Synergistic Effects of Ca2+ and High-Valence Nb5+ co-Doping on the Structural, Optical and Magnetic Properties of BiFeO3

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Abstract

The structural, optical and magnetic properties of BiFeO$_3$, BiFe$_{0.99}$Nb$_{0.01}$O$_3$ and Bi$_{1-x}$Ca$_x$Fe$_{0.99}$Nb$_{0.01}$O$_3$ (BCFNO, 0 ≤ $x$ ≤ 0.25) nanoparticles synthesized via sol-gel method are investigated. It has been found that a phase transition from the rhombohedral $R3c$ structure ($x$ ≤ 0.10) to the ideal cubic perovskite structure ($x$ = 0.25) which can be attributed to Ca$^{2+}$ doping. Increasing Ca$^{2+}$ dopants results in the increase of oxygen vacancies. As doping amount $x$ increase, the band gap of BCFNO decreases and the valence band spectra indicates that it’s a p-type semiconductor, which indicates their favorable potential in photocatalytic applications. The remnant magnetization $M_r$ of BCFNO reaches a maximum value (0.146 emu/g about 15 times compared with pure BFO) at $x$ = 0.10. This enhancement of magnetic properties in BCFNO can be ascribed to the synergistic effect of A and B site ions co-doping. Higher valence Nb doping cause the size effect and the magnetic polarons bounded to the impurities by Ca ions.

1. Introduction

Multiferroics are those materials which posses ferroelectric (or antiferroelectric) properties in combination with ferromagnetic (or antiferromagnetic) properties in the same phase and have emerged as new appealing materials thanks to their enormous properties in the field of spintronic devices, dual storage devices, sensors, high density memory and multi-state electric devices[1][2][3]. Among the multiferroic materials, the room temperature phase of BiFeO$_3$ possesses distorted rhombohedral perovskite structure as rhombohedral ($R3c$ space group) with high ferroelectric Curie point (T ≈ 830°C), high anti-ferromagnetic(AFM) Neel temperature (T ≈ 370°C) and narrow band gap(2.16 eV)[4][5]. It’s highly investigated that BFO is characterized as a distorted perovskite rhombohedral structure ($R3c$ space group) and a G-type antiferromagnetic (AFM) order modulated by a spatially spin structure along the [110]hex direction with a period of 62nm[6]. In spite of various interesting features, BiFeO$_3$ exhibits several drawbacks like high leakage current, low magnetization, difficult to synthesize in single phase etc. associated with it.

In order to overcome these shortcomings, many steps have already been taken including doping of divalent ions(Ca$^{2+}$,Sr$^{2+}$ and Ba$^{2+}$) and trivalent ions(La$^{3+}$,Nd$^{3+}$ and Eu$^{3+}$) at A-site[7][8][9] and high-valance ions (Nb$^{5+}$,Ti$^{4+}$) at B-site or co-doping[10][11][12][13][14] to greatly affect the ferroelectric, magnetic, optical and magnetoelectric properties of BiFeO$_3$. Sandhaya Jangra et al.[15] have reported that remanent magnetization increased for Bi$_{0.8}$Ca$_{0.2}$Fe$_{0.90}$Nb$_{0.10}$O$_3$ as compared with parent Bi$_{0.8}$Ca$_{0.2}$FeO$_3$ which was due to the presence of Nb. Ting Wang et al.[10] observed a decrease in the optical band gap in the Nd and Nb co-doped nanoparticles as well as an increase in magnetization for the Bi$_{0.85}$Nd$_{0.15}$Fe$_{0.95}$Nb$_{0.05}$O$_3$ nanoparticles which could be ascribed to the size effect and distorted octahedral structure. Zhai et al.[16] observed structural transition from rhombohedral to monoclinic in La$^{3+}$ doped BiFeO$_3$ (BLFO) and improved coercive field and remanent magnetization with Nb doping at B site of BLFO. In the view of above, we believe that structural, optical properties and saturation magnetization may be enhanced simultaneously by Ca and Nb co-doping. In the present study, BiFeO$_3$,
BiFe$_{0.99}$Nb$_{0.01}$O$_3$ and Bi$_{1-x}$Ca$_x$Fe$_{0.99}$Nb$_{0.01}$O$_3$ (0 ≤ x ≤ 0.25) nanoparticles are successfully synthesized via a tartaric acid-assisted sol-gel technique for the first time. The focus was placed on investigating the effect of Ca$^{2+}$ and Nb$^{5+}$ co-doping on the crystal structures, morphologies, and optical and magnetic properties of as-prepared nanoparticles.

2. Experimental Details

- Bi$_{1-x}$Ca$_x$Fe$_{0.99}$Nb$_{0.01}$O$_3$ (0 ≤ x ≤ 0.25) powders were prepared by a sol-gel method.
- Stoichiometric amounts of analytically pure Bi(NO$_3$)$_3$·5H$_2$O (99%), Fe(NO$_3$)$_3$·9H$_2$O (99%), Ca(NO$_3$)$_2$·5H$_2$O (99%), C$_{10}$H$_5$NbO$_{20}$ (99%) are dissolved in the pre-prepared dilute nitric acid. And calculated amounts of tartaric acid were added as a complexing agent. The concentration of Nb was fixed as 1% at Fe sites since previously content has been confirmed to be the most appropriate one for the Nb-doped BiFeO$_3$[17]. The solution was dried at 120°C and the resultant was grinded into powders. The powders were calcined at 300°C for one hour and heat preservation at 600°C for two hours to remove NO$_x$ and hydrocarbons. The crystal structure of the X-ray diffraction patterns were examined by a Bruker D8 ADVANCE X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å, Ni filter) with the scanning rate of 0.6°/min in a step size of 0.02°. The micro-structural properties of all specimens are measured by a field emission scanning electron microscopy (FE-SEM). The UV-Visible (UV-vis) absorption spectra over a range of 350–800 nm wave length were measured by an Ocean Optical Fiber Spectrometer (USB4000). X-ray photoelectron spectra (XPS) were collected by a Kratos Axis Ultra DLD photoelectron spectrometer with Al Kα source (hv = 1486.6 eV, with power setting of 10 mA × 12 kV) in a vacuum of 7 × 10$^{-7}$ Pa. Magnetic hysteresis loops were carried out on a vibrating sample magnetometer (VSM) in a physical property measurement system (PPMS, Quantum Design).

3. Results And Discussion

3.1 Structure analysis

Room temperature X-ray diffraction patterns of Bi$_{1-x}$Ca$_x$Fe$_{0.99}$Nb$_{0.01}$O$_3$ (BCFNO, x = 0.00 ~ 0.25) are shown in Fig. 1, where Nb1% means BiFe$_{0.99}$Nb$_{0.01}$O$_3$ sample. No major impurity phase was observed in the prepared samples. The XRD patterns of pure BiFeO$_3$ and Nb1% and x = 0.05, x = 0.10 samples in the BCFNO series could be labeled in a rhombohedral perovskite structure with $R3c$ phase (JCPDS no.86-1518). With the increasing of Ca doping concentration x, the (104) and (110) peaks tend to merge together when x ≤ 0.01 as shown in the inset of Fig. 1. It is found that the crystal structure of x = 0.25 sample(Bi$_{0.75}$Ca$_{0.25}$Fe$_{0.99}$Nb$_{0.01}$O$_3$) is a standard cubic perovskite structure with $Pm3m$ phase(JCPDS no.71–0878). This structural phase change is completely consistent with the change trend of the crystal structure of Ca-doped BFO alone[18], which shows that the main contribution of the change in the crystal structure of the Ca-Nb co-doped BCFNO sample comes from the replacement of Bi ions by Ca ions. With
an increasing Ca concentration $x$, all diffraction peaks shift toward higher angle since the twelve coordination ionic radius of Ca$^{2+}$ (134pm) is slightly smaller than that of Bi$^{3+}$ (139pm) and the six coordination ionic radius of Nb$^{5+}$ (64pm) is slightly smaller than that of Fe$^{3+}$ (64.5pm).

To studied structural properties of Ca and Nb co-doped BFO in detail, Rietveld refinement was adopted using the GSAS program. Patterns of refinements on XRD data were shown in Fig. 2. R3c space group was engaged in refining. As shown the remnant weight profile ($R_{wp}$) and and the fitness factor $\chi^2 \leq 2.564$ in Fig. 2, it suggested that the single phase with $R3c$ space group for $0 \leq x \leq 0.10$ and with $Pm3m$ phase group for $0.10 < x < 0.25$. The best fits was well consistent with XRD data and the phase transition in Ca-doped BFO[18]. The variation of lattice constant as a function of Ca concentration ($x$) of the BCFNO samples are shown in Fig. 3. With the increase of Ca content $x$, the lattice constant of BCFNO decrease which the overall trend was consistent with the Ca-doped BCFO sample[18].

Figures 4 shows the SEM images of BiFeO$_3$, BiFe$_{0.99}$Nb$_{0.01}$O$_3$, Bi$_{0.90}$Ca$_{0.10}$FeO$_3$, Bi$_{0.90}$Ca$_{0.10}$Fe$_{0.99}$Nb$_{0.01}$O$_3$ samples. The particle size of Bi$_{0.90}$Ca$_{0.10}$FeO$_3$ sample is larger than BiFe$_{0.99}$Nb$_{0.01}$O$_3$. The particles of Bi$_{0.90}$Ca$_{0.10}$Fe$_{0.99}$Nb$_{0.01}$O$_3$ are arranged more compactly, the particle size is about 70nm. It is found that a small amount(0.01) of Nb$^{5+}$ co-doping with Ca$^{2+}$ further refines the particles of the sample. The average grain sizes $D$ of the samples can be estimated by X-rays data using the Debye-Scherrer formula and the grain size corresponding to the BCFNO($x = 0.00$, $x = 0.05$, 0.10, 0.15, 0.20, 0.25) sample is 27.1nm, 49.5nm, 50.7nm, 46.1nm, 54.1nm, 53.1nm. The obtained results confirm that 1% Nb$^{5+}$ ions are the main cause of particle refinement, and the increased Ca$^{2+}$ dopants have little effect on the particle size of the samples.

The structure and phase transition confirmed by XRD can also been characterized by the Raman peaks. Figure 5 represents the Raman spectra of BCFNO nanoparticles. For BFO, Raman Raman active modes can be summarized using the following irreducible representation: $4A_1 + 9E$[19][20]. The main 13 vibrating modes observed are consistent with the results in Ca-doped BFO[18]. It can be seen that the 13 Raman activity peaks of pure BFO decrease and disappear gradually as the Ca doping amount increases to 0.25 in BCFNO, which indicates that the structure change from $R3c$ structure to $Pm3m$ structure in the Ca-Nb co-doped sample without Raman activity peak. Compare Raman Scattering Spectra of BCFNO and BCFO Samples, the similar evolution trend of Raman peaks also proves the structural phase transition is mainly caused by Ca$^{2+}$ doping[18]. Apparently, these Raman results are consistent with the XRD observations.

### 3.2 XPS Analysis

XPS spectrum analysis of BiFe$_{0.99}$Nb$_{0.01}$O$_3$($x = 0.00$) and Bi$_{0.90}$Ca$_{0.10}$Fe$_{0.99}$Nb$_{0.01}$O$_3$ ($x = 0.10$) samples were recorded to figure out valence state of Fe and oxygen vacancies(Vo) and the result is illustrated in Fig. 6(a)(b). As shown in Fig. 6(a), there is no shift of the fitting peaks(709.4/710.9eV) of Fe2p 3/2 which respectively could be ascribed to Fe$^{2+}$ and Fe$^{3+}$. The constant ratio of Fe$^{3+}$ and Fe$^{2+}$ indicates that the Ca$^{2+}$ doping does not cause the variation of the valence state of Fe ion. The O1s XPS spectrum (see
Fig. 6(b)) deconvoluted into two peaks, corresponding to the intrinsic O$^{2-}$ ions and the Vo [21]. As confirmed by the XPS patterns, the oxygen vacancies are increased with Ca concentration to maintain the electrical neutrality of the sample.

### 3.3 Optical Properties

BiFeO$_3$ can be used as a narrow band gap metal oxide semiconductor in applications such as photocatalytic materials. The room-temperature UV-Vis absorption spectra of BCFNO samples are displayed in Fig. 7. The absorption band is comparatively broad in the wave-length range of 480–560 nm, which indicates the high availability of visible light. The absorption edge shifts to higher wavelengths for the doped samples. The band gap can be determined from Kubelka-Munk function [22]: $(\alpha h\nu)^n = A(h\nu-E_g)$. $(\alpha h\nu)^2$ as a function of $h\nu$ is plotted in Fig. 7(a), which provides the value of $E_g$ by the tangent at $(\alpha h\nu)^2 = 0$. The calculated optical band gap $E_g$ decreases as $x$ increases as shown in the inset (b) of Fig. 7. BFO has a maximum value of $E_g$ (2.06 eV), which gradually decreases down to 1.78 eV for the Bi$_{0.90}$Ca$_{0.10}$Fe$_{0.99}$Nb$_{0.01}$O$_3$ nanoparticles (see Fig. 7(b)). Two major reasons should be considered to make $E_g$ shorten clear. As analyzed previously, on the one hand, the increased oxygen vacancy can act as a kind of defect induced energy levels below the conduction band(CB), which is closely associated with the shrinking of the band gap. Besides, it is reported the increased of the Fe-O-Fe angle, which could suppress the FeO$_6$-octahedral tilting, decreases the bandwidth of CB and VB of BFO [23][24]. Ting Wang et al.[10] evaluated the optical properties of pure BiFeO$_3$ and Bi$_{0.8}$Nd$_{0.2}$Fe$_{0.95}$Nb$_{0.05}$O$_3$ nanoparticles prepared by a sol-gel technique and obtained that the values of $E_g$ were approximately 2.16 and 2.05 eV for pure BiFeO$_3$ and Bi$_{0.8}$Nd$_{0.2}$Fe$_{0.95}$Nb$_{0.05}$O$_3$ nanoparticles. In addition, Kumar et al.[25] synthesized the Bi$_{1-x}$Ca$_x$Fe$_{1-x}$Ti$_x$O$_3$ nanoparticles ($x = 0, 0.05, 0.10, 0.15$ and $0.2$) prepared by a tartaric acid modified sol-gel technique and the direct band gap values were found to be about $2.17, 2.16, 2.11, 2.09$ and $2.05$ eV, respectively. Accordingly, the present $E_g$ values in our work compare favorably with the above-reported ones. Thanks to the energy band gap is located in the visible region, the as-prepared BiFeO$_3$ nanopowders can be used for photocatalysis in the decomposition of organic compounds.

Figure 7 The room-temperature UV-vis spectra of Bi$_{1-x}$Ca$_x$Fe$_{0.99}$Nb$_{0.01}$O$_3$ ($x = 0.00 \sim 0.25$) samples. Inset (a) shows $(\alpha h\nu)^2$ versus $h\nu$ plot. Inset (b) shows the band-gap $E_g$ versus doping amount $x$ plot.

Besides, XPS valence band spectra for Bi$_{1-x}$Ca$_x$Fe$_{0.99}$Nb$_{0.01}$O$_3$ ($x = 0.00, 0.05, 0.10$) samples are also given in Fig. 8. For Bi$_{0.90}$Ca$_{0.10}$Fe$_{0.99}$Nb$_{0.01}$O$_3$ sample, with the help of the optical band gap $E_g = 1.94$eV calculated by the UV-vis spectrum, we can determine the border between the Fermi energy ($E_F$) and valence band energy (VB) is about $\sim 0.49$ eV, suggesting that the $E_F$ is quite near to the VB. According to related reports, BFO is a p-type semiconductivity material [26][27][28], where the $E_F$ is near the VB, which means that the proportion of holes is higher than that of electrons. A schematic diagram(Fig. 8(b)) is introduced to better understand it. As the doping concentration $x$ increases, the Ca and Nb co-doped
samples gradually becomes a p-type semiconductor material, which might lead to a potential application in photocatalysis\cite{29}\cite{30}.

3.4 Magnetic Properties

The M-H hysteresis loops for pure BFO and Bi$_{1-x}$Ca$_x$Fe$_{0.99}$Nb$_{0.01}$O$_3$ ($x = 0.00, 0.10, 0.25$) samples are shown in Fig. 9. All our samples present weak ferromagnetism at room temperature. In order to study the magnetic enhancement mechanism of the BCFNO sample more clearly, the contrast diagram according to the change of the $M_r$ of BFO, BCFO, and BCFNO with the doping amount $x$ is shown in Fig. 10. It can be seen that the change of the remanence $M_r$ of Bi$_{1-x}$Ca$_x$Fe$_{0.99}$Nb$_{0.01}$O$_3$ (BCFNO) is similar to that of Bi$_{1-x}$Ca$_x$FeO$_3$ (BCFO). The $M_r$ is well improved to the maximum value (for $x = 0.10$) in R3c phase at the same concentration $x$. When the cubic Pm3m phase appears, with further Ca doping ($0.10 < x \leq 0.25$) in pure Ca doped and CaNb co-doped BFO, $M_r$ decreases continuously which is due to the increasing of the Pm3m phase in which the DM interaction vanishes since the Fe-O-Fe angle equals to 180° and the Fe$^{3+}$ moments are antiparallel to their nearest neighbors\cite{31}\cite{32}\cite{33}.

For the previous BCFO and BFNO series samples, in-depth discussion and analysis have been taken that the magnetic enhancement of pure Ca$^{2+}$ doped and Nb$^{5+}$ doped BFO samples are two different mechanisms\cite{17}\cite{18}. The incorporation of Ca impurity ions increases oxygen vacancies, forming bound magnetic polarons at the defects, which enhance the magnetization at low Ca$^{2+}$ doping content $x$\cite{18}. The enhancement of the magnetic property of the Nb doped BiFeO$_3$ samples is mainly attributed to the large ratio of surface to volume induced by the reduction of the particles size (size effect)\cite{17}. Interestingly, the particle size of the Ca-Nb co-doped BCFNO sample is slightly smaller than that of BCFO due to the small amount of Nb introduced as discussed above. Under the same doping amount $x$, the magnetic properties of the CaNb co-doped BFO samples are significantly better than that of BCFO. The remnant magnetization ($M_r$) of BCFNO at $x = 0.10$ reaches a maximum value (0.146 emu/g) which is about 15 times compared with pure BFO or larger than pure Nb-doped BFO. Therefore, the superior magnetic properties in BCFNO can be ascribed to the synergistic effect of A and B site ions doping:

1. One of the important contributions is the decreasing of the grain size by appropriate Nb doping at Fe site. The particle sizes of proper fixed content (1%) Nb$^{5+}$ doped samples decrease below the range of cycloid spin periodicity of BiFeO$_3$ (62 nm) and show a large ratio of surface to volume induced by the reduction of the particles size (size effect).

2. Ca$^{2+}$ dopants and the increased oxygen vacancies induce impurity levels within the forbidden band, and bound charge carriers to these impurity levels. The bound carriers polarize the localized magnetic cations in their neighbourhoods to form magnetic polarons (MPs), which interrupts the long range AF order\cite{34}\cite{35}.

As discussed above, the enhancement of magnetization in BCFNO is possible due to the synergistic effect of Ca$^{2+}$ and Nb$^{5+}$ ions doping, on the one hand, the size effect induced by Nb$^{5+}$ ions, on the other
hand, the magnetic polarons bounded to the impurities by Ca$^{2+}$ ions.

4. Conclusion

In summary, BiFeO$_3$, BiFe$_{0.99}$Nb$_{0.01}$O$_3$ and Bi$_{1-x}$Ca$_x$Fe$_{0.99}$Nb$_{0.01}$O$_3$ (BCFNO, $0 \leq x \leq 0.25$) have been successfully synthesized using tartaric acid-based sol–gel route. The Ca substitution causes a structural transition from a rhombohedral $R3c$ structure for $x \leq 0.10$ to a cubic $Pm3m$ structure at $x = 0.25$ which is observable from the Rietveld analysis of the XRD data and Raman spectra. Through XPS measurement, it is found that the increase of oxygen vacancies in Ca and Nb co-doped samples, which makes contribution to the formation of magnetic polarons. The optical band gap $E_g$ of the co-doped nanoparticles is apparently smaller than that of pure BiFeO$_3$. Furthermore, the enhancement of the magnetization for Bi$_{0.90}$Ca$_{0.10}$Fe$_{0.99}$Nb$_{0.01}$O$_3$ are nearly 15 times of those for pure BiFeO$_3$. which is due to the synergistic effect of the size effect and the formation of magnetic polarons.

Declarations

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References

1. P. Kozlenko, A.A. Belik, A.V. Belushkin, E.V. Lukin, W.G. Marshall, B.N. Savenko, E. Takayama-Muromachi, Antipolar phase in multiferroic BiFeO$_3$ at high pressure, Phys. Rev. B 84 (2011) 094108.
2. Saad Mabrouk Yakout, Spintronics: Future Technology for New Data Storage and Communication Devices, J. Supercond. Novel Magn. 33 (2020) 2557–2580
3. Sharma, V. Singh, R.K. Kotnala, R.K. Dwivedi, Comparative studies of pure BiFeO3 prepared by sol–gel versus conventional solid-state reaction method, J. Mater. Sci.-Mater. Electron. 25 (2014) 1915–1921.
4. Singh, G.D. Dwevedi, P. Shahi, D. Kumar, O. Prakash, A.K. Ghosh, S. Chatterjee, Effect of Pr- and Nd-doping on structural, dielectric, and magnetic properties of multiferroic Bi$_{0.8}$La$_{0.2}$Fe$_{0.9}$Mn$_{0.1}$O$_3$, J. Appl. Phys. 115 (2014) 134102
5. A. McDonnell, N. Wadnerkar, N. J. English, M. Rahman, D. Dowling, Photo-active and optical properties of bismuth ferrite (BiFeO$_3$): an experimental and theoretical study, Chem.Phys. Lett. 78 (2013) 572
6. Sosnowska, T. Peterlin-Neumaier, E. Steichele, Spiral magnetic ordering in bismuth ferrite, J. Phys. C: Solid State Phys. 15 (1982) 4835–4846.
7. Kaur, K.L. Yadav, P. Uniyal, Multiferroic and optical studies on the effects of Ba$^{2+}$ ions in BiFeO$_3$ nanoparticles, J. Mater. Sci.: Mater. Electron. 27 (2016) 4475–4482.

8. Ramachandran, A. Dixit, R. Naik, G. Lawes, M.S.R. Rao, Weak ferromagnetic ordering in Ca doped polycrystalline BiFeO$_3$, J. Appl. Phys. 111 (2012) 023910.

9. A. Khomchenko, J.A. Paixao, Ti doping-induced magnetic and morphological transformations in Sr- and Ca-substituted BiFeO$_3$, J. Phys.: Condens. Matter 28 (2016) 166004.

10. Ting Wang, Ting Xu, Shang Gao, S.-H. Song, Effect of Nd and Nb co-doping on the structural, magnetic and optical properties of multiferroic BiFeO$_3$ nanoparticles prepared by sol-gel method, Ceram. Int. 43 (2017) 4489–4495.

11. K. Jha, P.A. Jha, P. Kumar, K. Asokan, R.K. Dwivedi, Gradient core-shell microstructure in mixed valence multiferroic: TM (Ti, Nb, W) substituted bismuth ferrite, J. Alloys Compd. 667 (2016) 178-183.

12. Mao, X. Wang, L. Chu, Y. Zhu, Q. Wang, J. Zhang, J. Yang, X. Li, W. Huang, Simultaneous enhancement of magnetic and ferroelectric properties in Dy and Cr co-doped BiFeO$_3$ nanoparticles, Phys. Chem. Chem. Phys. 18 (2016) 6399-6405.

13. Mao, W. Chen, X. Wang, Y. Zhu, Y. Ma, H. Xue, L. Chu, J. Yang, X. Li, W. Huang, Influence of Eu and Sr co-substitution on multiferroic properties of BiFeO$_3$, Ceram. Int. 42 (2016) 12838-12842.

14. [14] M.A. Basith, O. Kurni, M.S. Alam, B.L. Sinha, B. Ahmmad, Room temperature dielectric and magnetic properties of Gd and Ti co-doped BiFeO$_3$ ceramics, J. Appl. Phys. 115 (2014) 024102.

15. Sandhaya Jangra, Sujata Sanghi, Ashish Agarwal, Manisha Rangi, Kavita Kaswan, Satish Khas, Improved structural, dielectric and magnetic properties of Ca$^{2+}$ and Nb$^{5+}$ co-substituted BiFeO$_3$ multiferroics, J. Alloys Compd. 722 (2017) 606e616.

16. Zhai, Y.G. Shi, S.L. Tang, L.Y. Lv, Y.W. Du, Large magnetic coercive field in Bi$_{0.9}$La$_{0.1}$Fe$_{0.98}$Nb$_{0.02}$O$_3$ polycrystalline compound, J. Phys. D. Appl. Phys. 42 (2009) 165004.

17. Hui-min Xian, Yi-quan Du, Jiang Zhang, Xi Chen, Structural, Magnetic and Optical Properties of BiFe$_{1-x}$Nb$_x$O$_3$, Chin. J. Chem. Phys. 29 (2016).

18. Hui-min Xian, Lingyun Tang, Zhongquan Mao, Jiang Zhang, Xi Chen, Bounded magnetic polarons induced enhanced magnetism in Ca-doped BiFeO$_3$, Solid State Commun., 287 (2019) 54-58.

19. Hermet, M. Goffinet, J. Kreisel, Ph Ghosez, Raman and infrared spectra of multiferroic bismuth ferrite from first principles, Phys. Rev. B 75 (2007) 220102.

20. Suresh, S. Srinath, Effect of synthesis route on the multiferroic properties of BiFeO$_3$: a comparative study between solid state and sol-gel methods, J. Alloy.Compd. 649 (2015) 843–850.

21. Fang, J. Liu, S. Ju, F. G. Zheng, W. Dong, M. R. Shen, Experimental and theoretical evidence of enhanced ferromagnetism in sonochemical synthesized BiFeO$_3$ nanoparticles, Appl. Phys. Lett. 97 (2010) 242501.
22. H. Yang, D. Kan, I. Takeuchi, V. Nagarajan, J. Seidel, Doping BiFeO$_3$: approaches and enhanced functionality, Phys. Chem. Chem. Phys. 14 (2012) 15953-15962

23. Y. Borisevich, H.J. Chang, M. Huijben, M.P. Oxley, S. Okamoto, M.K. Niranjan, J.D. Burton, E.Y. Tsymbal, Y.H. Chu, P. Yu, R. Ramesh, S.V. Kalinin, S.J. Pennycook, Suppression of octahedral tilts and associated changes in electronic properties at epitaxial oxide heterostructure interfaces, Phys. Rev. Lett. 105 (2010) 087204

24. L. Han, W.F. Liu, X.L. Xu, M.C. Guo, X.N. Zhang, P. Wu, G.H. Rao, S.Y. Wang, Room-temperature multiferroic and optical properties in Ba and Rb codoped BiFeO$_3$ nanoparticles, J. Alloy. Compd. 695 (2017) 2374-2380

25. Kumar, M. Kar, Effect of structural transition on magnetic and optical properties of Ca and Ti co-substituted BiFeO$_3$ ceramics, J. Alloy. Compd. 584 (2014) 566-572

26. Yang, H.M. Luo, H. Wang, I.O. Usov, N.A. Suvorova, M. Jain, D.M. Feldmann, P.C. Dowden, R.F. DePaula, Q.X. Jia, Rectifying current-voltage characteristics of BiFeO$_3$/Nb-doped SrTiO$_3$ heterojunction, Appl. Phys. Lett. 92 (2008) 102113.

27. K. Vasudevan, A.N. Morozovska, E.A. Eliseev, J. Britson, J.-C. Yang, Y.-H. Chu, P. Maksymovych, L.Q. Chen, V. Nagarajan, S.V. Kalinin, Domain wall geometry controls conduction in ferroelectrics, Nano Lett. 12 (2012) 5524-5531.

28. L. Han, W.F. Liu, X.L. Xu, M.C. Guo, X.N. Zhang, P. Wu, G.H. Rao, S.Y. Wang, Room-temperature multiferroic and optical properties in Ba and Rb codoped BiFeO$_3$ nanoparticles, J. Alloy. Compd. 695 (2017) 2374-2380

29. Soltani, M.H. Entezari, Photolysis and photocatalysis of methylene blue by ferrite bismuth nanoparticles under sunlight irradiation, J. Mol. Catal. A: Chem. 377 (2013) 197.

30. Xian, H. Yang, J. F. Dai, Z. Q. Wei, J. Y. Ma, W. J. Feng, Photocatalytic properties of BiFeO$_3$ nanoparticles with different sizes, Mater. Lett., 65, (2011) 1573.

31. K. Zvezdin, A. P. Pyatakov, On the problem of coexistence of the weak ferromagnetism and the spin flexoelectricity in multiferroic bismuth ferrite, Europhys. Lett. 99 (2012) 57003.

32. S. Chen, Y. H. He, J. Zhang, Z. Q. Mao, Y. J. Zhao, X. Chen, The oxygen octahedral distortion induced magnetic enhancement in multiferroic Bi$_{1-x}$Yb$_x$Fe$_{0.95}$Co$_{0.05}$O$_3$ powders, J. Alloys Compd. 604 (2014) 327-330.

33. S Chen, L. R. Zheng, Y. H. He, J. Zhang, Z. Q. Mao, X. Chen, The local distortion and electronic behavior in Mn doped BiFeO$_3$, J. Alloys Compd. 633 (2015) 216-219.

34. Chiorescu, J. L. Cohn, J. J. Neumeier, Impurity conduction and magnetic polarons in antiferromagnetic oxides. Phys. Rev. B, 76 (2007) 020404

35. H. Meskine, T. Saha-Dasgupta, and S. Satpathy, Does the Self-Trapped Magnetic Polaron Exist in Electron-Doped Manganites?. Phys. Rev. Lett. 92(2004) 056401

Figures
Figure 1

a) The XRD patterns of pure BFO and Bi$_{1-x}$Ca$_x$Fe$_{0.99}$Nb$_{0.01}$O$_3$ (BCFNO, x = 0.00~0.25) samples; b) Enlargement of the diffraction peaks located at about 2θ = 32°
Figure 2

The Rietveld-refined XRD patterns of Bi$_{1-x}$Ca$_x$Fe$_{0.99}$Nb$_{0.01}$O$_3$ (BCFNO, $x = 0.00, 0.10, 0.15, 0.25$)
Figure 3

The doping amount $x$ dependence of a) the lattice parameters $a_{R3c}$, $c_{R3c}$ and $a_{Pm3m}$
Figure 4

SEM images of a) BiFeO₃; b) BiFe₀.⁹⁹Nb₀.₀₁O₃; c) Bi₀.⁹₀Ca₀.₁₀FeO₃; d) Bi₀.⁹₀Ca₀.₁₀Fe₀.⁹⁹Nb₀.₀₁O₃
Figure 5

The room-temperature Raman spectra of Bi$_{1-x}$Ca$_x$Fe$_{0.99}$Nb$_{0.01}$O$_3$ (BCFNO, x = 0.00~0.25)
Figure 6

The XPS spectra of a) Fe2p 3/2; b) O1s for BiFe0.99Nb0.01O3(x = 0.00) and Bi0.90Ca0.10Fe0.99Nb0.01O3(x = 0.10) samples
Figure 7

The room-temperature UV-vis spectra of Bi1-xCaxFe0.99Nb0.01O3 (x = 0.00~0.25) samples. Inset (a) shows $(\alpha h\nu)^2$ versus $h\nu$ plot. Inset (b) shows the band-gap $E_g$ versus doping amount $x$ plot.
Figure 8

a) The XPS valence band spectra of Bi$_{1-x}$Ca$_x$Fe$_{0.99}$Nb$_{0.01}$O$_3$ (x = 0.00, 0.05, 0.10) samples; b) the energy band diagram of Bi$_{0.90}$Ca$_{0.10}$Fe$_{0.99}$Nb$_{0.01}$O$_3$ sample
Figure 9

The room-temperature magnetic loops for pure BFO and Bi$_{1-x}$Ca$_x$Fe$_{0.99}$Nb$_{0.01}$O$_3$ (BCFNO$_x$ = 0.00, 0.10, 0.25) samples. Inset shows the doping amount x dependence of remnant magnetization Mr.
Figure 10

The doping amount $x$ dependence of $M_r$ for BFO, $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_3$ (BCFO\(\x\) = 0.00~0.25)[18] and $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_3$ (BCFNO\(\x\) = 0.00~0.25) samples