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The effect of annealing on magnetic and transport properties of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ thin films

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Abstract
The effect of annealing on magnetic and transport properties in $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ thin films is studied. The samples were prepared by annealing amorphous films at different temperatures. With increase in annealing temperature, the resistivity decreases, and the Curie temperature (T_c) and negative magnetoresistance (MR) increase. These results arise from an increase of ferromagnetic coupling in grains and between grains, and a reduction of the spin dependent and disorder scattering. In addition, the conduction is very sensitive to oxygen deficiency. The thermopower (TEP) data for the films obtained by annealing at 600 and 1000 °C show totally different behaviours. The film obtained at 1000 °C shows temperature-linear dependence, and is typical of a metal, while the TEP of the film obtained at 600 °C increases sharply at about 150 K. This may arise from the transformation of intermediate spin Co(iii) to low spin Co(III) and the contribution from the amorphous and hole-poor matrix.

1. Introduction

Mn-based perovskite oxides $R_{1-x}A_xMnO_{3-\delta}$, where R is a rare earth element and A = Ca, Sr or Ba, have attracted much attention because of their colossal magnetoresistance (CMR) effect [1–4]. A large negative magnetoresistance (n-MR) ratio has been reported in another group of CMR oxides, (La, A)CoO_3 (A = Ca, Sr or Ba), by Briceno *et al* in 1995 [5]. These CMR oxides offer exciting possibilities for improved magnetic sensors, magnetoresistance read heads and magnetoresistance random access memory.

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$La_{1-x}Sr_xCoO_3$ exhibits diverse magnetic and transport properties with spin state transitions. Itoh *et al* [6] deduced the magnetic phase diagram of $La_{1-x}Sr_xCoO_3$ from magnetization measurements. The electrical and magnetic properties of $La_{1-x}Sr_xCoO_3$ are very sensitive to the Sr-doping level. In the low Sr region ($x < 0.18$), it is a semiconductor with spin-glass (SG) character at low temperatures. For $x > 0.18$, it becomes metallic cluster glass (CG) and is associated with long range magnetic order below a critical temperature [6]. It is a paramagnetic material above the critical temperature.

Highly strontium-doped $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) shows a good metallic conductivity and a large MR below the critical temperature where the paramagnetic to ferromagnetic transition occurs. Recently, many investigations have been done researching into physical properties and device applications for LSCO thin films [7–10]. We have studied the dynamics of crystallization and phase transition in $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ thin films. It is found that electron–grain boundary scattering plays a key role in various temperature regions during the resistance measurement [10]. The number of grain boundaries per unit volume decreases due to the increase of grain size with increase of the annealing temperature. In order to study the effect of annealing in LSCO thin films, amorphous films were prepared. Then they were annealed at different temperatures. The amorphous films start to nucleate at 400 °C, and become polycrystalline with very small crystal grains. The grains in the films continue to grow and reorient with increase of the annealing temperature. When the temperature reaches 560 °C, recrystallization occurs. The thin films should become metallic only after annealing at high temperature (>750 °C) [10]. In addition, annealing in ambient conditions results in an oxygen loss from LSCO films [11]. Oxygen deficiency also affects transport and magnetic properties of LSCO films. Therefore, annealing at different temperatures provides a way to obtain samples with different grain sizes and oxygen deficiencies δ. In addition, strain between film and substrate is another factor which affects transport and magnetic properties of films. In our samples, the lattice parameter of $LaAlO_3$ substrate (3.788 Å) matches well with that of LSCO (3.805 Å) [11]. Therefore, the effect of strain is small, and is ignored in our paper. In this paper, we study the effect of annealing by measurement of magnetic and transport properties for the three films which were obtained by annealing the amorphous films at 500, 600 and 1000 °C for 2 h. It is unfortunate that we cannot measure the precise value of the oxygen deficiency δ.

2. Experiment

The amorphous films were deposited on (001) $LaAlO_3$ substrates by pulsed laser ablation at room temperature in an atmosphere of 200 mTorr oxygen with a stoichiometric target. The film thickness was approximately 200 nm. Three films were obtained by annealing the as-prepared amorphous films at 500, 600 and 1000 °C in the atmosphere. They are called samples A, B and C, respectively. Resistance was measured using the four probe method. Magnetoresistance was measured with a dc magnetic field up to 10 T provided by a superconducting magnet system (Oxford Instruments). The thermopower was measured by a dc method in the temperature range 50–300 K. The magnetic susceptibility measurement was carried out with a superconducting quantum interference device magnetometer (SQUID).

3. Results and discussion

Figure 1 shows the temperature dependence of the resistivity for three films obtained by annealing the as-prepared amorphous films at 500, 600 and 1000 °C. It is observed that

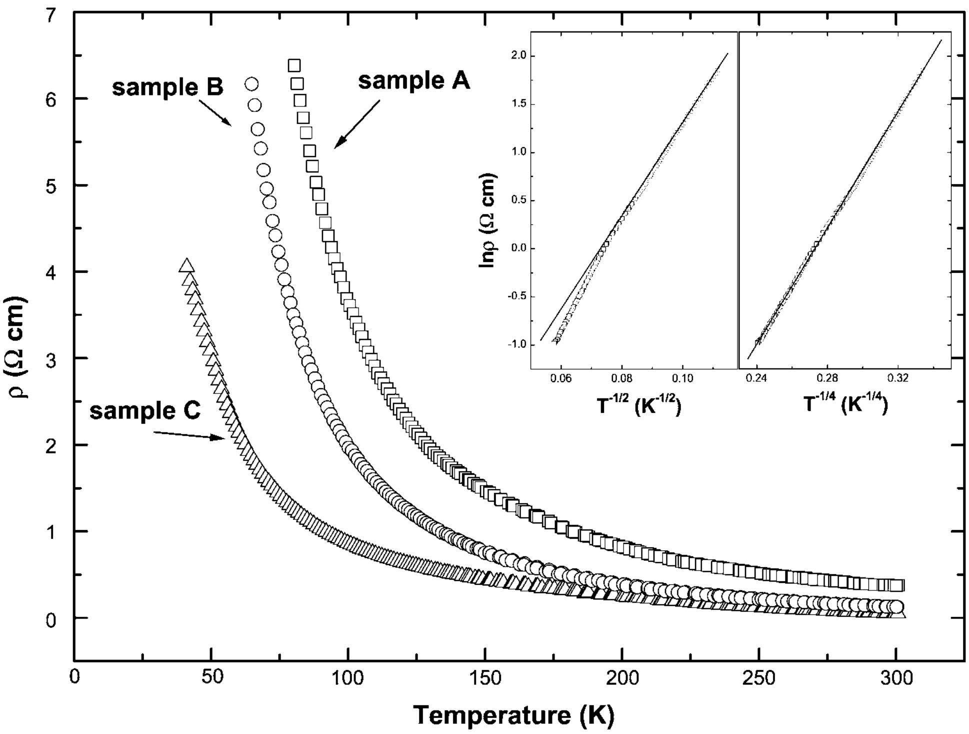

Figure 1. Temperature dependences of the resistivity for LSCO thin films obtained by annealing the as-prepared amorphous films at 500 °C (A), 600 °C (B) and 1000 °C (C). Inset: the $T^{-1/2}$- and $T^{-1/4}$-dependences of ln ρ(T) for sample C.

the resistivity at a given measurement temperature decreases with increasing annealing temperature. The grains grow from the amorphous matrix and become bigger with increasing annealing temperature. This suggests that a rapid decrease of the amorphous matrix leads to a reduction in grain boundary scattering, so that the resistivity decreases remarkably.

According to our previous report [10], the as-prepared amorphous LSCO thin film is semiconducting when it is prepared at room temperature and becomes metallic only after annealing at high temperature (>750 °C). As shown in figure 1, the resistivity of sample C shows semiconducting behaviour although it is obtained at 1000 °C, and its resistivity is much less than the others at low temperature. This semiconducting conduction behaviour may be caused by the depletion of oxygen. Previous studies give us the knowledge that the conductivity of LSCO can be reduced drastically with the depletion of oxygen [7]. The semiconducting behaviour was recorded even though the sample had slight oxygen loss [12, 13]. Annealing and long ageing in ambient conditions result in an oxygen loss from the LSCO thin films [11, 14]. In comparison with the case for the samples in [10], the oxygen loss in our samples is induced by long time annealing at high temperature and long ageing in ambient conditions before measurement. The oxygen loss will induce absence of Co^{4+}; these are the nuclei of the metallic clusters. This absence of Co^{4+} caused by oxygen deficiency will induce a variable-range hopping (VRH) behaviour of conduction in LSCO thin film. The conduction in LSCO thin film is very sensitive to the oxygen content, and the film with oxygen deficiency proceeds via VRH with the electron–electron interaction between ferromagnetic clusters. For the films with low oxygen deficiency δ, the conduction fits to $T^{1/2}$-VRH. With the increase of

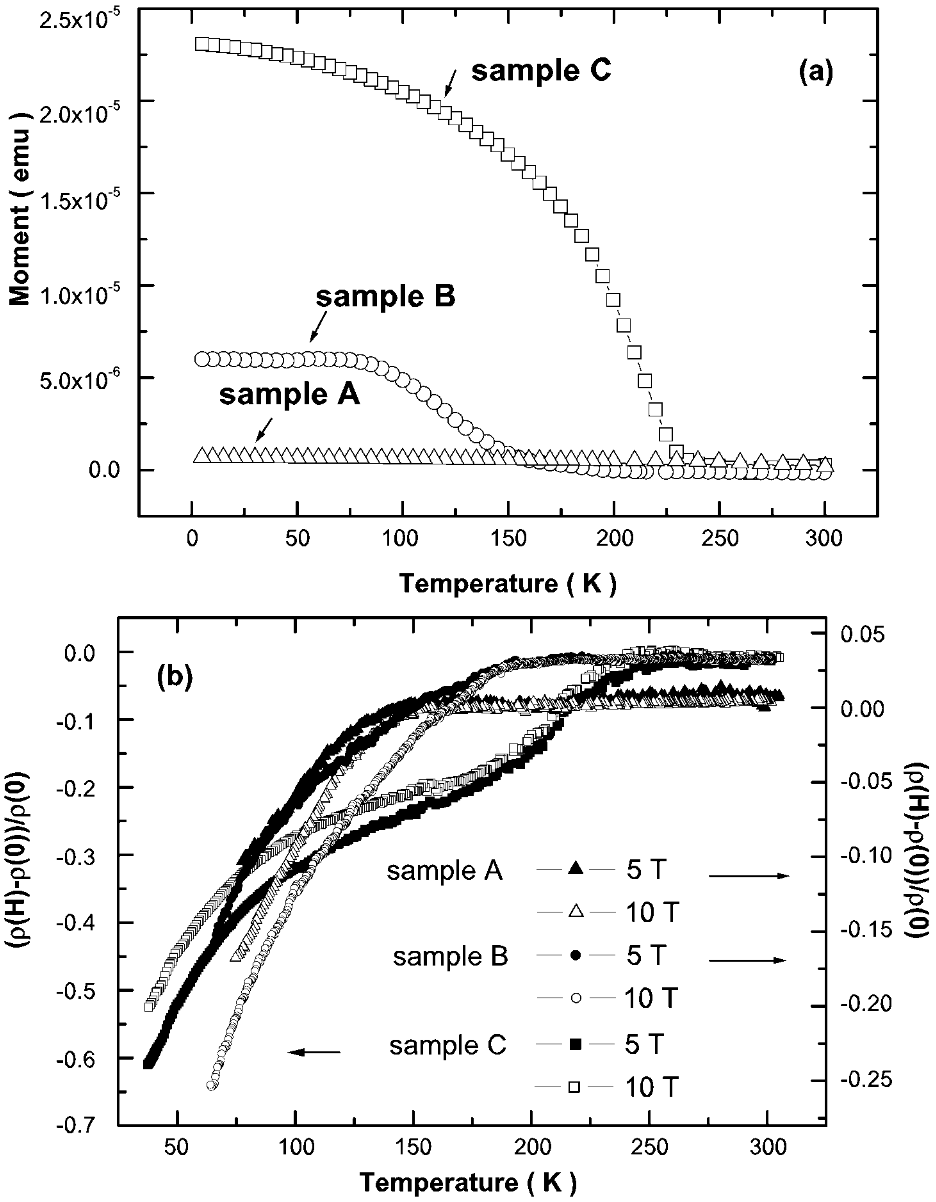

Figure 2. (a) The temperature dependence of the magnetization for LSCO thin films. (b) The temperature dependence of the magnetoresistance under magnetic fields of 5 and 10 T for samples A, B and C.

oxygen deficiency, the conduction changes from $T^{1/2}$-VRH to $T^{1/4}$-VRH. The data fit to $T^{1/4}$-VRH much better than $T^{1/2}$-VRH, as shown in the inset of figure 1. This suggests a higher oxygen deficiency δ in sample C. The oxygen deficiency of sample C leads to a semiconducting conduction behaviour.

Figure 2(a) shows the temperature dependence of the magnetization for three films in field-cooling processes (10 and 50 Oe). Sample A does not show a ferromagnetic transition. Samples B and C show a ferromagnetic transition, with Curie temperatures (T_c) of 160 K for sample B and of 230 K for sample C. With increasing grain size, the Curie temperature increases. Similar results have been reported in [3, 15]. When the amorphous thin film is annealed at 500 °C, it is polycrystalline with plenty of very small crystal grains [10]. On the one hand, the spin becomes heavily disordered at the grain boundary due to strain with lowering of the grain size [16, 17]. On the other hand, because the ferromagnetic ordering region is very small in every grain, the ferromagnetic coupling between grains is weak. Therefore, spontaneous magnetization directions between different grains array randomly. There is no long range ferromagnetic ordering.

When the annealing temperature is higher than 560 °C, recrystallization has occurred [10]. The grain size increases continuously and the ferromagnetic order appears inside the grains at low temperature for sample B. However, there are still plenty of grain boundaries with disordered spins.

According to the theory of recrystallization, grains become bigger with a corresponding reduction in the number of grain boundaries per unit volume during recrystallization [10]. After annealing at 1000 °C, the regions of grain boundaries decrease remarkably in sample C. There are large ferromagnetic clusters with a long range ferromagnetic order. The coupling between the ferromagnetic clusters is much stronger than that in samples A and B. These lead to an obvious increase of T_c.

In all samples, oxygen deficiency is another factor which will affect magnetic properties. In aged film samples and as-prepared bulk samples, the oxygen deficiency turned out to be $\delta \approx 0.08$ [14], and it increases after annealing [11]. According to double-exchange (DE) model [18], ferromagnetic (FM) correlation is realized by O^{2-} ions between Co^{4+} and Co^{3+} ions. The loss of oxygen will weaken the FM correlation and induce the decrease of T_c.

Figure 2(b) shows the temperature dependence of the magnetoresistance under magnetic fields of 5 and 10 T for sample A, B and C. The MR is defined by $[\rho(H) - \rho(0)]/\rho(0)$, where $\rho(H)$ and $\rho(0)$ are the resistivities at magnetic field H and zero field, respectively. As shown in figure 2(b), the MR for all three samples increases with decreasing temperature. The MR increases with increase of the annealing temperature under both the fields 5 and 10 T.

Theoretically, the resistivity ρ can be expressed by the extended Matthiessen rule [19]: $\rho = \rho_{def} + \rho_{ph}(T) + \rho_b$, where ρ_{def} is the resistivity contribution from electron defects, $\rho_{ph}(T)$ that from electron–phonon interactions and ρ_b from three parts: (1) the electron scattering induced by the Lorentz force; (2) the grain boundary scattering caused by spin disordering at the grain boundary; (3) the spin dependent scattering based on the double-exchange model [14]. The MR of the samples is mainly affected by ρ_b.

According to the DE model, the effective transfer t_{ij} of e_g electrons (or holes) between the nearest-neighbour pairs (i, j) of the Co site depends on the relative angle $\Delta\theta_{ij}$ between neighbour t_{2g} spins at sites i and j: $t_{ij} = t_0 \cos(\Delta\theta_{ij}/2)$. Therefore, the ferromagnetic state can reduce the spin disordering (of the localized t_{2g} spins) and the mobility of carriers increases in an applied magnetic field ($\Delta\theta_{ij} \to 0$), which results in a drop of resistance and negative MR effect. For sample A, the magnetoresistance is almost zero above 150 K, and independent of temperature. Below 150 K, the magnetoresistance increases with decreasing temperature as shown in figure 2(b). The negative MR arises from the spin ordering in grains at low temperature although the magnetization measurement shows no ferromagnetic transition. This is because the long range spin ordering is lacking due to there being no coupling between grains. With decrease of the temperature, the short range ordered spins in grains tend to the orientation of the applied field. The spin ordering in grains reduces the contribution to the resistivity from spin dependent scattering.

For sample B, the behaviour for the temperature dependent MR is similar to that in sample A. An apparent negative MR occurs at about 170 K, which is almost the same as the ferromagnetic transition temperature shown in figure 2(a). It should be pointed out that the negative MR of sample B is larger than that of sample A. This indicates that the large negative MR arises from the spin ordering in the ferromagnetic state, because the grain size of sample B is larger than that of sample A. Therefore, the ferromagnetic region inside grains of sample B is much larger, which leads to a stronger ferromagnetic coupling and long range ordering in grains. But the ferromagnetic coupling is very weak between the grains due to the big amorphous grain boundaries.

The temperature dependence of the MR for sample C is different from those for samples A and B. When sample C enters the ferromagnetic state, an apparent negative MR shows up. With decreasing temperature, the negative MR sharply increases because the spin dependent scattering reduces; this arises from the spin ordering in grains. A shoulder appears with further decreasing temperature, and the increase in negative MR is sharp again at low temperature. For sample C, the annealing temperature is as high as 1000 °C, the grains become much larger and the grain boundaries decrease sharply, so that there is a strong coupling between grains, which leads to a spin ordering in grain boundaries with decreasing temperature. Therefore, the grain boundary scattering caused by spin disordering at grain boundaries reduces remarkably, and the negative MR in sample C is much larger than those of samples A and B.

The contribution of oxygen vacancies to the MR property is complicated. The largest effect appears at an intermediate number of vacancies. The complex behaviour of the MR induced by oxygen deficiency is perhaps the cooperation of local electron spin ordering and scattering effects in a magnetic field [13]. We need more experiments to make this clear.

Figure 3 shows the temperature dependence of the thermopower (TEP) for samples B and C between 50 K and room temperature. As shown in figure 3, the TEP of sample C monotonically decreases with decreasing temperature. This is typical of a metal although the resistivity measurement shows a semiconductor-like behaviour. TEP shows a temperature-linear dependence; a slope change occurs at about 230 K which is the same as the Curie temperature T_c. The slope below T_c is larger than that above T_c; this arises from the reduction of spin disorder scattering. For sample B, the TEP slightly increases with decreasing temperature, while it sharply increases at 160 K from about 10 to 90 μV K^{-1} at 115 K. A similar sharp increase in TEP has been observed in bulk slightly Sr-doped $LaCoO_3$ at high temperatures of 500–600 K [20]. This has been explained as arising from the progressive transformation of intermediate spin Co(iii) to low spin Co(III) in the trivalent cobalt matrix. Since oxidation enhances the covalent mixing between Co e and O 2p orbitals, an increase in Sr content favours transformation of the localized e electrons to extended σ^* electrons, leading to a lowering of temperature corresponding to the sharp increase in TEP. In addition, it should be pointed out that the TEP of $La_{1-x}Sr_xCo_{3-\delta}$ with $x = 0.5$ is negative as reported by Señ arís-Rodríguez and Goodenough [20], while our TEP is positive. In $La_{0.5}Sr_{0.5}Co_{3-\delta}$, the contribution to the TEP comes from the ferromagnetic cluster and the matrix between ferromagnetic domains. The contribution to the TEP from the ferromagnetic clusters is negative, while the contribution from the matrix is positive [19]. For sample A, the small grains are separated by the amorphous matrix; the amorphous matrix is too large to form a long range ferromagnetic ordering. It is very difficult to measure the TEP. There is much less matrix for sample C than for sample B; the TEP shows a metal character. According to the above discussion, the resistivity of sample C is semiconducting behaviour due to the depletion of oxygen, mainly. The resistivity has two parts: one is the contribution from the regions of oxygen deficiency and matrix grain boundary, which is semiconducting; the other arises from ferromagnetic regions (metallic). With decrease of the temperature, the resistivity coming from the former increases dramatically, while the resistivity which comes from metallic part at room temperature is about three times larger than that at low temperatures [20]. Thus, the total resistivity is dominantly affected by the former

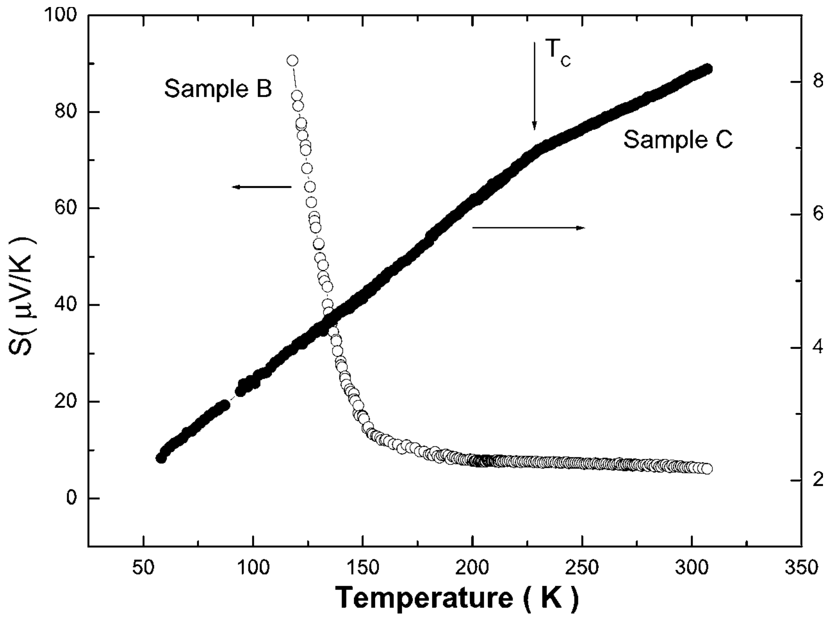

Figure 3. Temperature dependences of the thermopower (TEP) for samples B and C between 50 K and room temperature.

and presents a semiconducting behaviour; whereas, in the measurement of thermopower, the contributions from these two parts have opposite signs [19, 20]. In addition, the effect of the grain boundary on the thermopower is much less than that on the resistivity. This induces a small positive value and metallic character for the thermopower of sample C. In sample B, the contribution to the TEP from the matrix plays an important role, so that the TEP behaviour of sample B is very different from that of sample C.

4. Conclusion

In summary, the effect of annealing on magnetic and transport properties is studied for films annealed at different temperatures. With increasing grain size, the resistivity decreases and T_c increases. These results are explained by the ferromagnetic coupling between grains and spin disorder at grain boundaries. The negative MR depends strongly on the coupling inside grains and between grains. Oxygen deficiency is another factor which affects transport and magnetic properties of films. The samples show quite different TEP behaviours. The TEP of the sample annealed at 1000 °C shows a metallic behaviour, while the contributions from the amorphous and hole-poor matrix to the TEP play a critical role in sample B.

Acknowledgments

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References

[1] Shimakawa Y, Kubo Y and Manako T 1996 *Nature* **379** 53
[2] Ramirez A P, Cava R J and Krajewski J 1997 *Nature* **387** 268
[3] Das S, Chowdhury P, Gundu Rao T K, Das D and Bahadur D 2002 *Solid State Commun.* **121** 691
[4] Tamazyan R, van Smaalen S, Arsenov A and Mukovskii Y 2002 *Phys. Rev.* B **66** 224111
[5] Briceno G, Chang H Y, Sun X D, Schultz P G and Xiang X D 1995 *Science* **270** 273
[6] Itoh M, Natori I, Kubota S and Motoya K 1994 *J. Phys. Soc. Japan* **63** 1486
[7] Madlhukar S, Aggarwal S, Dhote A M, Ramesh R, Kishnan A, Keeble D and Poindexter E 1997 *J. Appl. Phys.* **81** 3543
[8] Yang B, Aggarwal S, Dhote A M, Song T K, Ramesh R and Lee J S 1997 *Appl. Phys. Lett.* **71** 356
[9] Sun J R, Yeung H W, Li H, Zhao K, Chan H N and Wong H K 2001 *J. Appl. Phys.* **90** 2831
[10] Chang H Y, Chen C L, Garrett T, Chen X H, Xiang X D, Chu C W, Zhang Q Y and Dong C 2002 *Appl. Phys. Lett.* **80** 4333
[11] Stemmer S, Jacobson A J, Chen X and Ignatiev A 2001 *J. Appl. Phys.* **90** 3319
[12] Liu J M and Ong C K 1998 *J. Appl. Phys.* **84** 5560
[13] Liu J M and Ong C K 1998 *Appl. Phys. Lett.* **73** 1047
[14] Prokhorov G, Kaminsky G G, Kravchenko I I and Lee Y P 2002 *Physica* B **324** 205
[15] Huang Y-H, Xu Z-G, Yan C-H, Wang Z-M, Zhu T, Liao C-S, Gao S and Xu G-X 2000 *Solid State Commun.* **114** 43
[16] Isaac S P, Mathur N D, Evets J E and Blamire M G 1998 *Appl. Phys. Lett.* **72** 2038
[17] Sanchez R D, Rivas J, Vazquez-Vazquez C, Lopez-Quintela A, Causa M T, Tovar M and Oseroff S 1996 *Appl. Phys. Lett.* **72** 134
[18] Zener C 1951 *Phys. Rev.* **82** 403
[19] Elliott S R 1990 *Physics of Amorphous Materials* 2nd edn (New York: Longman Scientific and Technical, Wiley)
[20] Señ arís-Rodríguez M A and Goodenough J B 1995 *J. Solid State Chem.* **118** 323