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Self-compensation in lanthanum-doped calcium titanate

U. BALACHANDRAN, N. G. EROR
Materials Science Department, Oregon Graduate Center, Beaverton, Oregon 97006, USA

The reversible change of oxygen content observed by gravimetric measurements on lanthanum (donor)-doped calcium titanate between specified states of reduction and oxidation is proportional to the lanthanum concentration. These measurements indicate that the lanthanum addition is compensated by additional oxygen up-take in the oxidized state. The range of this reversible change in oxygen stoichiometry is up to more than an order of magnitude larger than the oxygen non-stoichiometry of the undoped $CaTiO_3$. There is excellent agreement between the calculated amounts of oxygen necessary to compensate the donor-dopant and the measured reversible oxygen weight-change between the oxidized and reduced state of equilibration. A single-phase region from $La_{0.06}Ca_{0.94}Ti^{3+}_{0.06}Ti^{4+}_{0.94}O_3$ to $La_{0.06}Ca_{0.94}TiO_{3.03}$ has been confirmed. The gravimetric measurements can be explained by a model involving a shear structure.

1. Introduction

While the defect structure of $BaTiO_3$ and $SrTiO_3$ have been studied in considerable detail [1–11], $CaTiO_3$ has received comparatively little attention. George and Grace [12, 13] examined the electrical conductivity, Seebeck coefficient and diffusion of point defects in single-crystal $CaTiO_3$ in water–hydrogen atmospheres in the temperature range 1100 to 1300° C. The present authors [14, 15] have studied the defect structure of undoped and lanthanum-added polycrystalline $CaTiO_3$ by means of equilibrium electrical conductivity as a function of oxygen partial pressure (10^0 to 10^{-22} atm) and temperature (800 to 1100° C). $CaTiO_3$ can be converted into a good n-type semiconducting material at room temperature either by reduction or by doping with donors. The literature concerning the effect of dopant ions on the physical properties of $CaTiO_3$ is limited. Eror and Smyth [16] have reported that in $BaTiO_3$ up to 20 at% barium may be substituted by lanthanum to retain a single-phase fully-oxidized material. The solubility of lanthanum in strontium titanate has been estimated to be about 40 at% [17].

The disorder created by La^{3+} as a donor-dopant in $CaTiO_3$ should lend itself to description by Verwey's controlled valency model [18]. By this model, there would be compensation for the La^{3+} on Ca^{2+} sites by the creation of equal numbers of Ti^{3+} ions. The Ti^{3+} ions are then responsible for the increase in electrical conductivity. In this case the donor-dopant dominates the positive side of the charge neutrality equation and, as a consequence, the negative defect concentration would be independent of equilibrium oxygen activity. This compensation mechanism has also been referred to as controlled electronic imperfection [19]. Similarly, the donor-dopant may be compensated by the formation of charged-point defects that would also be independent of equilibrium oxygen activity. This compensation mechanism has been referred to as controlled atomic imperfection [19], self-compensation [16, 20–25], and stoichiometric compensation [16].

For $BaTiO_3$ with higher concentrations of donor-dopants, the theories that have been offered for the self-compensation range from the creation of compensating barium vacancies [26–28] to a change of the cation site occupied by the donor-dopant [29]. In considering these theories for donor-doped $CaTiO_3$, it must be kept in mind that $CaTiO_3$ is a ternary oxide and that the Ca/Ti ratio

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is fixed. For the case of the creation of calcium vacancies at higher donor-dopant concentrations, there should be an irreversible loss of calcium or precipitation of a calcium-rich phase. For the case of different site occupancy it would be possible to have compensation if some of the donor-dopant substituted for Ca^{2+} were to shift to Ti^{4+} sites and vice versa.

The present authors [10] have suggested from gravimetric studies that the extra oxygen in the over-stoichiometric composition can be accommodated by forming layers of SrO between the $SrTiO_3$ perovskite blocks in lanthanum-doped $SrTiO_3$. Incorporation of La^{3+} ion in strontium titanate decreases the cation/anion ratio and normally leads to an over-stoichiometric oxide, $La_xSr_{1-x}TiO_{3+x/2}$, under oxidizing conditions [10]. The purpose of the present work is to make a detailed study of the compensation mechanism in lanthanum-doped $CaTiO_3$ by gravimetric measurements. Lanthanum was selected as a dopant because of its stability in the tri-valent state which insures its incorporation in the lattice as La^{3+}.

2. Experimental procedure

Lanthanum-doped $CaTiO_3$ samples were prepared by a liquid mix technique [9, 10, 14, 16, 30]. Required amounts, according to the general formula $La_xCa_{1-x}TiO_3$, of calcium carbonate (obtained from Mallinckrodt Chemical Works), lanthanum carbonate (obtained from Rare-Earth Division) and tetraisopropyl titanate solution (obtained from Dupont Co., Tyzor) were dissolved in an ethylene glycol–citric acid solution. There was no evidence of any precipitation in the solutions as they were evaporated to a rigid, transparent, uniformly-coloured polymeric glass. The samples were then calcined at 700 to 900° C; there was no evidence of a second-phase in any of the as-calcined samples. The various calcined compositions were then pressed into circular discs under a load of 275 MPa and sintered in air at 1350° C for 10h. For gravimetric measurements, the samples were equilibrated in oxygen or carbon dioxide–carbon monoxide mixtures at 1100° C for the oxidized and reduced states, respectively, and quenched in the ambient gas. The CO/CO_2 mixture was adjusted to provide an oxygen partial pressure, P_{O_2}, of 10^{-16} atm at the equilibration temperature. All gravimetric measurements were made at room temperature on at least duplicate samples on a Cahn model 4100 electrobalance.

3. Results and discussion

Gravimetric measurements on calcium titanate doped with up to 6 at % La^{3+} have shown that the reversible change of oxygen content, between specified states of high and low oxygen activity, is proportional to the dopant concentration (see Fig. 1). As can be seen in Fig. 1, there is excellent agreement between the calculated amount of

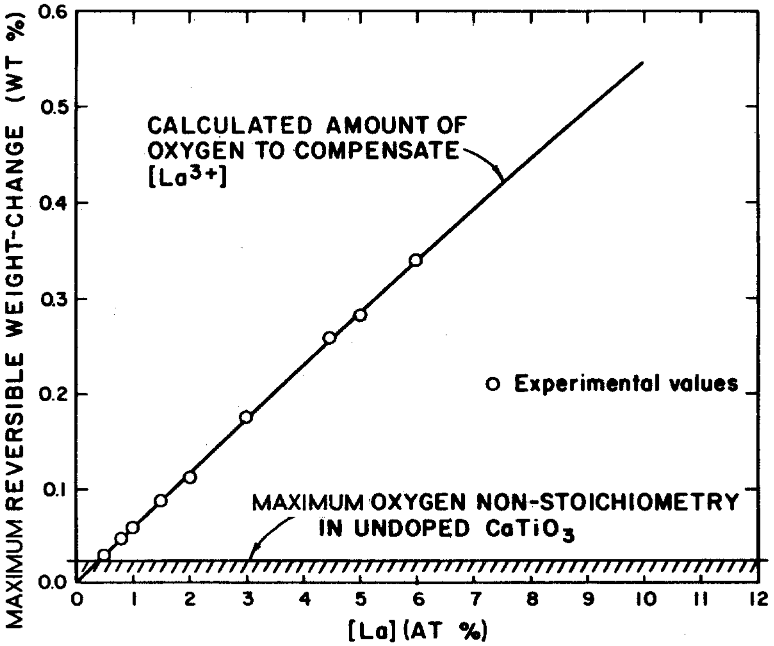

Figure 1 Maximum reversible weight-change observed in calcium titanate, between oxygen partial pressures established by CO/CO_2 mixture, or oxygen, as a function of La^{3+} concentration, at 1100° C.

oxygen necessary to compensate the La^{3+} dopant (assuming that each added oxygen will neutralize two La^{3+} dopant ions) and the measured reversible oxygen weight-change between the oxidized state at 1 atm oxygen and the reduced state of equilibration in a CO/CO_2 mixture ($P_{O_2} = 10^{-16}$ atm). The maximum oxygen non-stoichiometry measured in an undoped $CaTiO_3$ sample (a value of $\sim 2 \times 10^{-3}$ for x in $CaTiO_{3-x}$) is also shown in Fig. 1.

It is possible to increase the amount of electronic disorder created by a given donor-dopant concentration by substituting a 4+ valent dopant of the appropriate ionic size for Ca^{2+} or a 6+ valent dopant for Ti^{4+}. Such dopants would require twice as much reversible oxygen weight-change for electronic compensation as would an equal atomic concentration of La^{3+} on Ca^{2+} sites or Ta^{5+} on Ti^{4+} sites. Self-compensation of $BaTiO_3$ with up to 1 at % Th^{4+} substituted for Ba^{2+} has been measured by Eror and Smyth [16] and found to agree with the assumption that each added oxygen ion will neutralize one donor-dopant ion. Their results established that Th^{4+} substitutes for Ba^{2+} in $BaTiO_3$ when equilibrated with an atmosphere of high oxygen activity.

It is seen in Fig. 1 that for 6 at % La^{3+} concentration the measured reversible weight-change amounts to a 15-fold increase in oxygen non-stoichiometry, compared to that of the undoped $CaTiO_3$. No second phase was observed in the sample with 6 at % lanthanum in both oxidized and reduced states, indicating that the solubility limit of lanthanum in $CaTiO_3$ is above 6 at % for the conditions under which these samples were prepared. The measured reversible change in oxygen stoichiometry unequivocally explains that lanthanum additions to $CaTiO_3$ are self-compensated. The question of how the extra oxygen is accommodated remains to be answered. The possibility of accommodating the extra oxygen in the interstitial position is discounted because of the close-packed structure involved. Absence of any second phase studied optically, by X-ray diffraction or by Raman laser spectroscopy (a more sensitive technique than the first two), suggests that no discrete second phase that is stable in the fully-oxidized state is formed. The observation of self-compensation could be explained in the following ways:

(a) The addition of oxygen on oxygen sites, creating both calcium and titanium vacancies (although the latter is unlikely structurally)

$$\mathrm{La}^{\bullet}_{\mathrm{Ca}} + \mathrm{Ti}'_{\mathrm{Ti}} + \tfrac{1}{4}\mathrm{O}_2 \rightleftharpoons \tfrac{1}{2}\mathrm{O}^{x}_{\mathrm{O}} + \tfrac{1}{6}\mathrm{V}''_{\mathrm{Ca}} + \tfrac{1}{6}\mathrm{V}''''_{\mathrm{Ti}} + \mathrm{La}^{\bullet}_{\mathrm{Ca}} + \mathrm{Ti}^{x}_{\mathrm{Ti}}. \qquad (1)$$

The presence of B-site vacancies in perovskites has been reported for lanthana-substituted $PbTiO_3$ by Hennings and Rosenstein [31] and for lanthanum manganite by Tofield and Scott [32]. Rauser and Kemmler-Sack [33] have reported the ordered perovskites with B-site vacancies for a new series of composition $Ba_2^{2+}B^{3+}U^{6+}_{5/6}\square_{1/6}O_6$ for B^{3+} = Sm to Lu, Sc and Y. Kemmler-Sack and co-workers [34–37] have shown the presence of octahedral vacancies in hexagonal perovskites by structure-factor analysis and vibrational spectroscopic investigations. The existence of vacancies on both A and B sites in $CaTiO_3$, or in the structural analogs $BaTiO_3$ and $SrTiO_3$, is not reported in the literature.

(b) A shift in the cation site occupied by the donor-dopant when the samples are oxidized,

$$\mathrm{La}^{\bullet}_{\mathrm{Ca}} + \mathrm{Ti}'_{\mathrm{Ti}} + \tfrac{1}{4}\mathrm{O}_2 \rightleftharpoons \tfrac{1}{2}\mathrm{O}^{x}_{\mathrm{O}} + \tfrac{1}{6}\mathrm{La}'_{\mathrm{Ti}} + \tfrac{1}{3}\mathrm{V}''_{\mathrm{Ca}} + \tfrac{5}{6}\mathrm{La}^{\bullet}_{\mathrm{Ca}} + \mathrm{Ti}^{x}_{\mathrm{Ti}}. \qquad (2)$$

For the case of a 3+ valent dopant substituted for Ca^{2+} only $\frac{1}{6}$ of the dopant would have to shift from 2+ to 4+ valent sites for complete compensation to occur. The factor $\frac{1}{6}$ arises from the fact that the 3+ valent dopant removes itself as a donor when it shifts site, becomes an acceptor on a Ti^{4+} site, and results in two calcium vacancies which may become doubly-ionized (one since it now occupies and, therefore, creates a new Ti-site and one from the site it left behind). For the case of 5+ ion donor-dopant substituted for Ti^{4+} shifting to Ca^{2+} sites, $\frac{1}{6}$ of the dopant would have to occupy Ca^{2+} sites for complete compensation to occur. Lanthanum ions occupying octahedral sites in perovskites with the general formula $A^{2+}(B_1^{3+})_{0.5}(B_2^{5+})_{0.5}O_3$ have been found by Brixner [38, 39] and Galasso and Darby [40]. Takeda and Watanabe [41] have reported evidence of La^{3+} on Ti^{4+} sites in $BaTiO_3$. They obtained an electron paramagnetic resonance (EPR) signal characteristic of an F-centre, equivalent to the acceptor, $\mathrm{La}'_{\mathrm{Ti}}$. This signal was present only for the case of a Ba/Ti ratio of 1.02 plus an additional 1.0 at % La (Ba/Ti ratios of 1.01 and 1.03 had little or no signal). In the present investigation, the large cation to small cation ratio, Ca/Ti, is maintained at unity with a variation of about 20 ppm. From the results of Takeda and Watanabe [41] and the cation ratios used in this experiment, one can assume that La^{3+} ions mainly occupy the Ca^{2+} sites. Further, the possibility of a change in cation site occupied by the donor-dopant can be discounted because of the unlikely possibility of the creation of titanium vacancies in the perovskite structure that are required to compensate donor-dopants substituted for Ti^{4+}.

(c) A reversible change from a classic randomly-distributed point defect model in the reduced state to a compensated structure with ordered defects in the oxidized state,

$$\begin{aligned}&\mathrm{La}^{\bullet}_{\mathrm{Ca}} + \tfrac{1}{2}\mathrm{Ca}^{x}_{\mathrm{Ca}} + \mathrm{Ti}'_{\mathrm{Ti}} + \tfrac{1}{4}\mathrm{O}_2\\ &\rightleftharpoons \tfrac{1}{2}(\mathrm{CaO}) + \tfrac{1}{2}\mathrm{V}''_{\mathrm{Ca}} + \mathrm{Ti}^{x}_{\mathrm{Ti}} + \mathrm{La}^{\bullet}_{\mathrm{Ca}}. \qquad (3)\end{aligned}$$

The phase information available [42, 43] for the CaO–TiO_2 system shows the existence of $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$, in addition to $CaTiO_3$. The unit-cell dimensions for $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$ indicate that $Ca_3Ti_2O_7$ has double-$CaTiO_3$ perovskite blocks interleaved with CaO, while $Ca_4Ti_3O_{10}$ has triple perovskite blocks interleaved with a CaO layer [42]. The CaO formed, therefore, does not represent a separate phase but can be accommodated in the structure in an ordered fashion between $CaTiO_3$ perovskite blocks so as to form different compounds in the series $Ca_{n+1}Ti_nO_{3n+1}$. $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$ are the second ($n = 2$) and third ($n = 3$) members in this series. A similar series of compounds is known to exist in the SrO–TiO_2 system [44–47]. Eror and Smyth [16] have suggested from gravimetric studies that the extra oxygen in the over-stoichiometric composition can be accommodated by forming layers of BaO between the $BaTiO_3$ perovskite blocks. Similar results were also suggested for lanthanum-doped $SrTiO_3$ [10].

By this type of proposed model, the addition of lanthanum to $CaTiO_3$ is compensated by the formation of calcium vacancies, but since we have a ternary oxide the additional calcium that results from the calcium vacancies combines with oxygen, accounting for the gravimetric observations, to form CaO, which is built into the lattice in a reasonably ordered fashion. It should be noted that the perovskite layers may still contain a random distribution of dopant ions and calcium vacancies even in the fully-compensated oxidized state. The inter-layer ordering might not be detected by conventional X-ray powder diffraction pattern techniques because only one CaO layer would be required for each fifty perovskite $CaTiO_3$ layers for the case of 4 at % La^{3+} substitution for Ca^{2+}.

A Kroger–Vink diagram [19] is a useful representation to consider when discussing the defects in ternary oxides of the type ABO_3. Fig. 2 illustrates the variation of defect concentrations as a function of oxygen partial pressure for the case of fully-ionized atomic defects, electrons, [n], and electron holes, [p], in a ternary oxide ABO_3 with both A- and B-site vacancies. It is assumed that the A and B content of the oxide is constant. The familiar $[\mathrm{n}] \propto P_{\mathrm{O}_2}^{-1/6}$ relation in the region with charge neutrality condition, $[\mathrm{n}] \approx 2[\mathrm{V}_{\mathrm{O}}^{\bullet\bullet}]$, is illustrated in Fig. 2. Fig. 3 is for the case of a ternary oxide ABO_3 with a donor-dopant, $\mathrm{I_m}$, that is fully ionized, $\mathrm{I}^{\bullet}_{\mathrm{m}}$. It is seen from Fig. 3, that for sufficient departures from stoichiometry the charge neutrality condition is given by $[\mathrm{n}] \approx 2[\mathrm{V}_{\mathrm{O}}^{\bullet\bullet}]$ and the effect of the donor-dopant is not seen. When a donor element is added, the n to p transition is shifted to higher P_{O_2} while the metal-excess to metal-deficit transition is moved to lower P_{O_2} (see Fig. 3). This means that with the shift of the transition of metal-excess to metal-deficit disorder to lower P_{O_2} values there may be significantly larger concentrations of atomic disorder than for the undoped oxide. The possibility of self-compensation is built into the random defect model of non-stoichiometry if the oxide is stable over a sufficiently wide range of oxygen partial pressures. It should be pointed out here that Figs 2 and 3 represent the variations of the various defect concentrations for the general case of a ternary oxide ABO_3 in which vacancies on both A- and B-sites are considered to be present simultaneously.

4. Conclusions

The addition of lanthanum (up to 6 at %) to calcium titanate was found to be compensated by additional oxygen up-take in the oxidized state. The measured reversible oxygen weight-change of the lanthanum-doped $CaTiO_3$ between $P_{\mathrm{O}_2} = 10^{-16}$ to 1 atm at 1100° C is in excellent agreement with the calculated amount of oxygen needed to neutralize the donor-dopants. A single-phase region is observed for up to 6 at % lanthanum indicating that solubility limit of lanthanum in $CaTiO_3$ is beyond 6 at %. The additional calcium that results from the calcium vacancies in the oxidized state may combine with oxygen to form CaO layers which can be built into the lattice in an ordered fashion.

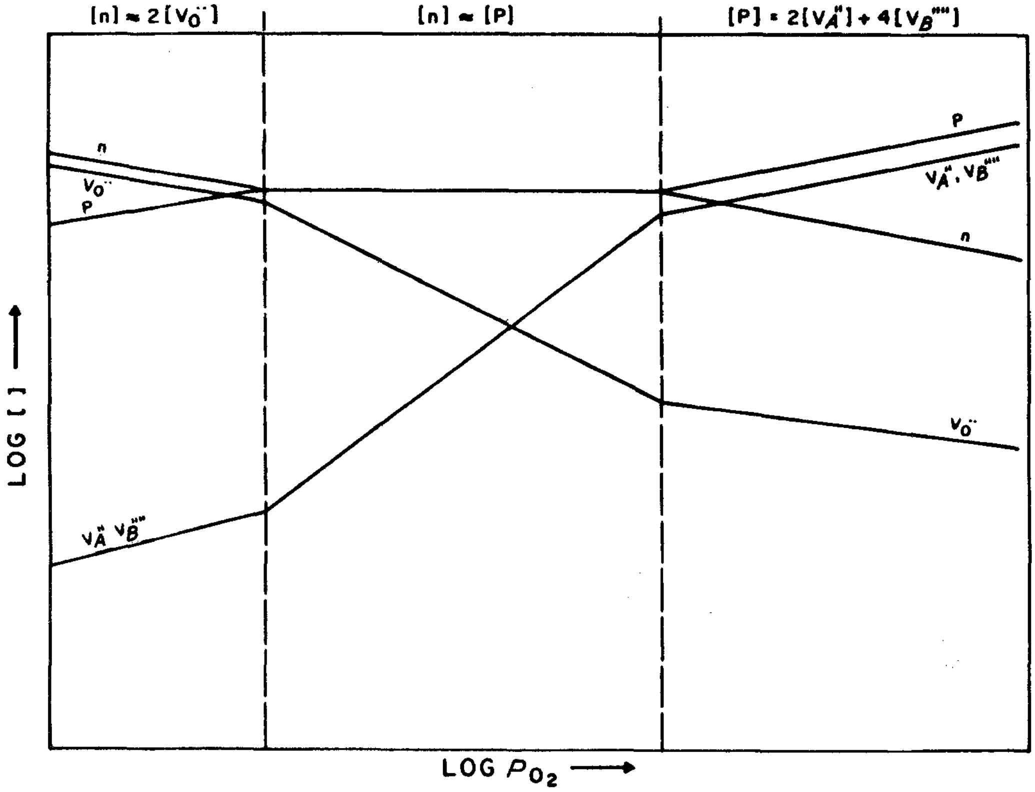

Figure 2 Defect concentrations plotted against the oxygen partial pressure in pure ternary oxide ABO_3 with Schottky–Wagner disorder.

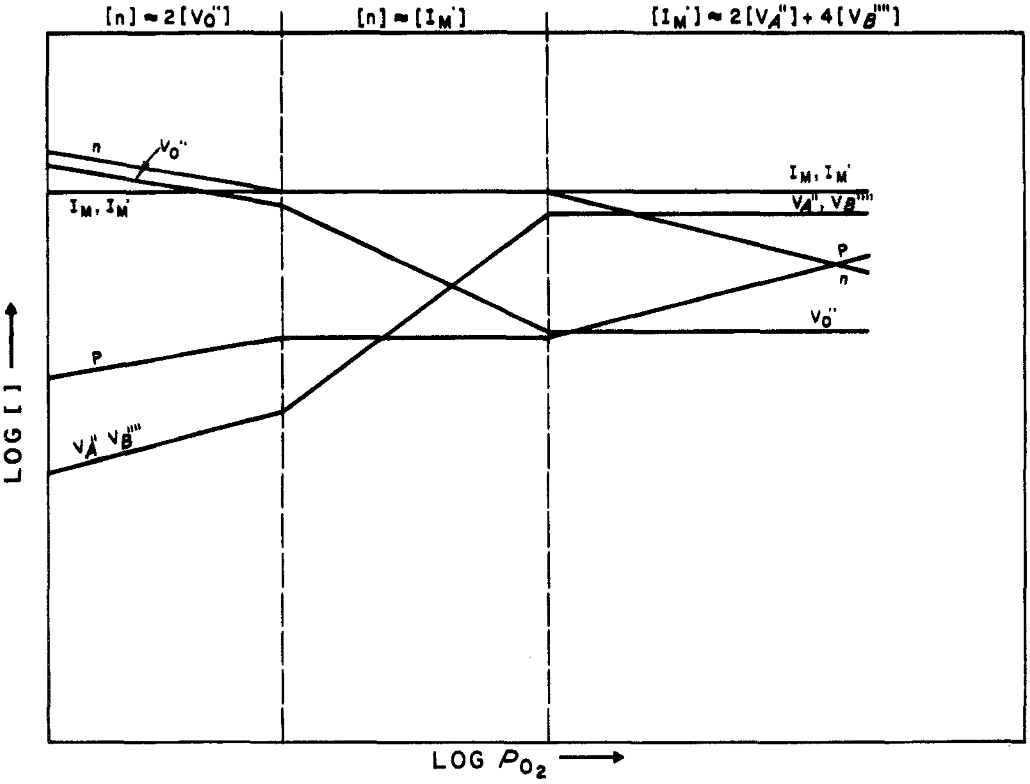

Figure 3 Concentrations of charged defects as a function of oxygen partial pressure for donor-doped ABO_3 with Schottky–Wagner disorder.

This work suggests a bridge between the two views held on non-stoichiometry: the case of random point defects in which aliovalent cations are incorporated into the host lattice without a change in either structure or cation/anion ratio, and the case of extended defect structures in which all cations retain their normal oxidation states and the resulting change in cation/anion ratio is accommodated by subtle structural changes [48–52].

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