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Crystal structure and Electron Density of $La_{0.64}(Ti_{0.92}Nb_{0.08})O_3$ at 1000 °C and 1350 °C

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Introduction

Doped-$La_{2/3}TiO_3$ materials have an *A*-site deficient perovskite-type structure (ABO_3) where A=$La_{2/3\pm y}$, B=$(Ti_{1-x}M_x)$ and M is dopant cation. These materials are attractive owing to their high oxide-ion conductivities and dielectric properties. Therefore, many researchers have studied the unit-cell parameters, phase transition and structural parameters of the compounds. To improve their properties, it is important to understand the precise chemical bonding nature. But no study has yet been reported on the bonding nature of $La_{0.64}(Ti_{0.92}Nb_{0.08})O_3$. Furthermore, no crystal structure data above 500 °C is available in the literature. Here, we have determined the crystal structure and electron density distribution by combining a Rietveld method, a maximum-entropy method (MEM) and whole pattern fitting using synchrotron X-ray diffraction intensity measured at 1000 °C and 1350 °C.

Experimental

Synchrotron X-ray powder diffraction data were collected using the multi-detector system installed at the beam line BL-4B$_2$ of Photon Factory, KEK, Tsukuba. The wavelength was determined to be λ=1.20667(1) Å. A furnace with $MoSi_2$ heaters[1] was used for the high-temperature measurements. Diffraction data were collected at 1000 °C and 1350 °C in the 2θ range from 7° to 154° in the step interval of 0.005° in 2θ. Computer programs RIETAN-2000[2], PRIMA[3] and VENUS[3] were utilized for Rietveld analysis, MEM calculation and visualization of the electron-density distribution, respectively.

Results and discussion

All the reflections in the synchrotron X-ray powder diffraction patterns measured at 1000 °C and 1350 °C were indexed on the basis of tetragonal symmetry with space group *P*4/*mmm* ($a \approx a_p \times b \approx a_p \times c \approx 2a_p$). The calculated profiles fit well with that of observed one (Fig. 1). The final unit-cell and structural parameters and *R*-factors for the two temperatures are summarized in Table I. The MEM analyses were performed using the structure factors obtained from the Rietveld analysis. The number of structure factors was 92 for both the data. The MEM calculations were done using PRIMA with the unit cell divided into 64 × 64 × 128 pixels and whole-pattern fitting using RIETAN-2000. Then, the MEM-based pattern fitting was applied which improved the reliability factors (value within parentheses in Table 1). Electron-density image is shown in Fig.2 to visualize the density derived from the MEM calculations for the data measured at 1350 °C. The electron density map shows the covalent bonding between the O3 and TiNb atoms and between Ti,Nb and O2 atoms.

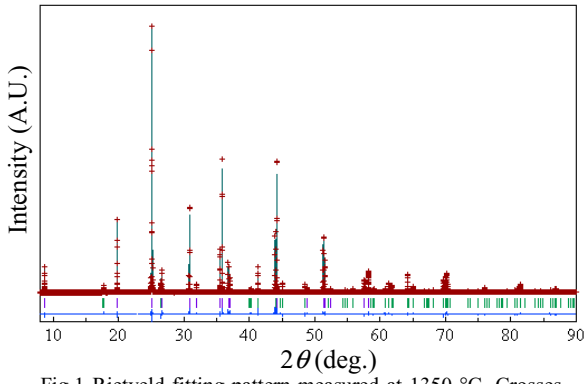

Fig.1 Rietveld fitting pattern measured at 1350 °C. Crosses (+ symbols) and line denote observed and calculated profile intensities, respectively. Short vertical bars represent Bragg reflection positions. A difference (observed-calculated) plot is shown bellow the profiles.

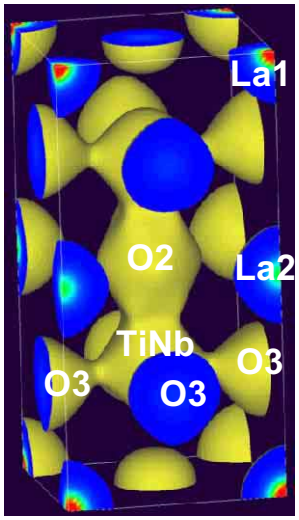

Fig.2 Equicontour surface of the electron-density distribution at 0.8 A^{-3} on the (001) plane of SR-XRD data of $La_{0.64}(Ti_{0.92}Nb_{0.08})O_3$ measured at 1350 °C

Table 1. Refined crystal parameters and reliability factors of the $La_{0.64}(Ti_{0.92}Nb_{0.08})O_3$

Temperature			1000 (°C)	1350 (°C)
Refined parameters	Atom			
		a	3.90047(1)	3.91930(1)
		c	7.90938(3)	7.92535(2)
	La1	*g*(La1)	0.911(1)	0.883(1)
		U (Å^2)	0.0087(2)	0.0144(2)
	La2	*g*(La2)	0.369(1)	0.397(1)
		U (Å^2)	0.0371(7)	0.0374(6)
	TiNb	*z*	0.2663(2)	0.2655(1)
		U (Å^2)	0.0123(3)	0.0160(3)
	O1	U_{eq}(Å^2)	0.023	0.045
	O2	*U* (Å^2)	0.016(2)	0.031(2)
	O3	*z*(O3)	0.2496(4)	0.2552(4)
		U_{eq}(Å^2)	0.035	0.041
Reliability factors	R_{wp} (%)		15.05(14.27)	13.43(11.69)
	R_p (%)		10.88(10.20)	10.03(8.70)
	R_I (%)		8.93(6.25)	10.46(5.54)
	R_F (%)		9.6294.86)	5.79(3.52)
	S		2.18(2.06)	1.92(1.62)

Tetragonal space group *P*4/*mmm* (No.123) *Z*=2. In the analyses the atom positions were: La1 1*a* (0.0, 0.0, 0.0); La2 1*b* (0.0, 0.0, 1/2); TiAl 2*h* (1/2, 1/2, *z*); O1 1*c* (1/2, 1/2, 0.0); O2 1*d* (1/2, 1/2, 1/2); O3 4*i* (1/2, 0.0, *z*). Reliability factors shown in the parentheses are obtained after REMEDY cycles.

References

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