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Martensite-like phase transformation and shape memory effect in orthomanganites

I.O. Troyanchuk, A.I. Akimov, L.A. Bliznjuk, N.V. Kasper

Institute of Physics of Solids and Semiconductors, Belorussian Academy of Sciences, P. Brovka str., 17, 220072, Minsk, Belarus

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Abstract

$RMnO_{3+x}$ (R is a rare earth ion) orthomanganites were examined in the temperature range 20–1500 °C by dilatometry and by differential thermal analysis and thermogravimetry. These compounds show first-order transitions to their orbital-disordered structures at 500–1100 °C. It was found that a uniaxial mechanical load changes the transition character. The behavior of the $\Delta l/l$ curves was quite different on heating and on cooling. Both jumps and smooth anomalies of the $\Delta l/l(T)$ dependences were observed on cooling. The temperatures and values of these pecularities coincide on repeated measurements. The results obtained are interpreted by considering the role of the thermoelastic character of the orbital order–disorder transition and oxidative non-stoichiometry in $RMnO_{3+x}$.

Keywords: Rare earth orthomanganites; First order phase transition; Shape memory effect

1. Introduction

The properties of the systems $A_{1-x}Ca_xMnO_3$ ($A \equiv$ La, Pr, Nd) have been studied by many investigators since van Santen and Jonker [1] showed that these compounds become ferromagnetic at $x \geq 0.15$. Structural (first-order) phase transitions were observed in $PrMnO_3$ at 810 K and in $NdMnO_3$ at 900 K [2,3]. These transitions were supposed to be caused by the d_{z^2}-orbital ordering of the Mn ions. However, the orthomanganites of Sm, Eu and heavy rare-earth ions have not been sufficiently studied. There are no literature data on structural phase transformations in these compounds. So we investigated the rare-earth orthomanganites by dilatometry and by differential thermal analysis and thermogravimetry (DTA-TG).

2. Experiment

The $RMnO_{3+x}$ samples (R ≡ Nd, Sm, Eu, Gd, Tb, Dy) were prepared by a standard ceramic method. R_2O_3 and Mn_2O_3 oxides of high purity were mixed in stoichiometric ratios and presintered at 900 °C for 2 h in air. The mixture was then pressed into pellets which were sintered at 1400 °C for 2 h in air and cooled in the furnace to room temperature at a rate of 200 °C^{-1} h. The X-ray diffractograms were recorded with a DRON-3M difractometer, using Fe Kα radiation. All the samples were single phase perovskites. The orthorhombic unit cell parameters of the samples were in agreement with the values obtained in Ref. [4]. The porosity was below 7%. The thermal expansion was measured with an inductance dilatometer (model D1-24 ADAMEL LHOMARGY). Samples at least 12 mm long and 7 mm in diameter were used. The initial load on the sample was as a rule 0.1 N. The heating and cooling rates were 2 °C min^{-1}. The DTA-TG study was performed in air at heating and cooling rates of 10 °C min^{-1} with a PC 92 SETARAM derivatograph. The reliability of the dilatometer and derivatograph and derivatograph data was checked by measurements of Al_2O_3, SiO_2, ZrO_2 and CaC_2O_4 specimens with standard $\Delta l/l$ and DTA curves, and by repeating the results many times.

3. Results

The thermal expansion of $DyMnO_{3+x}$ was first measured on heating to $T_{max} = 1390$ °C, exposure for 2 h and cooling (Fig. 1(a)). Anomalous behavior has

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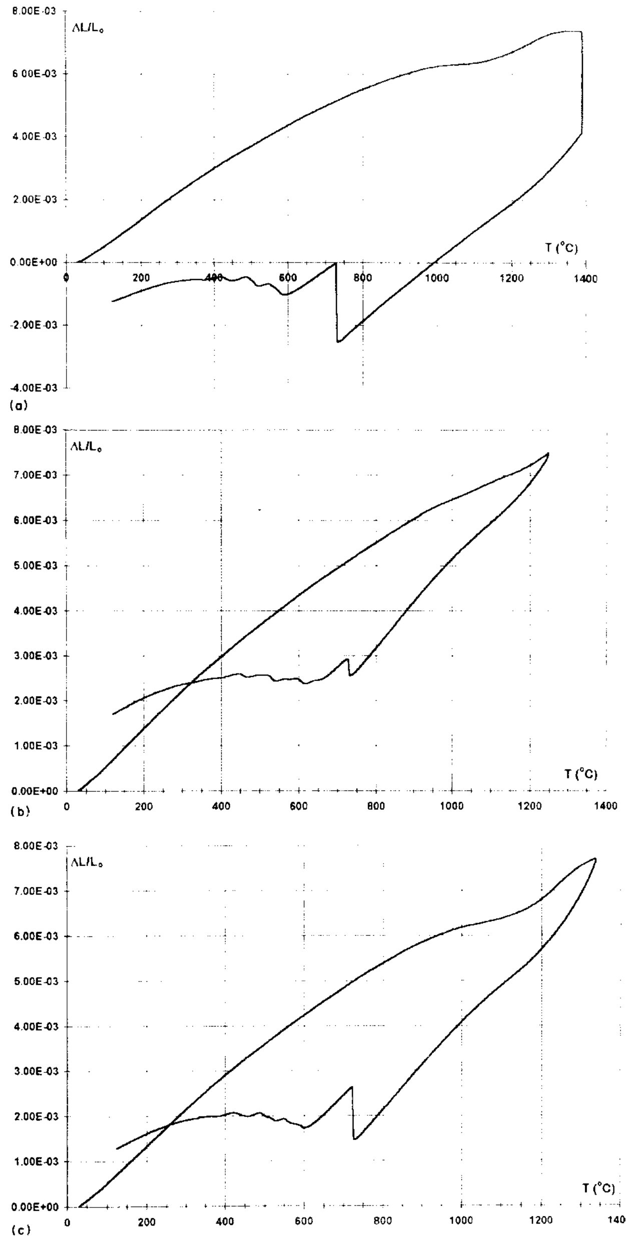

Fig. 1. $\Delta l/l(T)$ curves for DyMnO$_{3+x}$: (a) exposure at T_{max} for 2 h, T_{max} = 1390 °C, (b) T_{max} = 1220 °C, (c) T_{max} = 1340 °C.

been observed on heating at 1000 °C. This was caused apparently by the phase transformation into the orbitally disordered phase. On cooling an abrupt jump at T_r = 730 °C and three $\Delta l/l$ maxima at lower temperatures were found. The measurement were repeated seven times in this regime. Good reproducibility of the results was found. Further measurements were performed on heating to 1000, 1100, 1150, 1220, 1300, 1340, 1390, 1450 and 1500 °C as well as on cooling. In the first case the cooling curve was quite the same as the curve obtained on heating to 1000 °C. In the case of heating to 1220 °C the behavior of the heating and cooling curves was different. A small jump at T_r = 730 °C and three smooth anomalies were observed on cooling (Fig. 1(b)). The values of these anomalies increase with increasing temperature up to 1340 °C (Fig. 1(b)) and change slightly up to cooling from 1450 °C. Exposure of the samples to the maximal temperature (T_{max} < 1400 °C) does not affect the anomalies on cooling, but after heating up to 1500 °C the shape of the curves on cooling changes significantly.

The behavior of the $\Delta l/l$ curve on cooling tends to recover the shape change of the sample during the phase transition on heating. The sample deformation apparently can be recovered both smoothly and by jumps (Fig. 2(a),(b)). The sample deformation at high temperatures (T_{max} > 1300 °C) is irreversible.

The length changes of the sample caused by phase transformations are especially large for measurements performed on SmMnO$_{3+x}$ or EuMnO$_{3+x}$ samples on annealing at 1450–1500 °C (Fig. 3). The length changes on heating are always smooth while the length changes on cooling can take place by jumps (Fig. 3).

The DTA study of the RMnO$_{3+x}$ (R ≡ Nd to Dy) samples did not reveal abrupt anomalies on cooling from 1200–1400 °C to 600 °C. The difference between the DTA and dilatometric data might be caused by sample loading during the dilatometric measurements.

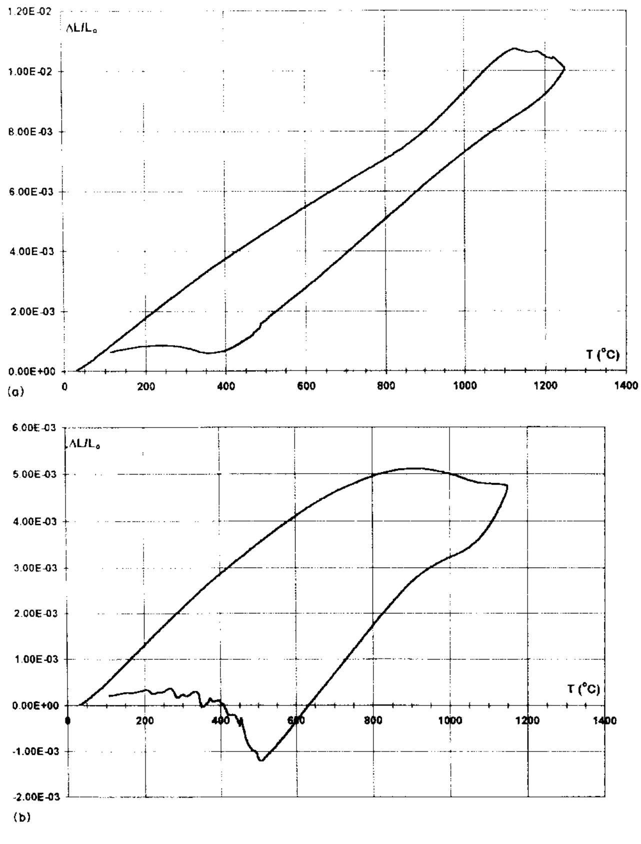

Fig. 2. $\Delta l/l(T)$ curves for GdMnO$_{3+x}$, (a) T_{max} = 1250 °C) and EuMnO$_{3+x}$, (b) T_{max} = 1150 °C.

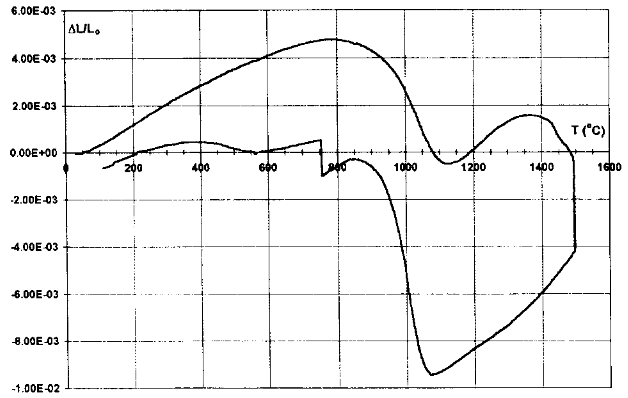

Fig. 3. $\Delta l/l(T)$ curves for $EuMnO_{3+x}$, $T_{max} = 1500\,°C$, exposure at T_{max} for 1 h.

The sample mass change can reach 0.3% on heating as was found by the TG investigation. Such a value should correspond to a change in oxygen concentration of more than 1.5%. Non-stoichiometry shows a trend towards lower values with decreasing size of the R cation.

4. Discussion

We believe that the phase transition of the first type is caused by orbital ordering which takes place in orthomanganites on heating. Such a transition was observed in $PrMnO_3$ by X-ray analysis [2]. It was found in Ref. [2] that both orbitally ordered and disordered phases could coexist in the wide temperature interval. This transformation also occurs in $RMnO_{3+x}$ ($R \equiv Sm$ to Dy), however, at higher temperatures (Figs. 1–3). The transformation hysteresis is not large (Fig. 3). It is characteristic of thermoelastic martensitic transformations in which a shape memory effect occurs [5]. The orthorhombic symmetry does not change during the transformation, as was shown in Ref. [2]. However, the unit cell volume changes significantly. So one can presume that twinning processes take place in the transformation temperature interval. The pecularity of the thermoelastic phase transition in orthomanganites is that it occurs under conditions of intensive chemical interaction with oxygen.

The results obtained can be interpreted on the basis of the following suppositions.

1. At the transition from the orbitally ordered phase to the paraphase the sample adopts a superplastic state. In such a state the load on the dilatometer is sufficient to produce deformation by twinning.

2. Interaction with oxygen leads to partially reversible changes in the system of defects.

3. Strong homogeneous internal stresses as well as strong inhomogeneous stresses (of first and second type respectively) occur in the sample on cooling. These stresses relax by way of stress-induced reorientation (switching) of the crystal domain structure.

Shape recovery can take place either smoothly (Fig. 2(a)) or by stochastic jumps (Fig. 2(b)) or by cooperative reconstruction of the domain structure (Fig. 3) depending on the character of the internal stress. Sometimes there is a mixture of different variants (Fig. 1). The temperature T_r at which shape recovery takes place does not coincide with that of the beginning of the phase transformation. The T_r value depends, apparently, on the changes in the defect system caused by the interaction with oxygen. T_r as a rule, increases with increasing temperature T_{max} of the dilatometric measurements and remains the same on further decreasing T_{max}.

Ferroelastic materials are usually characterized by a high value of coercive field σ_c (the stress necessary to switch the domain structure). In the case of $Pb_3(PO_4)_2$ one has $\sigma_c = 150\,N\,cm^{-2}$. This parameter is probably small in the case of $RMnO_{3+x}$.

For $LaMnO_{3+x}$ we did not observe the shape memory effect in the dilatometric study. This is apparently due to intensive interaction with oxygen during the measurement cycle.

It is possible that the mechanism of the burst-like recovery of the shape strain in $RMnO_{3+x}$ is similar to the burst-like transition in the ZrO_2–CeO_2 system [5].

Acknowledgement

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