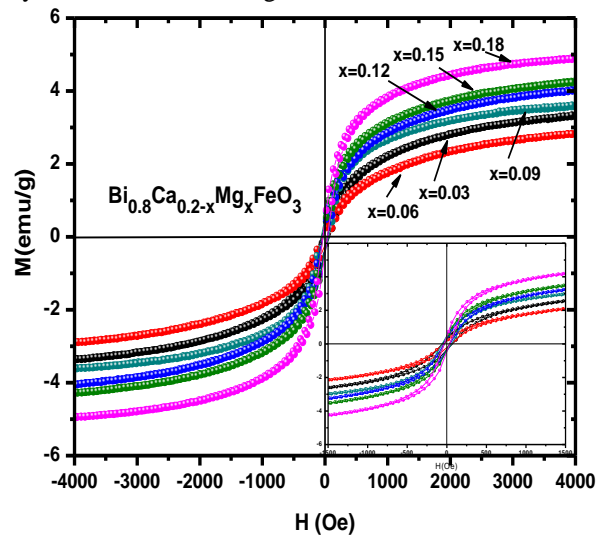


Fig.5. The magnetic hysteresis curves of $Bi_{0.8}Ca_{0.2-x}Mg_xFeO_3$ calcined at $600\text{ }^\circ\text{C}$ for 3 h.

Fig.5 shows the magnetic hysteresis curves for $Bi_{0.8}Ca_{0.2-x}Mg_xFeO_3$ which calcined at $600\text{ }^\circ\text{C}$ for 3h. According to the shape of the curve, when $x < 0.18$, all the sample show paramagnetic. And when $x=0.18$, the Curve open. With the increase of Mg^{2+} concentration has not obvious effect for the magnetic of the sample. The magnetic parameters of $Bi_{0.8}Ca_{0.2-x}Mg_xFeO_3$ is shown in Table 1. The value of M_s increase with the increasing of x value within the margin of error. Ca^{2+} , Mg^{2+} co-doping can improve the value of M_s . But from the change in Table 1, this change is not obvious.

TABLE 1. MAGNETIC PARAMETERS OF $Bi_{0.8}Ca_{0.2-x}Mg_xFeO_3$ CALCINED AT $600\text{ }^\circ\text{C}$ FOR 3 H

Content(x)	M_s (emu/g)	M_r (emu/g)	H_C (Oe)
0.03	3.317	0.606	121.516
0.06	2.824	0.385	120.333
0.09	3.586	0.891	117.990
0.12	4.013	0.747	118.945
0.15	4.247	0.869	119.517
0.18	4.884	1.149	119.587

The magnetic hysteresis curves of $Bi_{0.8}Ca_{0.2-x}Mg_xFeO_3$ ($x=0.06$) which calcined at different temperatures as show in Fig.6, the magnetic of the sample receded with the increasing of temperature. According to the interpretation of the literature is due to the gradual collapse of the space-modulated spin structure of

BiFeO₃^[20]. The value of Ms and Mr receded with increasing of temperature (Table 2), while the Hc increase. This associate to the doping-drive increase in the magnetic anisotropy^[20].

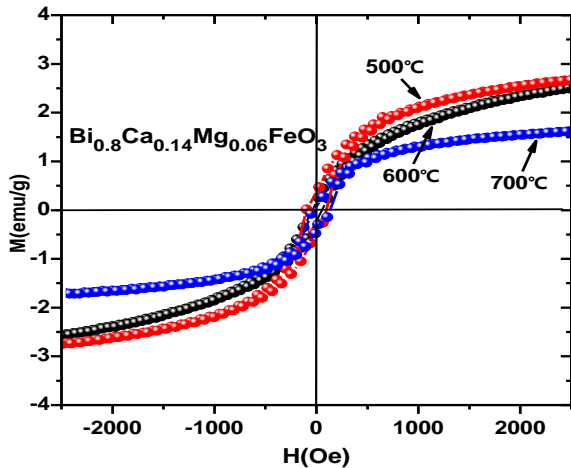


Fig. 6. Magnetic hysteresis curves of Bi_{0.8}Ca_{0.2-x}Mg_xFeO₃ (x=0.06) calcining at different temperatures.

TABLE 2. MAGNETIC PARAMETERS OF Bi_{0.8}Ca_{0.2-x}Mg_xFeO₃ (x=0.06) AT DIFFERENT TEMPERATURES.

Temperature (°C)	M _S (emu/g)	M _r (emu/g)	H _C (Oe)
500	3.126	0.463	94.585
600	2.824	0.420	114.50
700	1.830	0.284	183.50

The morphology of the samples Bi_{0.8}Ca_{0.2-x}Mg_xFeO₃ (x=0.03, 0.06, 0.12) were obtained as can be seen from SEM micrographs shown in Fig.7.It can also be seen that with increasing Mg²⁺ concentration, the morphology of the particle and grains change significantly.

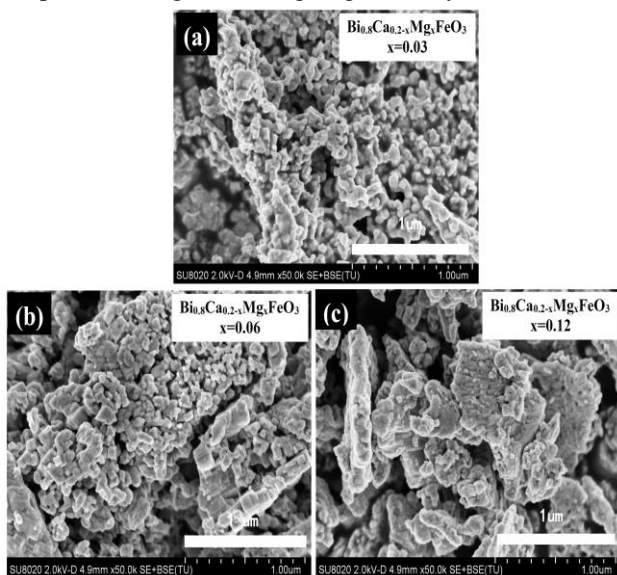


Fig.7. SEM of Bi_{0.8}Ca_{0.2-x}Mg_xFeO₃ (x=0.03, 0.06, 0.12) powder calcined at 600 °C for 3 h.

This is believed to be a direct consequence of the

modification in the unit cell of Bi_{0.8}Ca_{0.2}FeO₃ as a function of increasing Mg²⁺ concentration^[21-22]. With increase of x value, the grains increase and the reunion phenomenon intensified, this is because of the sample force between the particle surface enhancement^[18].

IV. CONCLUSION

In this paper, we prepared Bi_{0.8}Ca_{0.2-x}Mg_xFeO₃ (x=0.03~0.18) samples using sol-gel method, with the increase of Mg²⁺, half high width of the diffraction peak increase and due to the difference between ionic radius. When calcined at 600 °C the crystallization is complete. With the replace of Mg²⁺, all M-H curve show paramagnetic. The M-H curve which processing at different temperature displays that the magnetic of Bi_{0.8}Ca_{0.2-x}Mg_xFeO₃ reduce with the increasing of calcined temperature. The particle size increase with the increase of Mg²⁺ and display serious reunion phenomenon.

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