

Possible Weak Ferromagnetism in $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ Nanocrystals at Normal State

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Abstract. Nano-crystals of $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ (PCCO) with $x = 0$ and 0.15 have been successfully synthesized by chemically dissolved method employing HNO_3 as dissolving agent. The PCCO samples were calcinated at $900 - 1000^\circ\text{C}$ for $5 - 30$ h. The PCCO samples were characterized by x-ray diffraction (XRD) and vibrating sample magnetometer (VSM) for investigating the phase formation and crystals size, and for studying the magnetic properties at normal state, respectively. Based on the XRD data, PCCO with $x = 0.10$ and 0.15 calcinated at temperature of 1000°C for 15 h show no impurity phases with crystal size of around 50 nm using Rietveld analysis. It is shown that the non-superconductive PCCO nano-crystals have very weak ferromagnetic behavior at room temperature. This phenomenon is probably due to magnetic moments rising from oxygen vacancies of the nanocrystals surface.

1. Introduction

Researches on synthesis and magnetic properties of cuprate superconductors have shown a rapid development in both hole- and electron-doped cuprates. Generally, a micrometer particles and even single crystal bulk superconducting samples have been intensively produced in order to investigate the basic physical properties of the materials [1]. However, it is very rare to find superconducting materials in nanometer crystal size. There are some common methods to synthesis superconducting materials, such as solid state reaction [2-4] and ball milling [5-7], in which both synthesis techniques produce a sample with micrometer particle size (> 100 nm). In the case for producing a nanometer crystal size, precipitation method or dissolved method using NaOH, HCl and HNO_3 as dissolved agents have been successfully conducted [8-11].

Cuprate based superconductors with nanometer crystal size have been shown to have unique property so-called room-temperature ferromagnetism (RTFM). Shipra *et al.* [12] have shown that $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) with crystal size below 100 nm shows ferromagnetic properties at above critical temperature, T_c , as well as at room temperature. This phenomenon is indicated by the appearance of magnetic hysteresis at the normal state. However, in the micrometer bulk samples, it has been shown that a paramagnetic behavior was observed clearly [13]. The presence of ferromagnetism is expected due to the oxygen vacancies (crystal defects) on surface of the nanoparticles producing weak and localized magnetic moments. The RTFM phenomenon has also been reported by M. A. Baqiya and co-workers in the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (Bi-2212) nanoparticles. They have observed the existence of RTFM in the Bi-2212 nanoparticles prepared by dissolved method with crystal size less than 200 nm [8].

This paper is aimed to study the magnetic properties at normal state of $\text{T}'\text{-Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ ($\text{T}'\text{-PCCO}$) nanocrystals prepared by chemical dissolved method. As it is known that the physical properties of the T' -structure are strongly influenced by the presence of apical oxygen [14]. A small number of oxygen



vacancies either on the apical site or the other oxygen sites may affect the overall magnetic properties of the cuprates. Therefore, it is also important to investigate the magnetic behaviour of the PCCO nanocrystals at normal state.

2. Experimental

$\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ (PCCO) nanocrystals with $x = 0$ and 0.15 were prepared by dissolved method with HNO_3 as the dissolving agent. The dissolved method used in this present research was similar with previous works [8]. Pr_6O_{11} , CeO_2 , and CuO powders with high purity (99.9%) have been used as the raw materials. First, the raw materials were dried and weighted according to the desired stoichiometry. The dried raw materials were dissolved by HNO_3 separately at around 150°C and then mixed them together until it forms a precipitate. The step was continued by performing pre-calcination process for the precipitate at 400°C for 4 h. Finally, the precursor powder was calcinated at $900 - 1000^\circ\text{C}$ for 5 – 30 h. The structural properties and magnetic hysteresis curves of the PCCO samples were measured by XRD and VSM, respectively. Phase identification and crystal structure of the samples were investigated using XRD with scanning angle 2θ ranging from 10° to 70° and operated at 40 kV and 30 mA with $\text{CuK}\alpha_1$ radiation with wavelength of $1.54 \text{ \AA}$. The lattice parameter and the average crystal size were estimated by Rietveld analysis using Rietica [15] and materials analysis using diffraction (MAUD) [16] software, respectively. VSM (Dexing Magnet Ltd., VSM 250) measurements were conducted with external magnetic field ranging from -2 T to 2 T at room temperature (23°C) resulting magnetic hysteresis curves.

3. Results and Discussion

Figure 1(a) and 1(b) show the XRD patterns of PCCO nanocrystals with $x = 0$ and 0.15 at various calcination temperatures, respectively. Based on the phase identification, all peaks are detected as PCCO phase with PDF#080-2368. However, at the calcination temperature of 900°C , there is an impurity phase of Pr_6O_{11} . Matsuda *et al.* [17] reported that the single phase of 214 systems can be obtained using solid state reaction technique at 1030°C . In this research, the PCCO phase has been formed at calcination temperature of 1000°C for 15 h without any impurities. In fact, the formation of PCCO phase has been initiated at 900°C with small amount of impurities less than 15%. This means that the dissolved method used in this present research has successfully formed the 214 phase (PCCO phase) at a lower temperature than 1030°C . This is due to the dissolved method is one of bottom up synthesis method which give the particles easily to react each other even at relatively low temperature.

Figure 1(c) shows peak shift between PCCO nanocrystals without and with Ce doping. All diffraction peaks shift to larger diffraction angle with the addition of Ce doping meaning that all Ce atoms were successfully doped into the crystal. The values of lattice parameter and crystal size of PCCO samples obtained from the analysis results of Rietica and MAUD software, respectively, are shown in Table 1. PCCO phase (ICSD#72246 with tetragonal structure and space group $I4/mmm$) was used for Rietveld analysis achieving the goodness of refinement (GoF) less than 2%. It can be seen that the addition of Ce doping decreases the c-axis length. This is consistent with the former research by Matsumoto *et al.* [18] that there is doping dependence of lattice parameter in the cuprate system. The ionic radius of Ce^{4+} ($1.11 \text{ \AA}$) is smaller than that of Pr^{3+} ($1.27 \text{ \AA}$). Therefore, the c-axis length shrinks in the doped sample because the Pr^{3+} ions have been replaced by Ce^{4+} ions perfectly [18].

Based on analysis results in Table 1, it is found that PCCO samples with $x = 0$ and 0.15 have crystal size of $40 - 118 \text{ nm}$. These results show that the calcination temperature and the holding time affect the crystal size due to the thermal energy for resulting larger crystal size. As for the effect of doping, Table 1 shows that a- and b-axis lengths do not change significantly with additional Ce doping and different calcination time. However, c-axis length increases with the increase of calcination time because the longer calcination time provides more thermal energy to expand the lattice parameter (c-axis length).

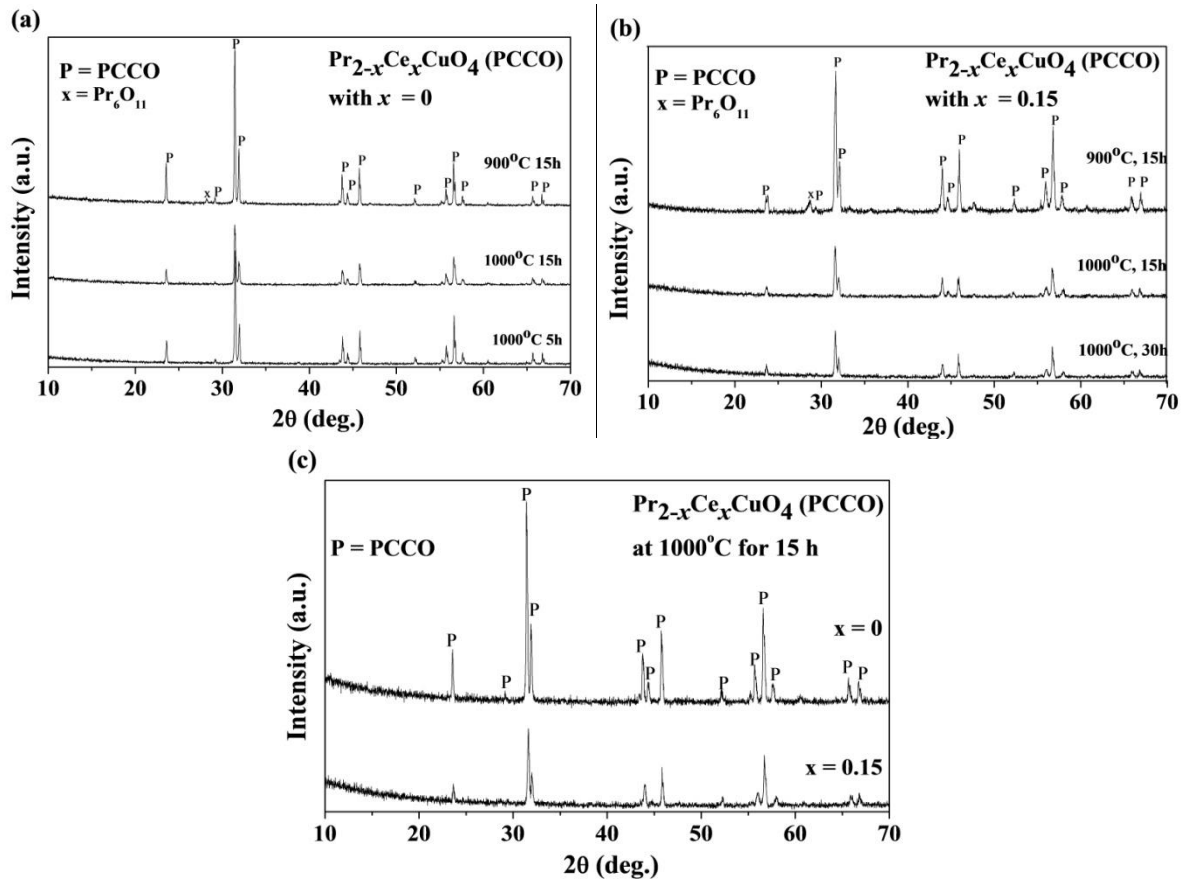


Figure 1. XRD patterns of PCCO nanocrystals with different calcination process and holding time: 900 - 1000°C for 5 - 30 h. (a) $x = 0$ and (b) $x = 0.15$; (c) Comparison between the XRD patterns of single phase PCCO with $x = 0$ and 0.15 (calcination at 1000°C for 15 h).

Table 1. The results of crystal analysis of PCCO samples with $x = 0$ and 0.15 using Rietveld analysis.

PCCO Samples	Calcination Temperature	Holding Time (h)	Crystal size (nm)	Lattice Parameter (Å)	
				a=b axis	c axis
$x = 0$	1000°C	5	118 ± 20	3.903(0)	12.058(1)
	1000°C	15	61 ± 1	3.904(0)	12.062(1)
$x = 0.15$	1000°C	15	40 ± 1	3.908(1)	12.012(2)
	1000°C	30	46 ± 1	3.902(0)	12.025(1)

Figure 2 shows magnetic hysteresis curves for PCCO nanocrystals with $x = 0$ and 0.15 measured at room temperature. Both samples are non-superconducting samples and show weak RTFM phenomena. This result is in accord to the former paper by Shipra *et al.* [12]. It can be seen that the hysteresis curves show no magnetic saturation up to 1 T representing dominant paramagnetic properties in both PCCO samples. Based on Figure 2, PCCO nanocrystals without Ce doping shows a higher value of paramagnetic susceptibility compared to the doped one. It seems that the increase of Ce doping results in the decrease of magnetic hysteresis and turns into relatively weak ferromagnetic at room temperature. This is probably due to the contribution of Ce^{4+} magnetic moments affecting the overall magnetization in the doped PCCO.

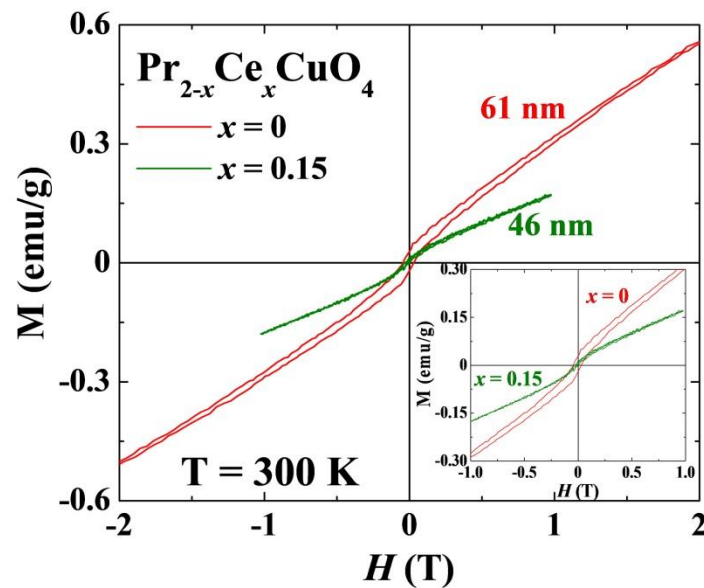


Figure 2. Magnetic hysteresis curves for PCCO nanocrystals with $x = 0$ and 0.15 at room temperature.

Both undoped and doped PCCO samples with crystal size less than 100 nm exhibit RTFM feature. The crystal size dependence on the magnetic properties of cuprates has been reported by S. K. Hasanain *et al.* [19]. The higher crystal size of the nanoparticles results in a smaller magnetization and finally becomes paramagnetic. Moreover, the increase of Ce doping in the PCCO crystal may be responsible for the disturbance of net magnetic moments leading to a competition between magnetic moments rising from Ce ions and oxygen vacancies. However, the appearance of RTFM in PCCO nanocrystals should be investigated in more detail to elucidate the correlation between crystal size effect and magnetic moments rising from oxygen defects.

4. Summary

PCCO nanocrystals with $x = 0$ and 0.15 have been successfully synthesized by chemically dissolved method. The XRD patterns show single phase of PCCO crystal obtained by calcination at 1000°C for more than 15 h . Based on Rietveld analysis, it is obtained the smallest crystal size of about 40 nm . The lattice parameters (a - and b -axis length) do not change significantly with different calcination temperatures. However, the c -axis length decreases with addition of Ce doping. Both PCCO nanocrystals with $x = 0$ and 0.15 have shown very weak RTFM behavior. It is found that PCCO nanocrystal with $x = 0$ shows a relatively strong magnetization without any magnetic saturation compared with $x = 0.15$. These results suggest that both PCCO nanocrystals have dominant paramagnetic properties with very weak RTFM feature.

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