

# Synthesis and Structure of New Perovskite Phase in the La–Ti–Al–O System

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In this paper we report the synthesis of a new phase in the La–Ti–Al–O system. A starting composition  $\text{La}_2\text{TiAlO}_{6.5}$  and synthesis conditions of 1400°C under  $\text{H}_2/\text{Ar}$  (5%/95%) resulted in a perovskite with a monoclinic ( $I2/a$ ;  $a = 7.686$ ,  $b = 5.435$ ,  $c = 5.424$  Å,  $\beta = 90.20^\circ$ ) cell. Although it was necessary to synthesize this material under reducing conditions, once prepared it was stable to subsequent oxidation at high temperatures in air. Structure refinement using neutron diffraction suggests the possible incorporation of a small amount of La on the small cation sites along with a La deficiency on the large cation sites, such that the composition may be written as  $\text{La}_{0.83}(\text{La}_{0.07}\text{Al}_{0.465}\text{Ti}_{0.465})\text{O}_{2.9}$ .

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**Key Words:** perovskite; titanate; neutron diffraction.

## INTRODUCTION

Perovskite systems, general formula  $\text{ABO}_3$  ( $A$  = large 12-coordinate cation,  $B$  = small 6-coordinate cation), exhibit a wide variety of technologically important properties and uses, ranging from high-temperature superconductivity to ionic conduction and catalysis. We have been investigating doped perovskite titanates for use as anodes in solid oxide fuel cells (1, 2). During this work an attempt was made to prepare a phase of composition  $\text{La}_2\text{TiAlO}_6$  containing  $\text{Ti}^{3+}$  by reaction of  $\text{La}_2\text{O}_3$  with  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  under  $\text{H}_2/\text{Ar}$  (5%/95%). A single-phase sample was prepared and we report here the identification of this material from a structural determination using powder neutron diffraction.

## EXPERIMENTAL

High-purity  $\text{La}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{Al}_2\text{O}_3$  were weighed out in the ratio La:Ti:Al 2:1:1, intimately ground and heated at 1400°C in  $\text{H}_2/\text{Ar}$  (5%/95%) for 3 days with intermediate regrinding. Phase purity and preliminary X-ray data for structural analysis were collected on a Phillips X'Pert

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PW3020 diffractometer. Powder neutron diffraction data were collected on diffractometer HRPD, ISIS (Rutherford Appleton Laboratory). Rietveld refinement was performed using the programs TF12LS and LX15LS based on the Cambridge Crystallographic Subroutine Library (CCSL) (3, 4). Scattering lengths of 0.827,  $-0.3438$ , 0.3449, 0.5805 ( $\times 10^{-12}$  cm) were used for La, Ti, Al, O respectively.

Thermogravimetric analysis was performed using a TA instruments thermal analyzer SDT 2960. Samples (approximately 30 mg) were heated at 10°C/min in  $\text{O}_2$  to 930°C and held for 15 min resulting in the oxidation of any  $\text{Ti}^{3+}$  to  $\text{Ti}^{4+}$ .

## RESULTS

X-ray diffraction indicated a single-phase perovskite material with broad peaks suggesting a possible deviation from cubic symmetry; however, the resolution of the diffractometer was not sufficient for this to be resolved. The high resolution of the powder neutron diffractometer, HRPD, was able to resolve the splitting and suggested either a rhombohedral or monoclinic cell similar to that observed in  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$  at high temperatures (500–1000°C) (5). Preliminary refinement of the neutron diffraction data was therefore attempted using the monoclinic and rhombohedral cells observed for  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ . It was found that the monoclinic cell resulted in the best fit. The final refined data suggested a higher Al content than that weighed out as well as a 17% La deficiency of the  $A$  sites, giving a final composition of  $\text{La}_{0.83}\text{Ti}_{0.4}\text{Al}_{0.6}\text{O}_{2.9}$ . To try to rationalize this, the X-ray diffraction data was also refined. In contrast to the neutron data, this data suggested a higher Ti content, composition  $\text{La}_{0.85}\text{Ti}_{0.58}\text{Al}_{0.42}\text{O}_{2.9}$ . It should be noted however that we were refining a cell with a slight monoclinic distortion using low-resolution data, and so the X-ray determined values should be viewed with this in mind.

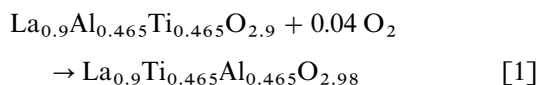
Nevertheless, the anomaly between X-ray and neutron data could be explained by the presence of a small amount

**TABLE 1**  
**Refined Structural Parameters for  $\text{La}_{0.83}(\text{La}_{0.07}\text{Ti}_{0.465}\text{Al}_{0.465})\text{O}_{2.9}$**

Atom	Position	x	y	z	ITF	Site occupancy
La1	4e	0.25	0.000(1)	0	0.67(3)	0.83(1)
Ti1	4b	0	0.5	0	0.9(2)	0.465(4)
Al1	4b	0	0.5	0	0.9(2)	0.465(4)
La2	4b	0	0.5	0	0.9(2)	0.071(7)
O1	4e	0.25	0.470(2)	0	1.4(1)	0.90(1)
O2	8f	0.4871(3)	0.7301(1)	0.2684(5)	0.97(4)	1.0

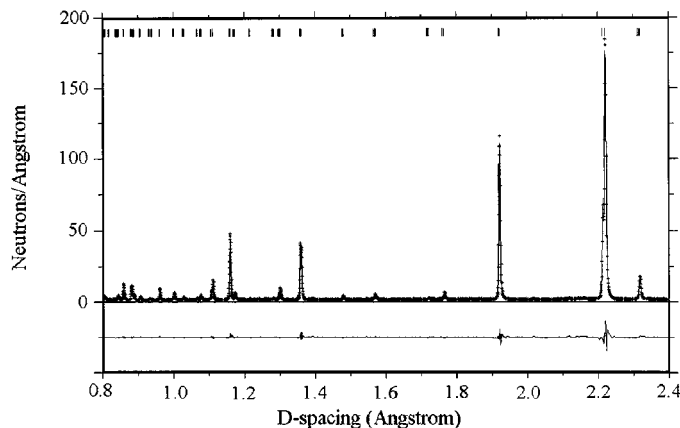
Note.  $a = 7.6855(1)$ ,  $b = 5.4347(1)$ ,  $c = 5.4243(1)$  Å,  $\beta = 90.221(1)$ ,  $R_1 = 2.59\%$ ,  $R_p = 5.96\%$ ,  $R_{wp} = 7.36\%$ ,  $R_E = 3.82\%$ .

of La on the Al sites. Refinement of the neutron data was then continued assuming this model with the Ti and Al contents being kept equal to one another. This gives a composition  $\text{La}_{0.83(1)}(\text{La}_{0.071(7)}\text{Ti}_{0.465(4)}\text{Al}_{0.465(4)})\text{O}_{2.90(1)}$  or an approximate La:Ti:Al ratio close to 2:1:1, consistent with that weighed out. The composition suggests a Ti oxidation state of  $3.67(4)^+$ , from which we would predict a mass increase after complete oxidation of  $\text{Ti}^{4+}$  according to Eq. [1] of 0.6(1)%.



This value is similar to the value of 0.4(1)% observed from the actual TGA data. The fact that there is no evidence of decomposition of this perovskite phase after such oxidation is also consistent with the structural data, by the fact that there are sufficient oxygen vacancies to allow oxidation to  $\text{Ti}^{4+}$  without requiring breakdown of the structure. The final refined structural parameters are given in Table 1, and the neutron diffraction profiles are shown in Fig. 1. Refinement of the X-ray data suggests a lower La content, but still a small La occupancy (0.02) of the small cation sites.

No attempt was made to do a combined X-ray and neutron refinement as we would lose the high resolution of the neutron data. This resolution is important as the compound represents only a small monoclinic distortion from rhombohedral symmetry. Attempts were also made to refine in a lower symmetry monoclinic cell, to investigate possible ordering on the B sites. These refinements were generally unstable, although there was the suggestion of a small degree of ordering. Since there appears to be La, Ti, and Al on the B sites and so the data could not give unique values for the occupancies of each and there seemed to be negligible improvements in the fits, we have preferred to keep the higher symmetry space group.



**FIG 1.** Observed, calculated, and difference neutron profiles for  $\text{La}_{0.83}(\text{La}_{0.07}\text{Ti}_{0.465}\text{Al}_{0.465})\text{O}_{2.9}$ .

## CONCLUSIONS

In conclusion, we have prepared a new perovskite phase of nominal composition  $\text{La}_2\text{TiAlO}_{6.5-x}$ . Powder neutron diffraction indicates a monoclinic cell with La vacancies on the A cation sites and the possible presence of some La on the small cation sites such that the formula may be written as  $\text{La}_{0.83}(\text{La}_{0.07}\text{Ti}_{0.465}\text{Al}_{0.465})\text{O}_{3-x}$ . The presence of La on both A and B cation sites is highly unusual and we hope to perform some anomalous X-ray scattering experiments to confirm this. It is interesting to note that the cation ratios observed here are very close to that for  $\text{La}_{0.92}\text{Ti}_{0.46}\text{Al}_{0.46}\text{O}_3$ , i.e.,  $A_{2x}\text{III}B_x\text{III}B_x\text{IV}O_z$ , where  $x = 0.46$ ,  $z = 3.0$ . A value of  $x$  higher than 0.46 would lead to the fully oxidised form exceeding  $\text{O}_3$  stoichiometry.

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