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Phase transformation and percolation effect in $PbO_2 - \frac{1}{12}Ag_2O - xC$ system

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Abstract

The structure and electronic transport properties have been investigated for composite $PbO_2 - \frac{1}{12}Ag_2O - xC$ ($0 \le x \le 2$) materials prepared by mechanical milling in an O_2 atmosphere. The solid-state reactions result in the occurrence of abundant phase transformations, when the graphite content increases. With the phase transformations occurring, the percolation effect is observed for the electronic transport of $PbO_2 - \frac{1}{12}Ag_2O - xC$ system, while its conductivity undergoes an insulator–metal transition. The percolation threshold is determined by DC conductivity measurement and analysis of X-ray diffraction patterns.

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Keywords: A. The $PbO_2 - \frac{1}{12}Ag_2O - xC$ system; D. Electronic transport; D. Percolation effect

1. Introduction

The percolation threshold effect is a well-known phenomenon widely observed in physical systems [1], like, filler-matrix systems as the extreme change of certain physical properties within a rather narrow range of filler concentration. The conductive composites [2,3], consisting of an insulting polymeric matrix and conductive filler, and the nanocomposite magnets [4], consisting of hard and soft magnetic phases, frequently demonstrate such a behavior. Several models have been proposed to describe the percolation behavior of electroconductive composites [5, 6]. The most frequently used electroconductive particles served as fillers for conductive composites are either various forms of carbon or finely dispersed metals. Recently, the systems of $PbCO_3 \cdot 2PbO - Ag_2O$ and $PbCO_3 \cdot PbO - Ag_2O$ were reported to exhibit possible superconductivity [7,8]. We investigated the electronic transport properties of $PbO_2 - Ag_2O - xC$ system, which shows metal–nonmetal transition and percolation effect [9]. In this work, we find that abundant phase transformations and percolation effect exist in $PbO_2 - \frac{1}{12}Ag_2O - xC$ system with increasing the graphite content. The percolation effect is analyzed for electronic transport properties of the $(2PbCO_3 \cdot PbO + PbCO_3)/Pb$ nanocomposite in which Pb serves as conductive filler. We also succeed in synthesizing $Ag_5Pb_2O_6$ compound by annealing the $PbCO_3 \cdot PbO/Ag$ nanocomposite in an O_2 atmosphere.

2. Experimental

The composite materials were prepared by analytical reagents of PbO_2 (rutile-type), Ag_2O and 99.7%-pure

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graphite with the mol ratio of $1{:}\frac{1}{12}{:}x$ $(0 \leq x \leq 2)$. The powder mixture of PbO_2, Ag_2O and graphite was sealed in a hardened steel can in an oxygen atmosphere and mechanically milled using a high-energy ball miller at a voltage of 110 V for 5 h. The mass ratio of balls to powders was kept at 20:1. The as-milled powders were pressed into pellets by using a 760 MPa axial-pressure with a steel die. The pellets were ground to a rectangular parallelepiped with dimensions of $2 \times 10 \times 0.6\ \mathrm{mm}^3$ to fit the test holder. X-ray diffraction (XRD) patterns were recorded at room temperature using Cu Kα radiation with a Rigaku D/Max-γA rotation target diffractrometer. The temperature dependence of electrical resistance was measured between 77 K and room temperature by the DC four-probe method using 15 mm silver wires and silver paint with contact resistance ranging from 3 to 20 Ω.

3. Results and discussion

The brown, dark or silver gray powders were produced after milling for 5 h. When the cans were opened, some gases were ejected from the cans. When the gases were collected, a part of the gases could be absorbed by a solution of ~20% NaOH, which was considered as CO_2. The gases produced during milling may be either oxygen or carbon dioxide, depending on the content of graphite in the precursors. XRD patterns (Fig. 1) of the as-milled powders show that different phases are produced during the milling progress, depending on the change of the graphite content. The broad peaks in the XRD patterns show that the crystal structures of the phases are not very perfect with the existence of defects that induced by mechanical milling as usual. From the phase constituents shown by XRD patterns, it is clear that some solid-state reactions occur indeed during milling. Without any graphite $(x = 0)$, PbO_2 can be decomposed to Pb_2O_3 and O_2 by the violent hurtling of the steel balls. The possible reaction is: $2PbO_2 \rightarrow Pb_2O_3 + \frac{1}{2}O_2$. When there exists a small amount of graphite $(0 < x \leq 0.25)$, lead oxide $PbO_{1.55}$ appears and its amount increases gradually because of the partial reduction by graphite. For $0.25 \leq x \leq 0.4$, Pb_2O_3 and $PbO_{1.55}$ phases disappear gradually, while lead oxycarbonate $PbCo_3{\cdot}PbO$ emerges, with possible reactions: $2PbO_2 + C \rightarrow PbCO_3{\cdot}PbO$ and $C + O_2 \rightarrow CO_2$. In this process for x less than 0.4, none of elemental Ag peaks can be found in XRD patterns. According to our recent work [9], it is evaluated that a very small amount of $Ag_5Pb_2O_6$ compound may exist, doping the other main phases, because the content of Ag_2O is far less than that of PbO_2 in the starting materials. The possible reaction is: $5Ag_2O + 4PbO_2 \rightarrow 2Ag_5Pb_2O_6 + \frac{1}{2}O_2$. When x is larger than 0.4, the elemental Ag appears according to XRD patterns, which can be ascribed by the reduction of graphite. When $x = 0.5$ and 0.6, we can easily obtain the composite of $PbCO_3{\cdot}PbO{-}Ag$ (with $Ag/Pb = 1/6$ in a simple process with one step, instead of the complicated preparation processes with experimental conditions of high press/high temperatures as described in literature [6,7]. With increasing the graphite content x up to 0.70, another lead oxycarbonate $2PbCO_3{\cdot}PbO$ can be synthesized and it is difficult to estimate the possible reactions. When $0.73 < x \leq 0.80$, the amount of $2PbCO_3{\cdot}PbO$ reduces gradually and it disappears at $x = 0.80$, while $PbCO_3$ and Pb appear. When $0.90 \leq x \leq 2.0$, lead oxides PbO also appear due to the oxidation of the very fine Pb powders. When x is larger than 1.20, the main phase is Pb, which is mixed by $PbCO_3$ and PbO. In this process, the role of graphite is not only to react to synthesize products, but also to create a CO_2 atmosphere during the milling synthesis. All the compounds have been produced in the mixture of O_2 and CO_2 atmospheres and the CO_2 partial pressure can be controlled by the amount of graphite in the starting compositions (except the sample $x = 0$).

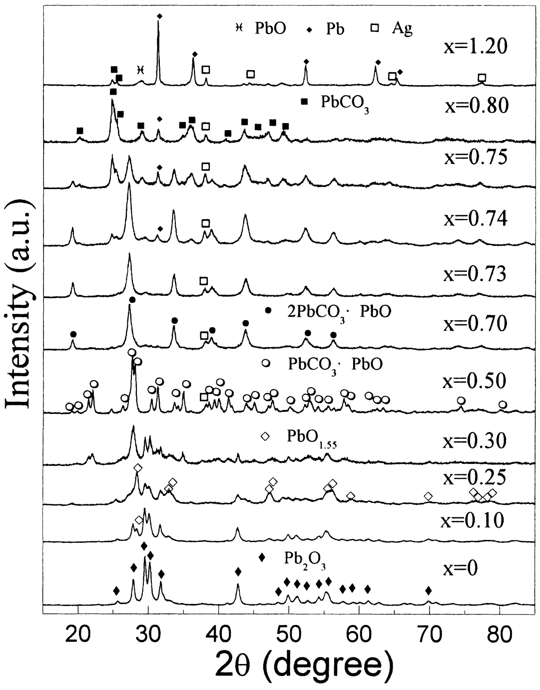

Fig. 1. X-ray diffraction patterns of as-milled $PbO_2-\frac{1}{12}Ag_2O-xC$ samples.

The as-milled samples of $x \leq 0.74$ are insulators, whilst other samples with more graphite in starting materials show metallic conductivity and the pellets pressed show metallic luster. With increasing x from 0.75 to 1.4, the resistivities of these samples at 290 K decrease from 0.29 to $6.12 \times 10^{-5}\ \Omega$ cm. The temperature dependences of resistivity of these metallic pellets are represented in Fig. 2, which are characterized by a linear function of $\rho = \rho_0 + AT$ (where ρ is resistivity of the composite, ρ_0 residual resistivity due to impurity scattering and A the temperature coefficient of resistivity) in the measurement temperature range. It can be illustrated by the scattering of conduction

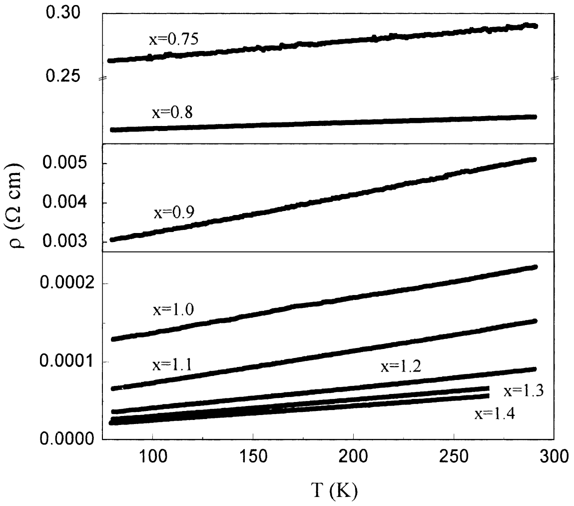

Fig. 2. Temperature dependence of resistivity of the as-milled $\mathrm{PbO_2}-\frac{1}{12}\mathrm{Ag_2O}-x\mathrm{C}$ ($0.75 \le x \le 1.4$) samples.

electron by thermal vibration of atoms, same as the curve of $x = 1$ and 1.25 in our recent work [9].

The graphite content dependence of the conductivity of the as-milled samples ($0.75 \le x \le 1.4$) is shown in Fig. 3. The normalized conductivities σ_c/σ_0 at 290 K are plotted as a function of x, which represent the graphite content in the starting materials. The relationship between the normalized conductivity σ_c/σ_0 and the graphite content x in the region of $0.75 < x \le 1.2$ can be fitted by the equation $\sigma_c/\sigma_0 = (V - V_c)^s \sim \alpha(x - x_c)^s$, same as the equation (1) in the literature [5]. Here, σ_c and σ_0 are the electrical conductivities of the composite and the conductive filler particles (Pb), V, V_c the volume fraction and the volume percolation concentration of the conductive filler. In the present case, the percolation phenomenon is slightly more complex because the conductive filler Pb is produced by reducing reaction with graphite and the relative amount of Pb depends on the graphite content in the starting materials. Hence, α is an adjustable parameter through which one can transfer graphite content x to the volume fraction of the conductive filler, and s a quantity determining the power of the conductivity increase above V_c. Kirkpatrick [5] gave the value for the exponent $s = 1.5 \pm 0.1$ as point percolation model. Our value of $s = 1.5 \pm 0.1$ support the mechanism of point percolation in the present system. With the graphite content increasing ($x > 1.2$), the normalized conductivities deviate from the fitting curve because of the excess graphite added and the increase of the amount of PbO in the samples.

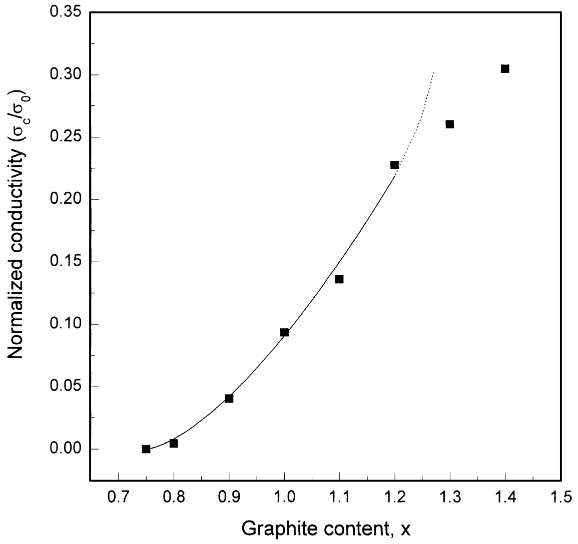

Fig. 3. Normalized conductivity σ_c/σ_0 of the as-milled $\mathrm{PbO_2}-\frac{1}{12}\mathrm{Ag_2O}-x\mathrm{C}$ ($0.75 \le x \le 1.4$) samples as a function of the graphite starting content (x). The solid curve is the fitting result $\sigma_c/\sigma_0 \sim \alpha(x - x_c)^s$ with fitting parameters of $x_c = 0.75 \pm 0.02$, $s = 1.5 \pm 0.1$, $\alpha = 0.72 \pm 0.02$.

From Figs. 1 and 3, we can infer that the value of percolation threshold for the graphite content x_c should be 0.75. In the $\mathrm{PbO_2}-\frac{1}{12}\mathrm{Ag_2O}-x\mathrm{C}$ system, the sample of $x = 0.75$ first shows a metallic conductivity. Compared to the XRD patterns of samples with $x = 0.73$, 0.74 and 0.75, it is evident that there is no trace of Pb in the sample of $x = 0.73$, whilst the conductive phase Pb has been produced in the samples of $x = 0.74$ and 0.75. However, the $x = 0.74$ sample is still an insulator because it is below the percolation threshold. The $x = 0.75$ sample becomes a conductor, due to the conductive particles Pb forming a conductive path through the sample. This transition is actually an insulator-metal transition, originating from the percolation effect of the conductive composite, which changes the electronic transport properties of the ($\mathrm{2PbCO_3{\cdot}PbO + PbCO_3}$)/Pb nanocomposite in which Pb serves as conductive filler.

The sample of $x = 0.5$, consisting of $\mathrm{PbCO_3{\cdot}PbO}$ and Ag, is interesting for comparing with the literature [7,8]. DSC curve of this sample, shown in Fig. 4, reveals that four transitions occur between 100 and 400 °C with the onset temperatures at 235.5, 327, 342 and 365 °C, respectively. Except for the very weak endothermal peak onset at 342 °C, the other three are exothermal peaks, among which the peak at 327 °C is the weakest, and that at 365 °C is much broader than that at 235.5 °C. We tried to identify these transitions by annealing the sample at temperatures just above the onset temperatures. The $x = 0.5$ sample was annealed at 250, 335, 350 and 380 °C, respectively, in 0.1 MPa $\mathrm{O_2}$ flow for 1 h. XRD patterns of the as-milled and annealed samples are shown in Fig. 5. It is identified that some reactions occur during annealing. The first peak, in Fig. 4, with the onset temperature of 235.5 °C is consistent with the decomposition of some unknown phases. As annealed at 335 °C, $\mathrm{PbCO_3{\cdot}PbO}$ starts to decompose to be $\mathrm{PbCO_3{\cdot}2PbO}$ and $\mathrm{CO_2}$. With increasing temperature to 350 °C, the amount of $\mathrm{PbCO_3{\cdot}PbO}$ gradually reduces and that of $\mathrm{PbCO_3{\cdot}2PbO}$ increases with the appearance of $\mathrm{Pb_3O_4}$. When annealed at

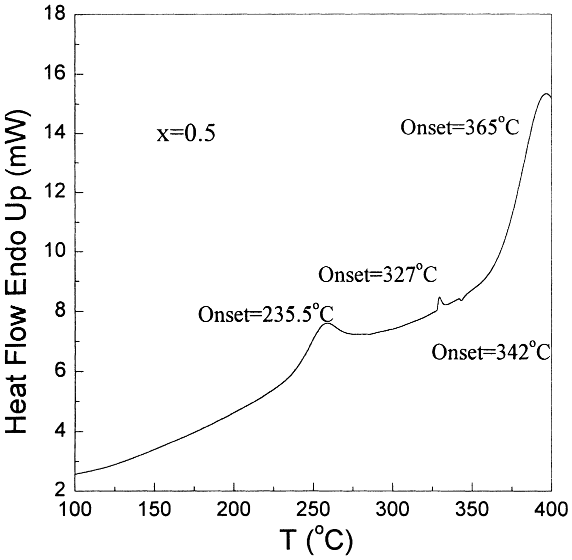

Fig. 4. DSC graph of the sample of $x = 0.5$ with increasing temperature.

380 °C, both $PbCO_3 \cdot PbO$ and $PbCO_3 \cdot 2PbO$ disappear and $Ag_5Pb_2O_6$ forms. Before annealing at 380 °C, the elemental Ag is mechanically mixed in other major phases. The conductive $Ag_5Pb_2O_6$ phase [10] is produced directly by reaction from Ag and $PbCO_3 \cdot 2PbO$ at ambient pressure, which is different from mechanical milling [9], hydrothermal method [11], and high pressure synthesis [12]. However, all these annealed samples are insulators, which is due to the small amount of $Ag_5Pb_2O_6$. X-ray data recorded from samples in Refs. [7,8] revealed the presence of diffraction line at $d = 321$ pm which were asserted to a novel unknown material (cited as phase 321 in Refs. [7,8]). Djurek et al. [7,8] assumed on the structure of the phase 321 as follows [7,8]. Pb layers could span hexanogal basal planes separated 321 pm along c-axis [7,8]. Pb^{2+} cations could be octahedrally co-ordinated by oxygen atoms with octahedra face and vertex shared giving rise to formation of $(Pb_2O_3)^{2-}$ complexes which form three-dimensional cage. They supposed the formation of Pb=Pb double bonds which enable to Pb cattons, in the environment of ligands [7,8]. Unlike the literature [7,8], the phase 321 cannot be obtained in the present work, which may be caused by the deficient pressures of O_2 and CO_2. We would like not to discuss in detail this phase in this paper.

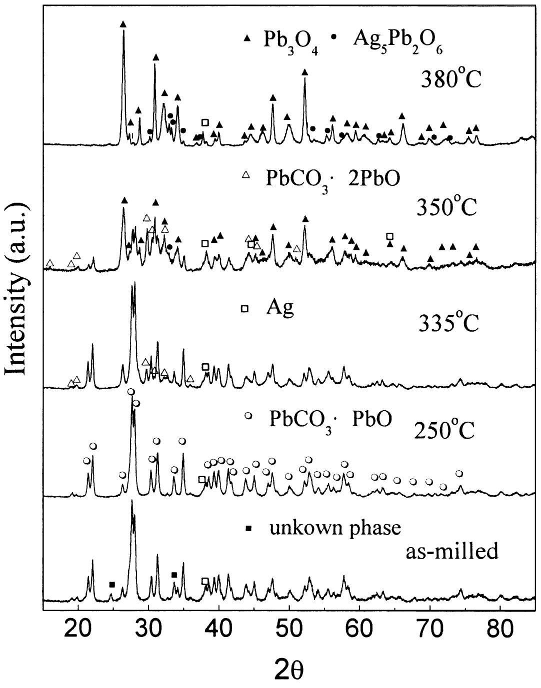

Fig. 5. X-ray diffraction patterns of the as-milled and annealed samples of $x = 0.5$.

4. Summary

In summary, the effects of oxygen atmosphere and graphite content on synthesizing the composite of $PbO_2-\frac{1}{12}Ag_2O-xC$ system by mechanical milling have been investigated. Under an oxygen and carbon dioxide atmosphere, there exist abundant phase transformations as the graphite content varies in this system. With the phase transformation occurring, the percolation threshold effect is observed for the conductivity of $PbO_2-\frac{1}{12}Ag_2O-xC$ system, changing from insulator to metallic conductivity. The percolation threshold ($x = 0.75$) of the $(2PbCO_3 \cdot PbO + PbCO_3)/Pb$ nanocomposite is found by DC resistivity and XRD measurements.

Acknowledgements

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References

[1] S. Kirkpatrick, Rev. Mod. Phys. 45 (1973) 574.
[2] D.M. Bigg, Adv. Polym. Technol. 4 (1984) 255.
[3] C. Klason, D.H. Mcqeen, J. Kubát, Macromol. Symp. 108 (1996) 247.
[4] X.K. Sun, J. Zhang, Y. Chu, W. Lui, B. Cui, Z.D. Zhang, Appl. Phys. Lett. 74 (1999) 1740.
[5] F. Lux, J. Mater. Sci. 28 (1993) 285.
[6] R. Zallen, The Physics of Amorphous Solids, Wiley, New York, 1983, Chapter 4.

[7] D. Djurek, Z. Medunić, A. Tonejc, M. Paljević, Physica C 341–348 (2000) 723.

[8] D. Djurek, Z. Medunić, A. Tonejc, M. Paljević, Physica C 351 (2001) 78.

[9] D. Li, D.Y. Geng, Y.T. Xing, G.W. Qiao, Y.Z. Wang, Q.F. Xiao, Z.D. Zhang, submitted for publication.

[10] D. Li, W.F. Li, D.Y. Geng, G.W. Qiao, Y.Z. Wang, X.P. Song, Z.D. Zhang, submitted for publication.

[11] A. Byström, L. Evers, Acta Chem. Scand. 4 (1950) 613.

[12] M. Jansen, M. Bortz, K. Heidebrecht, J. Less-Common Met. 161 (1990) 17.