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多铁性铁氧化物材料的设计、制备、性质和应用

Design, Synthesis, Properties and Application of
Multiferroic Ferrites

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**Design, Synthesis, Properties and Application of Multiferroic
Ferrites**

A Dissertation Submitted to the Graduate School in Partial Fulfillment of
the Requirements for the Degree of Doctor of Philosophy

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摘要

铁电材料是一类具有在外电场作用下翻转的自发电极化的重要的功能材料；铁磁材料则是具有稳定的可在磁场作用下翻转的磁矩的功能材料。多铁性材料作为一种同时具有两种以上铁性的材料，具有独特的物理性质，近年来已经成为功能材料和凝聚态物理领域最热门的话题之一。多铁性材料在基础研究和实际应用都有重要的研究价值，然而，由于铁电性和铁磁性的物理起源完全不同，很大程度上这两种性质是相互排斥的，因此，真正的单相多铁性材料非常稀少，而且其中绝大多数仅在很低的温度下同时具有两种铁性。本论文围绕多铁性材料有序温度低，磁电耦合弱的缺点开展研究工作。主要的内容是室温多铁性铁氧体的设计，合成，性质和应用，主要有以下几方面的内容：

1. BiFeO_3 ，作为目前极少数室温多铁性材料之一，受到研究者广泛的关注。然而，事实上 BiFeO_3 是性能很差的铁电材料和磁性材料，有很多严重的缺陷：比如难以合成纯相，室温下具有严重的漏导，很大的矫顽场，极弱的磁性等。我们首先尝试增强 BiFeO_3 在室温下的磁性。我们发现在 $\alpha\text{-Fe}_2\text{O}_3$ 中引入氧缺陷可以很大地增强磁性， $\alpha\text{-Fe}_2\text{O}_3$ 在空气中催化氧化酒石酸之后在室温时的磁矩增大了 13.6 倍。我们通过多种实验和测试手段分析了反应过程，化学组成和磁性起源，确认其磁性来源于其中的氧缺陷。

这种增强磁性方法对于多铁性材料 BiFeO_3 仍然适用。我们以 $\alpha\text{-Fe}_2\text{O}_3$ 和 Bi_2O_3 和酒石酸为原料，利用金属氧化物的催化作用使酒石酸在较低的温度下氧化，然后利用氧化放出的热快速的合成 BiFeO_3 ，这种方法相比于固相反应，具有简单，快速，高效的优点。同时，由于反应中涉及瞬间高温过程，使 BiFeO_3 中具有大量的本征氧缺陷，极大地增强了 BiFeO_3 在室温下的磁性。

2. 通过引入氧缺陷确实可以增强 BiFeO_3 的磁性，但是却不能改善其铁电性，为了同时获得较好的铁电性和磁性，我们研究了 $\text{BiFeO}_3\text{-DyFeO}_3$ 固溶体。我们合成了位于三方和正交准同型相界位置的 $0.9 \text{BiFeO}_3\text{-}0.1 \text{DyFeO}_3$ 固溶体，同时，为了减小漏导，在钙钛矿的氧八面体位置掺杂 1%-3% 的 Ti^{4+} 。我们采用剩余极化

强度的测量方法来测量电滞回线, 最终我们成功地测到了固溶体中典型的电滞回线和压电常数, 而且磁性也比单晶 BiFeO_3 也有一定地增强。我们发现固溶体在室温时具有较强磁电耦合能力, 所以 $0.9 \text{ BiFeO}_3\text{-}0.1 \text{ DyFeO}_3$ 固溶体是一种真正意义上的室温多铁性材料, 具有铁电性、磁性甚至磁电耦合能力。在研究 3% Ti^{4+} 掺杂的 $0.9 \text{ BiFeO}_3\text{-}0.1 \text{ DyFeO}_3$ 固溶体的磁性时, 我们发现当温度低于 100 K 时, 其磁矩在弱磁场下为负值。通过实验, 我们排除了超导态和抗磁性, 我们认为这种异常的磁行为来源于其中 Dy^{3+} 在低温时的自旋翻转。

3. 为了研究多铁性材料在信息记录材料方面的应用, 我们合成了多铁性材料 $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$, 并将其用做四态存储器原型。我们通过电场和磁场来实现信息的“写入”, 通过测量偏置磁场下磁电耦合系数来实现信息的“读取”。通过这一四态存储器原型地设计和测量, 完成了多铁性材料在信息领域的应用设计。

4. 我们用熔盐法合成了半反尖晶石结构的 ZnFe_2O_4 , 具有尖晶石铁氧体中最高的饱和磁矩, 高居里温度, 高电阻率, 低矫顽场和良好的烧结性, 是一种优秀的软磁材料。XRD, XPS 和 Mössbauer 谱研究认为, 其磁矩来源于半反尖晶石结构: 即一半的 Zn^{2+} 占据了八面体位置, 一半的 Zn^{2+} 占据了四面体位置。

关键词: 多铁性材料; 铁氧体; 四态存储; 软磁材料

Abstract

A ferroelectric material exhibits a spontaneous polarization and it can be switched by the application of an electric field. A ferromagnetic material exhibits a stable and switchable magnetization. Both ferromagnetic and ferroelectric materials are very important functional materials, which has promising application in many aspects of science and technology fields. Multiferroic materials, coexisting of ferroelectricity and ferromagnetism and exhibiting unique properties, arise extensive research interest recently. From scientific and technological point of view, the mutual control of electric and magnetic properties is attractive. However, ferroelectricity arises from off-center displacement while ferromagnetism arises through quantum mechanical exchange between spin or angular momentum. Ferroelectricity and magnetism tend to be mutually exclusive, and therefore the candidates of multiferroic are very few and most of them only exist at extremely low temperature. The main purpose of our research is to obtain room temperature multiferroics and enhance their properties. Main research progresses and results are shown in the following.

1. BiFeO_3 has attracted increasing attention because it is one of few room temperature multiferroics. However, BiFeO_3 presents some issues, such as, the difficulties in preparing single-phase samples, a large leakage current, a high coercive field and weak magnetism. Herein, we tried to improve the magnetic properties of BiFeO_3 . In our experiment, unusual room temperature enhanced magnetic properties was found in $\alpha\text{-Fe}_2\text{O}_3$ by introducing oxygen deficiency. The magnetic moment of $\alpha\text{-Fe}_2\text{O}_3$ increased 13.6 times by heating the mixture of $\alpha\text{-Fe}_2\text{O}_3$ and tartaric acid. The heating process results in the reaction involving a quick catalyzed oxidation process of tartaric acid, which generate large amount of heat and lead to the formation of oxygen deficient $\alpha\text{-Fe}_2\text{O}_3$. Careful chemical analyses confirmed that no any ferromagnetism impurities were present and the unusual magnetism was attributed to the formation of a large amount of oxygen deficiency.

This above synthetic strategy was used for the synthesis of BiFeO_3 to enhance its magnetism property. When the mixture of $\alpha\text{-Fe}_2\text{O}_3$, Bi_2O_3 , and tartaric acid was heated, the heat resulted from the oxidation reaction of the tartaric acid promoted the reaction of the $\alpha\text{-Fe}_2\text{O}_3$ and Bi_2O_3 to form BiFeO_3 . This is simple, fast and convenient method to synthesize BiFeO_3 . More interestingly, the magnetic moment of the as-prepared BiFeO_3 was increased a lot by introducing oxygen deficiency, which was formed during the fast reaction process during the rapid heating process.

2. Oxygen deficiency can increase magnetism, but cannot improve the ferroelectricity. In order to develop multiferroics with enhanced magnetization and polarization, we prepared $0.9\text{BiFeO}_3\text{-}0.1\text{DyFeO}_3$ solid solution, which was located at morphotropic phase boundary from rhombohedra to orthorhombic phase. We also used aliovalent ionic substitution of Ti^{4+} for Fe^{3+} with concentration of 1%-3%. The chemically modified solid solution exhibits a typical ferroelectric hysteresis loop and piezoelectric properties. By introducing of Dy^{3+} on the perovskite A site, the magnetic properties were improved. More interestingly, the solid solution exhibited strong magnetoelectric coupling effect at room temperature. These properties entitle Ti^{4+} doped $0.9\text{BiFeO}_3\text{-}0.1\text{DyFeO}_3$ to be true multiferroic at room temperature. The 3% Ti^{4+} doped $0.9\text{BiFeO}_3\text{-}0.1\text{DyFeO}_3$ solid solution exhibited negative magnetic susceptibility below 100 K. Superconductivity and diamagnetism have all been suggested, but each ruled out. The unusual property may be originated from the spin reorientation of Dy^{3+} at low temperature.

3. The combination of ferroelectricity and ferromagnetism in single phase offers the ability to obtain four physical polarization states. We synthesized single phase $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$, which exhibited multiferroic at room temperature. The $\text{Sr}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$ was used as a four-state memory prototype. The information was written by electric and magnetic fields, and read out by magnetoelectric coefficient with the help of a small bias magnetic field. The prototype makes a progress in data storage and the application of multiferroic.

4. We synthesized partially inverse spinel ZnFe_2O_4 by molten salt method. It exhibits the highest saturation magnetization among ferrites. It also exhibits high Curie temperature, high resistivity, low coercive field and good sintering properties. These excellent properties indicate the as-prepared ZnFe_2O_4 is an ideal kind of soft magnet. Though careful analyses, including powder X-ray diffraction, X-ray photoelectron spectroscopic and Mössbauer spectroscopic measurements, it was concluded that the strong ferromagnetism resulted from its partially inverse spinel structure, i.e. 1/2 of Zn^{2+} occupy tetrahedral oxygen site, 1/2 of Zn^{2+} occupy octahedral oxygen site.

Keywords : multiferroics; ferrites; four-state memory; soft magnet

第一章 绪论

1.1 课题背景及研究意义

铁电材料是一类非常重要的功能材料,指的是具有可在外电场作用下翻转的自发极化的介电材料,具有压电性,高介电常数和电滞回线的性质,广泛应用于传感器和制动器,高密度电容器和信息存储等。铁磁材料也是一类重要的功能材料,是指近邻的原子或者离子的磁矩由于相互作用而按照一定的顺序排列的材料,广泛应用于磁芯、永磁体、磁记录材料、自旋器件等。多铁性材料是指同时具有铁电和(反)铁磁性质而且电偶极矩和自旋还存在相互作用的一类材料。多铁性材料同时具有铁电材料和铁磁材料的性质,更重要的是,通过电场/磁场可以控制磁场/电极化,可用于超低磁场探测、自旋电子器件、高密度存储器等领域。由于具有这些特殊而且重要应用前景,多铁性材料已经成为国际上研究的热门方向,2008年被《科学》杂志评为全球七大研究热点之一。多铁性材料作为功能材料以及凝聚态物理新的热门领域,除了具有广阔诱人的应用前景外,还由于其本身蕴含丰富的物理现象。这些问题涉及电极化的有序排列与电子自旋和轨道的相互耦合,结构有序和弹性的相互作用等复杂的强关联电子问题,比如:电极化有序和磁极化有序是如何耦合,有序排列的方向如何确定,外加电场和磁场如何影响这些有序排列等。

然而,由于铁电和铁磁有序的相互排斥,使得多铁材料非常稀少,而且其中绝大多数磁电耦合作用非常弱,有序温度极低,使得这类材料还未能实际应用。本论文的研究目的是设计,合成具有室温多铁性质的铁氧体,研究其铁电性和铁磁性的起源,并初步将合成的多铁材料用作存储器件的原型。

1.2 “铁”性材料

铁(ferro-)性材料并不是指材料中含有大量的“铁”,而是指具有“回线”性质的一类材料^[1],如图 1-1 所示。当材料的某一物理量,比如电极化(P),磁矩(M),应变(S)(对应图 1.1 的纵轴)对于外加电场(E),磁场(H),应力(σ)(对应图 1-1 的横轴)的响应方式如图 1-1 所示时,称该类材料具有“铁”

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