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THE EFFECT OF OXYGEN SORPTION ON THE CRYSTAL STRUCTURE OF $La_{1-x}Sr_xCoO_{3-\delta}$

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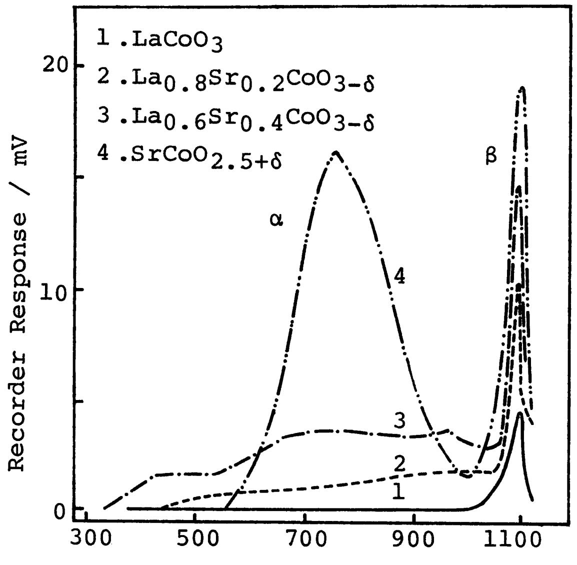
High temperature X-ray diffractometry was applied to investigate the effects of oxygen sorption on the structure of $La_{1-x}Sr_xCoO_{3-\delta}$. The lattice parameters of $SrCoO_{2.5+\delta}$ $(x = 1)$, which was found to have a tetragonal unit cell in this study, were markedly affected by oxygen sorption, while no such effects were observed for the samples $x = 0$, 0.2, and 0.4 with perovskite structure. It is suggested that the structural effects of oxygen sorption arise from the reordering of oxygen vacancies.

The defect perovskite oxide $La_{1-x}Sr_xCoO_{3-\delta}$ is attracting great attention as a catalyst for the complete oxidation of hydrocarbons and electrode processes. The partial or total substitution of Sr^{2+} for La^{3+} in $LaCoO_3$ has been shown to result in the formation of Co^{4+} and/or oxygen vacancies and such defect formation has been considered to be important for the catalytic activity of the compounds. We reported previously1) that $La_{1-x}Sr_xCoO_{3-\delta}$ sorbed a large amount of oxygen which far exceeded a surface monolayer and increased with increasing x. This behavior in oxygen sorption seems to be also related to the oxygen vacancies of the compound. In order to collect the imformation on the nature of sorbed oxygen, it is considered important to know whether the sorption or desorption of such a large amount of oxygen is accompanied by the change of crystal structure. In this paper, we have tried to reveal the effect of oxygen sorption on the crystal structure of $La_{1-x}Sr_xCoO_{3-\delta}$ by X-ray powder diffractometry.

Four samples, $LaCoO_3$ $(x = 0)$, $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ $(x = 0.2)$, $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ $(x = 0.4)$, and $SrCoO_{2.5+\delta}$ $(x = 1.0)$, were prepared by calcining the mixtures of the metal acetates at 1100 K in air for 10 h. The products were identified by X-ray diffraction with filtered CuKα radiation. X-Ray diffraction measurements at high temperatures were carried out by using a high temperature camera (Rigaku denki Model D-3F high temperature attachment) which allowed one to control the sample temperature and atmosphere. Silver powder was used as an internal standard for determining lattice constants. The powder samples were mixed with silver (99.9 %), and after mounting on a platinum specimen holder, heated or cooled to desired temperatures in vacuo (13 ~ 1.3 Pa) or in an oxygen atmosphere (13 kPa). After standing for 0.5 h at each desired temperature, the samples were subjected to X-ray diffraction measurement.

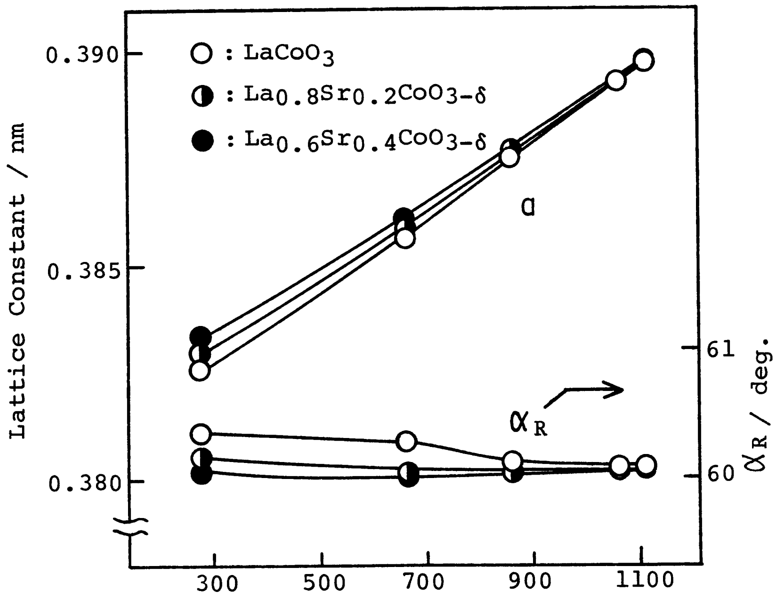
It would be appropriate to describe briefly the oxygen-absorptive properties of the four samples before going to the results of X-ray study. As shown in Fig. 1, the TPD chromatograms of oxygen are characterized by the appearance of two desorption peaks, α and β; α is a broad peak ranging from ca. 300 K to ca. 1000 K and in fact plateau-like for $x = 0$, 0.2, or 0.4, while β is a very sharp one centered at ca. 1100 K. Both α and β increase with increasing the Sr content. The amount of desorbed oxygen for each desorption peak is far larger than can be accomodated by the surface, except the case of α from $LaCoO_3$ in which the oxygen amount is equivalent to ca. 40 % of a surface monolayer. The amount, α + β, is estimated to be 0.02 (x = 0), 0.07 (x = 0.2), 0.13 (x = 0.4), or 0.20 (x = 1) mol-oxygen atom per mol-perovskite compound, respectively. This indicates that the desorbed oxygen is liberated not only from the surface but also from the bulk.



Temperature / K

Fig. 1 TPD chromatograms of oxygen from $La_{1-x}Sr_xCoO_{3-\delta}$.
(Oxygen preadsorption 1100 K→RT, 13 kPa)

Of the four samples investigated, the first three with x = 0, 0.2, and 0.4 have perovskite structure[2)] while the last one with x = 1.0 has not. The effects of oxygen sorption on crystal structure were found to be utterly different between these two groups. The perovskite structure of the first group (x = 0, 0.2, and 0.4) was somewhat distorted rhombohedrally. The distortion decreased with increasing x and almost disappeared at x = 0.4 in agreement with the previous reports.[3)] These samples were subjected to oxygen sorption by cooling from 1073 K to room temperature in an oxygen atmosphere (13 kPa), followed by X-ray diffractometry during heating stepwise up to 1100 K in vacuo. The parameters obtained are shown as a function of temperature in Fig. 2. The lattice constant a increases smoothly with raising temperature while the rhombohedral angle α_R for x = 0, and 0.2 decreased gradually to 60°, a value for the undistorted perovskite structure. These changes are regarded as thermal expansion or undistortion of the crystal lattice. There are no particular changes ascribable to the oxygen desorption of α or β. Nor we detected any significant differences in the lattice parameters at room temperature between the oxygen-sorbed sample and one which was evacuated at 1100 K.



Temperature / K

Fig. 2 Changes of lattice parameters on heating.
a : lattice constant
α_R : rhombohedral angle

In marked contrast with the above samples, the lattice parameters of $SrCoO_{2.5+\delta}$ (x = 1) were found to chage significantly with oxygen sorption. The crystallography of $SrCoO_{2.5+\delta}$ is rather complex. Watanabe and Takeda[4)] have reported that the calcination of a equimolar mixture of $SrCO_3$ and $CoCO_3$ gives various $SrCoO_{2.5+\delta}$ phases with brownmillerite, orthoferrite, tetragonal perovskite, cubic perovskite, or hexagonal $BaNiO_3$ type structure depending on the oxygen pressure and temperature of calcination. Such variety in phase formation seems to arise from the change in oxygen content (or δ) as reported in $SrFeO_{2.5+\delta}$.[5)] The present $SrCoO_{2.5+\delta}$ sample, which was prepared from metal acetates as stated before, however, did not coincide with any one of the phases reported above. The X-ray diffraction pattern of the sample which was cooled to room temperature in air after preparation could be indexed satisfactorily by assuming a tetragonal unit cell with $a = 0.5846$ nm and $c = 0.729$ nm at 298 K, as shown in Table 1. The unit cell seems to be structurally related to cubic perovskite lattice by $a = \sqrt{2}\, a_c$ and $c = 2\, a_c$, where a_c is the lattice constant of cubic perovskite structure. Such structural relation with perovskite structure has been observed for many other phases in $SrCoO_{2.5+\delta}$ and $SrFeO_{2.5+\delta}$ systems. The lattice constants of the present phase were found to be influenced significantly by oxygen sorption, as shown in Fig. 3. For comparison with the unit cell of perovskite structure, the pseudo lattice constants, $a/\sqrt{2}$ and $c/2$, are presented in the figure. In case 1, the sample was evacuated at 1100 K followed by cooling in vacuo to room temperature (preevacuated sample). Its unit cell had dimensions of $a = 0.554$ nm and $c = 0.757$ nm at 298 K. On heating, the lattice constants elongated simply by thermal expansion. In case 2, the sample was subjected to the same oxygen preadsorption as in the TPD experiments of Fig. 1. At room temperature the lattice constant a was expanded while c was shrinked, compared to those of the preevacuated sample. On heating in vacuo the lattice constants drew near and coincided respectively

Table 1. X-Ray diffraction data for $SrCoO_{2.5+\delta}$

h k l	d, obsd. nm	d, calcd. nm	Int.
1 0 2	0.3116	0.3093	56
1 1 2	0.2793	0.2734	100
2 1 2	0.2123	0.2125	14
2 2 0	0.2062	0.2067	43
0 3 0	0.1951	0.1949	13
1 1 4	0.1670	0.1668	7
1 3 2	0.1649	0.1649	26
2 3 1	0.1583	0.1583	16
1 2 4	0.1501	0.1495	13
3 3 0	0.1373	0.1378	14
2 2 4	0.1368	0.1367	13

($a = 0.5846$ nm, $c = 0.729$ nm at 298 K)

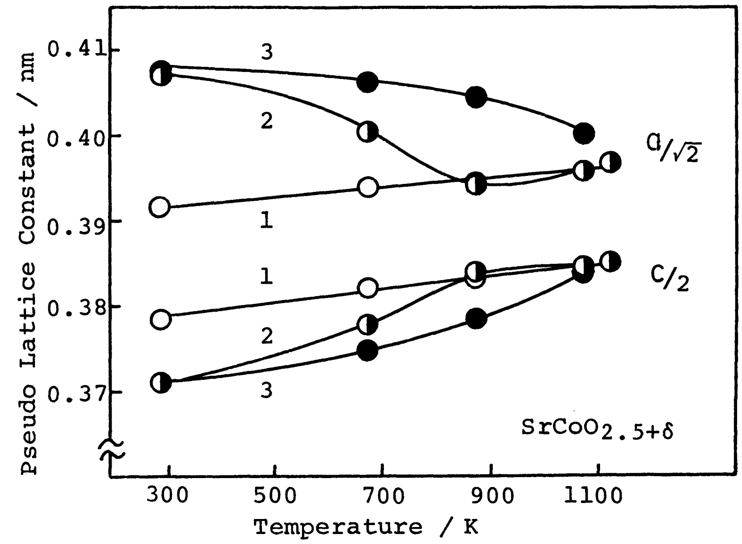


Fig. 3 Changes of pseudo lattice constants of $SrCoO_{2.5+\delta}$ on heating.

(1) : heating in vacuo after preevacuation at 1100 K
(2) : heating in vacuo after oxygen preadsorption at 1100 K
(3) : heating under oxygen atmosphere (13 kPa) after oxygen preadsorption at 1100 K

with those of the preevacuated sample at temperatures above 900 K. From the comparison of this behavior with the TPD chromatogram shown in Fig. 1, the rapid change in cell dimension below ca. 900 K is evidently due to the oxygen desorption ascribable to α. In constant, β desorption gave no effects on the unit cell. In case 3 where the oxygen preadsorbed sample was heated in an oxygen atmosphere, the lattice constants changed more slowly than in case 2. The differences in lattice constants between case 2 and 3 are contributed by such amounts of oxygen that are sorbed or desorbed reversibly at respective temperatures. It was confirmed in a separate gravimetric analysis that at high temperatures, e.g. 900 K, a considerable amount of oxygen was absorbed reversibly according to the atmospheric oxygen pressure.

As mentioned above, α sorption (or desorption) of oxygen in $SrCoO_{2.5+\delta}$ gave rise to large changes in unit cell dimension. This is direct evidence that the sorbed oxygen is taken into the oxygen vacancies of oxide lattice. It is noted that while the preevacuated sample has a pseudo unit cell ($a/\sqrt{2} = 0.392$ nm and $c/2 = 0.379$ nm) rather close to that of cubic perovskite structure ($a = 0.383$ nm), the oxygen preadsorbed sample has more anisotropic structure ($a/\sqrt{2} = 0.408$ nm and $c/2 = 0.371$ nm). This suggests that some anisotropic ordering of vacancies takes place with α desorption. We have reported that α sorption amounts to ca. 0.065 mol-O_2/mol of $SrCoO_{2.5+\delta}$ under the present conditions. On the other hand, β sorption exerted no effects on the unit cell, though its amount is comparable with that of α. Thus α and β sorptions in this sample have different meanings in the crystallographic view point. However, a question remains as to why β sorption does not affect the unit cell. A plausible reason may be that in β sorption oxygen is accepted by vacancies at random without causing the reordering of vacancies. In the other three samples ($x = 0$, 0.2, and 0.4) both α and β little affected the unit cells. In these cases, oxygen is accommodated at randomly distributed oxygen vacancies without affecting the vacancy ordering. Thus we suspect that in the $La_{1-x}Sr_xCoO_{3-\delta}$ system oxygen sorption affects the unit cell dimension only when reordering of oxygen vacancies takes place.

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