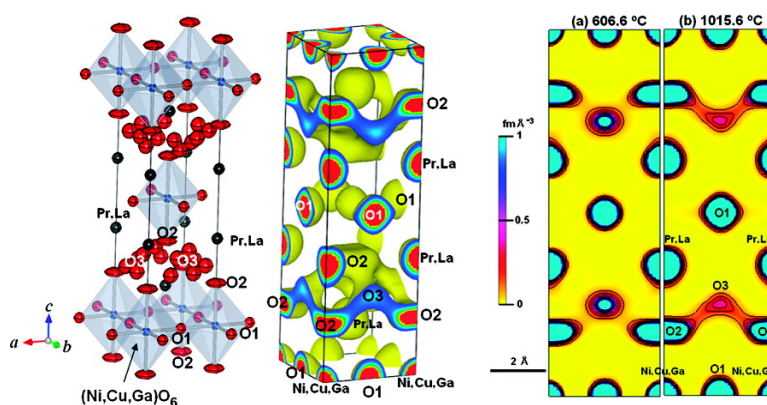


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J. Am. Chem. Soc., **2008**, 130 (9), 2762-2763 • DOI: 10.1021/ja7111478h

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Structural Disorder and Diffusional Pathway of Oxide Ions in a Doped Pr_2NiO_4 -Based Mixed Conductor

Masatomo Yashima,^{*,†} Makiko Enoki,[‡] Takahiro Wakita,[†] Roushoun Ali,^{†,§} Yoshitaka Matsushita,[§] Fujio Izumi,[§] and Tatsumi Ishihara[‡]

Department of Materials Science and Engineering, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta-cho 4259, Midori-Ku, Yokohama, Kanagawa 226-8502, Japan, Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Motoooka 744, Nishi-Ku, Fukuoka, Fukuoka 819-0395, Japan, and Quantum Beam Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Received December 30, 2007; E-mail: yashima@materia.titech.ac.jp

Mixed oxide-ionic and electronic conducting ceramics (MIECs) are attracting much interest as materials for oxygen separation membranes.¹ Oxygen can permeate through MIECs membranes when a gradient of oxygen chemical potential exists. $A_2\text{BO}_4$ -based oxides with K_2NiF_4 -type structure have extensively been studied as new mixed ionic-electronic conductors,^{2–7} where A and B are cations. The development of improved MIECs requires a better understanding of the mechanism of ionic conduction, and crucial to this is a comprehensive knowledge of the crystal structure.^{8,9} It was speculated that the oxide ion conduction in the $A_2\text{BO}_4$ -based oxides occurs by diffusion of excess oxide ions along the rock-salt-type AO layers.^{3–6} However, the diffusion path of oxide ion has not been determined yet. Pr_2NiO_4 -based oxides have a high oxygen permeability and high diffusivity of oxide ions.^{6,7} Here, we report for the first time the diffusion path of oxide ions in a K_2NiF_4 -type mixed conductor, $(\text{Pr}_{0.9}\text{La}_{0.1})_2(\text{Ni}_{0.74}\text{Cu}_{0.21}\text{Ga}_{0.05})\text{O}_{4+\delta}$ (PLNCG), through a high-temperature neutron powder diffraction study. We chose this chemical composition, because it exhibits high oxygen permeability. The present result would give hints for the design of K_2NiF_4 -type conductors.

A PLNCG sample was prepared by a solid-state reaction method at 1300 °C for 6 h in air.⁷ Neutron powder diffraction data of PLNCG were *in situ* measured at 606.6 and 1015.6 °C using a furnace¹⁰ and a 150 detector system HERMES¹¹ at a neutron wavelength of 1.82646 Å. Neutron diffraction patterns at both temperatures indicated a K_2NiF_4 -type structure with the $I4/mmm$ space group. Neutron-diffraction data were analyzed by a combination of Rietveld analysis,¹² the maximum-entropy method (MEM),¹³ and MEM-based pattern fitting (MPF).¹³ The computer program RIETAN-2000¹² was utilized for the Rietveld analysis and MEM-based whole pattern fitting, and VESTA,¹⁴ for visualization of nuclear density (scattering-length density) distribution. It is known that MPF makes it possible to determine nuclear densities in compounds containing disordered chemical species from neutron diffraction data.^{8,13}

Rietveld refinements of the neutron diffraction data of PLNCG at 606.6 and 1015.6 °C were successfully performed on the basis of the K_2NiF_4 -type structure with $I4/mmm$ space-group symmetry (Figure 1a). It was found that PLNCG has a crystal structure consisting of $(\text{Ni,Cu,Ga})\text{O}_6$ octahedron and $(\text{Pr,L a})\text{-O}$ layers. Refined occupancy factors indicated the excess oxygen of $\delta = 0.0154(3)$ in $(\text{Pr}_{0.9}\text{La}_{0.1})_2(\text{Ni}_{0.74}\text{Cu}_{0.21}\text{Ga}_{0.05})\text{O}_{4+\delta}$, which is ascribed to the interstitial O3 atom. The O3 atom is located at a $16n$ site,

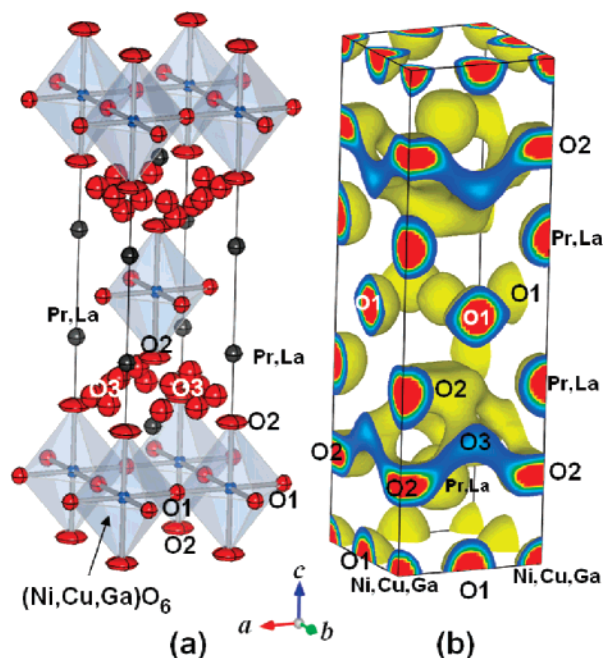


Figure 1. (a) Refined crystal structure and isosurface of nuclear density at 0.05 fm^{-3} of the mixed oxide-ionic and electronic conductor $(\text{Pr}_{0.9}\text{La}_{0.1})_2(\text{Ni}_{0.74}\text{Cu}_{0.21}\text{Ga}_{0.05})\text{O}_{4+\delta}$ determined *in situ* at 1015.6 °C. Unit cell: Tetragonal $I4/mmm$, $a = 3.875(3)$ Å and $c = 12.738(9)$ Å.

i.e., $(x, 0, z)$ where $x = 0.666(19)$ and $z = 0.223(9)$ at 1015.6 °C. Figures 1b and 2 show the isosurface and distributions of the MEM nuclear density of PLNCG. The oxygen atom at the O2 site ($4e$; $(0, 0, z)$; $z = 0.1752(4)$ at 1015.6 °C) exhibits highly anisotropic thermal motion ($U_{11} = U_{22} = 0.115(3) \text{ \AA}^2$ and $U_{33} = 0.021(3) \text{ \AA}^2$), which leads to the migration of oxide ions to the nearest-neighbor interstitial O3 positions. The striking feature in the nuclear density distribution is the curved O2–O3 diffusion path as shown in Figures 1b and 2. This feature is ascribed to the repulsion between (Pr,L a) and O atoms. In fact, the distance between the (Pr,L a) and O atoms is kept approximately constant along the diffusion paths. This fact suggests that the large-sized cations such as Pr and La ions at the A site in the $A_2\text{BO}_4$ -type conductor are effective in improving the oxide-ionic conduction on the $A\text{-O}$ layer. The conduction path is along the $\langle 100 \rangle$ directions near the O2 site and roughly along the $\langle 301 \rangle$ directions around the center of the paths (Figure 2b). The nuclear-density distribution also shows the two-dimensional (2D) network of the O2–O3–O2 diffusion paths of oxide ions. The 2D feature is consistent with the anisotropic transport of oxide ions in $\text{La}_2\text{NiO}_{4+\delta}$.⁵ The nuclear density on the diffusion path at

[†] Tokyo Institute of Technology.

[‡] Kyushu University.

[§] National Institute for Materials Science.

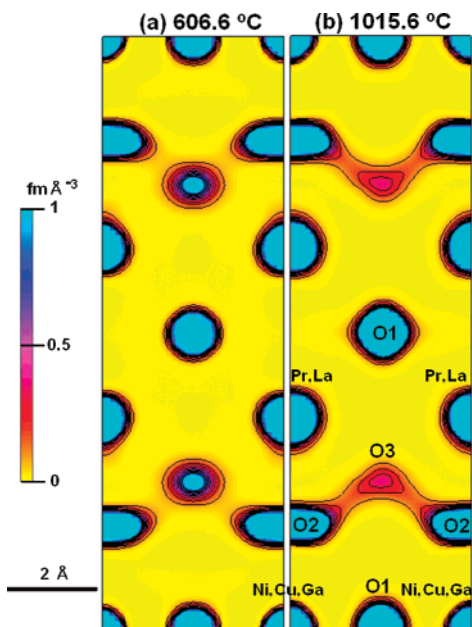


Figure 2. Nuclear density distribution on the (100) plane of the mixed conductor $(\text{Pr}_{0.9}\text{La}_{0.1})_2(\text{Ni}_{0.74}\text{Cu}_{0.21}\text{Ga}_{0.05})\text{O}_{4+\delta}$ at (a) 606.6 °C and (b) 1015.6 °C. Contour lines from 0.1 to 1.0 by the step of 0.1 $\text{fm} \text{ \AA}^{-3}$.

1015.6 °C (Figure 2b) is larger than that at 606.6 °C (Figure 2a), which is consistent with the improved oxygen permeability at higher temperatures.⁷

In conclusion, we have presented here the first visualization of structural disorder and diffusion path of oxide ions in K_2NiF_4 -type mixed conductors. We have experimentally confirmed that the anisotropic thermal motions of the O2 atom and the interstitial O3 atoms are essential for the high oxygen permeability of the $\text{K}_2\text{-NiF}_4$ -type mixed conductor. To design improved K_2NiF_4 -type mixed conductors with higher oxide-ion diffusivity, it might be useful to adopt larger A cations and A and B cations with higher valences, which yields a higher concentration of interstitial O3 atoms.

Acknowledgment. We thank Prof. K. Ohoyama and Mr. K. Nemoto for arranging the neutron-diffraction experiment and Mr. Y. Kawaike, Mr. T. Tsuji, Mr. T. Ueda, Mr. T. Komatsu, and Mr. Y. Phat for their help with the neutron-diffraction experiment. This research work was partially supported by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Scientific Research.

Note Added after ASAP Publication. The version of this paper published on February 8, 2008 contained errors in Figure 2 and the Table of Contents graphic. The version published on February 19, 2008 has the correct information.

Supporting Information Available: Neutron powder diffraction plot and crystallographic data of PLNCG. Figure of the 2D network of diffusion paths. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) ten Elshof, J. E.; Bouwmeester, H. J. M.; Verweij, H. *Appl. Catal., A* **1995**, *130*, 195–212. (b) Balachandran, U.; Dusek, J. T.; Mieville, R. L.; Poeppel, R. B.; Kleefisch, M. S.; Pei, S.; Kobylnski, T. P.; Udovich, C. A.; Bose, A. C. *Appl. Catal., A* **1995**, *133*, 19–29. (c) Tsai, C. Y.; Dixon, A. G.; Moser, W. R.; Ma, Y. H. *AIChE J.* **1997**, *43*, 2741–2750.
- (2) (a) Hundley, M. F.; Kwok, R. S.; Cheong, S. W.; Thompson, J. D.; Fisk, Z. *Phys. C (Amsterdam, Neth)* **1991**, *172*, 455–464. (b) Kharton, V. V.; Viskup, A. P.; Kovalevsky, A. V.; Naumovich, E. N.; Marques, F. M. B. *Solid State Ionics* **2001**, *143*, 337–353. (c) Kato, S.; Ogasawara, M.; Sugai, M.; Nakata, S. *Solid State Ionics* **2002**, *149*, 53–57. (d) Manthiram, A.; Prado, F.; Armstrong, T. *Solid State Ionics* **2002**, *152–153*, 647–655. (e) Li, C.; Hu, T. H.; Zhang, H.; Chen, Y.; Jin, J.; Yang, N. R. *J. Membr. Sci.* **2003**, *226*, 1–7. (f) Kharton, V. V.; Tsipis, E. V.; Yaremchenko, A. A.; Frade, J. R. *Solid State Ionics* **2004**, *166*, 327–337. (g) Kovalevsky, A. V.; Kharton, V. V.; Yaremchenko, A. A.; Pivak, Y. V.; Tsipis, E. V.; Yakovlev, S. O.; Markov, A. A.; Naumovich, E. N.; Frade, J. R. *J. Electroceram.* **2007**, *18*, 205–218.
- (3) Skinner, S. J.; Kilner, J. A. *Solid State Ionics* **2000**, *135*, 709–712.
- (4) Minervini, L.; Grimes, R. W.; Kilner, J. A.; Sickafus, K. E. *J. Mater. Chem.* **2000**, *10*, 2349–2354.
- (5) Bassat, J. M.; Odier, P.; Villesuzanne, A.; Marin, C.; Pouchard, M. *Solid State Ionics* **2004**, *167*, 341–347.
- (6) Boem, E.; Bassat, J.-M.; Dordor, P.; Mauvy, F.; Grenier, J.-C.; Stevens, Ph. *Solid State Ionics* **2005**, *176*, 2717–2725.
- (7) (a) Miyoshi, S.; Furuno, T.; Sangoanruang, O.; Matsumoto, H.; Ishihara, T. *J. Electrochem. Soc.* **2007**, *154*, B57–B62. (b) Ishihara, T.; Miyoshi, S.; Furuno, T.; Sangoanruang, O.; Matsumoto, H. *Solid State Ionics* **2006**, *177*, 3087–3091. (c) Miyoshi, S.; Furuno, T.; Matsumoto, H.; Ishihara, T. *Solid State Ionics* **2006**, *177*, 2269–2273.
- (8) (a) Yashima, M.; Nomura, K.; Kageyama, H.; Miyazaki, Y.; Chitose, N.; Adachi, K. *Chem. Phys. Lett.* **2003**, *380*, 391–396. (b) Yashima, M.; Itoh, M.; Inaguma, Y.; Morii, Y. *J. Am. Chem. Soc.* **2005**, *127*, 3491–3495. (c) Yashima, M.; Kobayashi, S.; Yasuda, T. *Faraday Discuss.* **2007**, *134*, 369–376.
- (9) (a) Skinner, S. J. *Solid State Sci.* **2003**, *5*, 419–426. (b) Aguadero, A.; Alonso, J. A.; Martinez-Lope, M. J.; Fernandez-Diaz, M. T.; Escudero, M. J.; Daza, L. *J. Mater. Chem.* **2006**, *16*, 3402–3408. (c) Skinner, S. J.; Amow, G. *J. Solid State Chem.* **2007**, *180*, 1977–1983.
- (10) Yashima, M. *J. Am. Ceram. Soc.* **2002**, *85*, 2925–2930.
- (11) Ohoyama, K.; Kanouchi, T.; Nemoto, K.; Ohashi, M.; Kajitani, T.; Yamaguchi, Y. *Jpn. J. Appl. Phys., Part 1* **1998**, *37*, 3319–3326.
- (12) Izumi, F.; Ikeda, T. *Mater. Sci. Forum* **2000**, *321–324*, 198–203.
- (13) Izumi, F.; Dilanian, R. A. *Recent Res. Develop. Phys.* **2002**, *3(2)*, 699–726.
- (14) Momma, K.; Izumi, F. *Commission on Crystallogr. Comput., IUCr Newsllett.* **2006**, *No. 7*, 106–119.

JA711478H