Superconductivity and X-Ray Crystallographic Structures of $La_xBa_{1+x}Cu_{1+2x}O_y$ (x = 2, 3, ...)†

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In present study, the thermal analysis, Rietveld refinement, magnetic susceptibility and electrical resistivity of $La_xBa_{1+x}Cu_{1+2x}O_y$ (x = 2, 3, ...) have been reported. It is possible to interpret the relationship between the crystal structures and the superconductivity. All the compounds have tetragonal structure with triple perovskite unit. A portion of La atoms occupied Ba site and more La atoms were in the Ba site as the composition of La increased. The oxygen atoms at the pyramid base responsible for the superconductivity migrated to vacancies around Ba site to neutralize the excess positive charge of La^{3+} ions. La-336 compound, which is the ultimate composition of the series, loses superconductivity as a result of pyramid collapse.

Key Words: Rietveld, $La_xBa_{1+x}Cu_{1+2x}O_y$, TGA, Perovskite, Superconductivity, Vacancy.

INTRODUCTION

Rare earth containing Re-Ba-Cu-O compounds have a high critical temperature near 93 K. The superconducting phase of these compounds usually have a fixed composition of Re:Ba:Cu = 1:2:3. La-Ba-Cu-O superconductors were originally investigated by Bednorz and Müller[1]. These compounds have a single phase with a wide variety of compositions. Michel *et al.*[2] confirmed that the structure of $BaLa_4Cu_5O_{13+y}$ was different from $ReBa_2Cu_3O_{7-x}$ (Re-123 hereafter) compounds by neutron diffraction analysis. $La_3Ba_3Cu_6O_y$ (La-336 hereafter) has a tetragonal structure with a triple perovskite unit. This compound has no superconducting properties and some La atoms occupy the Ba sites. The structure and properties of modified La-336 was published by Engelsberg[3]. Additional results were published by other researchers such as $La_3Ba_3Ca_xCu_{6+x}O_y$ ($0 \leq x \leq 3$)[4], $La_3Ca_xBa_{4-x}Cu_7O_y$[5,6]. The purpose of this research is to investigate the crystal structures and superconducting properties of $La_xBa_{1+x}Cu_{1+2x}O_y$ (x = 2, 3, ...) systems.

EXPERIMENTAL

All the compounds were made by representative solid state reaction under the same conditions. High purity (> 99.98 %) La_2O_3, $BaCO_3$ and CuO powders were used. Mixtures of powders were heated at 950 ºC, 24 h in the air, then formed into pellets. The pellets were heated again 48 h at the same temperature in an oxygen atmosphere then annealed at 500 ºC, 12 h to get the completely oxidized compounds. The specimens were shiny black after the final treatments. A Bruker D5005 X-ray diffractometer with a primary monochromator was used to get the diffraction pattern. Data were collected in the range of $2\theta = 20\text{-}100º$ with $\Delta\theta = 0.02º$ and a step time of 20 s. Rietveld analysis was performed with the program Rietan94 to analyze the crystal structure of the compounds. The tetragonal structure of La-336 with the space group P4/mmm was chosen as a model. A Lakeshore 7130 ac-susceptometer was used to measure the susceptibility in the temperature range of 12-295 K at 500 Hz and 4 Oe. Oxygen content was determined by iodometry. Thermal analysis was performed to identify the temperature for maximum oxygen content.

RESULTS AND DISCUSSION

All the compounds with the formula $La_xBa_{1+x}Cu_{1+2x}O_y$ (x = 2, 3, ...) had nearly same structure as $YBa_2Cu_3O_{7-x}$ (Y-123 hereafter). They had tetragonal symmetry with triple perovskite unit. All the compounds between x = 2 and x = 8 were single phase and the ultimate composition approached La-336 as x increased.

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Fig. 1 shows the result of thermal analysis. The weight of La$_2$Ba$_3$Cu$_5$O$_y$ (La-235 hereafter)specimen decreased during the heating process in an N$_2$ atmosphere and the weight of the same sample was restored on heating in an O$_2$ atmosphere. The annealing temperature for maximum O$_2$ content is 500 ºC.
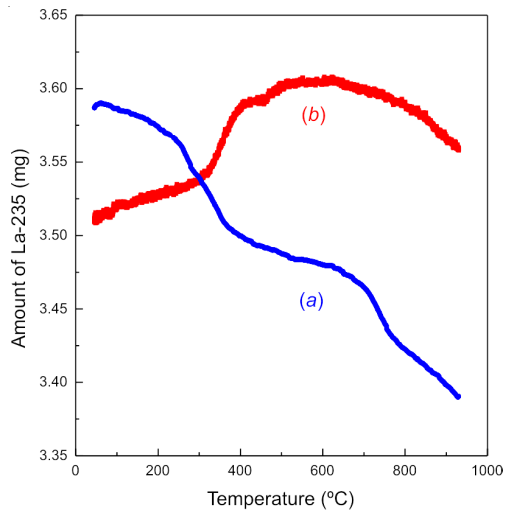

Fig. 1. TGA curves of La-235 phase (a) first run in N$_2$ (b) second run in O$_2$

Figs. 2 and 3 show the electrical resistivity and magnetic susceptibility of the compounds, respectively, as a function of temperature. The two sets of data coincide well and the critical temperature of each compound decreases as x increases.
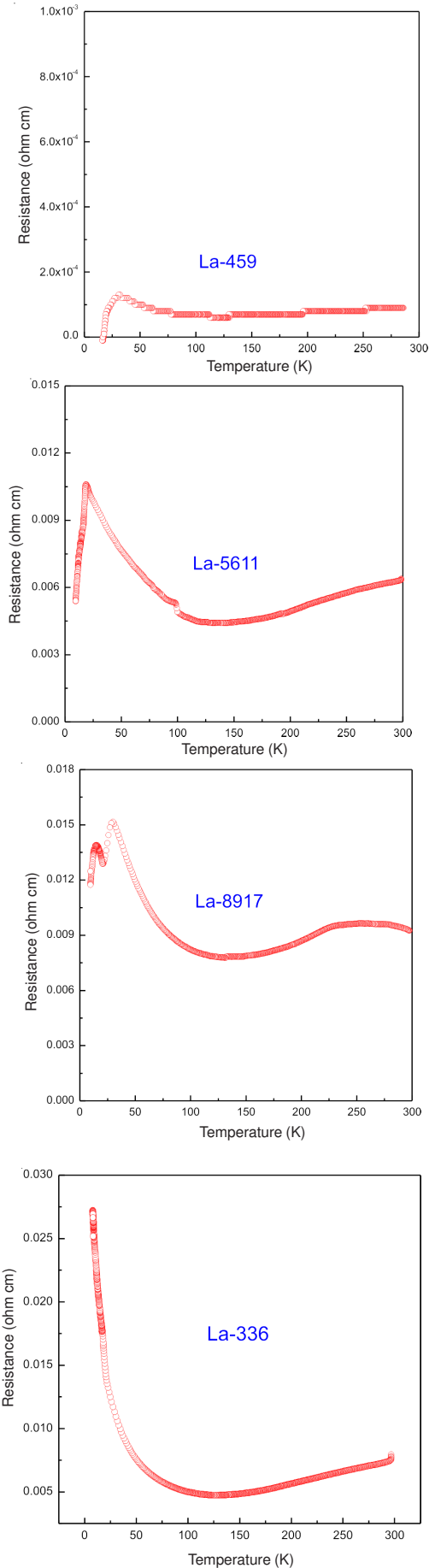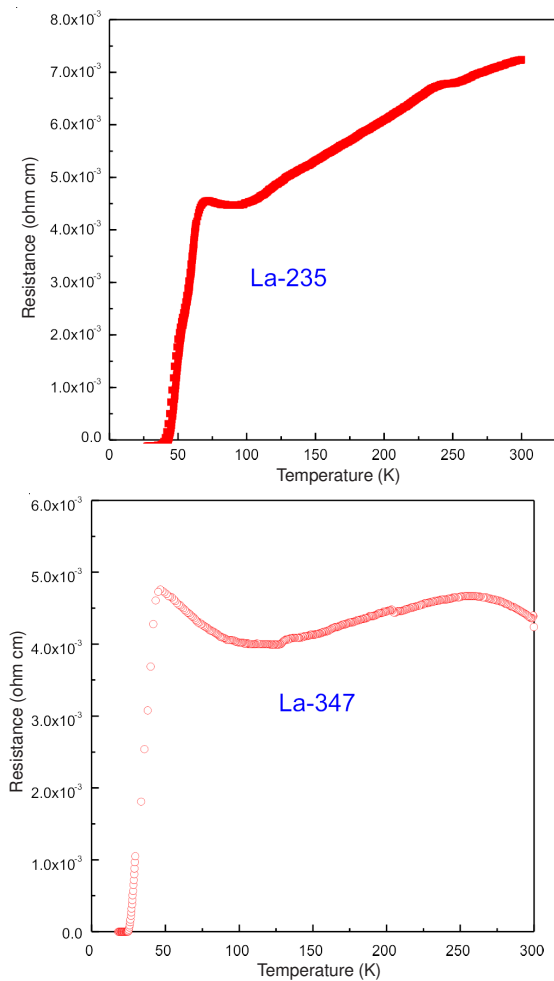

Fig. 2. Resistivity *versus* temperature for La$_x$Ba$_{1+x}$Cu$_{1+2x}$O$_y$ system
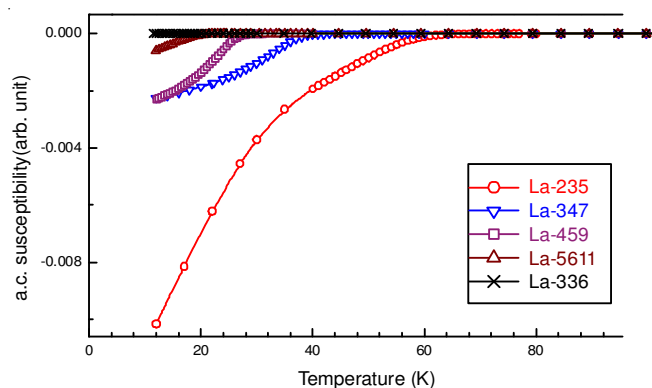
Fig. 3. Temperature dependence of the a.c. susceptibility for $La_xBa_{1+x}Cu_{1+2x}O_y$ system

Table-1 lists lattice parameter, oxygen content, Cu valency and critical temperature of the compounds. One Y^{3+} (La^{3+}) ion occupies the center of the middle perovskite unit, two Ba^{2+} ions occupy the center of the upper perovskite unit and the lower perovskite unit, respectively, at the triple perovskite unit in Y-123 (La-123). In our compounds, there were excess La atoms and fewer Ba atoms compared to Y-123 (La-123) compound. As a result, a portion of the La atoms occupied the Ba sites. Unit cell dimensions of the compounds gradually decreased as more La^{3+} (103 pm) ions occupy the Ba^{2+} (135 pm) site.

Table-2 lists the Rietveld analysis results. Measured intensity from the X-ray diffraction corresponded with the intensity from the Rietveld analysis. Because the scattering factors of La and Ba are similar, it is not possible to determine the relative amount of La^{3+} and Ba^{2+} ions occupying the same sites from X-ray diffraction. The amount of La atoms in the Ba sites could be determined successfully during the Rietveld refinement process with appropriate temperature factors. The majority of the values in the table are fractional coordinates

of each atom. The upper N corresponds to the site occupancy of Ba in the Ba sites. These values decrease as the relative amount of La increases. The lower N is the site occupancy of La in the Ba site. This demonstrates clearly that more La atoms occupy the Ba site as the amount of La increases.

As higher valent La^{3+} ions occupied lower valent Ba sites, there was an increase in oxygen atoms which surround the Ba sites to neutralize the excess positive charge of La^{3+} ions. Oxygen content did not change significantly from x = 2 to x = 5, but Cu valency decreased. A portion of the oxygen atoms, which construct pyramid bases in the unit cell, migrated to the vacancies around Ba sites. The reduction of Cu valency is directly related to a decrease of hole concentration in the compounds used in this study, thus T_c decreases.

The oxygen content and Cu valency of x = 8 and La-336 compounds increased remarkably and lost superconductivity. More oxygen atoms from the pyramid base migrated in this case and Cu-O pyramids began to collapse. The collapse of Cu-O pyramid, responsible for the superconductivity, will convert La-336 compound into a non-superconducting, anti-ferromagnetic state. Moreover, external oxygen atoms will occupy the vacant sites as more oxygen atoms are needed to neutralize the excess positive charge of La^{3+} ions. Therefore, superconductivity dissipates despite the increase of oxygen content and Cu valency.

It is almost impossible to get the occupation factor of oxygen in our compounds because the X-ray scattering factor of oxygen is very small compared to La and Ba. A neutron diffraction experiment would be required for the compounds in this study.

Conclusion

The oxygen atoms which construct the pyramid base migrated to the vacancies around Ba site as La^{3+} ions occupied the Ba site. More oxygen atoms migrated due to the increased

TABLE-1 LATTICE PARAMETER, OXYGEN CONTENT, COPPER VALENCY AND CRITICAL TEMPERATURE OF $La_xBa_{1+x}Cu_{1+2x}O_y$ SYSTEM								
La:Ba:Cu	a	b	c	c/a	Oxygen content (y)	Cu valency	T_c (K)	
							a.c. Susceptibility	Resistivity (onset)
1.15:1.85:3	3.8982	3.9331	11.7525	3.015	–	–	64.3	63.3
2:3:5	3.9172		11.7893	3.010	6.869	2.179	63.2	63.5
3:4:7	3.9139		11.7593	3.004	6.895	2.167	40.1	44.0
4:5:9	3.9158		11.7563	3.002	6.864	2.132	28.5	29.0
5:6:11	3.9140		11.7354	2.998	6.893	2.142	21.1	18.3
8:9:17	3.9130		11.7209	2.995	7.065	2.240	18.1	14.0
3:3:6	3.9087		11.7044	2.994	7.185	2.290	n.s.	n.s.

TABLE-2 RIETVELD ANALYSIS RESULTS					
	x = 2.0	x = 3.0	x = 4.0	x = 5.0	x = 8.0
Cu(2), (0, 0, z), z	0.3462	0.3459	0.3455	0.3458	0.3448
Ba, (0.5, 0.5, z), z	0.1827	0.1810	0.1821	0.1807	0.1794
N	0.9	0.857	0.835	0.82	0.794
La at Ba, (0.5, 0.5, z), z	0.1827	0.1810	0.1821	0.1807	0.1794
N	0.1	0.143	0.165	0.18	0.206
O(2), (0, 0.5, z), z	0.3726	0.3692	0.3708	0.3685	0.3695
O(3), (0, 0, z), z	0.1538	0.1597	0.1603	0.1612	0.1627
Rp	7.6	6.96	6.97	7.94	7.82
Rwp	9.88	9.47	9.24	10.40	10.25
Re	8.27	7.81	7.81	9.56	9.27

La composition. The reduction of Cu valencies decreased hole concentration in the compounds, therefore T_c decreased. If the amount of migrating oxygen exceeds critical values, superconductivity dissipates as in the case of La-336.

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