Physical Properties of Sol-Gel Lead Nickel Titanate Powder $\text{Pb}(\text{Ti}_{1-x}\text{Ni}_x)\text{O}_3$

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A series of sol-gel lead nickel titanate powder with composition of $\text{PbTi}_{1-x}\text{Ni}_x\text{O}_3$, where $x = 0.00, 0.03, 0.06, 0.08, 0.10$ and 0.12 , were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy, and magnetization (M - H) curves. XRD patterns show that $\text{PbTi}_{1-x}\text{Ni}_x\text{O}_3$ materials well crystallize in tetragonal phase. The tetragonal distorted ratio c/a of $\text{PbTi}_{1-x}\text{Ni}_x\text{O}_3$ was found to decrease with the increase of Ni content and to increase with increasing calcining temperature. The mean size of $\text{PbTi}_{1-x}\text{Ni}_x\text{O}_3$ crystal particles gradually decreased with increasing Ni content. Some Raman modes shifted to lower wavenumbers when Ni content increases, that is assigned to the variation of crystal structure due to the incorporation of Ni into PbTiO_3 crystal. In addition, the results of room temperature magnetization measurements present an obvious improvement of ferromagnetism when Ni content increases in the range from 3 to 12 mol%.

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1. Introduction

Perovskite ferroelectric PbTiO_3 is of fundamental scientific interest as well as varied technological application because of its extraordinary electromechanical properties in novel device development, such as nonvolatile memories, sensors, actuators, transducers, high-dielectric constant capacitors and tunable microwave circuits.¹⁻³⁾ Recent efforts in introducing ferromagnetic order into this material by partially substituting B sites with transition-metal elements were performed to seek out a facility route to prepare multiferroics materials and develop new realistic devices based on the coupling between ferroelectric and ferromagnetic orders. Ren *et al.*⁴⁾ showed the transition of hysteresis loop from an anti-S-type M - H curve for PT sample into typical S-type in Fe^{3+} -doped PbTiO_3 samples synthesized by hydrothermal process in which the author proposed that the mechanism leading to the ferromagnetism in the nanocrystals is F-center exchange (FCE) similarly to that in the Fe doped SnO_2 nanocrystals.^{5,6)} The largest ferromagnetic order was observed in 0.5% Fe-doped PbTiO_3 sample with $M_S \sim 0.01 \mu_B/\text{Fe}$ and a coercive field of ~ 100 Oe. Verma *et al.*⁷⁾ reported the largest ferromagnetic order in 1.2% Fe^{3+} -doped PbTiO_3 sample synthesized by chemical route with $M_S \sim 0.52 \mu_B/\text{Fe}$ and $H_C \sim 125$ Oe. Palkar *et al.*⁸⁾ presented the conversion of ferroelectric PbTiO_3 to magnetoelectric material by partially substituting Ti with Fe^{3+} . The significant improvement of ferromagnetic property as well as magnetoelectric coupling at room temperature was also reported in ceramic Mn^{4+} -doped PbTiO_3 series by Kumar *et al.*⁹⁾ On the contrary, S. Stoupin *et al.*¹⁰⁾ argued that multiferroicity at room temperatures is unattainable in $\text{PbTi}_{1-x}\text{Mn}_x\text{O}_3$. In addition, many theoretic calculations on doped and un-doped PbTiO_3 were carried out to interpret the origin of the variation in ferroelectric as well as ferromagnetic orders in this single phase magnetoelectric material.^{11,12)} However, the efforts to find out the appropriate element doping were limited to only a few transition-metal ions such as Fe^{3+} , Mn^{4+} . The studies have not yet been

extended base on the substituting of many other elements into Ti sites.

Here, we report for the first time the influence of Ni^{2+} substitution on crystal structure, vibration and magnetic properties of PbTiO_3 (PTO) nanocrystals synthesized by sol-gel process with Ni concentration ranging from 3 to 12 mol% (Ni_3 , Ni_6 , Ni_8 , Ni_{10} and Ni_{12}).

2. Experimental Procedure

Ni-doped PbTiO_3 nanoparticles, $\text{PbTi}_{1-x}\text{Ni}_x\text{O}_3$, were synthesized by sol-gel process using ethylene glycol (EG) as a surfactant. The Ni concentrations are designed as the molar ratio of $\text{Ni}/(\text{Ni} + \text{Ti})$ (in the form of Ni^{2+}). Starting materials were titanium (IV) tetraisopropoxide $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$, lead nitrate $\text{Pb}(\text{NO}_3)_2$ and nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Titanium (IV) tetraisopropoxide was added into solution of acid citric and distilled water. This solution was stirred for 2 h at 80°C to achieve a colorless transparent solution. Lead nitrate and nickel nitrate were dissolved in separate cups of distilled water then poured slowly into above solution of Titanium. The obtained mixture solution was stirred for 1 h at 80°C to get a uniform emerald green sol containing the cations of Pb^{2+} , Ti^{4+} and Ni^{2+} . Ethylene glycol was then added into this sol as a surfactant. This sol was then vaporized gradually under low stirring and temperature of 90 – 100°C until a clear gel was obtained. Gel was dried at 180°C for 5 h then calcinated for 3 h at various temperatures from 500 to 900°C to crystallize the specimens.

The crystal structure and surface morphology of Ni doped PbTiO_3 particles were characterized by XRD (SIEMENS D5000) with $\text{Cu K}\alpha$ radiation and scanning electron microscopes SEM (Hitachi S-4800), respectively. Raman scattering measurements were performed using a Jobin-Yvon T64000 spectrometer operated with 514.5 nm line of Ar ion laser. The magnetization vs. magnetic field was measured by a vibrating sample magnetometer (VSM-Micro Sence EZ-9).

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Fig. 1 (a) XRD patterns of $\text{PbTi}_{1-x}\text{Ni}_x\text{O}_3$ powders heat treated at 500°C and (b) the dependence of tetragonal distorted ratio c/a of $\text{PbTi}_{1-x}\text{Ni}_x\text{O}_{3-500^\circ\text{C}}$ and $\text{PbTi}_{1-x}\text{Ni}_x\text{O}_{3-800^\circ\text{C}}$ powders on Ni doping concentration.

Fig. 2 (a) XRD patterns of Ni8 samples calcinated at different temperatures and (b) the influence of lattice parameters and tetragonal distorted ratio c/a in Ni8 samples as a function of calcining temperatures.

3. Results and Discussions

The influence of the nickel content on PbTiO_3 crystal structure can be observed in Fig. 1(a). This figure illustrates the XRD patterns for the $\text{PbTi}_{1-x}\text{Ni}_x\text{O}_3$ powders heat treated at 500°C with x ranging from 0 to 12 mol%. By indexing, XRD patterns of these samples are consistent with tetragonal structure phase of PbTiO_3 . Single phase and crystalline powders are obtained after this treatment up to 12 mol% of Ni dopant. A gradual phase transformation from tetragonal to cubic with respect to the addition of Ni was evidenced by the left shift of XRD peaks such as (100), (110), (200), and (201) and the right shift of some other peaks such as (001), (101), (002), and (102). Consequently, tetragonal distorted ratio c/a of $\text{PbTi}_{1-x}\text{Ni}_x\text{O}_3$ samples decreases obviously from 1.051 for PTO to 1.020 for Ni12 (squares dotted line in Fig. 1(b)) in which lattice parameter c sharply decreases from 4.11 to 4.01 Å while lattice parameter a negligibly increases from 3.91 to 3.93 Å. This suppression in lattice distortion was also observed in many previous studies and was assigned to the replacing of dopant ions with different ion radius such as Fe^{3+} [4,7,8] and Mn^{4+} [9] into Ti^{4+} sites in the host PbTiO_3 crystal lattice. It was claimed that the off-center displacement D_B of ion Ti^{4+} and electric polarization P is proportional to tetragonality in ferroelectric PbTiO_3 -based solid solution, [8,13]

hence high c/a ratio is required for high electric polarization perovskite material.

Figure 2(a) shows the XRD patterns of Ni8 samples which are heat treated at different temperatures. In contrast to Fig. 1(a), the gradual splitting of (101) and (110) doublet with increasing calcining temperature is the obvious evidence of the increase of tetragonality. The variation of lattice parameters (a and c) as well as tetragonal distorted ratio (c/a) as the function of calcining temperature is showed in Fig. 2(b). Tetragonality of sample increases remarkably in the early stage of temperature, from $c/a = 1.029$ for $\text{Ni8}_{500^\circ\text{C}}$ sample to $c/a = 1.045$ for $\text{Ni8}_{700^\circ\text{C}}$ sample. In the temperature range from 700 to 800°C, c/a ratio increases more slowly, reaching 1.046 for $\text{Ni8}_{800^\circ\text{C}}$ sample. In addition, XRD analysis of $\text{PbTi}_{1-x}\text{Ni}_x\text{O}_3$ powders calcinated at 800°C for 3 h shows that tetragonality is well remained after substituting up to 12 mol% of Ni dopant (the circle dotted line in Fig. 1(b)). c/a ratio of $\text{Ni12}_{800^\circ\text{C}}$ sample is about of 1.044, much higher than that of 1.019 of $\text{Ni12}_{500^\circ\text{C}}$ sample. These results indicate that tetragonality (c/a) and hence electric polarization can be easily controlled by calcining temperature.

FESEM images of PTO, Ni6 and Ni10 samples heat treated at 500°C are displayed in Fig. 3. It is estimated that the particle size of PTO sample is within the range from 40 to 60 nm, averaging at about 50 nm. The PTO powder exhibits

Fig. 3 FESEM images of PTO, Ni6 and Ni10 samples heat treated at 500°C.

Fig. 4 (a) Raman spectra of $\text{PbTi}_{1-x}\text{Ni}_x\text{O}_3$ powders calcinated at 500°C and (b) the dependence of Raman peak position on Ni content.

some rod-shape grains beside a relatively regular round shape. The average grain size of $\text{PbTi}_{1-x}\text{Ni}_x\text{O}_3$ powders decreases gradually with Ni content which is estimated to be about 40 nm and 35 nm respectively for PNT6 and PNT10 sample. The suppression of particle growth process due to the replacement of Ni can be assigned to the difference in radii of Ni^{2+} and Ti^{4+} .

The replacement of Ni into Ti sites in PTO crystal lattice has a huge influence on the vibration property of PTO powders, which is exhibited obviously in Raman spectra. Figure 4(a) shows Raman spectra of $\text{PbTi}_{1-x}\text{Ni}_x\text{O}_3$ powders calcinated at 500°C. In the region of $100 \div 900 \text{ cm}^{-1}$, all samples exhibit 9 Raman peaks as assigned in Fig. 4(a). The variation of Raman peak position as a function of Ni content in Fig. 4(b) shows that A_1 peaks significantly shift to the lower wavenumber when Ni content increases. For example, $A_1(2\text{TO})$ and $A_1(3\text{TO})$ peaks respectively shift from 330 and 487 cm^{-1} to 321 and 478 cm^{-1} when Ni concentration increases from 0 to 12 mol%. Meanwhile, E and B_1 peaks almost do not change their position with the increase of Ni content up to 12 mol%. This can be explained from the sharp decrease of lattice parameters c with increasing Ni content in $\text{PbTi}_{1-x}\text{Ni}_x\text{O}_{3-500^\circ\text{C}}$ series as discussed above. A_1 modes consist of the displacements of Ti ion along the c axis relative to O ions and Pb ions while E modes consist the displacements of Ti ion along a or b axis and B_1 mode consists the

displacement of O ions in ab plane along c axis.¹⁴⁾ The significant decrease of c parameter only strong affects to the vibration of Ti ion along c axis hence resulting the left-shift of A_1 mode which is similar to the left-shift occurred under tetragonal-cubic transition with increasing temperature.¹⁴⁾ In addition, the decrease of frequency of Ti^{4+} -related Raman modes also can be originated from heavier atom weight of Ni^{2+} cations with respect to Ti^{4+} cations, implying the replacement of Ni^{2+} ions into Ti^{4+} sites.

Figure 5 displays M - H curves of high tetragonality $\text{PbTi}_{1-x}\text{Ni}_x\text{O}_3$ samples calcined at 900°C. M - H curve of PTO sample in the insert figure shows intrinsic diamagnetism of PbTiO_3 material which comes from $3d^0$ electron configuration of Ti^{4+} ion.⁴⁾ The existence of a weak ferromagnetic order in pure phase PbTiO_3 can be assigned to the oxygen vacancy which causes a very small saturation magnetization about of 0.0006 emu/g .^{11,12)} All $\text{PbTi}_{1-x}\text{Ni}_x\text{O}_3$ samples exhibit the S-type M - H curves of ferromagnetism with the gradually increase of both coercive force H_C and saturation magnetization M_S with increasing Ni content. For Ni12 sample, the values of saturation magnetization M_S and coercive field H_C reach to 0.0056 emu/g and 705 Oe , respectively. Bound magnetic polaron model, first proposed by Torrance,¹⁵⁾ can be employed to explain the ferromagnetism in $\text{PbTi}_{1-x}\text{Ni}_x\text{O}_3$ materials. In such model, an electron associated with an oxygen vacancy will be confined in a

Fig. 5 The M - H curve of PTO, Ni3, Ni6, Ni8 and Ni12 powders calcined at 900°C (the insert figure displays the intrinsic diamagnetism nature of pure PbTiO_3 material).

hydrogenic orbital which is called donor electron. These electrons tend to form bound magnetic polarons, coupling the 3d moments of the ions within their orbits.¹⁶⁾ The effective coupling between two Ni^{2+} magnetic ions in the same hydrogenic orbital is ferromagnetic. As the density of impurity ions increases, the number of Ni^{2+} ions in the same electron orbital increases leading to the increases of total magnetic moment. Otherwise, the electric neutralization condition also leads to the increase of oxygen vacancies density with increasing Ni^{2+} content which results to the overlapping between the different hydrogenic orbitals.¹⁶⁾ Thus, total magnetization will still increases until Ni^{2+} content is large enough to make the appearance of antiferromagnetic super-exchange interactions, which reduce the average magnetic moment per doping ion due to the antiferromagnetic order $\uparrow\downarrow\uparrow$.

4. Conclusions

In summary, the influences of Ni^{2+} substitution on crystal structure, vibration and magnetic properties were observed in $\text{PbTi}_{1-x}\text{Ni}_x\text{O}$ nanocrystals prepared by sol-gel method with Ni concentration ranging from 0 to 12 mol%. Tetragonal distorted ratio c/a decreased with increasing Ni content,

demonstrating the substitution of Ni into PbTiO_3 crystal lattice, and increased with increasing calcining temperature, benefiting for ferroelectric polarization. The substitution of Ni into PbTiO_3 crystal lattice was also proved by the left-shift of Raman peaks related to Ti vibration along c axis. Room-temperature ferromagnetism of $\text{PbTi}_{1-x}\text{Ni}_x\text{O}_3$ nanocrystals calcined at 900°C improved in the range of Ni doping concentration from 0 to 12 mol%. The observation of room temperature ferromagnetism in high tetragonality $\text{PbTi}_{1-x}\text{Ni}_x\text{O}$ series may provide an approach to widely explore more single-phase multiferroics.

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