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XPS study of adsorbed oxygen of nanocrystalline $LaFeO_3$ materials

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Abstract

The adsorbed oxygen and lattice oxygen of nanocrystalline $LaFeO_3$ materials have been studied by X-ray photoelectron spectroscopy at room temperature and under a compacting pressure of 0.0 and 1.0 GPa. It was found that the signal of the chemisorbed oxygen was less intense than that of the lattice oxygen at 0.0 GPa, but larger than that of the lattice oxygen at 1.0 GPa for an average crystal size larger than 15 nm. When the average crystal size was 2.0 nm, the chemisorbed/lattice oxygen ratio did not significantly change between 0.0 and 1.0 GPa.

1. Introduction

Perovskite-type nanocrystalline $LaFeO_3$ is an interesting material in which the amounts of adsorbed and lattice oxygen (O_c and O_l) under different compacting pressures change dramatically. The authors have already presented the results of an X-ray photoelectron spectroscopy (XPS) study of the chemisorbed and lattice oxygen of nanocrystalline $LaFeO_3$ from 0.0 to 1.5 GPa compacting pressure for an average crystal size of less than 15 nm [1]. It was shown there that the signal of the chemisorbed oxygen O_c is less intense than that of the lattice oxygen O_l for a crystal size of 70 nm but that the signal of the O_c is more intense than that of O_l for nanocrystals. It was further shown that the O_c/O_l ratio is increased at 1.0 GPa for nanocrystalline $LaFeO_3$ solid materials. In this paper, we try to determine the maximum particle size of uncompacted nanocrystal for which the O_c signal is still more intense than the O_l signal. We try to answer the question of how the O_c/O_l ratio will change if loose powders with an average particle size larger than 15 nm are compacted. For this purpose information on the nature of chemisorbed and lattice oxygen for nanocrystalline $LaFeO_3$ (larger than 15 nm) under a compacting pressure of 1.0 GPa is obtained by XPS.

2. Experimental details

In order to find out the regularity of the XPS spectra of $LaFeO_3$ nanocrystals prepared by various methods, we have prepared several samples. They are

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denoted sample A (prepared by citrate method, CTM, the average crystal size $d_A = 16.0$ nm) [2], sample B (polyethylene glycol method, PEGM, $d_B = 15.3$ nm) [3], sample C (polyvinyl alcohol method, PVAM, $d_C = 17.1$ nm) [4], sample D (stearic acid method, SAM, $d_D = 17.3$ nm) [5], and sample E (reverse drop coprecipitation in alcohol method, RDCAM, $d_E = 2.0$ nm) [6]. These samples exist in the single orthorhombic phase as determined by X-ray diffraction (XRD) and the average crystal size of the samples was examined by transmission electron microscopy (TEM). The XPS study was performed by means of a VG Scientific ESCA MK II spectrometer chamber (pressure 3×10^{-6} Pa). The binding energy (*BE*) was calibrated with reference to C(1s) = 285.0 eV.

3. Results and discussion

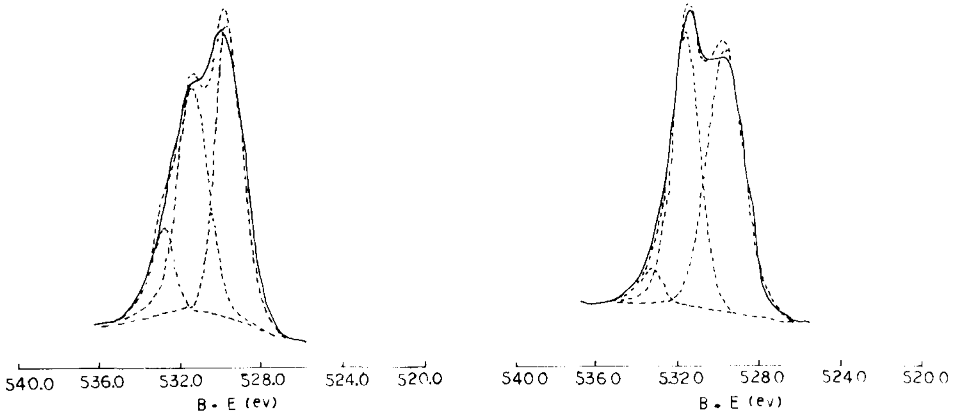
3.1 Resolution of O(1s)

XPS measurements were carried out for the O(1s) spectra of the samples from A to D at 0.0 and 1.0 GPa and room temperature as shown in Table 1, the average crystal size of these samples is larger than 15 nm. Every composite O(1s) spectrum can be resolved into three components: the lattice oxygen O_l (*BE* = 528.93–530.29 eV), the chemisorbed oxygen or adsorbed oxygen O_c (*BE* = 531.00–532.20 eV) and the physisorbed oxygen O_p (*BE* = 532.34–532.95 eV). The O(1s) spectra of samples A, C and E at 0.0 and 1.0 (1.5) GPa compacting pressure and room temperature are shown in Figs. 1, 2 and 3.

TABLE 1

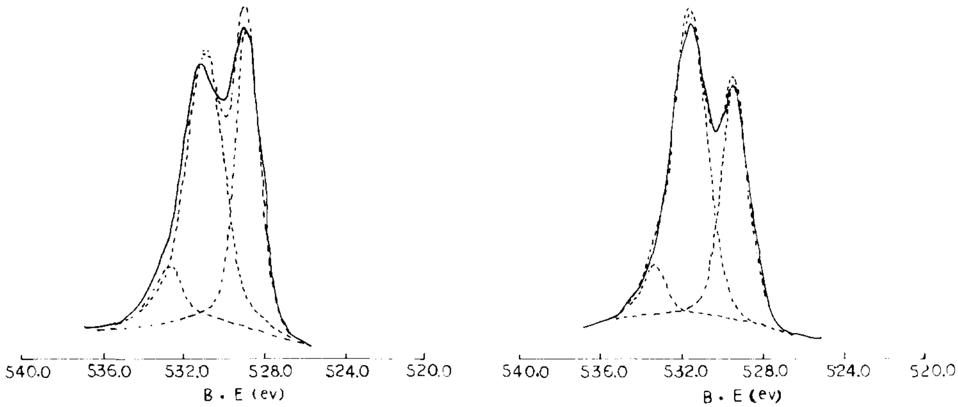
Binding energy and percentage of O_p, O_c and O_l in $LaFeO_3$

Sample	*d* (nm)	Pressure (GPa)	O(1s) (eV)						O_c/O_l ratio	Increase in ratio (%)
			O_p	%	O_c	%	O_l	%		
A	16.4	0.0	532.82	10.16	531.39	41.74	529.63	48.05	0.87	
		1.0	532.95	7.82	531.50	44.06	529.60	48.11	0.92	5.4
B	15.3	0.0	532.67	3.38	531.39	34.36	529.44	62.26	0.55	
		1.0	532.56	8.62	531.33	44.95	529.28	46.43	0.97	43.1
C	17.1	0.0	532.63	4.57	531.00	55.70	528.93	39.73	1.40	
		1.0	532.77	10.19	531.32	55.15	529.22	34.65	1.59	11.9
D	17.3	0.0	533.34	11.79	532.20	29.80	530.29	58.41	0.51	
		1.0	533.46	9.78	531.94	41.69	529.88	48.53	0.86	40.6
E	2.0	0.0	532.84	10.75	531.33	52.81	529.39	36.44	1.45	
		0.5	532.86	4.17	531.43	57.80	529.35	38.03	1.52	
		1.0	532.88	9.93	531.57	52.33	529.60	37.74	1.39	−4.1
		1.5	533.25	11.48	531.25	67.45	529.10	21.06	3.20	120.7
F	70.0	0.0	532.46	3.69	531.42	29.91	529.37	66.40	0.45	
		1.0	532.96	3.67	531.62	27.43	529.44	68.91	0.40	−11.1



(a) (b)

Fig. 1. O(1s) spectra of the $LaFeO_3$ nanocrystals for sample A: (a) 0.0 GPa; (b) 1.0 GPa.



(a) (b)

Fig. 2. O(1s) spectra of the $LaFeO_3$ nanocrystals for sample C: (a) 0.0 GPa; (b) 1.0 GPa.

3.2. Characteristic of O(1s) in uncompacted nanocrystals (larger than 15 nm)

In ref. 1 we discussed the fact that the signal of chemisorbed oxygen is always more intense than that of lattice oxygen whether the samples are compacted or uncompacted, when the average size of the samples is less than 15 nm. It can be seen from samples A to D in Table 1 that the signal of the chemisorbed oxygen was less intense than that of the lattice oxygen when the average crystal size of the uncompacted samples was larger than 15 nm. XPS analysis shows that despite the fact that there is a large difference in the average particle size between nanocrystals (15.3–17.3 nm) and conventional crystals (larger than 70 nm), nanocrystals of 15.3 nm already exhibit the O(1s) characteristic of conventional crystals (70 nm). The con-

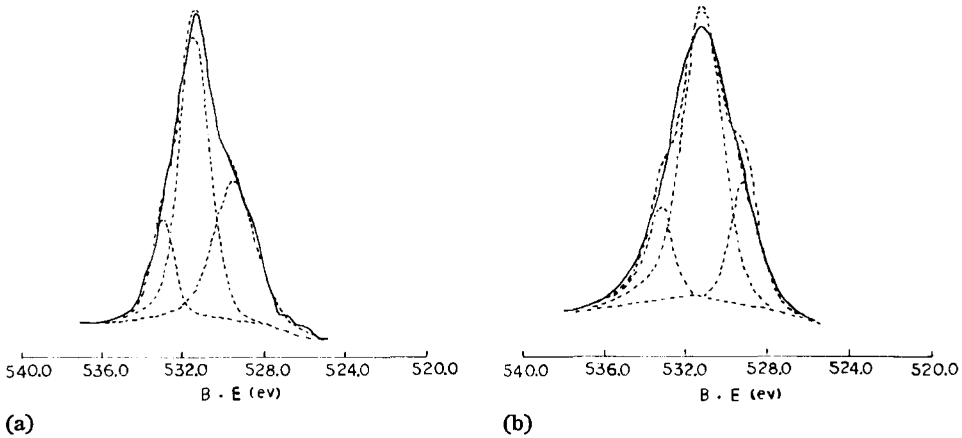


Fig. 3. O(1s) spectra of the $LaFeO_3$ nanocrystals for sample E: (a) 0.0 GPa; (b) 1.5 GPa.

clusion to be drawn from this investigation is that the different physical or chemical characteristics of nanocrystals might be transformed to those of conventional crystals with different sizes.

3.3. Characteristic of O(1s) of nanocrystalline solid materials (larger than 15 nm)

When the samples with 15.3–17.3 nm average crystal size were compacted into nanocrystalline solid materials at 1.0 GPa, the O(1s) spectra of these samples are different from those of the uncompacted samples, but are very similar to those of the compacted or uncompacted nanocrystals with crystal size less than 15 nm reported in ref. 1. For these samples the intensity of chemisorbed oxygen was stronger than that of lattice oxygen. The *BE* and the percentage of O_p, O_c and O_l for the samples are shown in Table 1. As can be seen from the table, the percentage of O_c and O_c/O_l ratio increased after the samples were compacted at 1.0 GPa. This shows that part of the nanocrystals has become displaced and fragmented under the stress of the contact zones in the interparticle. The interface of the crystalline in the compacted samples is therefore increased [1]. The displacement and fragmentation behaviour under the fixed compacting pressure are related directly to crystal size.

3.4. Characteristic of O(1s) for sample with 2.0 nm average crystal size before and after compacting

It can be derived from the spectra of O(1s) of sample E in Fig. 3 and Table 1 that with average crystal size of 2.0 nm the peak of O_c far exceeds the peak of O_l in intensity independently of whether the samples are compacted at 0.0, 0.5, 1.0 or 1.5 GPa; but the O_c/O_l ratio has not distinctly changed after compacting except for the sample which was compacted at 1.5 GPa, as seen in Table 1. It can be considered that such small nanocrystals have become displaced and fragmented at 0.5 GPa under the stress of the contact zones in the interparticles, but that new contact zones have formed, probably in the interparticles at 1.0 GPa, so that a part of interface of the nanocrystals has decreased. When the samples were further investigated at 1.5 GPa, it was found that the percentage of O_c and the O_c/O_l ratio were distinctly larger, and that the sample compacted at 1.5 GPa had the highest O_c/O_l ratio.

There is no distinct change in the O_c/O_l ratio for sample F, the 70 nm conventional crystal, after being compacted at 1.0 GPa [1].

It can be seen from the samples with various average crystal sizes that the O(1s) spectra of the samples changed with variation in crystal size and the compacting pressure. The smaller the average crystal size, the lower the compacting pressure needed to increase the O_c/O_l ratio.

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