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Dilatometric determination of phase transition temperatures and oxidation temperatures on the compounds $SrMnO_{3-y}$ and $Sr_2MnO_{4-y'}$

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Abstract

Dilatometric measurements were used to determine phase transition temperatures and oxidation temperatures of $Sr_2MnO_{4-y'}$ and several phases in the system $SrMnO_{3-y}$. The use of dilatometry is based on differences among the molar volumina of the various phases determined by XRD. Oxidation of $SrMnO_{3-y}$ and $Sr_2MnO_{4-y'}$ proceeds without change in the basic structure of perovskite and K_2NiF_4 type, respectively. Anion vacancies produce lattice expansion in reduced $Sr_2MnO_{4-y'}$ and $SrMnO_{3-y}$ compared with $Sr_2MnO_{4.00}$ and β-$SrMnO_{3.00}$. In the case of $SrMnO_{2.58}$, the ratio of lattice constants indicates narrow structural relations to β-$SrMnO_3$.

Keywords: Dilatometry; Phase transition temperature; Strontium manganate

1. Introduction

The system $SrMnO_{3-y}$ was investigated extensively by Negas and Roth [1] by gravimetric determination of oxygen content and XRD on quenched samples. They obtained hexagonal α-$SrMnO_{3-y}$ below 1400°C, cubic β-$SrMnO_{2.74-2.62}$ between 1400 and 1740°C (melting point) in air, and orthorhombic $SrMnO_{2.56}$ in vacuum at high temperatures.

The hexagonal α-modification is the stable phase up to 1400°C in air, but oxygen loss starts above 1035°C [1]. The structure was determined by Kuroda et al. [2]. The

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"hexagonal perovskite" α-$SrMnO_3$ has the layer sequence abac (chch) with a ratio of 1:1 of cubic:hexagonal packed layers. β-$SrMnO_{3-y}$ crystallises in the perovskite structure [3] with the layer sequence abc (ccc). The β-modification is metastable below 1400°C in air. At higher temperatures, the compound exists with a remarkable concentration of anion vacancies corresponding to the formula $SrMnO_{2.62-2.74}$.

The structure of $SrMnO_{3-y}$ formed at high temperatures [1] and at low oxygen partial pressure has not been clearly described. Mizutani et al. [4] obtained orthorhombic $SrMnO_{2.5}$ at 1500°C in a nitrogen atmosphere, but the lattice constants are not identical with the results of Negas and Roth [1]. Caignaert et al. [5] described another orthorhombic phase $SrMnO_{2.5}$ investigated by neutron diffraction. This compound prepared by reduction with hydrogen at 500°C crystallises in brownmillerite structure (Ca_2AlFeO_5) with high ordered vacancies. It cannot be excluded that the arrangement of the oxygen vacancies depends on the preparation route.

Sr_2MnO_4 was also investigated by Mizutani et al. [4]. They found a low- and a high-temperature modification. Bouloux et al. [6] described the same polymorphism. The high-temperature phase crystallises in K_2NiF_4 type but the structure of the low-temperature phase was not solved. However, Kriegel et al. [7] have shown that the low-temperature "α-modification" consists of a mixture of SrO and the compound $Sr_7Mn_4O_{15}$. The "phase transition" is actually the reversible reaction

$$SrO + Sr_7Mn_4O_{15} \rightleftharpoons 2Sr_2MnO_4$$

Kriegel et al. [8] also reported for the first time on $Sr_2MnO_{3.84}$ which crystallises in the K_2NiF_4 structure with anion vacancies.

XRD measurements have shown differences among the molar volumina of several compounds in the system Sr–Mn–O, dependent on the structure and oxygen content. In fact, phase transitions and oxidation by thermal treatment of dense samples produce significant expansions or contractions. In order to complete the knowledge of the phase transitions in the Sr–Mn–O system, dilatometry was used as a dynamic method making use of different molar volumina of the various modifications determined by XRD.

2. Experimental

2.1. Preparation

$SrCO_3$ and $MnCO_3 \cdot xH_2O$ (reagent grade, Merck) were used as starting materials. Element contents were determined by drying $SrCO_3$ at 500°C and by conversion of $MnCO_3$ into Mn_3O_4 at 1050°C in air, respectively. The mixtures of $SrCO_3$ and $MnCO_3$ (molar ratio 1:1 and 2:1) were ground in an agate vibration mill and calcined at 1000°C for 12 h in air. The black powders were ground again, compressed (90 MPa) to cylinders and calcined at 1200°C for 12 h in air. The procedure was repeated once more (this time with 250 MPa) and the samples were sintered in air ($SrMnO_{3-y}$ only) and then in a flow of purified argon ($10\,l\,h^{-1}$) at 1500°C for 3 h. Dense bodies of composition $SrMnO_{2.58}$ with 92% ($Sr_2MnO_{3.71}$ with 82%) of the theoretical density were obtained after cooling down at approx. 10 K min^{-1} to 100°C.

In agreement with the results of Negas and Roth [1], metastable β-$SrMnO_{3.00}$ was prepared by thermal treatment of $SrMnO_{2.58}$ at 400°C in air for 60 min. Several samples of β-$SrMnO_{3.00}$ were converted to α-$SrMnO_3$ (8 h, 1000°C), in contrast to the former process without mass gain. $Sr_2MnO_{4.00}$ was formed by oxidation of $Sr_2MnO_{3.71}$ at 400°C in air for 60 min. Oxygen content and purity of the produced compounds were determined by chemical analysis and XRD.

2.2. *Chemical analysis*

Oxygen contents of the compounds were determined by chemical analysis. Samples were dissolved in dilute perchloric acid containing a definite concentration of $VO(ClO_4)_2$ and titrated with 0.1 *n* $KMnO_4$ solution. The procedure has been described earlier in detail [9]. Oxidation of $SrMnO_{2.58}$ and $Sr_2MnO_{3.71}$ at 400°C forms phases with ideal oxygen content ($SrMnO_{3.00}$; $Sr_2MnO_{4.00}$). Therefore, the mass gain by oxidation was used to calculate the oxygen content of the samples in the reduced state. Comparison of the methods shows a very good agreement. Deviations were observed in the last numerical position of the formula $SrMnO_{3.00(0)}$.

2.3. *XRD measurements*

The several phases were characterised with X-ray powder diffraction (diffractometer HZG4 Freiburg and Guinier system 629). Lattice constants were obtained from Guinier photos with Cu $K\alpha_1$ ($\lambda = 154.056$ pm) and germanium standard ($a = 543.061$ pm). Intensities were computed with the program LAZY PULVERIX [10]. Atomic positions for α-$SrMnO_3$, β-$SrMnO_3$, Sr_2MnO_{4-y}, and Sr_2MnO_4 were taken from Refs. [2, 3, 8]. Deviations between calculated intensities and experimental values were lower than 5%.

Table 1 gives a summary of the X-ray diffraction results and attracts attention to the differences between the molar volumina of the various compounds. The most dense

Table 1
Summary of X-ray powder diffraction results

Phases	α-$SrMnO_3$	β-$SrMnO_3$	$SrMnO_{2.58}$	$Sr_2MnO_{3.72}$	Sr_2MnO_4
Crystal system	Hexagonal	Cubic	Orthorhombic	Tetragonal	Tetragonal
Space group	$P6_3/mmc$	$Pm\bar{3}m$		I4/mmm	I4/mmm
Formel units	4	1	4	2	2
a/pm	544.37(2)	380.37(2)	551.68(11)	380.67(3)	379.07(3)
b/pm	–	–	1076.50(16)	–	
c/pm	906.85(13)	–	380.91(59)	1254.03(11)	1249.44(11)
$V_{EZ}/(10^6\ pm^3)$	232.73	55.03	226.22	181.72	179.54
$V_{mol}/(cm^3\ mol^{-1})$	35.04	33.14	34.06	54.72	54.06

modification in the system $SrMnO_{3-y}$ is metastable β-$SrMnO_3$, whereas α-$SrMnO_3$ has a molar volume that is 5.8% larger. Compounds with reduced oxygen content ($SrMnO_{2.58}$ and $Sr_2MnO_{3.71}$) have a larger molar volume than the compounds with ideal oxygen stoichiometry, crystallising in perovskite and K_2NiF_4 structure, respectively.

2.4. Dilatometric measurements

Dilatometric measurements were carried out in a Push Rod Dilatometer 402 E (Netzsch) using samples with 92% (82%) of theoretical density. Phase transitions in the system $SrMnO_{3-y}$ observed by the measurement of the sample length up to 1570°C at a heating rate of 5 K min^{-1} are shown in Fig. 1. Sintering effects are not noticed. $SrMnO_{2.58}$ expands linearly up to approx. 300°C. A vague maximum indicates the oxidation to metastable β-$SrMnO_3$. The latter transforms to α-$SrMnO_3$ at 880°C, which forms β-$SrMnO_{3-y}$ again above 1400°C.

Fig. 2 presents the transition range of β-$SrMnO_3$ in detail. The decrease in heating rate from 5 to 1 K min^{-1} results in a lower transition temperature of 845°C. A linear expansion of 2.44% was observed. In contrast to the results of Negas and Roth [1], the phase transition proceeds quickly. Pure α-$SrMnO_3$ was found after cooling down, if the maximum temperature is lower than 1350°C.

The oxidation of $SrMnO_{2.58}$ to β-$SrMnO_3$ is clearly detectable by dilatometry with a lower heating rate of 1 K min^{-1} (Fig. 3). The process starts at 262°C in air and is associated with a linear contraction of 0.43%. If the maximum temperature is lower than 800°C, the reaction product is pure β-$SrMnO_{3.00}$ without oxygen vacancies. Taking into account the high density of this sample (92% of theoretical density) and the sample diameter of 10 mm, we can suppose that the reaction is very fast under these conditions.

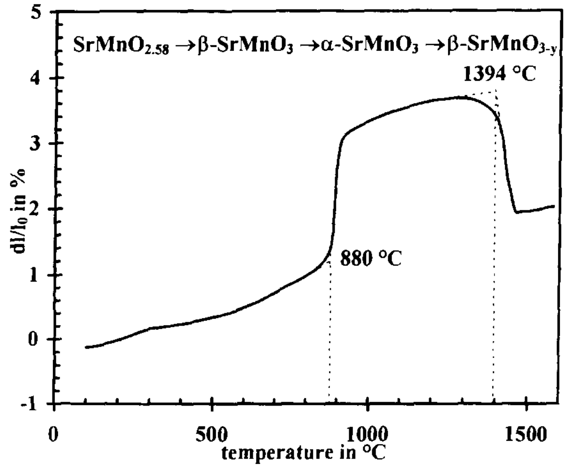

Fig. 1. Dilatometric measurement on $SrMnO_{2.58}$ with 5 K min^{-1} heating rate in air.

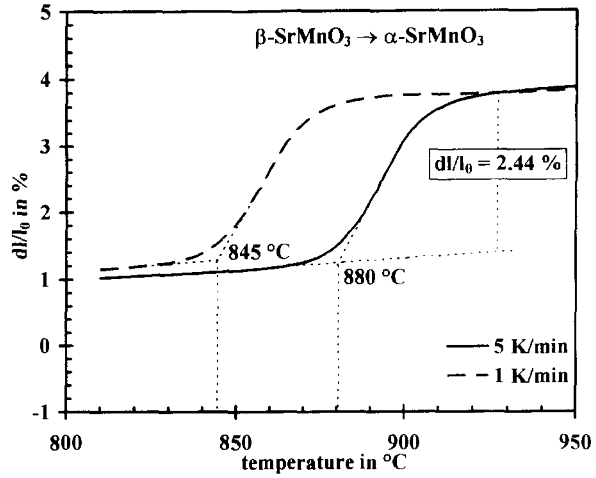

Fig. 2. Dilatometric measurements of the transition β-$SrMnO_3$ to α-$SrMnO_3$ with heating rates 5 and 1 K min^{-1} in air.

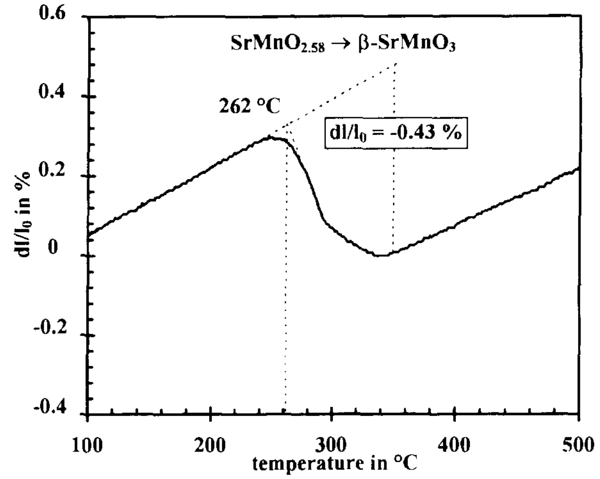

Fig. 3. Dilatometric measurement of the oxidation of $SrMnO_{2.58}$ to β-$SrMnO_3$ with 1 K min^{-1} heating rate in air.

Fig. 4 shows the oxidation of a sample of $Sr_2MnO_{3.72}$ with 82% of theoretical density in air. This reaction leads to a contraction of 0.45% with a heating rate of 5 K min^{-1}. The oxidation temperature of 387°C is more than 100 K higher in comparison with $SrMnO_{2.58}$. In an argon flow, a contraction was not observed. All the described phase transitions were determined by XRD.

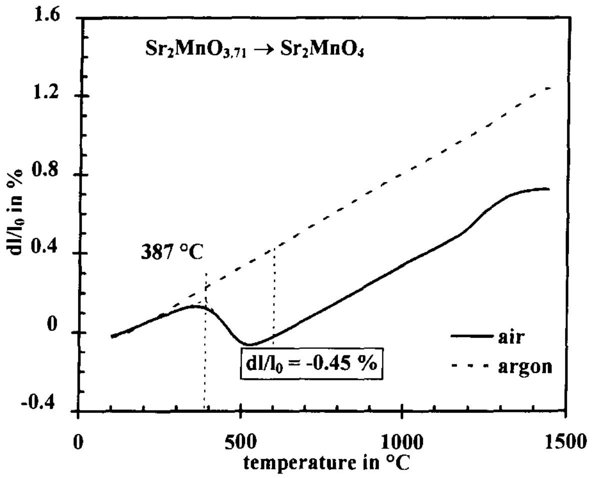

Fig. 4. Dilatometric measurement of the oxidation of $Sr_2MnO_{3.71}$ to Sr_2MnO_4 with 5 K min^{-1} heating rate in air and argon.

3. Results and discussion

The different molar volumina of various phases enabled dilatometry to be used to determine the temperatures of phase transitions. It is also necessary to understand the reasons for the structural changes in the $SrMnO_{3-y}$ system.

Both structures of α-$SrMnO_{3-y}$ and β-$SrMnO_{3-y}$ are built up of common most dense packed anions and Sr(II) ions. All SrO_3 layers in β-$SrMnO_{3-y}$ are packed in a cubic sequence abc (ccc, c = cubic, h = hexagonal), so that only corner sharing occurs between the $MnO_{6/2}$ octahedras. However, α-$SrMnO_{3-y}$ has the layer sequence abac (chch) with a ratio 1:1 of cubic:hexagonal packed layers. Facesharing $MnO_{6/2}$ octahedras occur only in the hexagonal dense packed layers (h). As discussed earlier [7], the repulsion within the $O_{3/2}MnO_3MnO_{3/2}$ units through the common faces in the (100) plane generates a noticeable expansion or distortion of the structure especially in the [001] direction. This explanation corresponds with results of hexagonal indexing of the cubic lattice of β-$SrMnO_3$ with

$$a_{\text{hex.}} = \sqrt{2}\, a_{\text{cub}} \qquad c_{\text{hex.}} = \frac{4}{3}\sqrt{3}\, a_{\text{cub}}$$

Lattice parameters of α-$SrMnO_3$ with $a = 544.48$ pm and $c = 906.85$ pm are larger (+1.2%, +3.2%) than the computed "hexagonal" lattice constants of cubic β-$SrMnO_3$ with $a_{\text{hex.}} = 537.9$ pm and $c_{\text{hex.}} = 878.4$ pm. The different expansion of the crystal lattice of α-$SrMnO_3$ in [100] and [001] directions compared with the structure of β-$SrMnO_3$ indicates a remarkable lattice distortion.

The lattice distortion initiates an enlargement of the Sr(II) sites and a reduction of the Mn(IV) sites. Therefore in compounds of formula ABO_3, the increase in the A ion

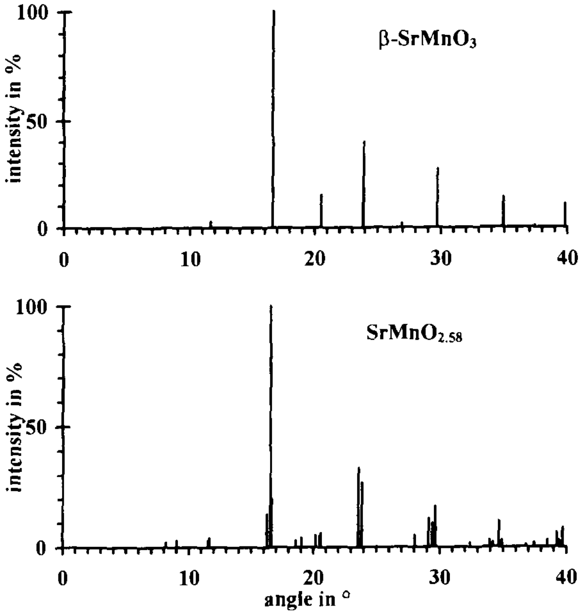

Fig. 5. Comparison of diffractograms (Cu Kα_1) of β-$SrMnO_3$ and $SrMnO_{2.58}$.

radius or the decrease in the B ion radius stabilises the hexagonal packing sequence of AO_3 layers. Syono et al. [11] discussed this point of view in their work on high pressure phases of $SrMnO_3$ and $BaMnO_3$.

Both fast oxidation of $SrMnO_{2.58}$ to β-$SrMnO_3$ at moderate conditions, and splitting of X-ray diffraction lines (Fig. 5), indicate narrow structural relations between the two phases, in the same way as relations between the lattice constants

$$a_{\text{orthorh}} \approx \sqrt{2}\, a_{\text{cub}} \quad b_{\text{orthorh}} \approx 2\sqrt{2}\, a_{\text{cub}} \quad c_{\text{orthorh}} \approx a_{\text{cub}}$$

Reller et al. [12,13] reported that oxidation and reduction (with hydrogen at 300–500°C) of $CaMnO_{3-y}$ (with $y = 0.25$; 0.50) proceeds in a topotactical reaction without changing the structural principle of the perovskite structure. Only the octahedral coordination of Mn(IV) is decreased to a square pyramidal coordination around Mn(III) and the crystal symmetry is reduced. In this respect, the structural principle of corner sharing of $MnO_{6/2}$ polyhedras in perovskite should also be kept in orthorhombic $SrMnO_{2.58}$. An anion vacancy produces two Mn(III) ions in the basic faces of square pyramids which are faced to each other. Therefore the repulsion between the Mn(III) ions can be understood as the driving force for the expansion of $SrMnO_{2.58}$ and the symmetry reduction compared with cubic β-$SrMnO_3$. Similar considerations about the role of anion vacancies in Sr_2MnO_{4-y}, which crystallises in the K_2NiF_4 structure have been published [8].

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