Experimental Report

Proposal: **5-23-657** **Council:** 10/2012

Title: Crystal structures of the A-site deficient Sr1-xLa0.67xTi1-yNbyO3-d perovskite thermoelectrics (0 < x < 1; 0 < y < 0.2).

This proposal is a new proposal

Researh Area: Materials

Main proposer: **BOS Jan-Willem**

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Samples: Sr1-xLa0.67xTi1-yNbyO3-d (0 < x < 1; 0 < y < 0.2).

Instrument	Req. Days	All. Days	From	To
D2B	2	2	16/07/2013	18/07/2013

Abstract:

The aim of the proposal is to determine the crystal structures of the A-site and oxygen deficient Sr1-xLa0.67xTi1-yNbyO3-d perovskites (0 < x < 1, 0 < y < 0.2). We have shown that these materials are promising thermoelectric materials. In particular because they show reduced thermal conductivities compared to SrTiO3. Knowledge of the the site occupancies, Glazer tilt systems and oxygen defect structures is needed to fully understand these materials, and enable further improvements in thermoelectric performance.

Crystal structures of the A-site deficient $Sr_{1-x}La_{0.67x}Ti_{1-y}Nb_yO_{3-d}$ perovskite thermoelectrics ($0 < x < 1$; $0 < y < 0.2$). (5-23-657).

Aim: The aim of the proposal was to determine the site occupancies, Glazer tilt systems and oxygen defect structures of the $Sr_{1-x}La_{0.67x}Ti_{1-y}Nb_yO_{3-d}$ ($0 < x < 1$; $0 < y < 0.2$) thermoelectric materials. These materials have A-site vacancies, which can be exploited to reduce the thermal conductivity, while the Nb doping is used to introduce charge carriers.

Results:
We successfully collected data on all two series of materials: $Sr_{1-x}La_{0.67x}Ti_{0.8}Nb_{0.2}O_{3-d}$ and $Sr_{0.8}La_{0.13}Ti_{1-y}Nb_yO_{3-d}$ (7 samples in total), and undertook a variable temperature study on the x = 0.2, y = 0.1 sample. The results from Rietveld fits are given in the Tables at the end of this document. All samples crystallise with the I4/mcm structure at room temperature. This corresponds to the $a^0a^oc^-$ Glazer tilt system.

Increasing the concentration of A-site vacancies in $Sr_{1-x}La_{0.67x}Ti_{0.8}Nb_{0.2}O_{3-d}$. The Rietveld fits confirmed the nominal A-site occupancies and that all samples, except for $Sr_{0.80(1)}La_{0.13(1)}Ti_{0.95}Nb_{0.05}O_{2.976}$, are oxygen stoichiometric. This also revealed a maximum Nb content of 15% ($y_{experimental} \leq 0.15$). The thermal displacement parameter for the A-site showed a maximum for equal amounts of Sr and La (x = 0.4, y = 0.2), suggesting this reflects static disorder (La/Sr size mismatch) which is maximum for this composition. In contrast, the displacement parameter for the oxygen sites increases up to the most A-site deficient composition (x = 0.8, y = 0.2), which has a glass-like thermal conductivity.[1] To fully understand the glass-like composition variable temperature studies (4-1100 K) are needed. The Ti/Nb-O bond distances and tilt angles are comparable in all samples, while somewhat more pronounced changes are evident in the Sr/La-O distances. Increasing the Nb concentration in $Sr_{0.8}La_{0.13}Ti_{1-y}Nb_yO_{3-d}$ revealed gradual changes in lattice parameter, bond distances and thermal displacement factors.

Variable temperature on the The $Sr_{0.80(1)}La_{0.13(1)}\square_{0.07}Ti_{0.90(1)}Nb_{0.10(1)}O_3$ sample (x = 0.2) revealed a transition to cubic between RT and 100 °C. No anomalies were observed in the temperature dependence of the lattice parameters or thermal displacement parameters as expected given the regular 1/T temperature dependence of the thermal conductivity for this composition.[1]

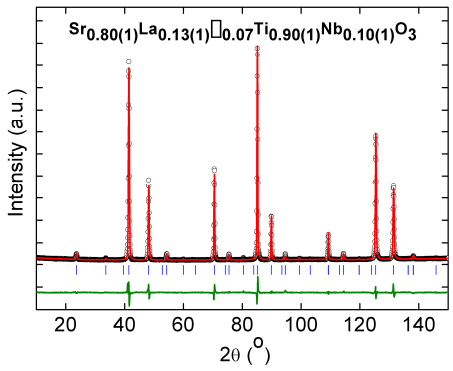

Fig. 1. Room temperature Rietveld fit to D2B data collected on $Sr_{0.80(1)}La_{0.13(1)}\square_{0.07}Ti_{0.90(1)}Nb_{0.10(1)}O_3$

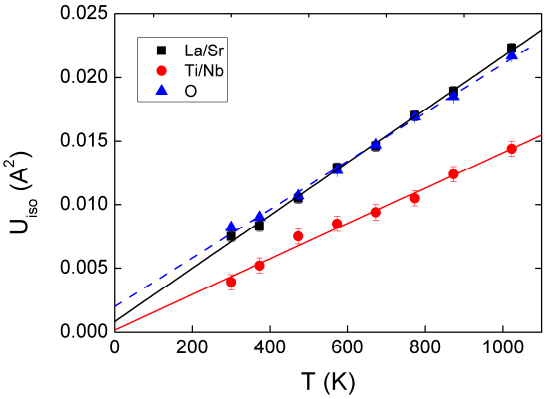

Fig. 2. Temperature dependence of the displacement parameters for $Sr_{0.80(1)}La_{0.13(1)}\square_{0.07}Ti_{0.90(1)}Nb_{0.10(1)}O_3$

[1] S. R. Popuri, A. J. M. Scott, R. A. Downie, M. A. Hall, E. Suard, R. Decourt,c M. Pollet and J.-W. G. Bos "Glass-like thermal conductivity in $SrTiO_3$ thermoelectrics induced by A-site vacancies" ***RSC Adv.***, 2014,**4**, 33720-33723

		$Sr_{0.80(1)}La_{0.13(1)}\square_{0.07}Ti_{1-y}Nb_yO_{3-\delta}$			$Sr_{1-x}La_{2x/3}\square_{x/3}Ti_{0.80}Nb_{0.20}O_{3-\delta}$				
		y=0	y=0.10	y=0.20	x=0	x=0.20	x=0.4	x=0.6	x=0.8
	S.G	I4/mcm	I4/mcm	I4/mcm	I4/mcm	I4/mcm	I4/mcm	I4/mcm	I4/mcm
	a (Å)	5.5202(3)	5.5317(9)	5.5397(3)	5.5415(4)	5.5397(3)	5.5297(1)	5.5298(1)	5.5206(1)
	c (Å)	7.808(1)	7.824(3)	7.838(1)	7.840(1)	7.838(1)	7.825(1)	7.8277(2)	7.8129(4)
Sr/La (4a)	Occ.	0.80/ 0.13	0.80/ 0.13	0.80/ 0.13	1.0	0.80/ 0.13	0.60/ 0.26	0.40/ 0.40	0.20/ 0.53
	$100*U_{iso}$	0.49(2)	0.75(4)	0.89(4)	0.77(4)	0.89(4)	0.91(4)	0.65(3)	0.56(4)
Ti/Nb (4c)	Occ.	1.0(1)	0.90(1)/ 0.10(1)	0.85(2)/ 0.15(2)	0.83(1)/ 0.171)	0.85(1)/ 0.15(1)	0.85(1)/ 0.15(1)	0.85(1)/ 0.15(1)	0.85(1)/ 0.15(1)
	$100*U_{iso}$	0.32(3)	0.39(1)	0.91(2)	0.14(1)	0.91(2)	0.87(1)	0.90(7)	0.84(1)
O1 (4a)	Occ.	0.98(1)	1.00(1)	1.00(1)	1.00(1)	1.00(1)	1.00(1)	1.00(1)	1.00(1)
	$100*U_{iso}$	0.71(2)	0.83(2)	1.05(1)	0.61(2)	1.05(1)	1.09(2)	1.18(2)	1.34(2)
O2 (8h)	Occ.	1	1	1	1	1	1	1	1
	$100*U_{iso}$	0.71(2)	0.83(2)	1.05(2)	0.61(2)	1.05(2)	1.09(2)	1.18(2)	1.34(2)
	δ	0.02(1)	0	0	0	0	0	0	0
	x	0.2458(2)	0.2468(3)	0.2450(3)	0.2447(3)	0.2450(3)	0.2402(2)	0.2346(1)	0.2366(2)
	R_p (%)	4.4	4.3	4.0	4.7	4.0	4.4	3.4	4.5
	wR_p (%)	6.3	6.0	6.3	6.9	6.3	6.3	4.9	6.3
	Ti/Nb-O1(×2)	1.9520(3)	1.9559(6)	1.9342(2)	1.9343(5)	1.934(2)	1.9343(5)	1.9343(5)	1.9533(9)
	Ti/Nb-O2(×4)	1.9520(1)	1.9559(3)	1.9546(2)	1.9555(9)	1.955(1)	1.9556(9)	1.9556(9)	1.9547(9)
	Ti/Nb-O1/O2-Ti/Nb	180/ 179.1(1)	180/ 178.6(1)	180/ 178.9(1)	180/ 178.8(1)	180/ 178.9(1)	180/ 178.8(1)	180/ 178.8(1)	180/ 176.9(1)
	Sr/La-O1 (×4)	2.760(1)	2.766(1)	2.764(2)	2.765(1)	2.764(2)	2.765(1)	2.765(1)	2.760(1)
	Sr/La-O2 (×4)	2.738(1)	2.749(2)	2.722(2)	2.721(1)	2.722(2)	2.721(1)	2.721(1)	2.688(1)
	Sr/La-O2 (×4)	2.783(1)	2.783(2)	2.778(2)	2.780(1)	2.778(2)	2.780(1)	2.780(1)	2.836(1)
Atomic Coordinates: Sr/La (0, 1/2, 1/4), Ti/Nb (0, 0, 0), O1 (0, 0, 1/4) and O2 (x, x+1/2, 0).									

	$Sr_{0.80(1)}La_{0.13(1)}\square_{0.07}Ti_{0.90(1)}Nb_{0.10(1)}O_3$							
T (K)	300	373	473	573	673	773	873	1023
S.G	I4/mcm	P m -3 m	P m -3 m	P m -3 m	P m -3 m	P m -3 m	P m -3 m	P m -3 m
a (Å)	5.5317(9)	3.9137(1)	3.9177(1)	3.9220(1)	3.9263(1)	3.9306(1)	3.9351(1)	3.9419(1)
c (Å)	7.824(3)	-	-	-	-	-	-	-
Occ.	0.80/ 0.13	0.80/ 0.13	0.80/ 0.13	0.80/ 0.13	0.80/ 0.13	0.80/ 0.13	0.80/ 0.13	0.80/ 0.13
100*U_{iso}	0.75(4)	0.83(4)	1.05(3)	1.29(3)	1.46(3)	1.70(3)	1.89(3)	2.23(4)
Occ.	0.90(1)/ 0.10(1)	0.90/ 0.10	0.90/ 0.10	0.90/ 0.10	0.90/ 0.10	0.90/ 0.10	0.90/ 0.10)	0.90/ 0.10
100*U_{iso}	0.39(1)	0.52(9)	0.75(5)	0.85(6)	0.94(6)	1.05(6)	1.24(6)	1.44(6)
Occu	1.0(1)	1.0(1)	1.0(1)	1.0(1)	1.0(1)	1.0(1)	1.0(1)	1.0(1)
100*U_{iso}	0.83(2)	0.90(2)	1.07(2)	1.27(2)	1.47(2)	1.69(2)	1.85(2)	2.17(2)
Occ.	1	-	-	-	-	-	-	-
100*U_{iso}	0.83(2)	-	-	-	-	-	-	-
x	0.2468(3)							
R_p (%)	4.3	4.1	4.0	4.0	3.8	3.7	3.6	3.5
wR_p (%)	6.0	5.9	5.8	5.8	5.6	5.4	5.3	5.2
Ti/Nb-O1 (×2)/ Ti/Nb-O2 (×4)	1.9559(6)/ 1.9559(3)	1.9569(1)	1.9589(1)	1.9610(1)	1.9632(1)	1.9653(1)	1.9675(1)	1.9709(1)
Ti/Nb-O1/O2-Ti/Nb	180/ 178.56(17)	180/180	180/180	180/180	180/180	180/180	180/180	180/180
Sr/La-O1 (×4)	2.766(1)	2.7674(1)	2.7702(1)	2.7732(1)	2.7763(1)	2.7794(1)	2.7825(1)	2.7873(1)
Sr/La-O2 (×4)	2.749(2)	-	-	-	-	-	-	-
Sr/La-O2 (×4)	2.783(2)	-	-	-	-	-	-	-

Atomic Coordinates: I4/mcm; Sr/La (4a) (0, 1/2, 1/4), Ti/Nb (4c) (0, 0, 0), O1 (4a) (0, 0, 1/4) and O2 (8h) (x, x+1/2, 0)
Atomic Coordinates: P m-3m; Sr/La (0, 0, 0), Ti/Nb (1/2, 1/2, 1/2) and O (0, 1/2, 1/2)