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Physical nature of the „stabilization“ effect of the oxygen content in $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3+\delta}$ thin films

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Received June 22, 2023

Revised July 7, 2023

Accepted July 7, 2023

Using *ab initio* calculations by the density functional theory in the LDA + U approximation, the features of the formation process of intrinsic defects in crystals of doped manganite with a perovskite-like structure are studied. It is shown that the nature of the energy barrier, which provides the relative stability of the material of high-quality $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3+\delta}$ films with a stoichiometric composition with respect to oxygen, due to the different energy of formation of metal and oxygen vacancies. In this case, the physical mechanism for the formation of an oxygen-excessive state of the crystal realizes in accordance with a well-known physical model, by forming additional cation-deficient crystal cells by means of the depletion of complete ones.

Keywords: doped manganite, *ab initio* calculations, defect formation mechanism, oxygen and cation vacancies, formation energy of point defects.

DOI: 10.61011/PSS.2023.09.57113.119

Most modern technologies for manufacturing high quality thin films based on doped manganites using magnetron, laser and chemical vapor deposition method use an additional heat treatment procedure for a film structure in order to adjust the oxygen content (OC) [1–3]. It is quite difficult [4] to provide a stoichiometric ratio by oxygen directly during *in situ* film growth. The main process task of thermal treating is to ensure full oxidation of the film material without inducing additional crystal defects in the form of cation vacancies.

Doped manganites crystallize in a perovskite-like structure with close packing of atoms. In accordance with the most widely used model, interstitial atoms in these crystals are not allowed, and anion and cation vacancies are the main type of point defects. In this case, oxygen-excessive state features high content of cation vacancies. Excessive OC formation mechanism in such crystals includes formation of additional lattice cells with cation deficiency due to depletion of several complete cells [5]. The crystal volume is not maintained. It is evident that this model is important for the objects with sufficiently well crystals structure and cannot follow the process of formation of major structural defects that occur, for example, when the sample is exposed to fast neutrons [6].

OC = 3 „stabilization“ effect has been detected and experimentally studied earlier in $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ series film with various thicknesses on LaAlO_3 single-crystal substrates [7]. This effect means that, within heat treatment procedure in air (at excessive partial pressure of oxygen [8]), there is an energy threshold that prevents formation of additional cation-deficient lattice cells at relatively low

temperatures. This fact, in particular, is expressed in the possibility to achieve the maximum allowable double phase transition temperature T_C in the vicinity of stoichiometric composition by oxygen at $T \leq 600^\circ\text{C}$. Heat treatment at higher temperature $T > 700\text{--}900^\circ\text{C}$ reduces T_C significantly, while achievement of the maximum allowable T_C within the smooth OC correction procedure in the film material is not possible any more. This confirms that formation of cation-deficient lattice cells is a completely irreversible process.

In practice, KC = 3 „stabilization“ process is extremely useful both to achieve the stoichiometric composition by oxygen and to optimize electrical and magnetic properties of films in terms of particular applications. However, the physical nature of the effect is still understudied. The authors show herein that the nature of the energy barrier that ensures crystal stability with stoichiometric ratio by oxygen is to a large extent associated with different energy of metal and oxygen vacancy formation. To verify this assumption, appropriate *ab initio* calculations based on the density functional theory with LDA + U approximation were performed.

Ab initio calculations have been extensively used before to calculate structural, electronic and magnetic properties of crystals with perovskite structure, including strontium system manganites [9–13]. Features of the existing approach to the *ab initio* calculations of point defect formation energy are described in review [14] using binary GaN and AlGaN as an example. There have been few calculations for manganite yet. The study [15] describing the calculations of oxygen vacancy formation energy in LSMO with various doping levels shall be pointed out. Numerical evaluations

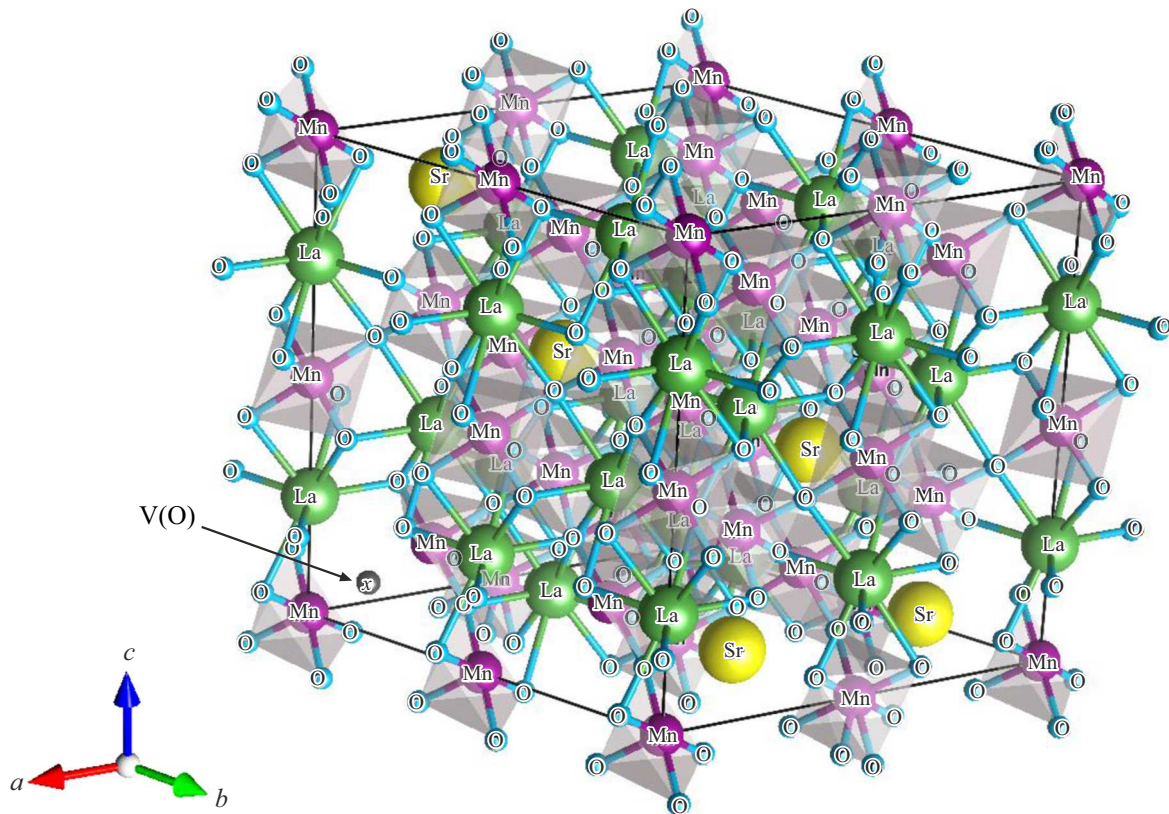


Figure 1. Diagram of design $\text{La}_{0.79}\text{Sr}_{0.21}\text{MnO}_{2.96}$ lattice cell with single oxygen vacancy.

of metal vacancy energy properties were provided only for pure LaMnO_3 [16].

Within the posed problem, a quadruplicate rhombohedral lattice cell containing 120 atoms was used to calculate the properties of the LSMO crystal with composition close to the required experimental cation ratio ($x = 0.2$). The general layout of the atomic structure of interest is shown in Figure 1.

Its is limited to a hexagonal structure with the following parameters: $a = b = 11.012 \text{ \AA}$; $c = 13.3291 \text{ \AA}$, that agrees with the experimental structural data for single crystals [17].

Electronic density distribution was calculated by the projector augmented wave method (PAW) [18], VASP (Vienna *ab initio* simulation package). For the exchange-correlation potential, generalized gradient approximation (GGA) was used in the form offered by Perdew–Burke–Ernzenhof [19] using standard VASP pseudopotentials. For Brillouin zone integration, a set of k -points $4 \times 4 \times 4$ and cutoff energy of $E_{\text{cut}} = 300 \text{ eV}$ were chosen for calculations. The self-consistent calculations provided optimized positions of all atoms and full system energy. For optimization, forces applied to the atoms were lower than 0.1 eV/\AA . As described in [20], optimization procedures were performed and Hubbard parameter $U = 4 \text{ eV}$ was calculated, which, in particular, considers the presence of manganese atom shell with localized and strongly interacting d -electrons.

Calculation of $E_{\text{for}}(j, q)$ defect formation energy by the procedure described in [14] and used in [16] involves not only the calculation of the difference of total energies of the crystal with and without defects, but also the use of additional corrections as follows:

$$E_{\text{for}}(j, q) = E_{\text{Defective}} - E_{\text{bulk}} + n_j \mu_j + q(E_v + \Delta E_F + \Delta V). \quad (1)$$

Here, $E_{\text{Defective}}$ and E_{bulk} are total energies calculated for the lattice cell with and without defect, n_j is the number of defects, μ_j is the chemical potential of the defect that, in case of vacancy, is the reservoir energy. The 4th term considers the chemical potential of an electron (Fermi energy — E_F), q is the defect charge state, E_v is the valence band top energy, ΔV is the correction for interaction of defects in adjacent computational atom cells. As discussed in [10], when cells with 96 atoms and more are used, ΔV is extremely low.

Quantitatively, the two first terms of (1) have the absolute value of the order of 10^3 eV , and their difference is by two orders of magnitude lower, that required high calculation accuracy. Further terms have lower values equal to unities of electron-volts.

In practice, half total energy of a lone oxygen molecule is often used as an assessment value of chemical potential of an oxygen atom μ_{O} for many oxide compounds. Evaluation of μ_j for metal atoms is less defined, it is evaluated

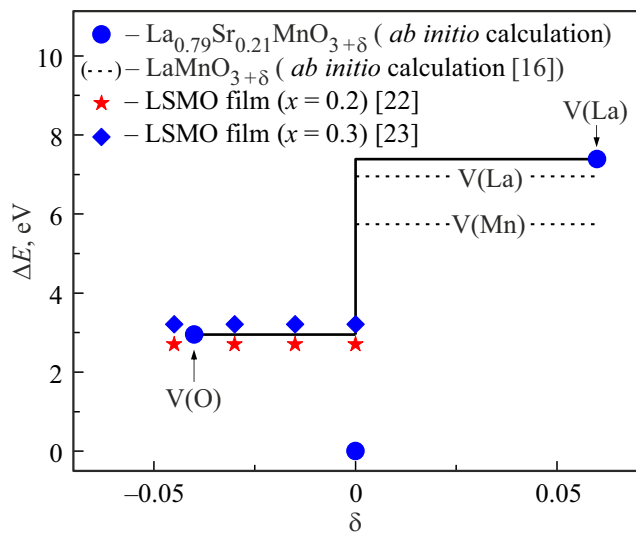


Figure 2. Point defect formation energy characteristics in the form of oxygen and cation vacancies in manganites. Circles — calculated oxygen V(O) and lanthanum V(La) vacancy formation energies (see the text). Stars and rhombs show experimental oxygen activation energies in LSMO films from [22,23]. Horizontal dashed lines in the region $\delta > 0$ show the metal vacancy formation energies in pure manganite from [16]. Solid line schematically shows the energy barrier that ensures relative temperature resistance of the crystal during transition from oxygen-deficient to oxygen-excessive state.

according to a wide range of implemented chemical bonds. For this, phase diagram of all possible binary compounds based on this element is addressed and then used to find the variation limits of μ_j . Considering this uncertainty, it should be noted that to compare the calculated values with the experimental data, it is important to choose adequate physical conditions.

Figure 2 shows the calculated assessment values of energy properties of point defects in the form of oxygen and metal vacancies.

It should be noted immediately that the oxygen vacancy formation energy ($\Delta E_{\text{O}} = 8.47 \text{ eV}$) and lanthanum vacancy formation energy ($\Delta E_{\text{La}} = 14.0 \text{ eV}$) calculated using only the first two terms of (1) [21] differ almost by a factor of two, showing an expected trend and indicating a cause of the energy barrier that ensures crystal stability in the vicinity of the stoichiometric composition by oxygen. I.e. oxygen vacancies are filled up during heat treatment, while cation vacancies are not formed effectively.

As shown in Figure 2, consideration of the chemical potential of vacancies reduces these values significantly, and it should be noted that the oxygen vacancy formation energy ($E_{\text{for}}(\text{O}) = 2.95 \text{ eV}$) agrees quite well with the experimental data shown in Figure 2.

Notwithstanding that the vacancies in manganites are electrically active defects, we represented the values corresponding to $q = 0$ [16] to compare the calculated data with macroscopic characteristics of the films. Macroscopic

properties of LSMO at $x = 0.2$ are characterized as ferromagnetic with high (metallic) hole-type conductivity [17]. Oxygen vacancies reduce charge carrier concentration, but since we are interested in the region of low deviations from stoichiometric ratio by oxygen, it can be considered that the potential pattern is well shielded by free charge carriers. As a result, when a vacancy is formed, free valence bonds of the adjacent ion vacancies are neutralized. Consider also the difference in formation of a single vacancy in the computational cell and in the macroscopic object. In the computational cell, due to a limited number of atoms, formation of one vacancy, for example, oxygen, results in significant change of the oxygen index ($\delta = -0.0416$). In the 100 nm film with an area of $1 \times 1 \text{ mm}^2$, this corresponds to the number of defects which by 5 orders of magnitude greater. I.e. the single vacancy formation process in the film has a relatively low influence on the macroscopic properties, including the chemical potential of electron, and, thus, meets $q = 0$ to a greater extent.

Stars and rhombs in Figure 2 show the oxygen atom activation energies corresponding to the oxygen-deficient state of films: $E_{\text{a}} = 2.7 \text{ eV}$ at $x = 0.2$ and $E_{\text{a}} = 3.21 \text{ eV}$ at $x = 0.3$. This data was obtained by numerical analysis of the time dependences of the oxygen concentration variation in a series of films during heat treatment [21,22]. It should be noted that the estimated oxygen vacancy formation energy $E_{\text{for}}(\text{O}) = 2.95 \text{ eV}$ quite well agrees with the values mentioned above.

Figure 2 also shows the assessment values of the lanthanum and manganese vacancy activation energies for pure $\text{LaMnO}_{3+\delta}$ obtained in [16]. Mn vacancies are characterized by a little lower formation energy than La, that not fully confirms the assumption, used in the quasi-chemical approach, concerning the generation of these vacancies in equal proportion. And the second trend to be pointed out — is the growth of lanthanum vacancy formation energy with growing strontium doping. Experimentally, similar dependence for the oxygen vacancy activation energy in manganites have been known long ago [24]. When deviations from the stoichiometric ratio are significant, it shall be probably exhibited also depending on the oxygen index. In the experimental data shown in Figure 2, it is absent due to slight changes of the oxygen index and possibly insufficient accuracy of the OC control in films.

Agreement between the calculated characteristics and macroscopic properties of crystals certainly depends on the hardware and procedures available for numerical simulation. Numerical values may be further updated, but the nature of the energy barrier (threshold) ensuring stability of the crystal with stoichiometric ratio by oxygen is quite obvious at the qualitative level. This effect is caused by the transition to a more energy-consuming physical defect formation mechanism associated with generation of cation vacancies.

Finally, it should be noted that the presence of barrier caused by relatively high cation vacancy formation energy could be exhibited in the form of previously observed effects associated, for example, with the appearance of phase

separation and temperature resistance of individual phases when samples are heated to 600°C and above [25].

Funding

The study was supported by the Ministry of Science and Higher Education of the Russian Federation under governmental job-order for the Federal State Budgetary Research Institution „Donetsk of Physics and Technology named after A.A. Galkin“.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by E.Ilyinskaya