Journal of Solid State Chemistry **159,** 19–25 (2001)
doi:10.1006/jssc.2001.9116, available online at http://www.idealibrary.com on IDEAL®

Synthesis and Crystal Structure of $(Sr_{1-x}La_{1+x})Zn_{1-x}O_{3.5-x/2}$ $(0.01 \leq x < 0.03)$

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Received August 29, 2000; in revised form January 2, 2001; accepted February 9, 2001

$(Sr_{1-x}La_{1+x})Zn_{1-x}O_{3.5-x/2}$ $(0.01 \leq x < 0.03)$, was prepared at 1373 K in the $SrO–La_2O_3–ZnO$ system. The X-ray and neutron powder diffraction peaks were indexed with a body-centered tetragonal unit cell ($a = 3.75$ and $c = 13.57$ Å for the sample $x = 0.01$). Weak diffuse superstructure reflections having periods of $\sim 2 \times a$ and $\sim 2 \times c$ were observed in electron diffraction patterns. The basic statistical structure of the superstructure was refined by Rietveld analysis for X-ray and neutron powder diffraction patterns of the sample $x = 0.01$ with a model related to an oxygen-deficient K_2NiF_4-type structure, space group *I*4/*mmm*, Z = 2, $R_{wp} = 0.1317$, $R_p = 0.1052$, $R_I = 0.0566$, and $R_F = 0.0371$ for X-ray data and $R_{wp} = 0.0796$, $R_p = 0.0615$, $R_I = 0.0395$, and $R_F = 0.0252$ for neutron data. In a local structure model, the Zn atom is coordinated by four oxygen atoms. Sr and La atoms are in the eightfold coordination of oxygen atoms. © 2001 Academic Press

Key Words: **$(Sr_{1-x}La_{1+x})Zn_{1-x}O_{3.5-x/2}$; strontium lanthanum zinc oxide; electron diffraction; X-ray powder diffraction; neutron powder diffraction; Rietveld analysis; K_2NiF_4-type structure; local structure; ZnO_4 tetrahedron.**

INTRODUCTION

Many quaternary oxides possessing the K_2NiF_4-type structure (space group *I*4/*mmm*) have been synthesized to study their electric, magnetic, and superconducting properties (1). A series of lanthanum strontium metal oxides, $LaSrMO_4$ (M = Al, V, Fe, Ni, Cu, and Ga) belong to the group of oxides with the K_2NiF_4-type structure (2–9). The trivalent M atoms situate in the octahedral site of the structure. Partial occupation of Zn atoms in the octahedral site was shown in the K_2NiF_4-type structure of $Sr_{3x}La_{2-3x}Zn_{1-x}Ru_xO_4$ $(1/3 \leq x \leq 2/3)$ (10). One-third of Zn atoms in the M site were replaced by Ru atoms at $x = 1/3$, $SrLa(Zn_{0.66}Ru_{0.33})O_4$. As far as we know, there has not been any reports on the oxide with the K_2NiF_4-type structure in which the octahedral site is fully occupied by Zn atoms.

In the Sr–La–Zn–O system, ternary oxides of $SrZnO_2$ (11), $Sr_2La_2O_5$, $SrLa_4O_7$ (12), and $Sr_3La_4O_9$ (13) have been reported. A new quaternary oxide was prepared at 1100°C in air with compositions close to the molar ratio Sr:La:Zn = 1:1:1. The X-ray diffraction pattern of this compound was similar to the patterns of $LaSrMO_4$. The present paper reports the preparation and crystal structure of the compound.

EXPERIMENTAL

Powders of $SrCO_3$ (99.99% purity), La_2O_3 (99.99% purity), and ZnO (99.99% purity) were used as starting materials. Before weighing, $SrCO_3$ powder was heated at 500°C for 24 h in a CO_2 stream. La_2O_3 powder was heated at 1000°C for 6 h. ZnO powder was heated at 200°C for 48 h. These starting powders were weighed to give various compositions, listed in Table 1. The powders were mixed with an agate mortar and pestle (dry mixing) or mixed in an appropriate amount of ethanol in an agate mortar (wet mixing). The powder mixtures were pressed into pellets. The pellets were placed on an alumina plate and heated at 900°C for 36 h and then at 1100°C for 48 h in air. The samples were cooled in the furnace by shutting off the electric power. The temperature dropped from 1100 to 500°C within 2 h.

Chemical analysis was carried out for Sr, La, and Zn by inductively coupled plasma (ICP) emission spectrometry.

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0022-4596/01 $35.00

TABLE 1
Compositions of the Samples and Products Prepared at 1100°C in Air in the $SrO–LaO_{1.5}–ZnO$ System

	Mixing composition/mole fraction			
No.	SrO	ZnO	$LaO_{1.5}$	Compounds
1	0.250	0.250	0.500	SLZO, La_2O_3
2	0.286	0.286	0.429	SLZO, La_2O_3
3	0.327	0.327	0.346	SLZO $\gg$ La_2O_3
4	0.329	0.329	0.342	SLZO
5	0.330	0.330	0.340	SLZO
6	0.331	0.331	0.338	SLZO
7	0.332	0.332	0.336	SLZO $\gg$ $SrZnO_2$
8	0.333	0.333	0.333	SLZO $\gg$ $SrZnO_2$
9	0.400	0.400	0.200	SLZO, $SrZnO_2$
10	0.500	0.500	0.000	$SrZnO_2$
11	0.550	0.350	0.100	SLZO, $SrZnO_2$, SrO
12	0.600	0.200	0.200	SLZO, SrO
13	0.500	0.150	0.350	SrO, La_2O_3, SLZO
14	0.340	0.130	0.530	La_2O_3, SrO, SLZO
15	0.140	0.430	0.430	ZnO, La_2O_3, SLZO
16	0.300	0.550	0.150	SLZO, $SrZnO_2$, ZnO

Note. SLZO: $(Sr_{1-x}La_{1+x})Zn_{1-x}O_{3.5-x/2}$ $(0.01 \leq x < 0.03)$.

Specimens for electron microscopy were prepared by dispersing crushed samples onto holey carbon films. Electron diffraction patterns were taken using a 200-kV electron microscope (Jeol JEM-2000EX).

The pellet samples were powdered and characterized by X-ray diffraction using Cu$K\alpha$ radiation with a pyrolitic graphite monochromator, a scintillation counter, and a diffractometer (Rigaku RINT2500). The X-ray diffraction data for the Rietveld refinement was collected at 25°C from 10° to 130° in 2θ with a sampling step of 0.04° (total number of reflections, 72).

Neutron powder diffraction data were collected at room temperature from 10 to 153° in 2θ on the Kinken powder diffractometer for high-efficiency and high-resolution measurements, HERMES, of the Institute for Materials Research (IMR), Tohoku University, installed at the JRR-3M reactor in the Japan Atomic Energy Research Institute (JAERI), Tokai (14). Neutrons with a wavelength of 1.8196 Å were obtained by the 331 reflections of the Ge monochromator and 12′–blank–sample–22′ collimation. The fine powder sample was sealed in a vanadium cylinder with helium gas.

Rietveld analysis was carried out with a Macintosh version of RIETAN-97 (15). The analytical forms of X-ray scattering factors for neutral atoms and correcting for both real and imaginary components of anomalous dispersion and the coherent neutron scattering lengths and cross sections of atoms were used as given in the RIETAN-97 software. A pseudo-Voigt function was used to fit the lineshape of the X-ray and neutron diffraction pattern.

RESULTS AND DISCUSSION

The phases in the samples prepared at 1100°C with various compositions are shown in Table 1 and Fig. 1. The ternary oxide, $SrZnO_2$, reported in the SrO–ZnO system (11) was confirmed. Formation of any ternary oxides such as $Sr_2La_2O_5$, $Sr_3La_4O_9$, and $SrLa_4O_7$ was not recognized in the LaO–SrO system at 1100°C. These Sr–La–O compounds were prepared above 1600°C in the previous studies (12, 13). A new phase was obtained near the composition Sr:La:Zn = 1:1:1.

We carefully weighed the well-dried starting powders with the 1:1:1 composition (sample 8) and mixed them two ways (dry mixing and wet mixing). However, besides the X-ray diffraction peaks of the new phase, small peaks of $SrZnO_2$ were seen in both samples prepared by the two methods. The single phases of the new compound were white and prepared at the ratios from 1:1.02:1 (sample 6) to 1:1.04:1 (sample 4). All X-ray diffraction peaks were indexed with body-centered tetragonal cells. In the diffraction pattern of sample 3 (Sr:La:Zn = 1:1.06:1), weak peaks of La_2O_3 were included. The composition region of the new phase is $0.333 < r < 0.346$, where r is a mole fraction of La/(Sr + La + Zn). Figure 2 shows the plots of the lattice parameters against the mole fraction r. The a-axis length increased from 3.749(1) to 3.753(1) Å and the c-axis length decreased from 13.572(4) to 13.533(4) Å with increasing r in the narrow range.

Sample 6 was used for the following structure analysis. The structural formula, $(Sr_{0.99}La_{1.01})O_2\,Zn_{0.99}O_{3.495}$, was deduced from the metal compositions of the starting oxide mixture and formal valences of Sr(II), La(III), and Zn(II). The chemical composition of the sample analyzed by ICP emission spectroscopy was Sr, 24.8(2), La, 40.4(5), and Zn, 18.6(1) wt%, which equals the ideal composition of this

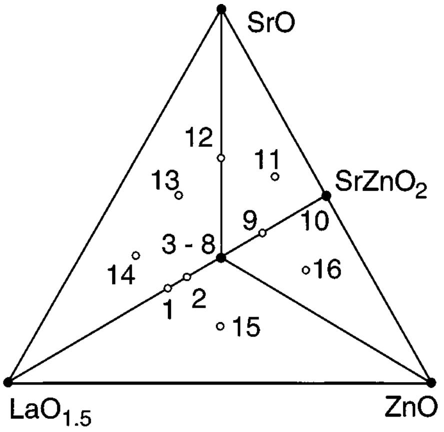

FIG. 1. Compounds obtained at 1100°C in air in the $SrO–La_2O_3–ZnO$ system.

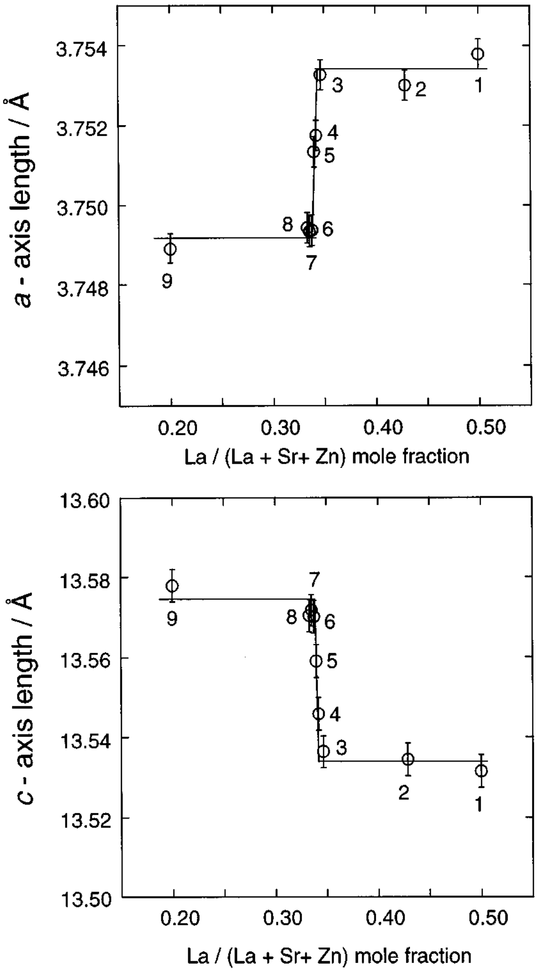

FIG. 2. Lattice parameters of $(Sr_{1-x}La_{1+x})Zn_{1-x}O_{3.5-x/2}$ versus La/(Sr + La + Zn) mole fractions in the starting mixture. The numbers in the figures correspond to the sample number in Table 1.

formula (24.99, 40.40, and 18.64 wt%) within the standard deviations.

The electron diffraction pattern of sample 6 is shown in Fig. 3. The fundamental spots of this and other electron diffraction patterns taken from different incident beam directions were explained with the body-centered tetragonal cell, which was the same as those obtained from the X-ray diffraction patterns. Weak diffuse diffraction spots were observed perpendicular to the a^* axis and between the fundamental spots with an interval around $c^*/2$. These diffuse spots suggest the local ordering of atoms in the structure with a periodicity of about $2 \times a$ and $2 \times c$.

Figure 4 shows the profile-fit and difference patterns of the Rietveld analysis for X-ray and neutron powder diffraction patterns of sample 6. The results of the final Rietveld refinement and the atomic coordinates are summarized in Tables 2 and 3, respectively. All peaks observed in the neutron diffraction pattern as well as those in the X-ray diffraction pattern were indexed with the basic tetragonal cell, and the peaks from the $2 \times a$ and $2 \times c$ superstructure were not detected.

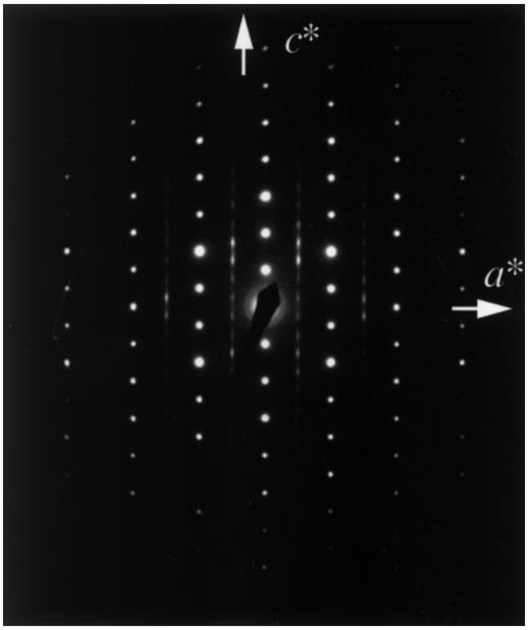

FIG. 3. Electron diffraction pattern of $(Sr_{0.99}La_{1.01})Zn_{0.99}O_{3.495}$.

In the beginning of the structure analysis, we used the K_2NiF_4-type structure model, space group *I*4/*mmm*. However, the value of the atomic displacement parameter for the O2 site was large in the results from the X-ray and neutron diffraction data (Table 2). We made a basic statistical-site occupation structure model, considering the diffuse peaks of the superlattice observed in the electron diffraction patterns. A projection of the refined atomic sites in the statistical model for $(Sr_{0.99}La_{1.01})Zn_{0.99}O_{3.495}$ was shown in Fig. 5. The 4*c* site of O2 in the K_2NiF_4-type structure was split into

TABLE 2
Crystallographic Data for $(Sr_{0.99}La_{1.01})Zn_{0.99}O_{3.495}$

Formula	$(Sr_{0.99}La_{1.01})Zn_{0.99}O_{3.495}$	
Formula weight	347.68	
Space group	*I*4/*mmm* (No. 139)	
Z	2	
	X-ray	Neutron
Wavelength (Å)	1.540562 (Cu$K\alpha_1$) 1.544390 (Cu$K\alpha_2$)	1.8196
Unit cell dimensions (Å)		
a	3.74935(5)	3.74522(10)
c	13.5722(2)	13.5589(4)
Cell volume (Å^3) *V*	190.793(5)	190.186(9)
Density (calculated, Mg/m^3)	6.05	6.07

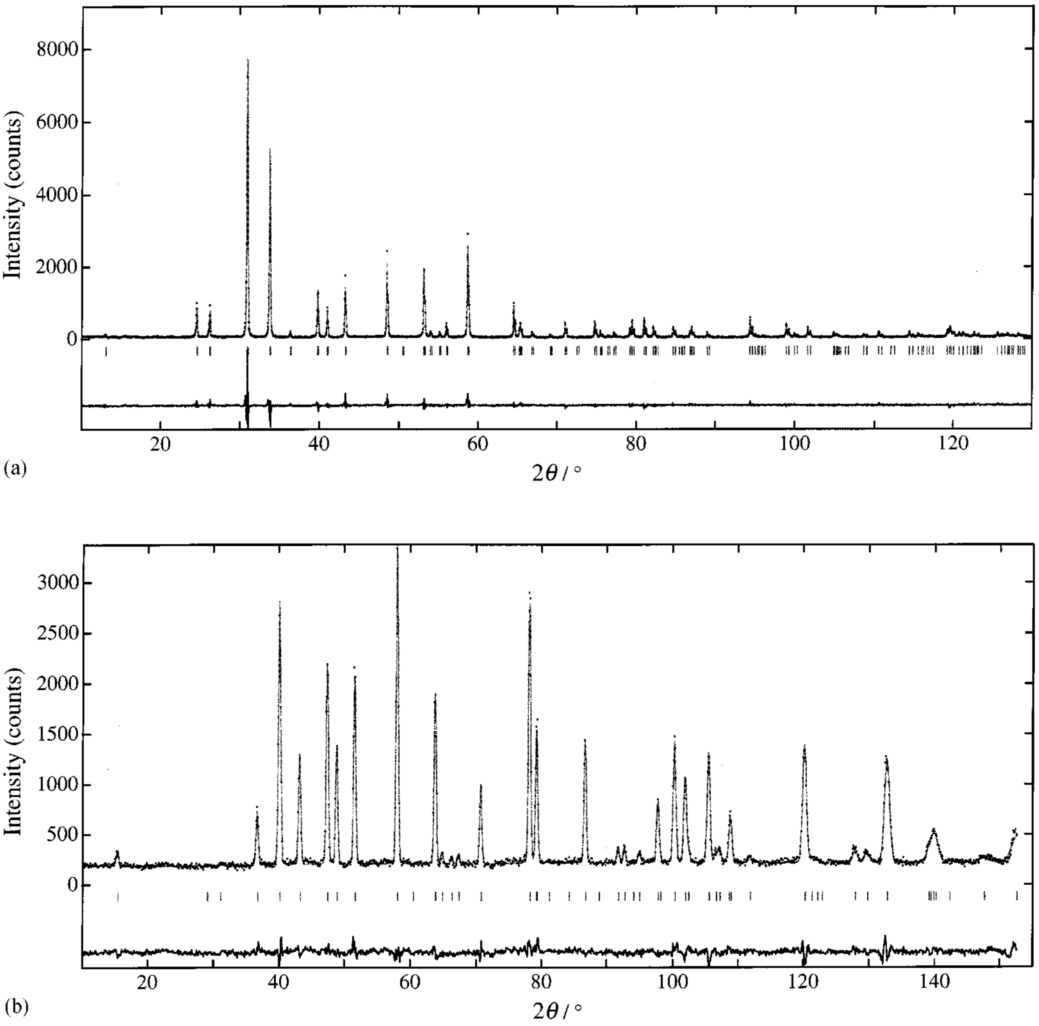

FIG. 4. Rietveld refinement profile of the X-ray diffraction pattern (a) and neutron diffraction pattern (b) for $(Sr_{0.99}La_{1.01})Zn_{0.99}O_{3.495}$. The dotted line represents the observed intensities. Difference plots are shown beneath the patterns. Positions of the Bragg reflections are represented by vertical bars.

an 8*j* site with statistical occupation. In the refinement of X-ray diffraction data, the occupancy was fixed with the ideal value (0.3738) calculated from the formula $(Sr_{0.99}La_{1.01})Zn_{0.99}O_{3.495}$. The occupancy of the O2 site was refined to be 0.384(5) in the basic statistical site-occupation model using the neutron data. This value is close to the ideal value of 0.3738. Splitting the 2*a* site of Zn into a 4*e* site along the *c*-axis direction improved the *R* indexes for the X-ray data analysis about 1% lower. The positional parameters of *y* and *z* in a 16*n* site of O1 occupied statistically with oxygen atoms were also refined with the X-ray and neutron data. The refined occupancy of 0.255(3) at the split site of O1 revealed that there is no oxygen vacancy in the $(La/Sr)_2O_2$ rock-salt layer.

We examined seven other space groups of lower symmetries in which the same systematic extinction was observed in the case of *I*4/*mmm*. When we placed the O2 atoms at general or special positions in the lower symmetry cell, the *R* values became large and the positional parameters often could not be refined with small deviation. Adding a site for statistical occupation reduced the *R* values. The positions refined for the statistically occupied sites were almost identical to the positions of the sites in the model of *I*4/*mmm*. Therefore, we adopted the highest symmetry for the description for the basic model of $(Sr_{0.99}La_{1.01})Zn_{0.99}O_{3.495}$.

In the local structure, we postulated the fourfold coordination of oxygen atoms around the Zn atom. A proposed local structure of $(Sr_{0.99}La_{1.01})Zn_{0.99}O_{3.495}$ is illustrated in Fig. 6, together with the K_2NiF_4-type structure. Table 4 lists the selected interatomic distances. Zn–O bond lengths are in the range from 1.9177(11) to 2.162(9) Å. The average value (1.98 Å) of the distances are close to the Zn–O distance

TABLE 3
Occupancy, Atomic Coordinates, Isotropic Displacement Parameters, and Structure Refinement for $(Sr_{0.99}La_{1.01})Zn_{0.99}O_{3.495}$

	X-ray		Neutron	
	K_2NiF_4 model	Statistical model	K_2NiF_4 model	Statistical model
La/Sr site	4*e*	4*e*	4*e*	4*e*
Occupancy	0.505/0.495	0.505/0.495	0.505/0.495	0.505/0.495
x	0	0	0	0
y	0	0	0	0
z	0.35349(9)	0.35386(9)	0.3537(2)	0.35390(14)
B/Å^2	0.74(3)	0.68(3)	1.11(7)	1.29(5)
Zn site	2*a*	4*e*	2*a*	4*e*
Occupancy	0.990	0.495	0.990	0.495
x	0	0	0	0
y	0	0	0	0
z	0	0.0150(5)	0	0.0152(6)
B/Å^2	1.66(8)	0.60(10)	1.73(11)	1.09(12)
O1 site	4*e*	16*n*	4*e*	16*n*
Occupancy	1.0	0.25	1.050(14)	0.255(3)
x	0	0	0	0
y	0	0.077(6)	0	0.047(3)
z	0.1736(9)	0.1758(8)	0.1729(3)	0.1741(2)
B/Å^2	1.8(3)	0.09(47)	2.39(11)	1.3(2)
O2 site	4*c*	8*j*	4*c*	8*j*
Occupancy	0.7475	0.3738	0.81(2)	0.384(5)
x	0	0.093(5)	0	0.096(1)
y	0.5	0.5	0.5	0.5
z	0	0	0	0
B/Å^2	3.9(5)	0.4(4)	6.6(2)	1.4(2)
Goodness-of-fit, S	1.548	1.4579	1.9366	1.4315
R indexes				
R_{wp}	0.1397	0.1317	0.1078	0.0796
R_p	0.1118	0.1052	0.0835	0.0615
R_I	0.0740	0.0566	0.0825	0.0393
R_F	0.0516	0.0371	0.0471	0.0252

observed in the tetrahedral coordination of oxygen atoms in $SrZnO_2$ (1.97–2.01 Å) (11), $BaZnNd_2O_5$ (1.95–1.96 Å) (16, 17), $BaZnLa_2O_5$ (1.94–1.98 Å) (17, 18), and ZnO (1.99 Å) (19). However, the positions refined are just average positions of the local structure model. The positions in the local structure probably deviate from the refined positions of the statistical structure listed in Table 3.

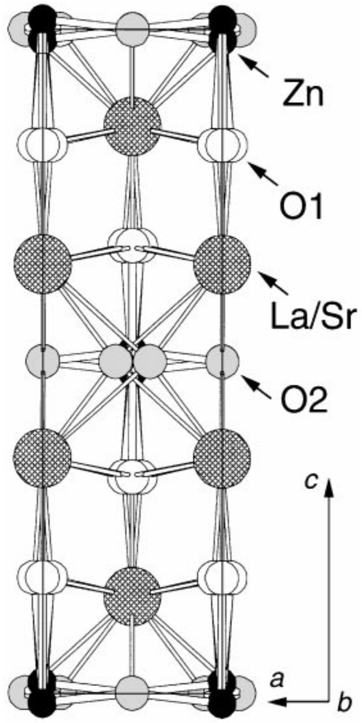

FIG. 5. The refined site positions in a basic statistical structure model of $(Sr_{0.99}La_{1.01})Zn_{0.99}O_{3.495}$.

The K_2NiF_4-type structure of $SrLaMO_4$ (M = Al, V, Fe, Ni, Cu, and Ga) can be explained as $(Sr/La)_2O_2$ rock-salt block layers and MO_2 sheets between the layers. Sr and La atoms statistically occupy a 4*e* site in $SrLaMO_4$ and are coordinated by ninefold oxygen atoms. Five O atoms are from the rock-salt layer and four O atoms from the MO_2 sheets. In the case of $(Sr_{0.99}La_{1.01})Zn_{0.99}O_{3.495}$, the structure consists of rock-salt $(Sr_{0.99}La_{1.01})O_2$ layers and oxygen-deficient $Zn_{0.99}O_{1.495}$ sheets. Thus, the average coordination number of Sr/La is nearly equal to 8. The Sr/La–O interatomic distances are from 2.44 to 2.98 Å and the average is 2.67 Å. The average distance is consistent with that for La/Sr–O distances in the ninefold coordination of $SrLaAlO_4$ (2.48–2.67 Å, average 2.61Å) (2), $LaSrVO_4$ (2.39–2.75 Å, average 2.67 Å) (3, 4), $LaSrFeO_4$ (2.41–2.77, average 2.68 Å) (5), $LaSrNiO_4$ (2.34–2.74 Å, average 2.63 Å) (6), $LaSrCuO_4$ (2.53–2.69 Å, average 2.65 Å) (7), $LaSrGaO_4$ (2.43–2.75, average 2.66 Å) (8, 9), and $SrLa\,(Zn_{0.66}Ru_{0.33})O_4$ (2.39–2.80, average 2.69 Å) (10).

We observed second harmonic generation from the powder of $(Sr_{0.99}La_{1.01})Zn_{0.99}O_{3.495}$ by irradiation of a laser

TABLE 4
Selected Interatomic Distances (Å) Calculated from the Statistical Model Analyzed with the Neutron Diffraction Data for $(Sr_{0.99}La_{1.01})Zn_{0.99}O_{3.495}$

La/Sr–O1	2.444(4) × 1	Zn–O1	2.162(9) × 1
–O1	2.556(8) × 2	–O2	1.9177(11) × 3
–O1	2.800(9) × 2		
–O2	2.494(3) × 6/4		
–O2	2.983(3) × 6/4		

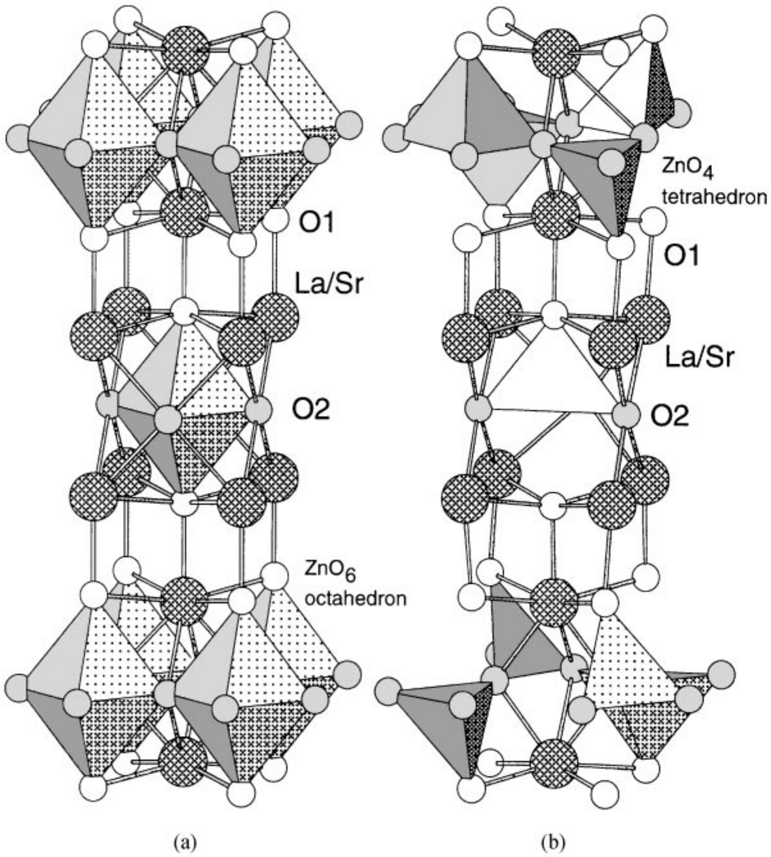

FIG. 6. K_2NiF_4-type structure (a) and a local structure of $(Sr_{0.99}La_{1.01})Zn_{0.99}O_{3.495}$ (b) illustrated with $ZnO_{6/4}$ octahedra and ZnO_4 tetrahedra, respectively.

beam using neodymium yttrium aluminum garnet (Nd: YAG). This means that the local structure of $(Sr_{0.99}La_{1.01})Zn_{0.99}O_{3.495}$ is non-centrosymmetric, although the statistical structure was analyzed with the centrosymmetric space group of *I*4/*mmm*.

Since the formation of the disordered $(Sr_{1-x}La_{1+x})Zn_{1-x}O_{3.5-x/2}$ $(0.01 \leq x < 0.03)$ from the starting mixture at 900°C was confirmed by X-ray diffraction, we annealed the sample at 850°C for 100 h in air to obtain an ordered superstructure. However, the sample decomposed into $SrZnO_2$ and La_2O_3 by annealing. We are trying to synthesize a long-range ordered superstructure phase by substituting other rare-earth atoms for the La atom.

ACKNOWLEDGMENTS

We thank Eiji Aoyagi and Yuji Hayasaka for aid with electron diffraction and Jun-ichi Shikata for laser irradiation. This work was supported in part by the Ministry of Education, Science, Sports and Culture through a Grant-in-Aid for Scientific Research.

REFERENCES

1. C. N. R. Rao and B. Rabeau, "Transition Metal Oxides." Wiley-VCH, New York, 1998.
2. R. D. Shannon, R. A. Oswald, J. B. Parise, B. H. T. Chai, P. Byszewski, A. Pajaczkowska, and R. Sobolewski, *J. Solid State Chem.* **98,** 90 (1992).
3. J. M. Longo and P. M. Raccah, *J. Solid State Chem.* **6,** 526 (1973).
4. J. E. Greedan and W. Gong, *J. Alloys Compd.* **180,** 281 (1992).
5. J. L. Soubeyroux, P. Courbin, L. Fournes, D. Fruchart, and G. L. Flem, *J. Solid State Chem.* **31,** 313 (1980).
6. H. Pausch and Hk. Müller-Buschbaum, *Z. Naturforsch. B* **34,** 378 (1979).
7. M. M. J. B. Goodenough, G. Demazeau, M. Pouchard, and P. Hagenmuller, *J. Solid State Chem.* **8,** 325 (1973).
8. I. Rüter and Hk. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **584,** 119 (1990).
9. J. F. Britten, *Acta Crystallogr. C* **51,** 1975 (1995).
10. S. H. Kim and P. D. Battle, *J. Solid State Chem.* **112,** 262 (1994).
11. H. G. Schnering and R. Hoppe, *Z. Anorg. Allg. Chem.* **312,** 87 (1961).
12. L. M. Lopato, V. N. Pavlikov, and L. I. Lugin, *Russ. J. Inorg. Chem.* **14,** 449 (1969).
13. A. R. Schulze and Hk. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **471,** 59 (1980).
14. K. Ohoyama, T. Kanouchi, K. Nemoto, M. Ohashi, T. Kajitani, and Y. Yamaguchi, *Jpn. J. Appl. Phys.* **37,** 3319 (1998).

15. F. Izumi, "RIETAN97. A Rietveld Refinement Program for Angle-Dispersive X-ray and Neutron Powder Diffraction." National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305, Japan, 1997.
16. Hk. Müller-Buschbaum and P. Sonne, *J. Less-Common Met.* **167,** 193 (1990).
17. C. Michel, L. Er-Rakho, and R. Rabeau, *J. Solid State Chem.* **42,** 176 (1982).
18. Hk. Müller-Buschbaum and S. Möhr, *J. Less-Common Met.* **170,** 127 (1991).
19. S. C. Abrahams and J. L. Bernstein, *Acta Crystallogr. B* **25,** 1233 (1969).