Iğdır Üniversitesi Fen Bilimleri Enstitüsü Dergisi, 11(4): 2737-2745, 2021
Journal of the Institute of Science and Technology, 11(4): 2737-2745, 2021
ISSN: 2146-0574, eISSN: 2536-4618
Fizik / *Physics* **DOI: 10.21597/jist.952882**
Araştırma Makalesi / *Research Article*
Geliş tarihi / Received: 15.06.2021 **Kabul tarihi / Accepted: 19.08.2021**

Atıf İçin: Topkaya R, Çiçek K, Koçyiğit A, 2021. Synthesis and Investigation of Structural and Magnetic Properties of Nickel Doped $BiFeO_3$, Journal of the Institute of Science and Technology, 11(4): 2737-2745.

To Cite: Topkaya R, Çiçek K, Koçyiğit A, 2021. Synthesis and Investigation of Structural and Magnetic Properties of Nickel Doped $BiFeO_3$, Journal of the Institute of Science and Technology, 11(4): 2737-2745.

Synthesis and Investigation of Structural and Magnetic Properties of Nickel Doped $BiFeO_3$

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ABSTRACT: Ni doped $BiFeO_3$ powders were synthesized by sol-gel method. The effect of annealing temperature and solvent type on the structural and magnetic properties of the synthesized powders has been studied by XRD, SEM, EDX, VSM and FMR techniques at the room temperature. XRD results highlighted that the Ni doped $BiFeO_3$ powders were successfully synthesized. The morphology changes with annealing temperature and solvent material. With EDX analysis, all the elements in Ni doped $BiFeO_3$ powders were confirmed. The magnetic properties of the samples were observed to strongly depend on annealing temperature and solvent material. The saturation magnetization is observed to increase with an increasing annealing temperature. The broad resonance lines indicate ferromagnetic property.

Keywords: Multiferroics, Spintronics, Ferromagnetic, Ferroelectric, $BiFeO_3$

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INTRODUCTION

The multiferroic materials having ferroelectric and ferromagnetic properties have attracted a great attention due to their applications in magnetoelectronics, nanotechnology, spintronics and optoelectronics (Hur et al. 2004; Wang et al. 2009; Dong et al. 2015; Tokura et al. 2014). A variety of promising technological applications: non-volatile memory elements having much control freedom (Ruan et al. 2016), sensors (Surowiak and Bochenek 2008), actuators and modulators (Ramesh and Spaldin 2010), diodes (Choi et al. 2009), spin wave generators (Kampfrath et al. 2011) and spintronic devices (Bibes and Barthelemy 2007) whose spins are manipulated with electric field (Fischer et al. 1980; Catalan and Scott 2009). In all these applications of multiferroic materials, it is intended to produce and develop the high-capacity and low-cost information devices.

Utilization of multiferroics has expanded greatly in the last few years, especially with the discovery of many different types of multiferroic materials. $TbMnO_3$ (Kimura et al. 2007), $MnWO_4$ (Kundys et al. 2008), $BiFeO_3$ (Mohanty and Choudhary 2015), $BiMnO_3$(Hanif et al. 2017), and many more are studied for a variety of multiferroic applications.

Among all these materials, Bismuth ferrite ($BiFeO_3$) has been utilised as multiferroic material in both film/heterostructure and bulk forms due to its high critical temperature, strong magnetization and large spontaneous polarization. As a magnetoelectric material, $BiFeO_3$ has high critical temperatures of T_C~1103 K for ferroelectricity and T_N~643 K for antiferromagnetism which are both above room temperature (Fischer et al. 1980; Catalan and Scott 2009). Therefore, it is put in more effort to explore the new aspects of $BiFeO_3$ for possible applications.

In this study Nickel (Ni) element is utilized as doping element to enhance the ferroelectric and magnetic properties of $BiFeO_3$. For the heterostructure formation, sol gel deposition method is utilized. Structural and magnetic techniques are used for the characterization. The outcomes of the study are discussed here.

MATERIALS AND METHODS

Materials

Ni doped $BiFeO_3$ powders were synthesized by the sol-gel method. The high purity analytical grade powders of $Bi(NO_3)_3 \cdot 5H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and $Ni(CH_3CO_2) \cdot 4H_2O$ were used as raw materials. The materials were purchased from Sigma-Aldrich.

Experimental procedure

The above mentioned powders were dissolved in separately ethylene glycol and acetic acid (solvent) in proper stoichiometry proportions. The mixtures were stirred at constant temperature of 100°C for 1 hr to obtain a homogeneous solution. The resulting solutions were heated and stirred at constant temperature of 150°C on magnetic stirrer to evaporate the solvent. Finally, the powders were annealed at 500 and 600 °C for 30 minutes. The basic steps of synthesis are shown in Figure 1.

The structural analysis of the powders was carried out by x-ray diffraction (XRD) (Rigaku SmartLab X-ray diffractometer) technique. The particle morphology were analysed using scanning electron microscopy (SEM, JSM-6510, JEOL). The magnetization curves were obtained by using vibrating sample magnetometer (VSM) of Quantum Design (PPMS, 9 T) at room temperature (300 K). Magnetic resonance spectra were obtained using JEOL JES-FA300 x-band spectrometer.

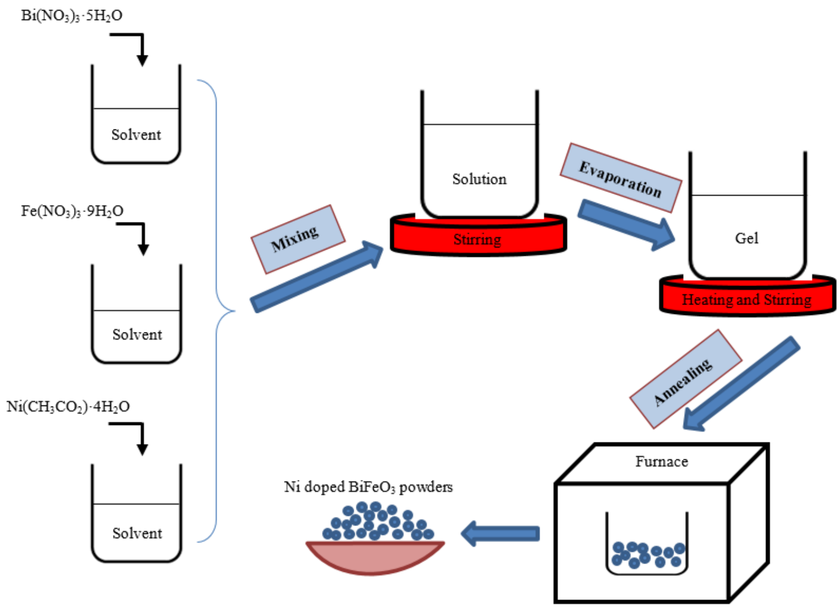

Figure 1. Schematic representation of synthesis process

RESULTS AND DISCUSSION

XRD, SEM and EDX Analysis

XRD patterns of the Ni doped $BiFeO_3$ powders have been shown in Fig. 2 in the ranges of the 15-65 degrees for the various annealing temperatures at 500 ºC and 600 ºC and both ethylene glycol and acetic acid solvents. The obtained XRD patterns are in good agreement for $BiFeO_3$ powders (Sheoran et al. 2019; Srinivas et al. 2016). The impurities or other phases of $BiFeO_3$ powders such as $Bi_2Fe_4O_9$, $Bi_{36}Fe_2O_{57}$ and $Bi_{24}Fe_2O_{39}$ also were detected in the XRD patterns with low intensity. However, Ni based impurity was not detected in any of the samples. While annealing temperature increases from 500 ºC to 600 ºC, the intensity of the peaks increases due to the increasing crystallinity (Karoblis et al. 2020). In terms of the solvents, the sharper peaks were obtained for the acetic acid solvents. While $Bi_{36}Fe_2O_{57}$ and $Bi_{24}Fe_2O_{39}$ impurity phases were obtained for acetic acid solvents, $Bi_2Fe_4O_9$ impurity phase was detected for the ethylene glycol solvents as well as acetic acid solvents. The solvent is another important parameter in order to change the crystalline structure of the $BiFeO_3$ powders (Clarke et al. 2018). The XRD results highlighted that the Ni doped $BiFeO_3$ powders were successfully synthesized.

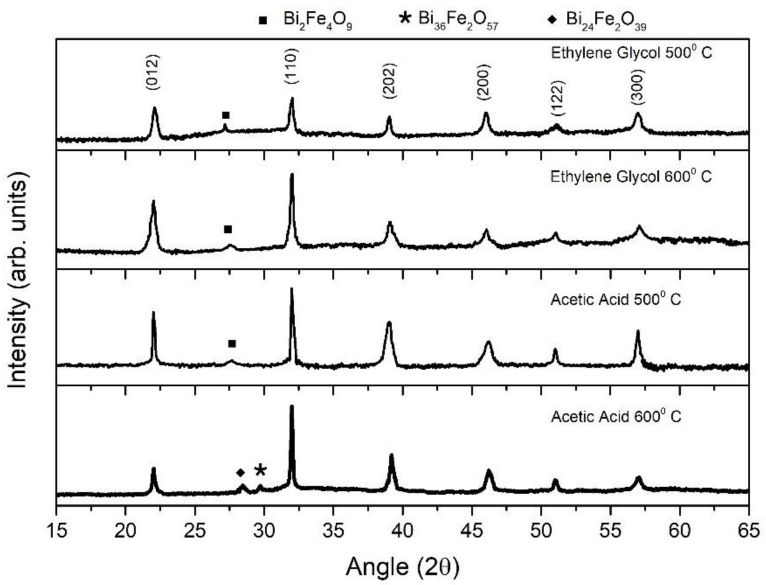

Figure 2. XRD graph of Ni doped $BiFeO_3$ powders

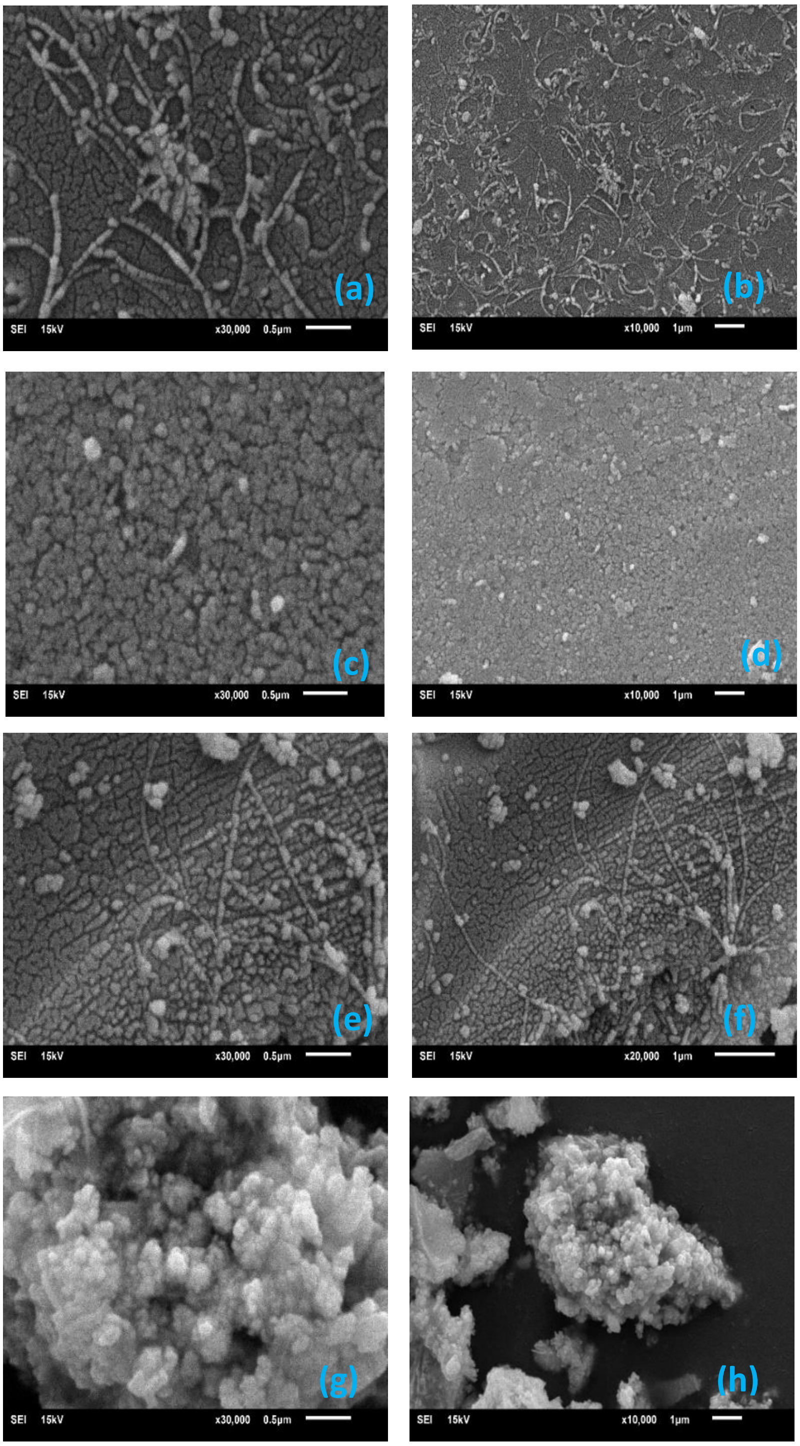

Figure 3. SEM images of Ni doped $BiFeO_3$ powders: a, b) ethylene glycol (500^o C), c, d) ethylene glycol (600^o C), e, f) acetic acid (500^o C), g, h) acetic acid (600^o C)

The surface morphology of Ni doped $BiFeO_3$ powders was studied by scanning electron microscopy technique. SEM images of Ni doped $BiFeO_3$ powders synthesized in ethylene glycol and acetic acid solvents for the annealing temperature at 500 ºC and 600 ºC temperatures have shown in Fig. 3a-3h for various magnifications. Fig. 3a and 3b exhibit surface morphology of Ni doped $BiFeO_3$ powders annealed at 500 ºC with the ethylene glycol solvent. There are some cracks and rod like structure on the surface. Fig. 3c and 3d shows SEM image of Ni doped $BiFeO_3$ powders annealed at 600 ºC with the ethylene glycol solvent. Surface morphology changed from rod like and cracked structures to cauliflower shapes after increasing annealing temperature. This type of change with increasing temperature can be attributed to the changing of the crystallinity (Hasan et al. 2016; Ryu et al. 2010). Fig. 3e, 3f and Fig. 3g, 3h illustrate the SEM images of the powders annealed at temperatures of 500 ºC and 600 ºC with the acetic acid solvents. SEM images of Ni doped $BiFeO_3$ powders annealed at 500 ºC obtained by acetic acid solvent show almost good homogeneity as well as fine granule sizes with some of rod-like structures. When the annealing temperature increased to 600 ºC, $BiFeO_3$ powders exhibited aggregated structures. This result can be attributed to increasing the grain size of Ni doped $BiFeO_3$ with increasing temperature (Ahmed et al. 2019).

Energy dispersive x-ray (EDX) spectroscopy was employed to determine the elemental composition of Ni doped $BiFeO_3$ powders. EDX analysis and EDX maps of Ni doped $BiFeO_3$ powders obtained in ethylene glycol and acetic acid solutions for various annealing temperatures have been shown in Fig. 4 and Fig. 5, respectively. According to EDX spectra (in Fig. 4), all the samples have enough amounts of Bi, O, Fe and Ni. Moreover, the increasing annealing temperature from 500° C to 600° C caused to increase the amounts of the O due to the annealing in the air. According to EDX map in Fig. 5, almost all the Ni doped $BiFeO_3$ powders have homogenous distribution of the Bi, O, Ni and Fe on the surfaces. The obtained EDX results of Ni doped $BiFeO_3$ powders are in good agreement with literature (Dao et al. 2016; Nadeem et al. 2018).

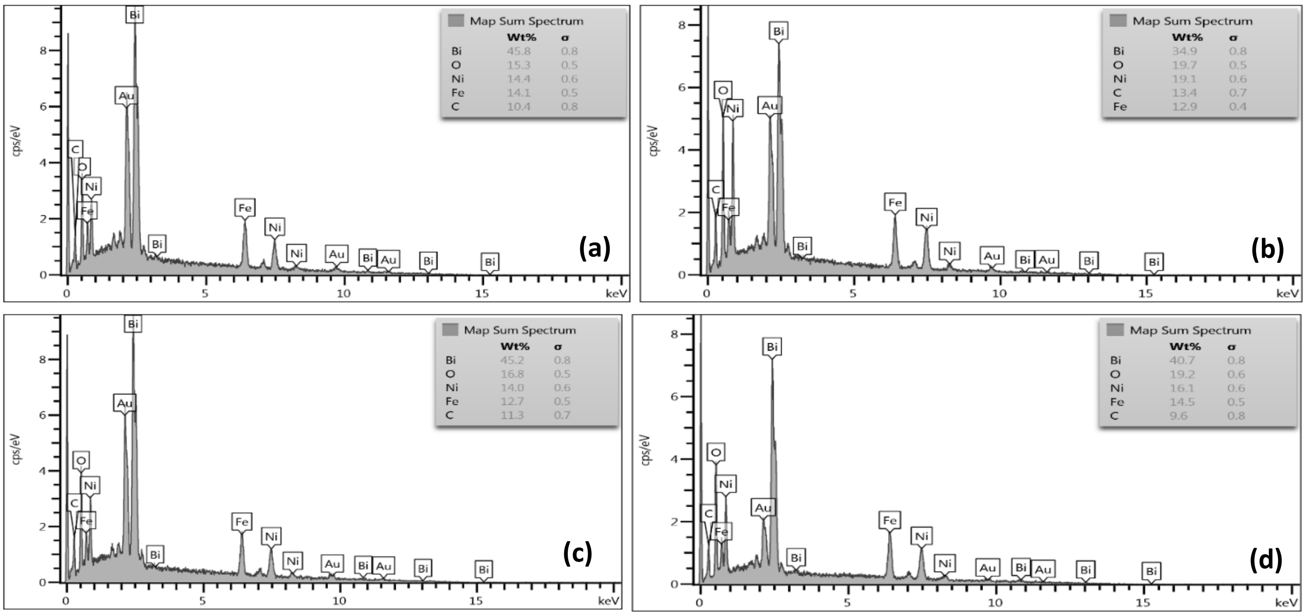

Figure 4. EDX spectra of Ni doped $BiFeO_3$ powders: a) ethylene glycol (500° C), b) ethylene glycol (600° C), c) acetic acid (500° C), d) acetic acid (600° C)

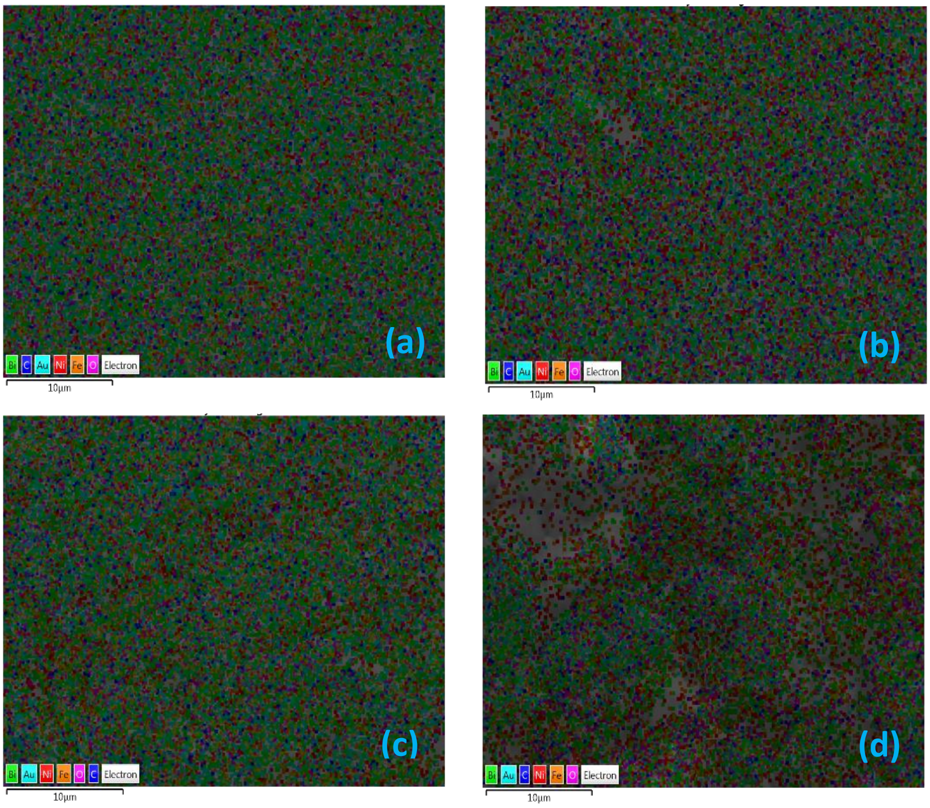

Figure 5. EDX maps of Ni doped $BiFeO_3$ powders: a) ethylene glycol (500^o C), b) ethylene glycol (600^o C), c) acetic acid (500 ^{o} C), d) acetic acid (600 ^{o} C)

Magnetic Properties

Figure 6 indicates the ferromagnetic resonance spectra of Ni doped $BiFeO_3$ powders. FMR spectra are generally described by a single, broad and asymmetric resonance line (Topkaya 2017). These magnetic curves recorded in this study indicate that the samples have ferromagnetic behaviour. These broad curves originate from the anisotropy axes of the powders randomly oriented (Sukhov et al. 2008). As can be seen from the figure, the resonance field decreases with annealing temperature and using ethylene glycol. The internal magnetic field arising from the demagnetization field and dipole-dipole interaction between neighbouring magnetic powders changes the resonance field of the magnetic spectrum (Topkaya et al. 2013).

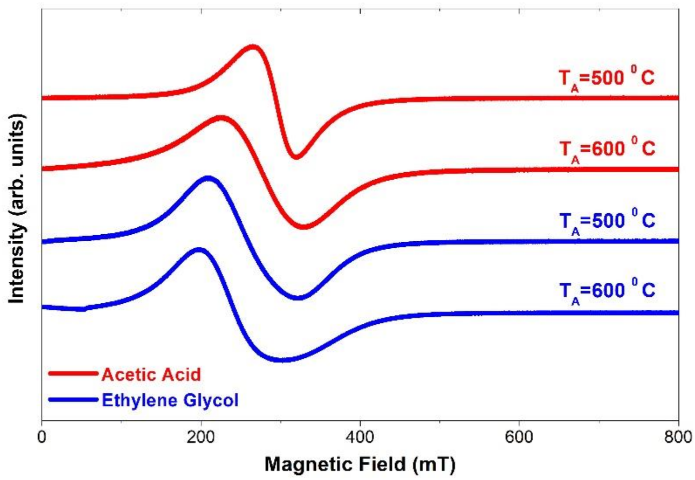

Figure 6. FMR spectra of Ni doped $BiFeO_3$ powders

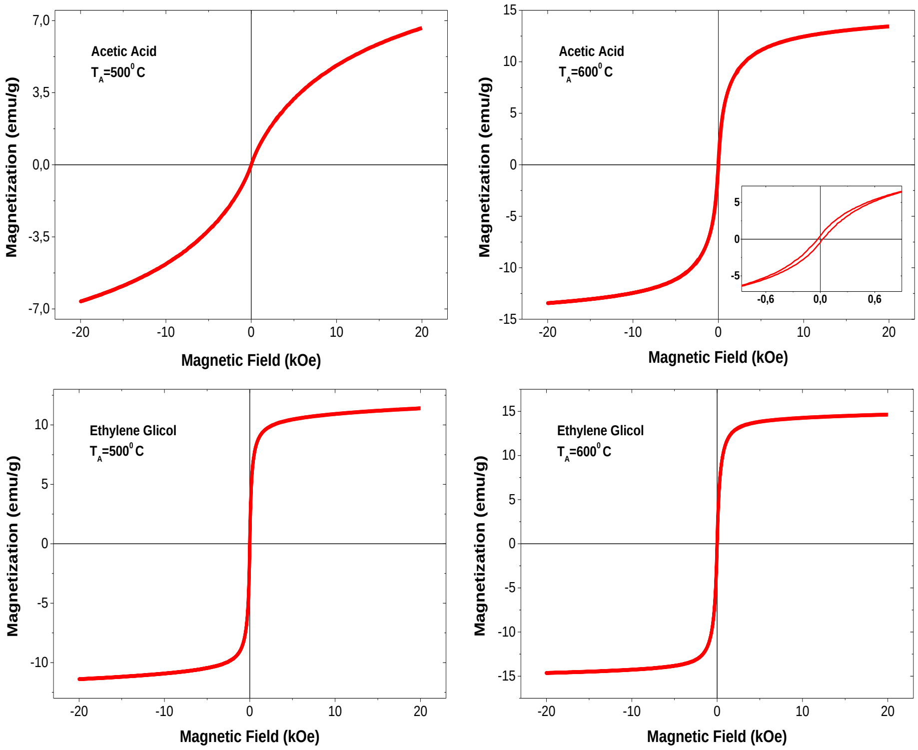

Figure 7. Magnetic hysteresis curves of Ni doped $BiFeO_3$ powders.

The magnetization curves for Ni doped $BiFeO_3$ samples are shown in Fig. 7. The magnetization graphs of all the samples were gotten at room temperatures (300 K) up to a magnetic field strength of 20 kOe. As shown from the figure, Ni doped $BiFeO_3$ samples have ferromagnetic behaviour. With increasing of the annealing temperature from 500 to 600 ^{o} C, the saturation magnetization (M_s) values of the samples increase. The recorded magnetization values of the samples solved in ethylene glycol are larger than that of the samples solved in acetic acid. In this studies, the obtained M_s values of the samples are larger than the values recorded in the previous studies about $BiFeO_3$ (Layek et al. 2013; Goswami et al. 2014; Du et al. 2010; Hasan et al. 2016)

CONCLUSION

Sol gel method were used to prepare Ni doped $BiFeO_3$ powders. Annealing and solvent material strongly affect the magnetic properties of the samples. XRD results indicate the formation of $BiFeO_3$ phase. The morphology was analysed by scanning electron microscopy. The large saturation magnetization values were obtained for all the samples. It has been observed that the annealing increases the saturation magnetization values. FMR measurements indicate that the samples have the ferromagnetic character. The obtained Ni doped $BiFeO_3$ powders can be a good candidate for the applications in spintronics.

ACKNOWLEDGEMENTS

This work was supported by Iğdır University Department of Scientific Research Projects (BAP) under project number 2017-FBE-A24.

Conflict of Interest

The article authors declare that there is no conflict of interest between them.

Author’s Contributions

The authors declare that they have contributed equally to the article.

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