Achieving fast oxygen diffusion in perovskites by cation ordering

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The oxygen-exchange behavior has been studied in half-doped manganese and cobalt perovskite oxides. We have found that the oxygen diffusivity in Gd$_{0.5}$Ba$_{0.5}$MnO$_{3-\delta}$ can be enhanced by orders of magnitude by inducing crystallographic ordering among lanthanide and alkali-earth ions in the A-site sublattice. Transformation of a simple cubic perovskite, with randomly occupied A-sites, into a layered crystal GdBaMn$_2$O$_{5+x}$ (or isostructural GdBaCo$_2$O$_{5+x}$ for cobalt oxide) with alternating lanthanide and alkali-earth planes reduces the oxygen bonding strength and provides disorder-free channels for ion motion, pointing to an efficient way to design new ionic conductors.

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Oxygen ion conductors - solids exhibiting very fast oxygen diffusion - constitute the basis for such emerging technologies as the membrane oxygen separation or the solid-oxide fuel cell (SOFC) power generation. These technologies offer enormous economical and ecological benefits provided high performance materials can be developed: The scientific challenge is to design materials demonstrating high oxygen diffusivity at low enough temperature.

In general, a crystal must meet two fundamental requirements to be a good oxygen-ion conductor: (i) it must contain a lot of vacancies in the oxygen sublattice, and (ii) the energy barrier for oxygen migration from one site to another must be fairly small, typically less than \( \sim 1 \) eV. Only a few types of oxides, and perovskites \( \text{ABO}_3 \) (A is a rare-earth or an alkali-earth element and B is typically a transition metal) among them, have been found to possess these features. Doped perovskites, which possess a high electronic conductivity in addition to the ionic one, are considered for using as electrodes in SOFC and as oxygen-selective membranes; for example, strontium-doped lanthanum manganese oxide, \( \text{La}_{1-y}\text{Sr}_y\text{MnO}_3\sim\delta \), is a standard cathode material for SOFC applications operating at temperatures around \( \sim 1000^\circ\text{C} \). Recently, serious efforts are made to reduce the operation temperature of SOFC, and for the operation at 700 - 800\(^\circ\text{C}\), strontium-doped lanthanum cobalt oxide, \( \text{La}_{1-y}\text{Sr}_y\text{CoO}_3\sim\delta \), is considered to be the most promising cathode material.\cite{6} The performance of perovskite oxides has been already optimized as much as possible mostly by means of various ion substitutions in both A and B sublattices, but they still fail to operate at low enough temperatures \( \sim 500^\circ\text{C} \) required for successful commercialization of the fuel cell technology.

In this Letter, we show that the oxygen-ion diffusion in a doped perovskite can be enhanced by orders of magnitude if a simple cubic crystal [schematically shown in Fig.1(a)] transforms into a layered compound with ordered lanthanide and alkali-earth ions [Fig. 1(b)], which reduces the oxygen bonding strength and provides disorder-free channels for ion motion.

Recently, the A-site-ordered manganese and cobalt perovskite oxides have been synthesized by several methods.\cite{7,8,9} We have succeeded in growing high-quality single crystals of these compounds by the floating-zone (FZ) technique.\cite{10} What makes these layered oxides promising for searching a high oxygen mobility is their remarkable variability of oxygen content: Oxygen atoms can be partially or even completely removed from the

![FIG. 1: Ordering of lanthanide \( A'^{3+} \) and alkali-earth \( A''^{n+} \) ions in the A-site sublattice of half-doped perovskites. (a) A simple cubic perovskite \( A'^{0.5}A''^{0.5}\text{BO}_3 \) with random occupation of A-sites is transformed into (b) a layered crystal \( A'A''\text{B}_2\text{O}_6 \) by doubling the unit cell, provided the difference in ionic radii of \( A' \) and \( A'' \) ions is sufficiently large. (c) Oxygen atoms can be partially or completely removed from lanthanide planes in \( A'A''\text{B}_2\text{O}_{5+x} \), providing a variability of the oxygen content, \( 0 \leq x \leq 1 \). (d, e) X-ray Bragg's (00L) peaks obtained for cubic Gd$_{0.5}$Ba$_{0.5}$Mn$_2$O$_{5+x}$ (d) and layered GdBaMn$_2$O$_{5+z}$ (e), which demonstrate the doubling of the unit cell along the c axis with the cation ordering (for convenience, the peak intensity is multiplied by a factor indicated near each peak).]
lantanide planes [as shown in Fig. 1 (c)], creating a lot of vacant sites in the crystal lattice. While polycrystalline air-sintered samples of GdBaMn$_2$O$_{5+x}$ adopt the cubic perovskite crystal structure (and thus should be expressed as Gd$_{0.5}$Ba$_{0.5}$MnO$_{3.5+\delta}$), the ordered phase can be grown under strongly reducing atmosphere of pure argon. The fortunate opportunity to obtain both layered GdBaMn$_2$O$_{5+x}$ and cubic Gd$_{0.5}$Ba$_{0.5}$MnO$_{3.5+\delta}$ phases allows direct comparison of the oxygen behaviour in materials with and without the A-site sublattice ordering. For the cobalt oxide, on the other hand, only the ordered GdBaCo$_2$O$_{5+x}$ phase can be obtained even at high oxygen pressure.

The homogeneity and cation stoichiometry of our crystals are confirmed by the electron-probe microanalysis (EPMA) and the inductively-coupled plasma (ICP) spectroscopy. Ordering of the Gd and Ba ions into consecutive (001) layers is confirmed by the X-ray diffraction measurements [Fig. 1(d) and (e)], which clearly demonstrate the doubling of the unit cell along the c axis for GdBaMn$_2$O$_{5+x}$ single crystals. The behaviour of dc resistivity shows that both GdBaMn$_2$O$_{5+x}$ and GdBaCo$_2$O$_{5+x}$ undergo an insulator-to-metal transition upon increasing temperature; at high temperatures, they possess a metallic conductivity $\sigma$ of the order of $10^2$ and $10^3$ S/cm, respectively. These values are much larger than any ionic conductivity available in solids, indicating that these compounds should be mixed ionic and electronic conductors (MIECs).

It is well known that in MIECs, the ionic conductivity $\sigma_i$, which is typically much smaller than the electronic conductivity $\sigma_e$, may be determined from diffusion measurements. In oxides with variable oxygen stoichiometry, like GdBaMn$_2$O$_{5+x}$ and GdBaCo$_2$O$_{5+x}$, a sharp change in conditions (oxygen pressure or temperature) results in a gradual transition into a new equilibrium state that differs in oxygen content; this means that the oxygen concentration in crystal samples changes with time, which can be measured as a weight change. The observed relaxation time depends on two processes: the oxygen exchange at the interface between the gas and the solid, and the oxygen bulk diffusion. In the present study, both the surface exchange coefficient $K$ and the chemical diffusion coefficient $D$ are obtained by examining the weight change of crystals as a function of time.

The oxygen-exchange behaviour in cubic manganese oxide and its layered counterpart, studied in polycrystalline samples with comparable morphology, is shown in Fig. 2. There are two clear consequences of the A-site ordering: First, as shown in Fig. 2(a), the change in the equilibrium oxygen content $x_{eq}$ upon decreasing oxygen pressure from 1 to $10^{-5}$ bar at 700°C is much more pronounced in the layered oxide. Thus, it is much easier to remove oxygen from the layered GdBaMn$_2$O$_{5+x}$ than from cubic Gd$_{0.5}$Ba$_{0.5}$MnO$_{3.5+\delta}$. Second, and more important, is a huge difference in the rate of the oxygen uptake. Figure 2(b) shows a normalized change in the oxygen content $\Delta x_{norm} = (x-x_0)/(x_{eq}-x_0)$ ($x_0$ is the initial oxygen content and $x_{eq}$ is the equilibrium one), measured during the annealing in the oxygen gas flow at 350°C and 650°C, for samples with ordered (open symbols) and disordered (filled symbols) A-site sublattice. The relaxation time is about two orders of magnitude smaller in the layered oxide. Surprisingly, the oxygen accumulation in the layered GdBaMn$_2$O$_{5+x}$ even at 350°C turns out to be faster than that in the cubic Gd$_{0.5}$Ba$_{0.5}$MnO$_{3.5+\delta}$ at 650°C.

Having established that the ordering of the A-site sublattice into a layered structure significantly enhances the oxygen relaxation rate, we now turn to a more quantitative analysis of the oxygen diffusion. For that purpose, however, large single-crystal samples of GdBaMn$_2$O$_{5+x}$ appear to be unsuitable: depending on $x$, the orthorhombicity $(b-a)/a$ in GdBaMn$_2$O$_{5+x}$ varies from 0 up to 7%, and the enormous strains emerging upon the oxygen intercalation into large single crystals result in the formation of a regular array of cracks on the crystal surface. We therefore focus our quantitative analysis on another layered material GdBaCo$_2$O$_{5+x}$, which does not have such a problem. To separate the surface-exchange and bulk-diffusion contributions to the overall oxygen exchange rate, we study the oxygen kinetics in GdBaCo$_2$O$_{5+x}$ single crystals of different size: the oxygen kinetics is mostly limited by the surface exchange for small-size crystals, while for large-size crystals it is mostly limited by the bulk diffusion. The change in weight with time in a rectangular-shape sample of a given size has an analytical solution which is a function of both the chemical diffusion coefficient $D$ and the surface exchange coefficient $K$. Figure 3 shows the experimental data (symbols) and analytical fits (solid lines) of the change in the oxygen content with time for GdBaCo$_2$O$_{5+x}$ single-crystal samples of different sizes upon annealing in the oxygen flow at 350°C. From this set of data, the parameters $D$ and
obtained in our experiments, is related to the diffusion (or trace-diffusion) coefficient of conductivity, which is uniquely determined by the self-diffusion process. Keeping in mind that the chemical diffusion coefficient of conductivity can be uniquely determined to be $D = 3 \cdot 10^{-7}$ cm$^2$/s and $K = 2 \cdot 10^{-6}$ cm/s. We note that the oxygen kinetics does not show any detectable difference upon varying the sample size along the $c$-axis in the range of 30-500 $\mu$m, implying an essentially two-dimensional character of the oxygen diffusion in this layered material.

Using the technique described above, we have determined the parameters $D$ and $K$ for the temperature range of 250-600°C at 1 bar oxygen pressure [Fig. 4(a)]. These data are well fitted by the activation laws $D(\text{cm}^2/\text{s}) = 0.15 \cdot \exp(-0.7 \text{eV}/k_B T)$ and $K(\text{cm/s}) = 15 \cdot \exp(-0.85 \text{eV}/k_B T)$, revealing quite low activation energies for both processes. As a result, the oxygen diffusion in GdBaCo$_{2}O_{5+x}$ becomes very fast already at rather low temperatures, exceeding $10^{-5}$ cm$^2$/s at 600°C. To appreciate the true merit of this high oxygen diffusivity in GdBaCo$_{2}O_{5+x}$, it is worth estimating the ionic bonding strength of oxygen, which is uniquely determined by the self-diffusion (or trace-diffusion) coefficient $D^*$. One should keep in mind that the chemical diffusion coefficient $D$, obtained in our experiments, is related to $D^*$ through a so-called thermodynamic factor $\Theta \equiv (\partial \ln P/\partial \ln x)/2$. $D = \Theta \cdot D^*$, reflecting the fact that the true driving force for diffusion is a gradient in the chemical potential but not a gradient in the oxygen concentration. In GdBaCo$_{2}O_{5+x}$, $\Theta$ turns out to be quite low and does not exceed $\sim 10$ in the whole temperature and oxygen-pressure range studied [Fig. 4(b)]. Thus, the ionic conductivity of 0.01 S/cm, which is considered as a criterion for SOFCs to be valuable, can be achieved in GdBaCo$_{2}O_{5+x}$ already at $\sim 500^\circ$C. Clearly, there should still be a possibility for further improvement of properties in ordered perovskite oxides, and the most obvious way is a substitution of different rare earths for Gd.

| Energy (eV) | Activation Energy (eV) |
|------------|------------------------|
| 0.7         | $-0.7 \text{eV}/k_B T$ |
| 0.85        | $-0.85 \text{eV}/k_B T$ |

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