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Short communication

Investigation of structural, optical and magnetic properties in $PbTi_{1-x}Fe_xO_3$ ceramics

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Abstract

We have been successful in preparation of $PbTiO_3$ by partly substituting Ti site by Fe ions using solid state reaction method. $PbTi_{1-x}Fe_xO_3$ perovskite has been studied as a function of Fe concentration using X-ray diffraction, absorption, Raman scattering and magnetization measurements. $PbTi_{1-x}Fe_xO_3$ system exhibits ferromagnetic ordering at room temperature. There appears an anomalous change in the lattice constants, optical band gap, Raman spectroscopy as well as magnetization of sample with $x = 0.30$. The result also suggests the limit of dissolubility of Fe ions doped in $PbTiO_3$.

Keywords: Fe doped $PbTiO_3$; Raman scattering; Absorption; Magnetization

1. Introduction

Lead titanate ($PbTiO_3$) has been widely studied [1–3] during last few decades because of its importance in science and technology. It has relatively a simple structure among many perovskite-based ferroelectrics and shows a typical displacive transition character. In ferroelectrics (FE), mechanical and electronic structures are competing parameters; the FE structure is realized at the cost of the lattice distortion. Their properties are further modified by introducing various species with controlled amount of dopants. Random lattice disorder, produced by chemical substitution in $PbTiO_3$, can lead to the formation of dipolar impurities and defects that have larger influence on the static and dynamic properties of these materials.

Recently, diluted magnetic dopant such as Fe^{3+} ion has been introduced into $PbTiO_3$ nanocrystals in order to obtain room-temperature ferromagnetism [4] and reduce the size of the nanocrystals has been demonstrated to significantly improve ferromagnetism of the doped $PbTiO_3$ [5]. Remarkably, magnetic transition occurs above room temperature in this newly synthesized $PbTi_{1-x}Fe_xO_3$ system. In addition, the origins of the ferroelectric order and its coupling to magnetic order are closely related to the lattice dynamics which is in turn directly connected to ferroelectric order. The Raman spectroscopy is known to be a powerful tool for studying the vibration and magnetic excitations. Some studies on Raman scattering of $PbTiO_3$ have indeed been reported [6,7], but most of those studies were focused on pure $PbTiO_3$. Although a number of Raman and XRD experiments have also been performed to study the influence of temperature and dopant concentration variations, very little works have been reported on the Fe dopant induced changes in the structure and optical as well as electromagnetic properties of $PbTiO_3$. In this paper, we report the result of a study on the Fe doping effects in $PbTi_{1-x}Fe_xO_3$ perovskites by means of measurements and analyses of the XRD, Raman scattering and optical absorption as well as impedance and magnetization measurements.

2. Experiments

The various forms of $PbTi_{1-x}Fe_xO_3$: $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5, where x is the molar content of Fe, were synthesized by solid state reaction method. The composition of $Pb_{1-x}Fe_xTiO_3$ was weighed using PbO (99.9%), TiO_2 (99.99%) and Fe_2O_3 (99.99%) powders. The mixed powders were calcined at 900 °C for 8 h in air then pressed into cylindrical pellets and finally sintered at 1150 °C for 10 h in air for three times.

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Structural characterization was performed by means of X-ray diffraction using a SIEMENS D5005 diffractometer with Cu Kα radiation and with 2θ varied in the range of 20–70° at a step size of 0.02°. The absorption spectra of $PbTi_{1-x}Fe_xO_3$ were measured using UV–visible diffuse reflectance spectrometry (Jasco 670 UV–vis spectrometer). Raman scattering measurements were performed in a back scattering geometry using a Jobin Yvon T 64000 triple spectrometer equipped with a cryogenic charge-coupled device (CCD) array detector and operated with 514.5 nm line of Ar ion laser. The magnetization vs. magnetic field was measured by a vibrating sample magnetometer (VSM – 7404 LakeShore, USA).

3. Results and discussion

Fig. 1 shows the XRD pattern of $PbTi_{1-x}Fe_xO_3$ powders derived from solid state reaction method, which exhibits sharp diffraction peaks indicating that the samples are well crystallized. All of the diffraction peaks of pure $PbTiO_3$ can be indexed as the tetragonal perovskite structure of $PbTiO_3$ with the lattice parameters: $a = 3.92$ Å and $c = 4.16$ Å, corresponding well with that of Joint Committee on Powder Diffraction Standards (JCPDS) Card No. 77-2002, which illustrates that the products are composed of $PbTiO_3$ perovskite structure and without the trace of any impurity phase. The change of the peak positions (inset in Fig. 1) and abrupt change in *c*/*a* ratio (see Fig. 4) are the evidences of some other phases or disorders in doped samples. The *c*/*a* ratio decreases as increasing substituted Fe content. However, it monotonously decreases in the range of $x < 0.3$. Above this content, the tendency seems more complex and appears an abrupt change at $x \sim 0.3$. The small decrease of the tetragonal distortion leads to a deformation of the TiO_6 octahedra in Fe-doped $PbTiO_3$, resulting in a decrease of the disorganization of the crystal. The reason might be related to the existence of some secondary phases or disorders in the samples as mentioned above.

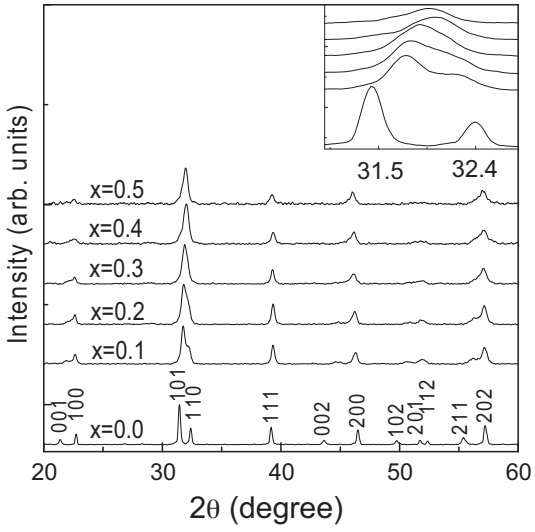

Fig. 1. XRD patterns of $PbTi_{1-x}Fe_xO_3$ powders. The inset is to enlarge the peak ~32°.

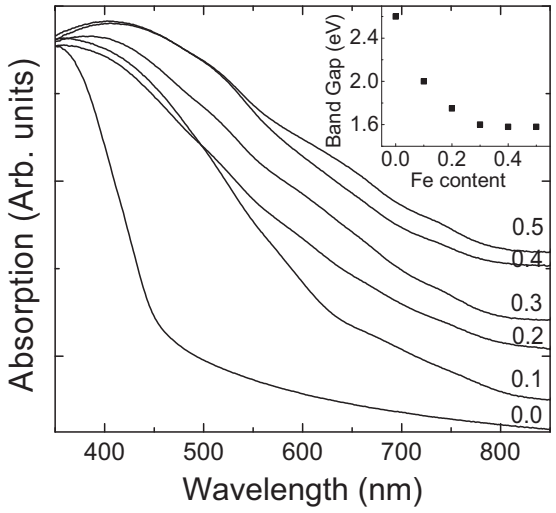

Fig. 2. Absorption spectra of $PbTi_{1-x}Fe_xO_3$ powders. The inset shows optical band gap vs. Fe content.

In Fig. 2, the dependence of the absorption spectra of the $PbTi_{1-x}Fe_xO_3$ samples on the Fe content is shown. The optical gaps, obtained by extrapolation of the linear curve regions according to the Wood and Tauc method [8], are shown in the inset of Fig. 2. These results indicate that optical absorption edge and the optical band gap are controlled by the degree of structural disorder in the lattice of the $PbTi_{1-x}Fe_xO_3$ samples. The change in the band gap can be ascribed to defects or impurities that give rise to intermediary levels of energy in the range of the band gap promoted by the $PbTi_{1-x}Fe_xO_3$ disordered structure [9]. The band gap strongly deceases in the range of Fe content from 0.00 to 0.30; and higher this, band gap seems to be lightly changed. This tendency is in agreement to the change in ratio of *c*/*a* (see inset of Figs. 2 and 4).

The further effect of Fe doped is describe by the Raman spectra of the $PbTi_{1-x}Fe_xO_3$ ceramics which are plotted in Fig. 3 with respect to variation of Fe concentration *x* at room temperature. It was known that, the ferroelectric phase of

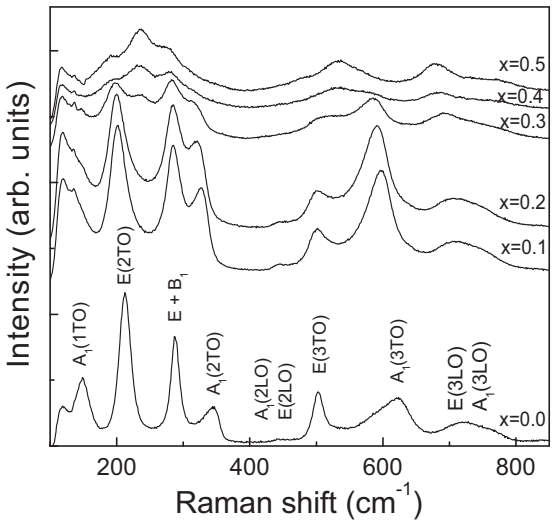

Fig. 3. Raman spectra of $PbTi_{1-x}Fe_xO_3$ samples vs. Fe content.

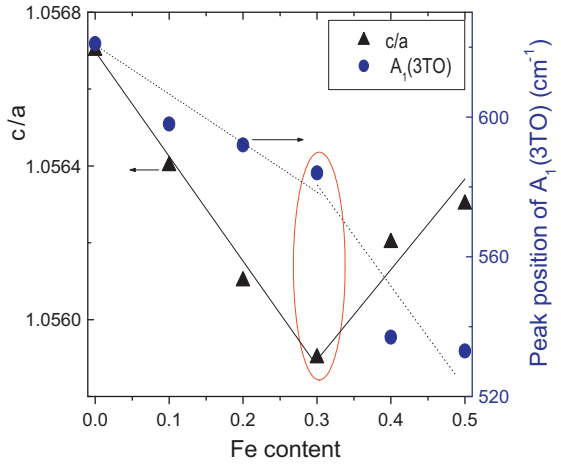

Fig. 4. The dependence of *c/a* ratio and position of A_1(3TO) mode on the Fe content in the $PbTi_{1-x}Fe_xO_3$ samples.

$PbTiO_3$ at room temperature exhibits a tetragonal symmetry with C^1_{2v} space group. According to Burns and Scott [1], there are 12 optical modes for the C_{2v} point group: $3A_1(TO) + 3A_1(LO) + 3E(TO) + 3E(LO)$, where LO and TO refer to longitudinal and transverse optical modes. The Raman scattering spectrum of the $PbTi_{1-x}Fe_xO_3$ samples recorded at room temperature is shown in Fig. 3. It can be seen that, five characteristic major bands are centered at around 163, 216, 281, 497, and 728 cm^{-1}, which are assigned to the lattice vibration mode A_1(1TO), E(2TO), $E + B_1$, A_1(2TO), and A_1(3LO), respectively.

The changes in *c/a* ratio and A_1(3TO) mode vs. Fe content are shown in Fig. 4. Both of them exhibit an abrupt change at $x = 0.3$. This is in agreement with the Raman spectra in Fig. 3. It is clear that, with $x > 0.3$ the sample becomes multiphase. The softening of modes, in accordance with the XRD results discussed earlier, indicate a decrease in tetragonality (*c/a* ratio) with increasing x.

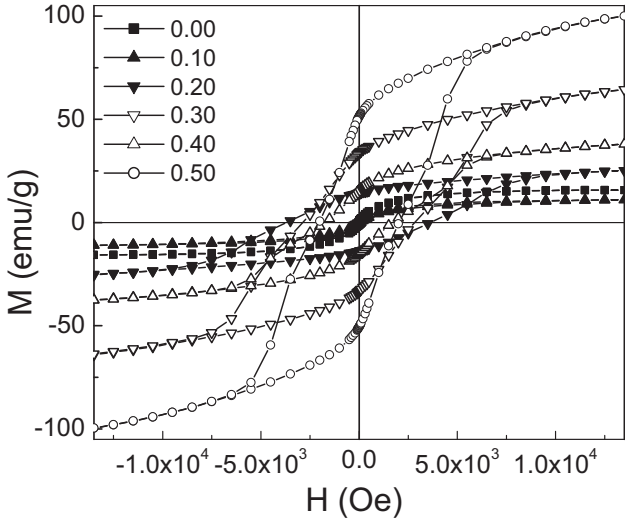

Fig. 5. Magnetization vs. magnetic field of $PbTi_{1-x}Fe_xO_3$ samples with different Fe content.

Fig. 5 presents the magnetization vs. magnetic field of $PbTi_{1-x}Fe_xO_3$ samples with different values of x. The coercivity reaches to maximum value at $x \sim 0.2$. Above this content, the coercivity decreases.

Qiu et al. [10] stated that both tetragonal and hexagonal phases coexisted in the Fe-doped $BaTiO_3$ ceramics. Hexagonal phase component was to be ferromagnetic.

In this case, individually measurement of the ferromagnetism originated from either of the two phase components is impossible since they basically form a composite material. However, it is possible to increase the volume fraction of the hexagonal phase component in the Fe-doped $PbTiO_3$ ceramics by increasing the Fe content, and then monitor the variation of ferromagnetism.

It should be noted that the loop of $PbTi_{1-x}Fe_xO_3$ with $x \geq 0.3$ exhibited two phases. This behavior normally happens in composite materials but rarely found in multiferroics, which gives one more evidence of multiphase that exists in sample with $x \geq 0.3$.

4. Conclusion

In summary, the effect of Fe doping on the $PbTi_{1-x}Fe_xO_3$ samples have been investigated using XRD, absorption, Raman scattering and magnetization measurements. $PbTi_{1-x}Fe_xO_3$ ceramics prepared from solid state reaction with varying Fe dopant concentration were found to exhibit a decrease in tetragonality *c/a* ratio with increase in x. The phonon modes observed in the Raman scattering spectra of $PbTi_{1-x}Fe_xO_3$ ceramics are in agreement with the reported modes for bulk $PbTiO_3$ before. It is important to point that the *c/a* ratio and A_1(3TO) mode abruptly changes around $x = 0.3$ as an evidence of structural change. This signal is also in agreement with Raman scattering and magnetization data. It is clear that, Fe doping is the cause of ferromagnetism in $PbTiO_3$ perovskite.

Acknowledgments

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