Importance of structural tuning in manganites[†]

D BAHADUR* and R A DUNLAP[‡]

Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology, Bombay 400 076, India

[‡]Department of Physics, Dalhousie University, Halifax, Nova Scotia, Canada B3H 3J5

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Abstract. Properties of substituted La-manganites are known to be very sensitive to La site substitution. The critical parameters appear to be (a) the charge and concentration of the substituted ions, which determine the Mn³⁺/Mn⁴⁺ ratio, (b) the average ionic radius at the A site and (c) the tolerance factor, *t*. The latter two parameters determine the distortion and structural tuning of the perovskite structure. Here we report the influence of minor variations in the above parameters on the magnetotransport of compounds around the basic composition La_{0.6}M_{0.07}Ca_{0.33}MnO₃ (M = Er, Yb and Bi). The influence of the method of synthesis on different properties is also discussed. The ionic radii of Er³⁺, Yb³⁺ and Bi³⁺ ions are 1.00, 0.985 and 1.11 Å, respectively, compared to 1.32 Å for La³⁺ and this provides a systematic variation for the investigation of the effects of A site substitution. The zero field resistivity data are essentially similar above the maxima which corresponds, at least approximately, to the Curie temperature as determined by magnetization measurements. However, there are variations below the transition temperature, where there is magnetic ordering, and large variations are often seen in the magnetic data between samples which are very similar in composition. Substantial similarities between field dependent magnetization and resistivity measurements appear to be related to domain wall displacement and rotation. These results will be discussed in the framework of structural tuning which has a strong influence on exchange parameters such as the Mn–O–Mn bond length and angle.

Keywords. Giant magnetoresistance; electronic structure; perovskites; magnetic phase transitions.

1. Introduction

Rare earth–manganese oxide-based perovskites with the substitution of divalent ions at the rare earth site have attracted considerable attention in recent years as a result of their giant magnetoresistance (GMR) behaviour (Hwang *et al* 1995; Jin *et al* 1995; Ju *et al* 1995; Mahendiran *et al* 1995; Mahesh *et al* 1995a; Raveau *et al* 1995). On the basis of a wide variety of studies in these materials, it is known that the details of the GMR effect in ABO₃ based perovskites are quite sensitive to variations in the A site substitution (Mahesh *et al* 1995b; Fontcuberta *et al* 1996; Kumar and Rao 1997). Such substitutions influence the GMR behaviour through their effect on (a) average ionic radius of the A site atoms, (b) the Mn³⁺/Mn⁴⁺ ratio and (c) the tolerance factor. This last factor is defined as (Hwang *et al* 1995)

$$t = \frac{R_A + R_O}{\sqrt{2} (R_B + R_O)}, \quad (1)$$

where *R_i* is the ionic radius of the A, B or O ions. It is generally believed that the GMR effect is optimized

when the Mn³⁺/Mn⁴⁺ ratio is around 7/3. This situation is ideal for the existence of ferromagnetic interactions and metallic behaviour resulting from the double exchange mechanism (Hwang *et al* 1995), where doped charge carriers (e.g. holes) mediate the ferromagnetic interaction between localized spins (Jonker and VanSanten 1950; Zener 1951a,b; Goodenough and Longo 1970). The ferromagnetic Curie temperature is related to the strength of the exchange integral between Mn³⁺ and Mn⁴⁺ ions and this influences the electronic conductivity. In addition to the Mn³⁺/Mn⁴⁺ ratio the GMR behaviour is also known to be very sensitive to the oxygen stoichiometry (Ju *et al* 1995) and recent investigations have also provided evidence that grain boundary effects are an important factor (Ju and Sohn 1997a,b). The partial substitution of La by other rare earth atoms in La–Ca–Mn–O perovskites has yielded some interesting results (e.g. Jin *et al* 1995). In recent work we have undertaken systematic investigations of the effects of A site substitutions on the GMR properties of these compounds. Specifically, we have looked at the effects of substituting Er, Yb and Bi into La–Ca–Mn–O perovskites. Ionic radii of Er³⁺, Yb³⁺ and Bi³⁺ as given by Shannon and Prewitt (1969) are 1.00, 0.985 and 1.11 Å, respectively, as compared to 1.32 Å for La³⁺, and this provides a systematic

*Author for correspondence

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method for the investigation of the effects of both atomic sizes and electronic structure. Here we review the most significant results from these investigations with specific emphasis of the following points: (a) the effects of different substitutions in $\text{La}_{0.6}\text{M}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$ ($\text{M} = \text{Er}, \text{Yb}, \text{Bi}$) and (b) the effects of different Er and Ca compositions and processing methods in $\text{La}_{0.67-x}\text{Er}_{x+y}\text{Ca}_{0.33-y}\text{MnO}_3$.

2. Experimental

Perovskite samples were prepared by either conventional ceramic processing methods or by the sol-gel technique as described in the literature (Bahadur *et al* 1996, 1997). The X-ray diffraction patterns were recorded with a Siemens D-500 X-ray diffractometer using CuK_α radiation. The X-ray diffraction patterns of all samples showed them to be of the single phase cubic perovskite structure and no evidence of any secondary phase was seen in any of the samples. The electrical resistivity and magnetoresistivity were measured as a function of temperature between 4.2 K and 300 K and in applied magnetic fields up to 6 T.

3. Results and discussion

3.1 Er, Yb and Bi substitutions in $\text{La}_{0.6}\text{M}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$

Table 1 gives the measured lattice parameter, average ionic radius at the A site and the tolerance factor, t , for the $\text{La}_{0.6}\text{M}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$ samples. Samples with Er, Yb and Bi substitutions are referred to as *E*, *Y* and *B*, respectively. The lattice parameter is the largest for sample *Y* and goes in the order $Y > E > B$. On the contrary, the ionic radius of Bi^{3+} is the largest and the ionic radii of the 3+ ions have the order $B > E > Y$. The size of Bi^{3+} may vary depending upon the degree of $6s^2$ lone pair character. When the Bi^{3+} ion resides in a high symmetry site its size is smaller than La^{3+} , while for a higher degree of lone pair character, its size is larger than La^{3+} (Zustao and Yufang 1996). Another possible reason for this discrepancy could be variations in the Yb and Bi valence states. It is known that Yb and Bi can also exist in 2+ and 5+ states, respectively, with ionic radii of 1.14 and 0.85 Å.

Figure 1 shows the zero field resistivity as a function of temperature for these three samples. All three sets of data exhibit a maxima above which semiconductor-like behaviour is observed, while below this temperature, a positive $\partial\rho/\partial T$ is seen. This transition temperature is given in table 1 and is in good agreement with the magnetic ordering temperature obtained by magnetic methods for these materials (Bahadur *et al* 1997). Sample *B* exhibits the highest transition temperature at around 260 K. Compared to the behaviour of the other samples studied here, the transition in sample *B* is also remarkably sharp. The transition temperatures for samples *E* and *Y* and their behaviour above the transition temperature are essentially similar. The resistivity as a function of temperature for sample *Y* in different applied fields up to 5.0 T is illustrated in figure 2. This shows a shift in the maxima to higher temperatures as the field increases indicating a spin dependent mechanism responsible for these effects. This behaviour is consistent with that typically seen in related GMR perovskites (Ju and Sohn 1997b). The magnetoresistivity ratio (MR) is defined to be

$$\text{MR} = \frac{\rho(B = 5 \text{ T}) - \rho(B = 0)}{\rho(B = 0)}, \quad (2)$$

where $\rho(B = 5 \text{ T})$ is the resistivity in an applied field of 5.0 T and is given in table 1. The table also gives resistivity values measured at 4.2 K. While the MR for sample *Y* is around 85%, sample *B* shows a MR of only about 35%. It is of relevance to point out that sample *B* exhibits a resistivity (at 4.2 K) which is at least one order of magnitude smaller than in samples *E* and *Y*.

The close association between the electron transport data and the magnetic properties of these materials indicates that magnetic spins and their interaction play a crucial role in determining the magnetotransport behaviour. This spin dependent mechanism is a function of the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio and the strength of the Mn–Mn exchange interaction, which proceeds via the oxygen 2p electrons. This interaction depends upon the lattice distortion, which in turn is very sensitive to substitutions at the lanthanide site (Hwang *et al* 1995; Raveau *et al* 1995). Antiferromagnetic coupling between Mn^{3+} ions in

Table 1. Measured lattice parameters, a , of the elementary perovskite cell, average ionic radii of the A site atoms, $\langle r_A \rangle$, and calculated tolerance factors, t , of $\text{La}_{0.6}\text{M}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$ samples with Er, Yb and Bi substitutions. Also given is the magnetoresistivity ratio, MR, defined in the text, the transition temperature, T_c , given by the peak in the resistivity and the resistivity at 4.2 K.

Sample	a (Å)	r_A (Å)	t	MR(4.2 K)	T_c (K)	$\rho_{4.2\text{K}}$ ($\Omega\text{-cm}$)
<i>E</i>	3.8504	1.1356	0.9480	0.84	185	2.4×10^{-2}
<i>Y</i>	3.8526	1.1342	0.9474	0.82	185	3.5×10^{-3}
<i>B</i>	3.8415	1.1433	0.9518	0.35	260	7.6×10^{-4}

the parent LaMnO_3 compound is modified in compounds with *A* site substitutions to a layered spin structure with antiferromagnetic coupling between adjacent layers and ferromagnetic order within layers (Yoshizawa *et al* 1995). Therefore, in these systems there is a competition between double exchange ferromagnetism and superexchange antiferromagnetism which may result in a canted antiferromagnetic structure (Yoshizawa *et al* 1995; von Helmolt *et al* 1994).

The strength of the ferromagnetic and antiferromagnetic interactions is determined by the overlap of the *d* orbitals directly or indirectly through the oxygen *p* orbital and this is very sensitive to interatomic distances and bond angles (Goodenough and Longo 1970). Therefore, very small lattice distortions or changes in the lattice parameter can give rise to combinations of magnetic sublattices

determined by different Mn–Mn distances and different Mn–O–Mn bond angles. There have been several reports in the literature where the coexistence of antiferromagnetic and ferromagnetic lattices in these materials has been demonstrated through neutron diffraction and other techniques (Radelli *et al* 1995; Yoshizawa *et al* 1995). The magnetic properties of sample *Y* has been attributed to such mixed magnetic behaviour (Bahadur *et al* 1997). The sharp transition seen in both the zero field resistivity and the magnetization data for sample *B* may be attributed to the existence of only ferromagnetic interactions in this system. In the perovskite lattice, the substitution of a small quantity of atoms with a different ionic radius at the lanthanide site influences the Mn–O–Mn angles much more than the Mn–O–Mn distances in the MnO_6 octahedra and such subtle changes are known to substantially affect the magnetic and electronic properties through the modifications of the exchange coupling (Torrance *et al* 1992; Fontcuberta *et al* 1996). When the Mn–O–Mn distances are larger than about 3.8 Å and the distortion of the lattice is minimal, only ferromagnetic order can exist. However, when there is some distortion in the lattice, some of these Mn–O–Mn bond angles may deviate considerably from 180° giving rise to a (canted) antiferromagnetic interaction. This canted antiferromagnetism can, in some cases, be driven to ferromagnetism through the spin flip mechanism by (for example) the application of a magnetic field.

Sample *E* exhibits the maximum MR ratio of 84% whereas sample *B* exhibits the minimum MR. On the other hand, the transition temperature for sample *B* is maximum. The following comments can be made concerning this behaviour. It is known that spin dependent scattering is the physical origin of the GMR effect. The MR ratio and the temperature where the maximum GMR

Figure 1. Zero field resistivity as a function of temperature for samples (a) *E*, (b) *Y* and (c) *B*.

Figure 2. Resistivity as a function of temperature for different field values for the sample *Y*. Curves with decreasing peak height correspond to applied fields of 0, 0.5, 1.0, 2.0 and 5.0 T, respectively.

effect is observed are controlled by the distortion or bending of the Mn–O–Mn bond through modifications of the exchange coupling (Torrance *et al* 1992; Fontcuberta *et al* 1996). This in turn will have a strong influence on the magnetic interactions. GMR effects in multilayers and heterogeneous alloys have been ascribed to spin dependent scattering near the interface between the ferromagnetic and nonmagnetic phases (Baibich *et al* 1988; von Helmolt *et al* 1994). In the manganese based perovskites this effect could be due to scattering at the interfaces between antiferromagnetic and ferromagnetic domains and the MR ratio may depend on the concentration of such interfaces. Another significant result for sample *B* is its unusually high transition temperature. The ferromagnetic to paramagnetic transition strongly depends upon the strength of the magnetic interaction $\text{Mn}^{3+}\text{--O}^{2-}\text{--Mn}^{4+}$ and hence on Mn–O–Mn distance and bond angle. The Mn–O–Mn distance and angle in these perovskite structure is a strong function of the tolerance factor. As the tolerance factor decreases the structure becomes more distorted and the MnO_6 octahedra tilt and rotate in order to fill the available space around the rare earth ion resulting in a smaller Mn–O–Mn bond angle (Torrance *et al* 1992). Among the three samples given in table 1, sample *B* has the highest tolerance factor. Therefore, the Mn–O–Mn bond angle has the smallest deviation from 180° and this supports the assumption of enhanced magnetic interactions.

3.2 Stoichiometry and processing effects in $\text{La}_{0.67-x}\text{Er}_{x+y}\text{Ca}_{0.33-y}\text{MnO}_3$

The lattice parameter, the average ionic radius of the A site ions, the tolerance factor and resistivity values of the $\text{La}_{0.67-x}\text{Er}_{x+y}\text{Ca}_{0.33-y}\text{MnO}_3$ samples are given in table 2. Samples are referred to by number as indicated in the table. Figure 3 shows the zero field resistivity as a function of temperature for these four samples. While samples 1, 2 and 3 show generally similar results, sample 4 shows a substantially higher transition temperature and a much greater resistivity peak at the transition.

A comparison of the results from samples 1 and 2 is

informative in understanding the effects of sample preparation technique on the resulting sample property. A comparison of the results from samples 2, 3 and 4 allows for an assessment of the influence of composition. In these samples, either the calcium content or the oxygen stoichiometry would decide the ratio of Mn^{3+} to Mn^{4+} . It is assumed that the oxygen stoichiometry is same for all ceramic samples as they have been synthesized under identical conditions. It is well known that the metallic and ferromagnetic behaviour result from double exchange interactions between Mn^{3+} and Mn^{4+} ions in these oxides. Therefore, this ratio is critical in determining properties such as the Curie temperature. From the zero field resistivity data as shown in figure 3, it appears that the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio is more influential than the other parameters tested here in determining sample properties. Most of the features as discussed above are different for sample 4 where the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio has been changed by a small amount.

A measure of the resistivity as a function of applied magnetic field provides additional insight into the behaviour of these materials. Figure 4 shows typical experimental results. It is interesting to note that this plot shows two distinct regions corresponding to the two distinct regions in the magnetization versus field behaviour. Up to about 0.5 T the magnetoresistance drops sharply and above this field value, the slope is much smaller. These effects seem to be related to the movement and rotation of the domain walls consisting of Mn^{3+} and Mn^{4+} spins coupled through the double exchange mechanism (Ju *et al* 1995; von Helmolt *et al* 1995; Xiong *et al* 1995). We suggest the following explanation for this behaviour based on the movement and rotation of the domain walls. When the applied field is low, there are a large number of domains and hence a large density of domain walls. Within the domain walls, spins are not parallel but change direction slowly with respect to adjacent domains so as to minimize the sum of the exchange and anisotropy energies. In these regions, electron transfer between Mn^{3+} and Mn^{4+} does not occur as readily as it does within the domain wall itself. This results in a higher resistivity in the low field region where the domain wall density is large. As the applied

Table 2. Properties of the $\text{La}_{0.67-x}\text{Er}_{x+y}\text{Ca}_{0.33-y}\text{MnO}_3$ perovskite samples; lattice parameter, average ionic radius at the A site, tolerance factor and resistivity, ρ at 5 K and 300 K. *g* in parentheses indicates that the sample was made by the citrate gel process, all other samples have been made by the ceramic route.

Sample	Composition	a (Å)	R_A (Å)	t	$\rho_{5\text{ K}}$ ($\Omega\cdot\text{cm}$)	$\rho_{300\text{ K}}$ ($\Omega\cdot\text{cm}$)
1	$\text{La}_{0.6}\text{Er}_{0.07}\text{Ca}_{0.33}\text{MnO}_3(g)$	3.858	1.136	0.9399	0.045	0.13
2	$\text{La}_{0.6}\text{Er}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$	3.850	1.136	0.9399	0.024	0.09
3	$\text{La}_{0.57}\text{Er}_{0.1}\text{Ca}_{0.33}\text{MnO}_3$	3.858	1.129	0.9382	0.02	0.11
4	$\text{La}_{0.57}\text{Er}_{0.13}\text{Ca}_{0.30}\text{MnO}_3$	3.862	1.126	0.934	1.39	0.13

field is increased, the number of domain walls is reduced significantly resulting in a rapid drop in resistivity. The field where the slope of the magnetoresistance changes corresponds to the near saturation field in the magnetization curves. Here the sample consists, primarily of a single domain and subsequent changes in magnetization occur principally as a result of domain rotation and changes in the spin canting angle within the domain. This results in much smaller changes in the magnetoresistance as seen in figure 4.

Typical resistivity data in fields up to 5 T as a function of temperature are illustrated in figure 5. The magnetoresistance ratio, MR, as defined above varies between 73 and 98% for these samples. The maximum change is observed for sample 4; about 98% in an applied field of 5 T. This is comparable to that reported by Jin *et al* (1995) in $\text{La}_{0.6}\text{Y}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$ where a maximum change of 99% in an applied field of 5 T was observed. These plots exhibit a shift in the maxima to higher temperatures as the field increases. This feature has been reported for several other systems (Yoshizawa *et al* 1995; Ju and Sohn 1997b) and appears to be characteristic of materials exhibiting GMR effects. The fact that the transition is field dependent and lies close to the ferromagnetic transition temperature indicates that the spin dependent mechanism is responsible for these effects. This spin dependent mechanism which results from the $\text{Mn}^{3+}\text{--O}^{2-}\text{--Mn}^{4+}$ interaction is a strong function of the distortion of the lattice, if the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio remains constant. This is also reflected in the studies of Hwang *et al* (1995) and Jia *et al* (1995), where they have introduced lattice distortion by the substitution of smaller ions at the A sites. Interestingly this affects the transition tem-

perature and the change in the magnitude of the resistivity in much the same way as the application of a magnetic field. An important parameter for the measurement of lattice distortion in this family of perovskites is the tolerance factor. For $t \approx 1$ a cubic structure results giving a Mn–O–Mn bond angle, θ , close to 180° . However, the factor, t , is generally less than unity resulting in a deviation of this angle from 180° . Experimental evidence shows that the Curie temperature is proportional to the angle, θ (Torrance *et al* 1992; Hwang *et al* 1995). In

Figure 4. Normalized resistivity as a function of applied magnetic field at 5 K for (a) sample 1 and (b) sample 2.

Figure 3. Zero field resistivity as a function of temperature for the samples identified in table 1; (a) sample 1, (b) sample 2, (c) sample 3 and (d) sample 4.

Figure 5. Resistivity as a function of temperature for different field values for sample 4. Decreasing values of the peak resistivity correspond to the field values of 0, 0.5, 1.0, 2.0, 3.0 and 4.0 T.

RNiO_3 type compounds (R = rare earth), Torrance *et al* (1992) have shown that as the tolerance factor and/or temperature increases, the bandwidth increases and the compounds become more metallic. The magnetic ordering temperature also simultaneously increases and this is accompanied by slight reduction in unit cell volume. These authors have shown that as the average rare earth ion size at the A site decreases (i.e. as the tolerance factor decreases), the ABO_3 structure becomes more distorted and the BO_6 octahedra tilt and rotate in order to fill the space otherwise present around the rare earth ion giving a lower $B\text{--}O\text{--}B$ angle. A substantial effect of temperature on the $B\text{--}O\text{--}B$ angle has also been reported by Torrance *et al* (1992). Other reports have also emphasized the importance of the interpolated cation and the tolerance factor in relation to the GMR effect in these manganites (Caignaert *et al* 1995; Mahesh *et al* 1995b; Raveau *et al* 1995; Kumar and Rao 1997). The applied magnetic field is known to bring about a change in the canting angle or even induce a structural phase transition in these manganites (Asamitsu *et al* 1995). Both the $B\text{--}O\text{--}B$ bond angle and spin canting angle could be responsible for the spin dependent mechanism. Hence, compositional variations and applied magnetic fields may have similar effects on the resistivity.

4. Conclusions

In the work described above we have shown that the substitution of trivalent ions into $\text{La}\text{--}\text{Ca}\text{--}\text{Mn}\text{--}\text{O}$ perovskites has substantial and systematic effects on their magnetotransport properties. Specifically it has been shown that the important parameters are (a) the charge and concentration of the substituted ions, which determine the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio, (b) the average ionic radius at the A site and (c) the tolerance factor, t . The structure of the material may be tuned by appropriately choosing the size and concentration of the substituted ions. As the average A site atomic radius and the tolerance factor vary in a predictable way as a function of the properties of the substituted ions, magnetoresistive behaviour may also be varied in a controlled manner. It has been shown that the magnetoresistive properties are closely related to the measured magnetic properties of the materials. A consideration of the effects of substitutions on the $\text{Mn}\text{--}\text{O}\text{--}\text{Mn}$ bond angle can give a consistent picture of the behaviour of these perovskites.

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References

- Asamitsu A, Moritomo Y, Tomioka Y, Arima T and Tokura Y 1995 *Nature* **373** 407
- Bahadur D, Yewondwossen M, Koziol Z, Foldeaki M and Dunlap R A 1996 *J. Phys. Condens. Matter* **8** 5235
- Bahadur D, Foldeaki M, Mandal S K, Yewondwossen M H, Koziol Z and Dunlap R A 1997 *J. Alloys and Compounds* **256** 76
- Baibich M N *et al* 1988 *Phys. Rev. Lett.* **61** 2472
- Caignaert V, Maignan A and Raveau B 1995 *Solid State Commun.* **95** 357
- Coe J M D, Viret M, Ranno L and Ounadjela K 1995 *Phys. Rev. Lett.* **75** 3910
- Fontcuberta J, Martinez B, Seffar A, Pinol S, Garcia-Munoz J L and Obradors X 1996 *Phys. Rev. Lett.* **76** 1122
- Goodenough J B and Longo J M 1970 *Landolt-Börnstein Tabellen* (Berlin: Springer Verlag) V. III/4a
- Hwang H Y, Cheong S W, Radaelli P G, Marezio M and Batlogg B 1995 *Phys. Rev. Lett.* **75** 914
- Jia Y X, Lu L, Khazeni K, Yen D, Lee C S and Zettl A 1995 *Solid State Commun.* **94** 917
- Jin S, O'Bryan H M, Tiefel T H, McCormack M and Rhodes W W 1995 *Appl. Phys. Lett.* **66** 382
- Jonker G H and VanSanten J H 1950 *Physica (Utrecht)* **16** 337
- Ju H L and Sohn H 1997a *J. Magn. Magn. Mater.* **167** 200
- Ju H L and Sohn H 1997b *Solid State Commun.* **102** 463
- Ju H L, Gopalakrishnan J, Peng J L, Li Q, Xiong G C, Venkatesan T and Greene R L 1995 *Phys. Rev.* **B51** 6143
- Kumar N and Rao C N R 1997 *J. Solid State Chem.* **129** 363
- Mahendiran R, Mahesh R, Raychaudhuri A K and Rao C N R 1995 *J. Phys. D: Appl. Phys.* **28** 1743
- Mahesh R, Mahendiran R, Raychaudhuri A K and Rao C N R 1995a *J. Solid State Chem.* **114** 297
- Mahesh R, Mahendiran R, Raychaudhuri A K and Rao C N R 1995b *J. Solid State Chem.* **120** 204
- Radaelli P G, Cox D E, Marezio M, Cheong S W, Schiffer P E and Ramirez A P 1995 *Phys. Rev. Lett.* **75** 4488
- Raveau B, Maignan A and Caignaert V 1995 *J. Solid State Chem.* **117** 424
- Shannon R D and Prewitt C T 1969 *Acta Crystallogr.* **B25** 925
- Torrance J B, Lacorre P, Nazzari A I, Ansaldo E J and Niedermayer Ch 1992 *Phys. Rev.* **B45** 8209
- von Helmolt R, Wecker J, Somwer K, Haupt L and Bärner K 1994 *J. Appl. Phys.* **76** 6925
- von Helmolt R, Wecker J, Lorenz T and Somwer K 1995 *Appl. Phys. Lett.* **67** 2093
- Xiong G C, Li Q, Ju H L, Baghat S M, Lofland S E, Greene R L and Venkatesan T 1995 *Appl. Phys. Lett.* **67** 3031
- Yoshizawa H, Kawano H, Tomioka Y and Tokura Y 1995 *Phys. Rev.* **B52** 13147
- Zener C 1951a *Phys. Rev.* **81** 440
- Zener C 1951b *Phys. Rev.* **82** 403
- Zustao Z and Yufang R 1996 *J. Solid State Chem.* **121** 138