Effect of La Doping on the Phase Conversion, Microstructure Change, and Electrical Properties of Bi2Fe4O9 Ceramics

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Undoped and La-doped Bi2Fe4O9 ceramics were synthesized using a soft chemical method. It is observed that in calcining Ladoped Bi2Fe4O9, Bi(La)FeO3 phase rather than Bi2-xLaxFe4O9 gradually increases with increasing La doping content. The phase conversion from mullite-type structure of Bi2Fe4O9 to rhombohedrally distorted perovskite one of Bi(La)FeO3 with increasing La doping content indicates that La doping can stabilize the structure of BiFeO3. This is further evidenced that Bi2Fe4O9 can be directly converted to Bi(La)FeO3 by heating the mixtures of nominal composition of Bi2Fe4O9/xLa2O3. Furthermore, the microstructure changes and the room temperature hysteresis loops and leakage current for Bi2-xLaxFe4O9 with x=0 and 0.02 were characterized.

I. Introduction

BISMUTH-BASED complex oxides have attracted a lot of attention because they usually display interesting electrical properties, especially, the multiferroics. Among them, BiFeO3 is the most promising one and exhibits a high Currie temperature (TCB1103 K) and Ne’el temperature (TNB643 K), which are important for theoretical research and various applications. In synthesizing BiFeO3, Bi2Fe4O9 was frequently observed as an impurity phase, whose structure is orthorhombic (space group: Pbam) and belongs to the family of mullite-type crystal structures. A unit cell of Bi2Fe4O9 contains two formula units with evenly distributed FeO6 octahedral and FeO4 tetrahedral. In addition, the Bi31 ions are surrounded by eight oxygen ions with mutually orthogonal shorter BiO3 and longer BiO5 units.

Bi2Fe4O9 has been known several decades ago, which displays various functional applications. Moreover, though Bi2Fe4O9 was known as antiferromagnetism at room temperature (TNB260 K), the ferroelectric properties were not taken into account due to the centrosymmetric crystal structure. Nevertheless, unexpected multiferroic effects were reported recently in polycrystalline Bi2Fe4O9, attributed to the frustrated spin system coupled with phonons. Moreover, it was also reported as a poor ferroelectric material.

While the effect of La dopant on the electrical polarization and magnetic moment of BiFeO3 was reported, the related study in Bi2Fe4O9 was still lacking. In this investigation, synthesis and electrical properties of undoped and La-doped Bi2Fe4O9 ceramics are reported. One interesting result should be highlighted, namely, La doping indeed can suppress the development of Bi2Fe4O9 and stabilize the structure of BiFeO3.

II. Experimental Procedure

Fine powders of Bi2-xLaxFe4O9 (x=0.02, 0.05, 0.08, 0.10, 0.20, and 0.30) ceramics were fabricated using a soft
chemical method. The precursor solution was prepared by mixing appropriate amounts of high-purity Bi2O3 and Fe (NO3)3 _ 9H2O, dissolved in a diluted nitric acid solution. Tartaric acid with respect to metal nitrates of 1:1 molar ratio was added to the solution. The solution was heated under stirring on a hot plate until all the liquids evaporated out from the solution and then heated in an oven at 420°C for 10 h, becoming dried fluffy powders. The powders were then ground and calcined at 750°C for 6 h. The calcined powders were milled again, and then pressed into disks of 10 mm in diameter. Finally, the disks were sintered at 950°C for 2 h with a high heating rate and then furnace cooled rapidly to room temperature.

X-ray diffraction (XRD) data were collected by a Rigaku diffractometer (Rigaku-D/Max, Rigaku, Tokyo, Japan) using CuKa radiation. The morphologies of the sintered samples were characterized using a Hitachi S4100 field emission scanning electron microscope (FE-SEM; Hitachi, Tokyo, Japan). For electrical measurements, the ceramic disks were polished to 0.1 mm thick and pasted with silver electrode on both surfaces. The polarization and leakage current versus electric field measurements were carried out at room temperature using a Taisiant RT6000 test system.

III. Results and Discussion

The XRD spectra of undoped and La-doped Bi2Fe4O9 ceramics are shown in Fig. 1. The sample of undoped Bi2Fe4O9 is single phase without any observable impurity phases. All diffraction peaks can be indexed as an orthorhombic mullite-type structure of Bi2Fe4O9 (space group: Pbam) with lattice constants of a=57.965 Å, b=58.440 Å, and c=55.994 Å, which are in good agreement with literature results (JCPDS: 25-0090). In addition, it reveals quite interesting results, retaining the structure of Bi2Fe4O9 at low-doping content (x=0.02) and converting gradually to that of BiFeO3 at high-doping content. It should be noted that rhombohedral (R) BiFeO3 can be identified even in the x=0.02 sample, as indicated by the most strong intensity peak of R-phase BiFeO3 at 2θ=52°. The peak intensity of BiFeO3 increases with increasing La doping content. When x=0.2, Bi(La)FeO3, indicating that La dissolves in BiFeO3, becomes dominant, and the peaks of Bi2Fe4O9 completely disappear at x=0.3. Extra peaks, identified as the impurity phase of Fe2O3, are observed in the XRD patterns of x=0.2 and 0.3 samples. Note that samples with x=0.4, 0.5, and 1.0 also contain Bi(La)FeO3 phase (not shown).

![Fig. 1. X-ray diffraction patterns of undoped and La-doped Bi2Fe4O9 at room temperature.](image1)

![Fig. 2. X-ray diffraction patterns of preprepared Bi2FeO3 powders and Bi2Fe4O9-xLa2O3 composites.](image2)

Obviously, the result of Fig. 1 shows that La doping can stabilize the structure of BiFeO3. While the mechanism for the stabilization of BiFeO3 by La doping is not known, we further evidence that the Bi2Fe4O9 phase can directly be converted to Bi(La)FeO3 phase via the reaction with nominal compositions of Bi2Fe4O9/xLa2O3 with x=1/3 and 1/9, shown in Fig. 2. (Note that the preprepared powders of Bi2Fe4O9 were thoroughly mixed with La2O3 in appropriate
proportion and then compacted and sintered at 950°C for 2 h.) It displays that the X-ray intensity of Bi(La)FeO₃ phase increases while that of Bi₂Fe₄O₉ decreases with increasing La₂O₃ doping. Thus, the above results provide plausible explanation why the La dopant can suppress the formation of the impurity phase of Bi₂Fe₄O₉ during synthesis of BiFeO₃. Similar case had been reported in the calcium ferrites, wherein by adding La₂O₃, CaFe₂O₄ could be converted to a magnetoplumbite structure of CaFe₁₂O₁₉. The driving force for the transformation was mainly attributed to ionic radius effect, which would be our future investigation. The effect of La doping on the microstructure change of Bi₂Fe₄O₉ has been shown in Fig. 3, wherein the grain-size distribution of the matrix is basically uniform with the grain size varies in the range of 0.5–2 mm. However, aggregated fine particles are present in the matrix (as indicated by arrows in Fig. 3(d)), which are gradually increased with the increase of the La doping content and can be attributed to Bi(La)FeO₃ phase (Fig. 1).

The electric polarization (P) and the leakage current versus applied electric field (E) of the samples of Bi₂₋ₓLaxFe₄O₉ (x=0 and 0.02) at room temperature are shown in Fig. 4. The hysteresis loops were measured at a frequency of 100 Hz. As observed, both curves (Fig. 4(a)) reveal typical lossy dielectrics, indicating that La doping cannot improve dielectric property of Bi₂Fe₄O₉. Nevertheless, Fig. 4(b) shows that the leakage current can be reduced at high-applied fields by adding a small amount of La doping.

IV. Conclusions

Bi(La)FeO₃ phase has been observed to develop instead of Bi₂₋ₓLaxFe₄O₉ in synthesizing La₂O₃-doped Bi₂Fe₄O₉, indicating that La₂O₃ can stabilize the structure of Bi(La)FeO₃ but suppress the development of Bi₂Fe₄O₉. This is further evidenced that Bi₂Fe₄O₉ can be directly converted to the phase of Bi(La)FeO₃ by heating the mixtures with nominal composition of Bi₂Fe₄O₉/xLa₂O₃. The occurrence of microstructure inhomogeneity with aggregated fine particles at high La doping can be ascribed to the development of Bi(La)FeO₃. Bi₂₋ₓLaxFe₄O₉ ceramics basically is a lossy dielectric material, and the leakage current can be reduced at high-applied fields by adding a small amount of La doping.

Fig. 3. Scanning electron micrographs of Bi₂₋ₓLaxFe₄O₉ pellets sintered at 950°C for 2 h: (a) x = 0, (b) x = 0.02, (c) x = 0.05, and (d) x = 0.08. The arrows indicate the microstructure inhomogeneity with low-sinterability fine particles.
Fig. 4. (a) P–E hysteresis curves of Bi$_2$$_x$La$_x$Fe$_4$O$_9$ with x0.0 and 0.02 and (b) leakage current versus electric field, measured at room temperature.
A STUDY OF THE RELATIONSHIP BETWEEN SEMI-CIRCULAR SHEAR BANDS AND POP-INS INDUCED BY INDENTATION IN BULK METALLIC GLASSES

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Intermetalics 18 (2010) 1572-1578
SCI Category: Metallurgy & Metallurgical Engineering, Impact Factor 2.231 Ranking 4/70=5.71%

The mechanical properties of bulk metallic glass (BMG) materials are quite different from those of conventional crystalline alloys. BMGs have a higher hardness, higher fracture strength, and better corrosion resistance than those of crystalline counterparts. However, the poor ductility and formation of shear bands induced by highly-localized inhomogeneous deformation limit BMGs applications. It was found that the load-displacement curve (P-h curve) represents the pop-ins during the indentation process of BMGs. Generally, it was considered that the pop-ins are associated with the emission of shear bands. However, few mathematical models have been developed to predict the relationship between shear bands pattern and pop-ins. In the present study, an analytical model is developed first to prove that the pop-ins in P-h curve are associated with the emission of the semi-circular shear bands induced by indentation in BMGs. It was confirmed that the depths of pop-ins are a geometric series with a common ratio of C, which is the same with the radius ratio of any two adjacent semi-circular shear band circles. Furthermore, the ratio of the deformation zone to the contact radius induced by an indentation is a constant, which depends on the constraint factor of the material. The ratios, predicted using the present model, were consistent with experimental results.
Fig. 3 Shear band morphology of Vickers indentation. Four radii of shear band circles were obtained and the average ratio of these radii were calculated.

Fig. 4 The contact radius and the deformation zone of shear band morphology induced by Vickers indentation.
Characterization of aqueous dispersions of Fe₃O₄ nanoparticles and their biomedical applications

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Biomaterials, 2005, 26, 729-738
Times Cited: 205

Studies of nanoscale materials have captured significant scientific and industrial interest in recent years. Magnetite (Fe₃O₄) nanoparticles have been extensively exploited as ferrofluids. Various approaches were developed to synthesize iron oxides. In recent advanced nanoparticles synthesis, Sun and co-workers manipulated mono-dispersed Fe₃O₄ nanoparticles. Following high-temperature decomposition of an iron precursor in an organic solution phase, they were able to produce magnetite with several controllable particle diameters. Conversely, well-dispersed aqueous Fe₃O₄ colloids fabrication has met with very limited success. Although the Fe(II) acetate sonication method has been reported by Gedanken et al., most of the common protocols involve ferrous and ferric ions coprecipitation with aqueous NH₄OH or NaOH. In any case, severe particles aggregation accompanied with facile precipitation are the inevitable outcomes. The synthesis of biocompatible superparamagnetic materials has long been of interest in biomedical applications including magnetic resonance imaging for clinical diagnosis, magnetic drug targeting, hyperthermia anti-cancer strategy, and enzyme immobilization.

The efficacy of many medical applications may strongly rely upon generating narrow size distribution and well-dispersed nanoparticles in an aqueous solution. Iron-oxide of nanometer size presents superparamagnetic property and is ideal for MR contrast enhancement by alterations of proton relaxation in the tissue microenvironment. However, magnetic nanoparticles without polymer coating often suffered from the aggregation problem in water or tissue fluid, which may limit in vitro magnetic-based isolation and detection strategies, as well as clinical MRI applications. Polymer coated iron-oxide particles (SPIO and USPIO) reduced aggregation problems and has been developed for various fields of clinical MR imaging. In fact, all SPIO or USPIO MR contrast agents already approved for clinical usage nowadays, as well as most of the currently developing contrast agents, were stabilized by dextran or its derivatives. The polymer coating significantly increases their overall size and therefore may limit their tissue distribution, penetration, and metabolic clearance. Polymer-coated particles are often uptaken rapidly by the reticuloendothelial system, such as Kupffer cells of the liver. In general, the biodistribution of these polymer-based nanoparticles was mainly influenced by their size and surface chemistry. In the surface chemistry aspect, hydrophobic surface may enhance the uptake of the nanoparticles by the liver, while hydrophilic coating and surface charges may influence their retention period in the circulation and the chance to penetrate into interstitial spaces. Although these polymer coatings are generally considered to be biocompatible, adverse reactions have also been reported. On the other hand, only limited recent reports have investigated non-polymer
coated superparamagnetic nanoparticles in MR imaging. These particles were stabilized by citrate monomer and presented adequate performance in coronary MR angiography. In this study, we have prepared another type of non-polymer dispersive superparamagnetic iron oxide nanoparticle and demonstrated their potential as a new class of MR contrast agent for the future development.

In the current study, a modified Fe(II) and Fe(III) salt coprecipitation synthesis using tetramethylammonium hydroxide (N(CH₃)₄OH) was used to produce well dispersed Fe₃O₄ colloidal solutions. The physical properties and the crystalline structure of the newly formed magnetite nanoparticles were characterized by Transmission electron microscopy (TEM) and X-ray diffraction (XRD). Fourier transform infrared spectrometer (FT-IR) and X-ray photoelectron spectrometer (XPS) were performed to analyze the surface characteristics of the nanoparticles. The magnetization was determined from superconducting quantum interference measurement device (SQUID) measurements. Furthermore, the in vitro cytotoxicity test and in vitro hemolysis assay were performed to evaluate the biocompatibility of the prepared Fe₃O₄ nanoparticles in vitro. To further investigate the potential usage of the nanoparticles in MR imaging, the T1 longitudinal and T2 transverse relaxation times were measured using the NMR spectrometer at 9.4 T. Although the ability of a given contrast agent to enhance the longitudinal and transverse relaxation rates is usually specified in terms of the in vitro dipolar relaxivity values (r₁ and r₂) of the agent, the observed T1 and T2 effects in MR imaging may not be directly deduced from these values alone since r₁ and r₂ only describe the agent’s ability to enhance the respective relaxation rates in a perfectly homogeneous medium, typically water without interactions with their local micro-environment.

Fig. 1 shows TEM images of the iron oxide suspensions. In addition to the dispersed and well-separated features, the prepared colloids also exhibited some degree of aggregated morphology, as shown in Fig. 1a. The particle diameter was calculated as 9.1±2.1 nm. Following centrifugation at 10000 rpm for 10 min, the particles in suspensions exhibited mostly the well-dispersed appearance. The average size decreased to 6.2±1.4 nm, as seen in Fig. 1b.

![Fig. 1. TEM imaging showing Fe₃O₄ nanoparticles (a) from the as-synthesized colloidal suspensions and (b) after following centrifugation at 10000 rpm.](image)

The XRD indicates that magnetite (Fe₃O₄) was the resulting material and FT-IR and XPS analysis were performed to characterize the surface nature of the resulting magnetite nanoparticles. SQUID shows the magnetization loop of the Fe₃O₄ nanoparticles measured at room temperature. The as-synthesized magnetites indicate a
superparamagnetic behavior, as evidenced by zero coercivity and remanance on the magnetization loop. A saturation magnetization of ~40 emu/g was determined for the fine Fe₃O₄ particles.

The viability of cells evaluated by MTT assay was apparently unaltered upon exposure to various concentrations of Fe₃O₄ nanoparticles for 4 h, ranging from 0.92 to 23.05 mM of iron concentrations (Fig. 2). According to cell viability assay, Fe₃O₄ nanoparticles are generally considered to be biocompatible. The in vitro hemolysis test, by detecting free hemoglobin in the serum after incubation with various concentrations of the nanoparticles, indicated that significant hemolysis (0.5 g/dL) could only be detected in 0.1 M iron concentration of the nanoparticle. Other samples presented undetectable hemoglobin concentration to the instrument’s detection limit. 0.1 M concentration was below the dose required for MR contrast enhancement in whole blood.

Superparamagnetic nano-ferrofluids have been recognized to hold great potential in clinical diagnostic applications as the magnetic resonance (MR) imaging contrast agents that could exhibit the ability to alter the proton relaxivity of water. Water proton relaxation for the as-synthesized Fe₃O₄ was performed using standard and solid state NMR spectrometer at 9.4 T. The magnetic nanoparticles strongly reduce both relaxation times (T₁ and T₂) with T₂ significantly lower than T₁. At a concentration of 0.86 mM magnetite particles (4.61 mM of iron concentration), the longitudinal relaxation time (T₁) was reduced from 3000 ms for pure water to 22.88 ms, while the T₂ relaxation time was reduced from 212.8 to 0.36 ms. In conclusion, the calculated r₁ and r₂ relaxivities of the newly synthesized nanoparticles were 9.4 s⁻¹mM⁻¹ and 605.5 s⁻¹mM⁻¹, respectively. Both r₁ and r₂ of the synthesized nanoparticles were much shorter than Resovist (commercial product). These results present the evidence that the newly prepared Fe₃O₄ nanoparticles strongly reduce both T₁ and T₂ relaxation times. Therefore, the magnetite material presented here may have great potential for clinical MR imaging as a contrast agent.

Conclusion

Newly formed Fe₃O₄ nanoparticles of 9 nm diameter were developed using ferrous and ferric ions with N(CH₃)
The resulting superparamagnetic magnetite exhibited a well-dispersed property. From the FT-IR and XPS analysis, the surface nature of the iron oxides was viewed as the electrostatic interaction between quaternary \((\text{CH}_3)_4\text{N}^+\) cations and the surface hydroxyl groups. The Cos-7 monkey kidney cells were used for estimating the biological effect of the superparamagnetic fluids on cell viability and proliferation. No apparent cytotoxic effects were observed at various \(\text{Fe}_3\text{O}_4\) doses.
An understanding of emotional fear in terms of its underlying cellular and molecular mechanisms is not only an essential piece of information for pharmacological intervention of anxiety and posttraumatic stress disorders but also provides some insight into the long-term memory formation in the brain. Accumulated evidence indicates that the amygdala is a crucial neural locus for the induction and expression of fear memory. When rats encounter a tone (conditioned stimulus [CS]) that was previously paired with noxious stimulus (unconditioned stimulus [US]), such as foot-shock, information flows from the auditory thalamus and cortex to the lateral (LA) and basolateral amygdala (BLA) where alterations of synaptic transmission are thought to subserve the encoding of fear memory.

PI-3 kinase has been suggested to participate in oncogenic and mitogenic signal transduction. Although a recent study implied that PI-3 kinase may play a role in the expression of long-term potentiation (LTP) in hippocampal dentate gyrus, data conflicted, as it was found that PI-3 kinase-deficient mice displayed an enhanced hippocampal CA1 LTP, but with normal spatial memory. Therefore, we investigated the role of PI-3 kinase in fear conditioning.

We first demonstrated that PI-3 kinase was selectively activated in the amygdala following fear conditioning, and pharmacological blockade of PI-3 kinase impaired fear memory in a dose-dependent manner. In in vitro slice preparation, we showed that bath application of PI-3 kinase inhibitors attenuated tetanus-induced L-LTP in the amygdala. Tetanus and forskolin-induced activation of mitogen-activated protein kinase (MAPK) was blocked by PI-3 kinase inhibitors, which also inhibited cAMP response element binding protein (CREB) phosphorylation. These results provide the first evidence of a requirement of PI-3 kinase activation in the amygdala for synaptic plasticity and memory consolidation, and this activation may occur at a point upstream of MAPK activation.
Fear memory formation in the amygdala requires activation of PI-3 kinase, which may lead to MAPK and CREB phosphorylation, resulting in the initiation of gene transcription and translation.