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Non-Stoichiometric $LaVO_3$. I. Synthesis and Physical Properties

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The effects of non-stoichiometry in lanthanum vanadium(III) oxide on unit-cell dimensions and thermal and magnetic properties are described. Samples with nominal composition $La_{1-x}VO_{3-y}$ were synthesized form citrate solutions. The final reduction of V^V intermediates was achieved using zirconium getter or reductive gas mixtures. Two types of non-stoichiometry were proven. The La deficiency, $La_{1-x}VO_3$, is substantial. According to powder X-ray diffraction, the homogeneity width is $0.00 \leqslant x \leqslant 0.09 \pm 0.01$ for samples annealed at 1273 K. Unit-cell data show that the range is clearly temperature dependent. In addition there are clear indications for La-excessive non-stoichiometry, $LaV_{1-z}O_{3-y}$. According to high-temperature powder X-ray diffraction, non-stoichiometric $La_{1-x}VO_3$ of the orthorhombic $GdFeO_3$-type undergoes a phase transition to the rhombohedral $LaAlO_3$-type around 770 K. Stoichiometric $LaVO_3$ does not show such behaviour. The non-stoichiometry has a pronounced effect on the magneto-structural phase transition occurring for $LaVO_3$ at 140 K. For $La_{0.92}VO_3$ magnetic susceptibility data indicate antiferromagnetic ordering below 70 K, whereas for $La_{0.90}VO_3$ paramagnetic behaviour was observed down to 5 K. Anomalous, negative magnetization was observed for field-cooled samples of $La_{1-x}VO_3$ ($x \leqslant 0.08$) with average formal oxidation number of vanadium higher than three.

Perovskite-type related oxides of $LaMO_3$ (M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, etc.) have been widely studied owing to their many potential applications and interesting structure–property relationships[1,2] Most of these materials possess some kind of non-stoichiometry which influences the physical properties quite dramatically. Since the range of existence for the non-stoichiometry is strongly influenced by temperature and oxygen partial pressure, monitoring of these parameters is important in material processing. In the case of oxygen non-stoichiometry, a reduced phase ($LaMO_{3-x}$) with oxygen vacancies is the most frequent situation. Such phases can normally be well described by defect cluster models.[3] In contrast to reduced oxides like $LaNiO_{3-x}$[4] and $LaCoO_{3-x}$,[5] oxidative non-stoichiometry exists in a few perovskites with easily oxidizable M cations,[6,7] e.g. $LaMnO_{3+\delta}$ and $LaTiO_{3+\delta}$. For M = V one can foresee the possibility of both oxygen deficiency and excess, corresponding to V^{II} and V^{IV} formation, respectively. For $LaCoO_3$ and $LaNiO_3$ the fully oxidized state corresponds to a rather high oxidation state for the M atoms, and they can easily be reduced. In fact, $LaNiO_3$ is not stable at $p(O_2) \approx 1$ bar at temperatures above 1073 K.[8] $LaCoO_{3-x}$ exhibits a substantial non-stoichiometry at high temperatures, e.g. at 1300 K, $x \leqslant 0.10$.[5] At low temperatures (say 700 K) $LaCoO_3$ and $LaNiO_3$ can be reduced (via intermediates) topotactically to $La_2Co_2O_5$ and $La_2Ni_2O_5$, respectively.[4,9] At more severe reduction conditions $LaCoO_3$ will decompose into $La_4Co_3O_{10}$, Co_3O_4 and CoO. In many cases the topotactically reduced phases are considered as metastable.

In $LaMnO_{3+\delta}$ the oxygen excess may correspond to as much as 40% Mn^{IV} ($\delta = 0.20$). This can be reached on heating sol–gel precursors in air at 1070 K.[6] The non-stoichiometry arises from random cation vacancies on the La and Mn sublattices rather than from oxygen interstitials.[10] $LaMnO_{3+\delta}$ is an excellent example of the strong influence of non-stoichiometry on crystal structure and physical properties.[11] At very reducing conditions, reduction to $LaMnO_{3-x}$ can be achieved.[12] A related situation exists for $LaTiO_{3+\delta}$; however, a number of distinct phases exist in the composition range between $LaTiO_3$ and $LaTiO_{3.5}$.[7] For example, reduction of $La_2Ti_2O_7$ gives a series of phases, among them $La_5Ti_5O_{17}$ ($LaTiO_{3.4}$) and an orthorhombic perovskite variant ($LaTiO_{<3.2}$).[7]

$LaVO_3$ is an interesting candidate for extending the knowledge on structure–property relations in defect

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perovskite-type oxides. Only sparse data are available in the literature. Tofield and Scott[13] reported that slight oxidation non-stoichiometry exists for $LaVO_{3+\delta}$, $\delta \leqslant 0.05$. No reports providing the existence of reduced $LaVO_{3-x}$ exist. The stoichiometric phase is reported to be stable down to an oxygen partial pressure of at least $p(O_2) = 10^{-21.1}$ bar at 1273 K.[14]

Recently the structural and magnetic properties of $LaVO_3$ have been in focus owing to observations of anomalous diamagnetism for field-cooled samples.[15–17] Shirakawa *et al.*[16] observed diamagnetic behaviour below 135 K. The large negative susceptibility, -2.4×10^{-2} cm^3 mol^{-1} (measurements in a field with $H =$ 200 Oe), was confirmed by Mahajan *et al.*[17] and others. The correct symmetry of the crystal structure has been debated. Early studies reported cubic or tetragonal symmetry.[17–21] It is now settled that the structure is orthorhombic ($GdFeO_3$-type) at ambient, but with pseudocubic metric ($a = 555.5$, $b = 784.8$ and $c =$ 555.3 pm; the relation to simple cubic perovskite cell being $a = c = a_p 2^{1/2}$, $b = 2a_p$). Recent TEM and synchrotron high-resolution X-ray studies show that the structure is slightly monoclinically distorted below the magneto-structural phase transition around 135 K.[22] To our knowledge, no data exist on the influence of non-stoichiometry on the intriguing low-temperature properties, although indications for non-stoichiometry were found by Kestigan *et al.*,[18] and Dougier *et al.* performed conductivity measurements for nominal $La_{0.9}VO_3$.[23]

The present study focuses on the syntheses of various, nominally non-stoichiometric $La_{1-x}VO_{3-y}$ samples. For samples exhibiting a homogeneity range, the effect of non-stoichiometry on the unit-cell dimensions, thermal expansion and thermal stability, low-temperature magnetostructural phase transition and magnetic properties is described.

Experimental

Synthesis. In earlier studies of $LaVO_3$, the samples were either prepared by heating solid mixtures of La_2O_3 and V_2O_5 at high temperatures, using a reducing atmosphere or a vacuum furnace,[13,14,21] or by arc-melting mixtures of La_2O_3 and V_2O_3 in an argon atmosphere.[16,17] In order to reduce problems arising from the high temperatures required for solid-state reactions, the present La–V–O samples were synthesized from citrate solutions where mixing at an atomic level in the precursor phase provides improved control on the overall composition of the samples and reduces sample inhomogeneities.

The La–V–O samples, typically in 0.1–0.2 g batches, were prepared for compositions with 41.5–50 mol% La_2O_3. The samples were synthesized by first dissolving La_2O_3 (99.9%, Aldrich; preheated to 1173 K to remove any hydrated and/or carbonated species) and V_2O_5 (99.5%, Riedel-de-Häen AG) in melted citric acid monohydrate $C_3H_4(OH)(COOH)_3 \cdot H_2O$ (P.T. Bundi Alarn, Sungai Budi) in about 1 : (30–50) ratio by weight with a few drops of water added. La_2O_3 dissolved in the melt during heating up to 420–450 K, and a clear solution was obtained. The vanadium component was then added along with additional water. The citrate solution was dehydrated at 453 K overnight, and a porous, X-ray amorphous material was formed. The organic components of this xerogel material were thereafter burned off at 723 K. The fluffy powder obtained was pressed into (white to yellow/brown) pellets. The pellets were annealed in air at 1173 K for 18–20 h. Prolonged or repeated heating did not alter the phase composition as judged from powder X-ray diffraction data. The adopted method gives V^V materials, hence a final reducing step is required. Tests on dissolving V^{III} compounds (V_2O_3, VCl_3) directly in citric acid and other solvents in order to avoid the final reduction step, were unsuccessful with respect to producing phase-pure samples.

Reduction of $LaVO_4$ to $LaVO_3$ requires an oxygen partial pressure $p(O_2) \leqslant 10^{-12.8}$ bar.[14] Two routes of performing the reduction were followed: (i) using weighed amounts of zirconium in evacuated, sealed silica glass ampoules and temperatures 1173–1373 K, or (ii) using a tube furnace with reductive gas mixtures of 10% H_2 in N_2/CO_2 at 1273 K (the oxygen partial pressure being monitored by an oxygen sensor of yttrium stabilized zirconia, Dansensor).

Two series of samples were synthesized, their nominal compositions being $La_{1-x}VO_3$ and $La_{1-x}VO_{3-y}$, $y > 0$; both for $0.00 \leqslant x \leqslant 0.17$. In addition, one sample with an La excess of the type $La_{1+x}VO_{3+\delta}$ (or $LaV_{1-z}O_{3-p}$), was prepared. The intermediate $LaVO_4$ phase during synthesis exhibited no major non-stoichiometry. The nominally $La_{1-x}VO_4$ intermediate samples consisted of a two-phase mixture of $LaVO_4$ and a V-rich phase, probably V_2O_5. However, powder X-ray diffraction could not verify V_2O_5, probably owing either to a high detection limit or to an amorphous nature. Thermal analysis (DTA) supports the latter assumption. DTA recordings of $La_{1-x}VO_4$ samples show an exothermal reaction at 573 K and an endothermal one at around 923 K. The exotherm is believed to signalize crystallization of V_2O_5. A similar exothermal effect was observed for a V_2O_3 sample after prolonged exposure to air, turning the sample into an almost X-ray amorphous substance. After annealing at 673 K this substance was converted into crystalline V_2O_5. Further support for the assumption of $LaVO_4$ and V_2O_5 two-phase mixtures was obtained from comparison of DTA measurements. For pure V_2O_5 the endothermal melting reaction occurred at 943 K, whereas for a mechanical mixture between V_2O_5 and $LaVO_4$, partial melting was observed at 923 K, i.e. the same temperature as found by DTA measurements of the intermediates (see above).

The melting of V_2O_5 (at 923–943 K) represents a potential problem for the synthesis, since melted V_2O_5 could react with or enter pores of the crucible during heating. Judged from weighing of the alumina crucibles prior and after calcining, any loss of V_2O_5 from the

sample was considered reasonable within uncertainty limits. In addition, selected control samples were synthesized. For these, all heating cycles prior to reduction were performed below the melting point of V_2O_5.

Characterization. Qualitative phase analysis, checking of sample homogeneity and deduction of unit-cell dimensions were based on powder X-ray diffraction (PXD) data obtained by Guinier–Hägg cameras (Cu $K\alpha_1$ radiation $\lambda = 154.0598$ pm, Si as internal standard, $a = 543.1061$ pm[24]). Low- and high-temperature PXD photographs were obtained with a Guinier–Simon camera (Enraf Nonius FR 553; Cu $K\alpha_1$ radiation). The samples were kept in open or sealed rotating silica glass capillaries, and the temperature change was synchronized with movement of the film cassette. Temperature calibration was based on measurements of thermal expansion for Ag.[25] Unit-cell dimensions were obtained by means of the CELLKANT program[26] using 13–15 Bragg reflections. Aid in indexing was obtained from pattern simulation using the LAZY PULVERIX program.[27]

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed with Perkin Elmer DTA7 and TGA7 instruments. Low-temperature differential scanning calorimetry (DSC) measurements were performed with a Mettler TA3000 system. Data evaluation was done using standard programs of the systems.

Magnetic susceptibility was measured between 5 and 320 K using a SQUID system (MPMS; Quantum Design). The samples were kept in gelatine capsules. Measurements were performed for zero field-cooled (ZFC) and field-cooled (FC) samples, in both cases upon heating in an applied magnetic field $H = 1$ kOe. Instrument calibration was done using a Pd standard (from NIST).

Results and discussion

Non-stoichiometry of $La_{1-x}VO_{3-y}$. In discussing the results on non-stoichiometry in $La_{1-x}VO_{3-y}$ it is convenient to differentiate between four categories of samples; those with (intended) nominal compositions (a) $La_{1-x}VO_3$, (b) $La_{1-x}VO_{3-y}$, $y = 3x/2 > 0$, (c) $LaVO_{3-y}$ and (d) $La_{1+x}VO_{3+\delta}$. The oxygen contents of all these samples were monitored by means of reduction of the $LaVO_4$ and V_2O_5 intermediates by a zirconium getter in closed ampoules (see Experimental). For $La_{1-x}VO_3$ the span in average oxidation number for V is between 3.00 and 3.51 ($0.00 \leqslant x \leqslant 0.17$), for $La_{1-x}VO_{3-3x/2}$ the average oxidation number for V is 3.00 and for $LaVO_{3-y}$ it is less than three.

$La_{1-x}VO_3$. The non-stoichiometric range of $La_{1-x}VO_3$ is substantial. According to the variation in unit-cell dimensions shown in Fig. 1 for samples reduced at 1273 K, a homogeneity range exists for $0.00 \leqslant x \leqslant 0.09 \pm 0.01$. The unit-cell dimensions decrease with increasing x, i.e. with increasing formal oxidation number for V. This fits the sparse data in Ref. 18. The width of

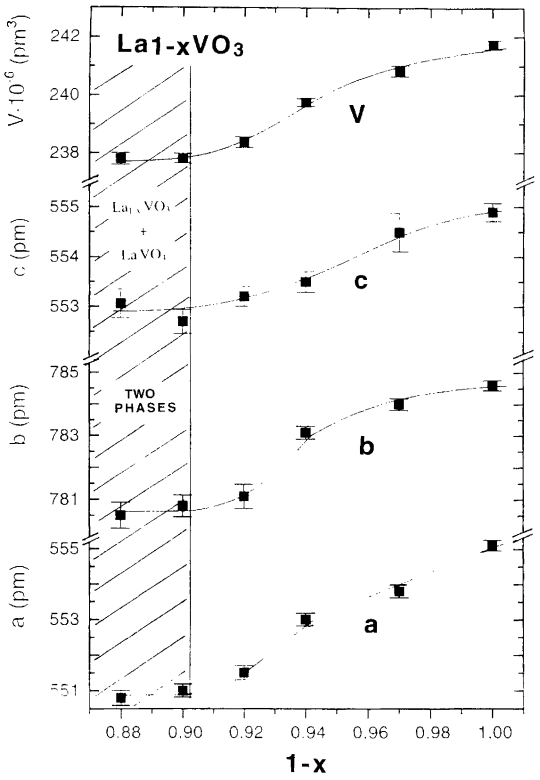

Fig. 1. Unit-cell dimensions (space group *Pnma*) of $La_{1-x}VO_3$ as a function of nominal non-stoichiometry. The two-phase region for $x \leqslant 0.09 \pm 0.01$ is indicated.

the non-stoichiometry range increases with increasing reduction temperature, and covers for samples prepared at 1373 K $0.00 \leqslant x \leqslant 0.11 \pm 0.01$. Samples outside the homogeneity range contain additional $LaVO_4$; however, no V-rich phase could be detected by PXD.

The unit-cell data in Fig. 1 are consistent with a $GdFeO_3$-type crystal structure (the *Pnma* setting being used). The orthorhombic splitting of the axes is small, which actually caused erroneous unit-cell descriptions in several earlier reports.[14,17,18] The degree of deformation in terms of $(1 - a/c)$ increases significantly with increasing La deficit. This is clearly seen as an increased line splitting on the Guinier films.

$La_{1-x}VO_{3-3x/2}$ and $LaVO_{3-y}$. All $La_{1-x}VO_{3-3x/2}$ samples gave PXD patterns identical to that of $LaVO_3$. Hence, any larger non-stoichiometry of the type indicated by the formula does not exist. Additional Bragg reflections from V_2O_3 were identified in the PXD patterns for samples with $x \leqslant 0.12$, in accordance with a detection limit for V_2O_3 of ~3 wt% in the present sample mixtures. The lack of variation in the PXD pattern (and in derived unit-cell dimensions) could be fortuitous if effects introduced by La and O deficiency cancelled out. However, since there is in addition no effect on the magnetostructural phase transition (see below), non-existence of $La_{1-x}VO_{3-3x/2}$ is highly probable. Likewise, no indications were found for the existence of reduced $LaVO_{3-y}$. Although handling was done under inert conditions, one

can not completely rule out blurring of the real situation owing to rapid reoxidation. Reduction of $LaVO_4$ at 1273 K using a $H_2/CO_2/Ar$ gas mixture with $p(O_2) = 10^{-14}$ bar gave stoichiometric $LaVO_3$ in accordance with earlier results.[14]

$La_{1+x}VO_{3+\delta}$. Only one sample with nominal composition $La_{1.05}VO_{3+\delta}$ was studied. Prior to reduction, the intermediate consisted of $LaVO_4$ and $La_8V_2O_{17}$ (the latter identified from its PXD pattern[28]). After reduction at 1273 K the sample appeared as a single phase with slightly smaller unit-cell dimensions than stoichiometric $LaVO_3$; viz. $a = 554.6(2)$, $b = 784.0(3)$ and $c = 554.2(3)$ pm versus $a = 555.3(1)$, $b = 784.8(2)$ and $c = 555.2(3)$ pm. Further support for such non-stoichiometry was obtained by observing a reduction in the magneto-structural phase transition temperature from 140 K for $LaVO_3$ to 125 K for $La_{1.05}VO_{3+\delta}$. La interstitials are unlikely in the perovskite-type structure, and the formula should be rewritten with basis in a structure determination.

$La_{1-x}VO_3$; phase transitions, thermal expansion and decomposition reactions. Low-temperature Guinier–Simon data show that $LaVO_3$ undergoes a discontinuous (magnetostructural) phase transition around 140 K into a more strongly orthorhombically deformed unit cell. This fits recent reports which, on the basis of TEM and high-resolution synchrotron powder X-ray diffraction data, actually show that the deformed phase is monoclinic ($\gamma = 90.125°$).[22] However, the slight monoclinic distortion could not be resolved in the present data. The effect of non-stoichiometry on the transition was followed by PXD, DSC and magnetic susceptibility measurements.

The temperature dependence of the unit-cell dimensions for $LaVO_3$ in Fig. 2 and the qualitative representation of changes in the diffraction pattern in Fig. 3 show the discontinuous nature of the structural transition. The transition temperature is strongly reduced on increasing the La deficit. Results from DSC (T_t) and magnetic measurements (T_N) are given in Table 1. For DSC the peak in heat flow, and for magnetic measurements, the peak in susceptibility, were chosen as transition temperatures. The listed temperatures represent means of all parallels for samples with the same nominal composition. For $LaVO_3$ and $La_{0.97}VO_3$, the difference in T_N and T_t appears significant. This would be in line with the model proposed by Nguyen and Goodenough[29] in which onset of long-range magnetic order is claimed as a prerequisite prior to a cooperative Jahn–Teller structural distortion.

Thermal expansion and temperature dependence of unit-cell dimensions for $LaVO_3$ between 293 and 1073 K were determined from Guinier–Simon PXD measurements (Fig. 4). In this range the linear volume expansion coefficient is $\alpha_V = 2.6 \times 10^{-5}\ K^{-1}$.

Similar experiments on $La_{1-x}VO_3$, $x > 0$, brought out a quite different behaviour. In contrast to $LaVO_3$ (and $La_{1-x}VO_{3-3x/2}$), the sealed capillaries for $La_{1-x}VO_3$

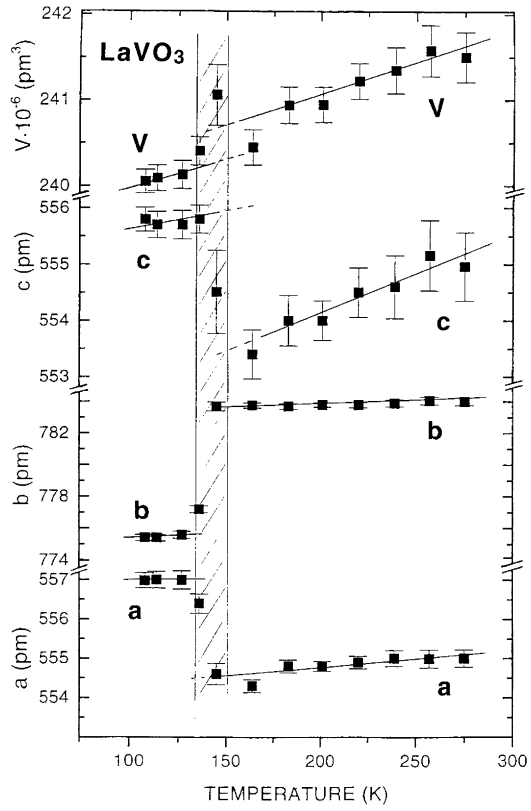

Fig. 2. Temperature dependence of unit-cell dimensions for $LaVO_3$ between 100 and 300 K.

generally broke (exploded) at around 770 K during the recordings. Nevertheless, from the film data it was possible to determine that a phase transition (or reaction) occurs prior to the breakdown, as evidenced by line splittings and a few additional reflections. The latter could be described to $LaVO_4$. The line splittings, cf. the schematic representation in Fig. 3, could be ascribed to a first-order phase transition from the $GdFeO_3$-type structure to the related, rhombohedral $LaAlO_3$-type structure. Help in indexing was obtained from a comparison with data for $LaCoO_3$; observed d-values with indexation are listed in Table 2. The unit-cell dimensions for rhombohedral $La_{0.92}VO_3$ at 700 K are $a = 552.7(2)$ pm and $\alpha = 60.43(1)°$. For all non-stoichiometric $La_{1-x}VO_3$ samples the structural phase transition is reversible. The explosion of the capillaries must be forced by a gas evolving reaction. A possible scheme involving a structural phase transition (step A), phase decomposition (step B) and oxidation (step C) is proposed:

(A) $La_{1-x}VO_{3\,(ORT)} \rightarrow La_{1-x}VO_{3\,(RH)}$

(B) $La_{1-x}VO_{3\,(RH)} \rightarrow (1-x)\ LaVO_{3\,(ORT)} + (x/2)V_2O_3 + (3x/4)O_2\ (g)$

(C) $LaVO_{3\,(ORT)} + (1/2)O_2\ (g) \rightarrow LaVO_4$ and/or

$La_{1-x}VO_{3\,(RH)} + [(2-3x)/4]O_2\ (g) \rightarrow (1-x)\ LaVO_4 + (x/2)V_2O_5$

and/or $V_2O_3 + O_2(g) \rightarrow V_2O_5$

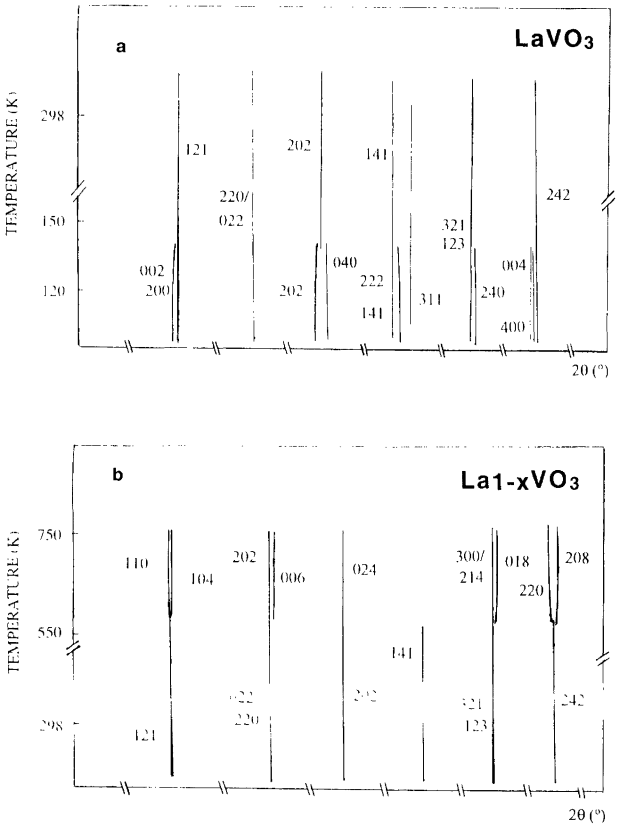

Fig. 3. Schematic illustration of temperature induced changes in position of Bragg reflections during (a) a low-temperature magnetostructural phase transition and (b) a high-temperature orthorhombic-to-rhombohedral phase transition for $La_{1-x}VO_3$. Intensities not to scale, splittings exaggerated.

Table 1. Phase transition temperatures for $La_{1-x}VO_3$: values for the magnetic (T_N) and structural transition (T_t) derived from magnetic susceptibility and DSC measurements, respectively.

$1-x$	T_N/K	T_t/K
1.00	140±1	133±2
0.97	125±1	118±2
0.94	110±1	110±2
0.92	70±1	*a, b*
0.90	*a*	*a, b*

[a]Not observed. [b]Temperature limit of equipment 100 K.

The observation of two structurally related modifications of '$LaVO_3$' fits well into the general scheme for $LaMO_3$, M = Ti–Ni, perovskite-type oxides. $LaCrO_3$, $LaMnO_3$ and $LaFeO_3$, being orthorhombic at 298 K, turn rhombohedral on heating to, respectively, T_t = 533,[30] 850[31] and 1203,[32] whereas $LaCoO_3$ and $LaNiO_3$ are rhombohedral at 298 K. This variation concurs with the assumption that lower values for the Goldschmidt tolerance factor $t=(r_{RE}+r_O)/[2(r_M+r_O)]^{1/2}$, favour the orthorhombic variant. The unit-cell volume per formula unit, V/Z, correlates reasonably with T_t for M = Cr–Ni.

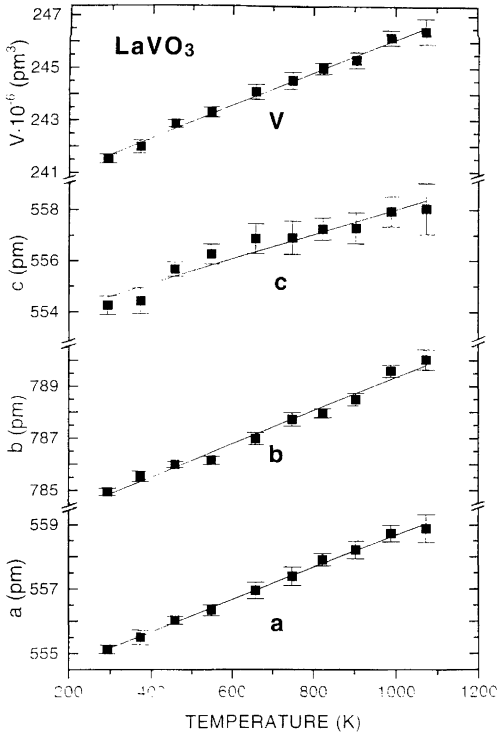

Fig. 4. Variation in unit-cell dimension of $LaVO_3$ between 293 and 1073 K.

Table 2. Miller indices (hexagonal setting) and *d*-values for rhombohedral $La_{0.92}VO_3$ at 700 K.

hkl	*d*/pm
110	278.0
104	276.4
202	227.1
006	*a*
024	196.1
300/214	160.6
018	*a*
220	139.1
208	138.1

[a]Observed, position uncertain.

For stoichiometric $LaVO_3$ no transition was observed below 1073 K, which is approximately where a transition should be expected assuming a $V(T)$ correlation. Unfortunately, no PXD experiment could be performed at higher temperatures. On the other hand, for $La_{0.90}VO_3$ (with 30% V^{IV}) the transition occurs at 590 K. In this respect $La_{1-x}VO_3$ may behave similarly to $LaMnO_{3+\delta}$, which show a pronounced dependence of T_t on non-stoichiometry (or Mn valence).[32]

Reoxidation. $LaVO_3$ is not oxidized at ambient temperature into $LaVO_4$. However, on heating in air oxidation is initiated around 550 K; cf. the TGA curves in Fig. 5. Stoichiometric $LaVO_3$ seems to be oxidized in two steps, first into $LaVO_{3.12}$, thereafter into $LaVO_4$ (Fig. 5a). Assuming the product $LaVO_4$ to be stoichiometric, the

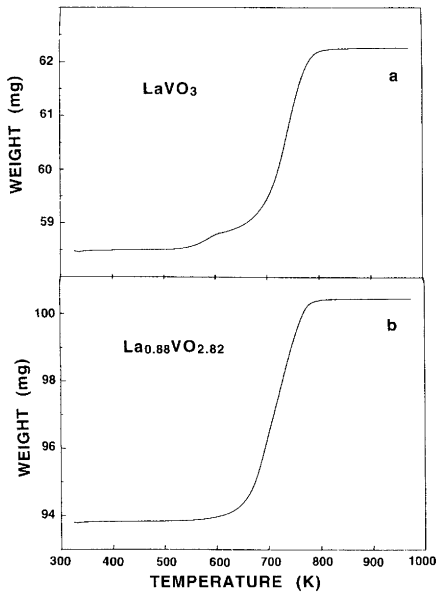

Fig. 5. Representative thermogravimetric curves for oxidation of (a) $LaVO_3$ and (b) $La_{0.88}VO_{2.82}$ (nominally) on heating in air at a heating rate of 10 K min^{-1}.

$LaVO_3$ starting materials were always calculated to have a slight oxygen excess, i.e. the content being 3.01–3.03. Also with respect to reoxidation, the non-stoichiometric samples behave differently than pure $LaVO_3$. The non-stoichiometric samples are oxidized in one step (Fig. 5b), including here also samples containing V_2O_3 impurities. According to Guinier–Simon photographs, the orthorhombic to rhombohedral phase transition occurs just prior to the onset of oxidation.

Magnetic properties. Magnetic susceptibility data for $La_{1-x}VO_3$, are shown in Fig. 6. The knick-points in the curves at T_N indicate an antiferro- to paramagnetic phase transition. The ordering temperature decreases from $T_N = 140$ K for $LaVO_3$ to 70 K for $La_{0.92}VO_3$, cf. also Table 1. For $La_{0.90}VO_3$ no indications for magnetic long-range order is found. As a curiosity it should be mentioned that the $La_{1-x}VO_3$ samples showed an extraordinary tendency to adsorb oxygen on the sample surface. Direct measurements of loaded samples into the MPMS system gave a large cusp around 60 K attributed to surface oxygen (Fig. 7). On repeated purging of the sample at 300 K with He, the cusp disappeared.

The magnetic susceptibility obeys the Curie–Weiss law above T_N. Table 3 lists the deduced Weiss temperature (Θ) and the paramagentic moment μ_{eff}. Literature reports give very different values for Θ and μ_{eff}, respectively ranging from -400 to -1000 K and from 2.83 to 4.2 μ_B.[21,23,33,34] The moment values are much higher than the spin-only value for a d^2 ion, indicating a substantial orbital contribution.

The existence of anomalous diamagnetism[16,17,34] for field-cooled samples of $LaVO_3$ was confirmed (cf. Fig. 8). A systematic study of the present $La_{1-x}VO_3$ samples revealed that the phenomenon is present for all samples with an average formal oxidation state of vanadium larger than three. Samples with solely trivalent vanadium exhibited positive magnetization (note that one out of ten measured samples did not fit this trend). Also, samples of $LaVO_3$ studied earlier seem to fit this pattern. Mahajan *et al.*[15,17] estimate the oxygen content of their studied samples to be 3.020–3.061. It appears that a mixed valence state for vanadium is required for the presence of the unusual behaviour.

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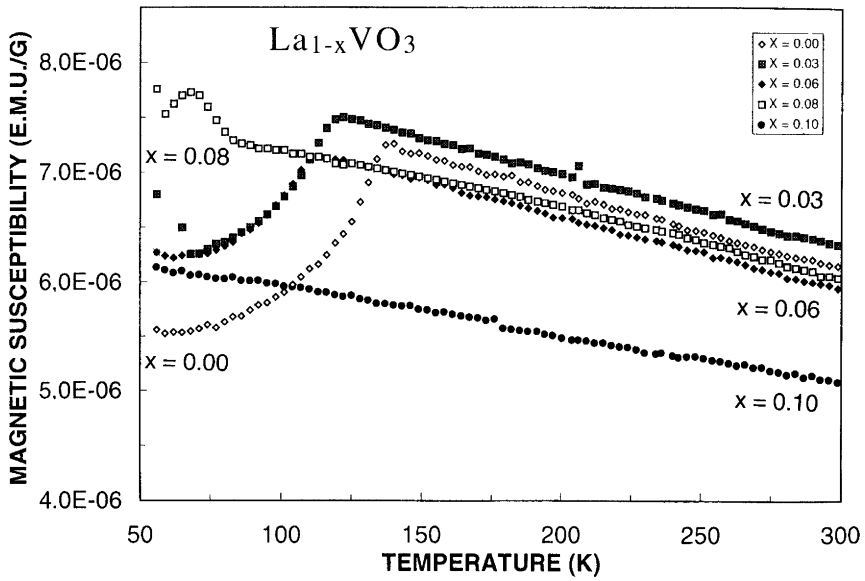

Fig. 6. Magnetic susceptibility versus temperature for zero-field-cooled $La_{1-x}VO_3$ measured for $H = 1$ kOe during heating.

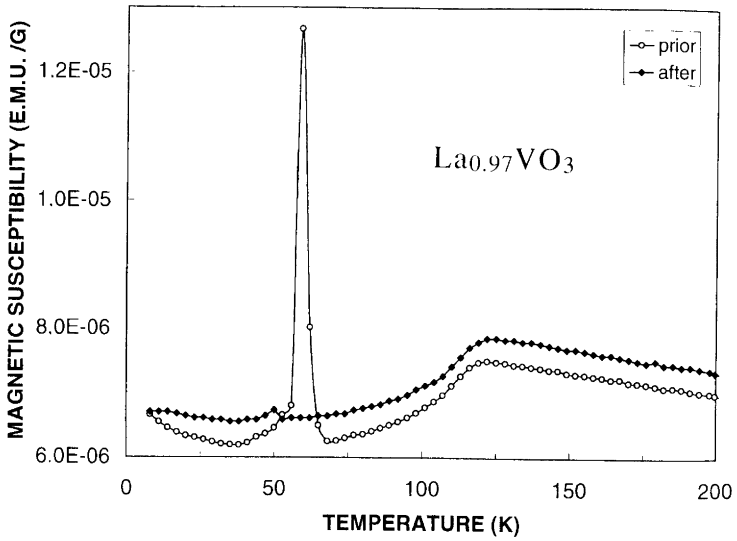

Fig. 7. Magnetic susceptibility of $La_{0.97}VO_3$ prior to (open circles) and after (filled diamonds) removal of surface oxygen by He flushing.

Table 3. Paramagnetic Weiss temperature and magnetic moment for $La_{1-x}VO_3$.[a]

$1-x$	Θ/K	μ_{eff}/μ_B
1.00	−735	3.50
0.97	−805	3.60
0.94	−750	3.40
0.92	−805	3.50
0.90	−1020	3.50

[a]Estimated uncertainty ±30 K in Θ and ±0.05 in μ_{eff}.

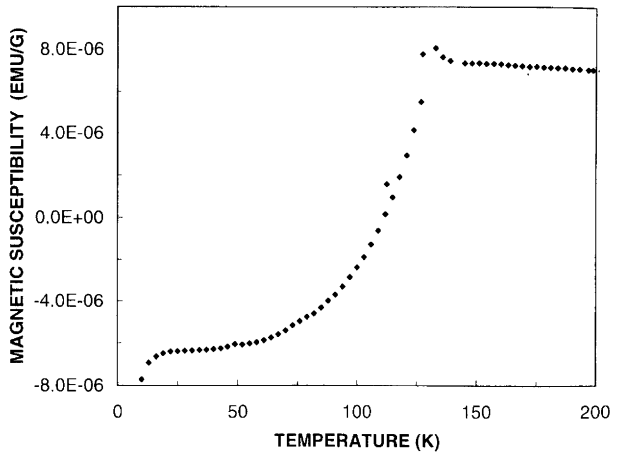

Fig. 8. Representative magnetic susceptibility versus temperature curve for field cooled samples of $LaVO_{3+y}$ measured for $H = 1$ kOe upon heating.

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