High Temperature Thermoelectric Properties of $(1-x)SrTiO_3 – (x)La_{1/3}NbO_3$ ceramic solid solution

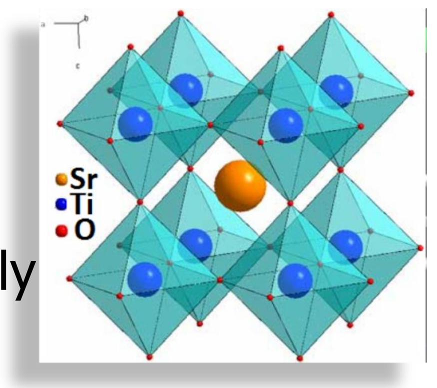
Deepanshu Srivastava, F. Azough, R. Freer

University Of Manchester, UK

INTRODUCTION

Ceramics based on $SrTiO_3$ (STO) are of growing interest as thermoelectric materials because of their high temperature stability and non-toxicity. STO is stable wide band gap semiconductor with a perovskite cubic structure.

Doped STO have demonstrated maximum ZT of 0.35 at 1000K[1]. Nanostructuring has limited effect on ZT through grain boundary scattering[2]. Microstructure modification, control of processing conditions can effectively increase the thermoelectric (TE) properties.



[1] *Koumoto, K.; Annual Review of Materials Research, Vol 40 2010, 40, 363-394.*

[2] *Yadav, G.G., Nanoscale, 2011, 3, 4078*

OBJECTIVES

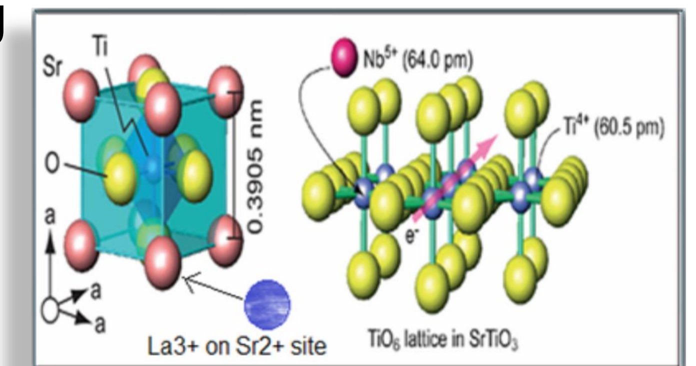
- Study of TE properties of $(1-x)SrTiO_3 – (x)La_{1/3}NbO_3$
- Study of effect of sintering atmosphere on TE properties and microstructure and improve ZT.

EXPERIMENTAL METHODOLOGY

$Sr_{1-x}La_{x/3}Ti_{1-x}Nb_xO_3$= Lx is prepared by mixed oxide route using conventional solid state sintering. L(x) is prepared in stoichiometric ratio hence creating A-site vacancy by aliovalent substitution of La^{3+} on Sr^{2+}.

Nb^{5+} is substituted on Ti^{4+} sites.

Level of doping is optimized for improved TE properties.



Charge carrier concentration and improved electrical conductivity can be achieved by reduction of Ti^{4+} sites to Ti^{3+} and creation of oxygen vacancies with normal pressure sintering

CHARACTERISATION METHODS

Electrical conductivity and Seebeck coefficient, are measured by ZEM-III ULVAC.

Thermal diffusivity is measured by laser flash method (Netzsch STA 449 C); differential scanning calorimeter is used to measure specific heat capacity.

Philips XL 30 and TITAN were used to study the structure in SEM and TEM mode.

Author's Contact Details

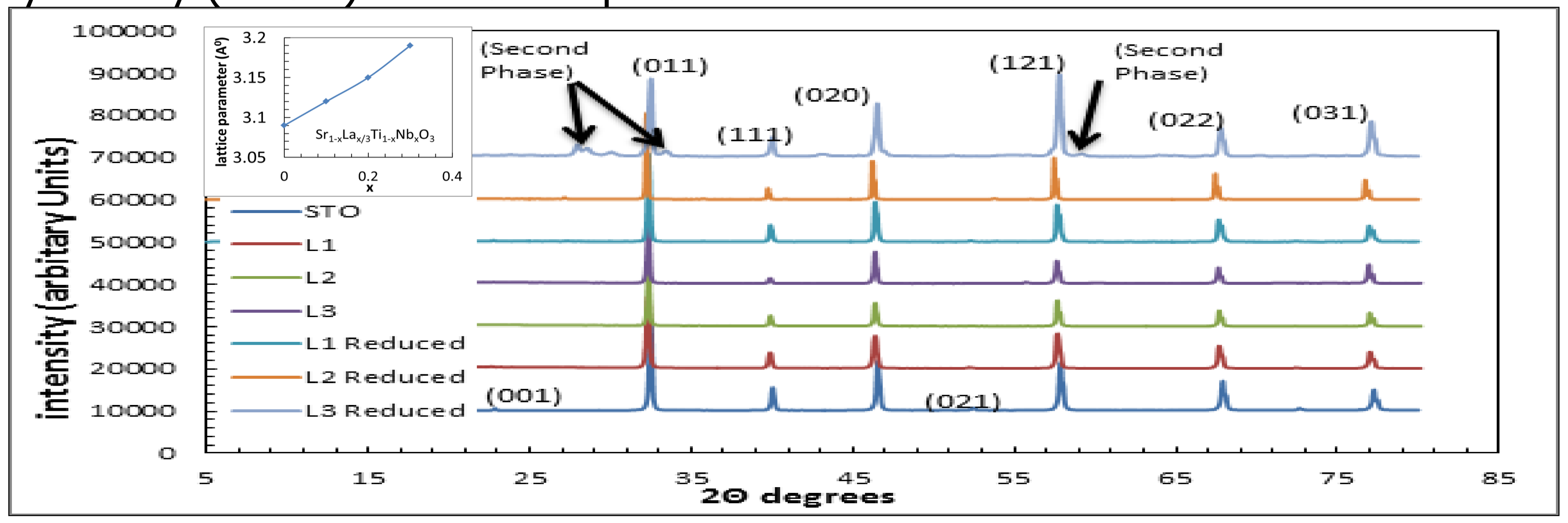
Position : PhD Candidate, University Of Manchester, UK

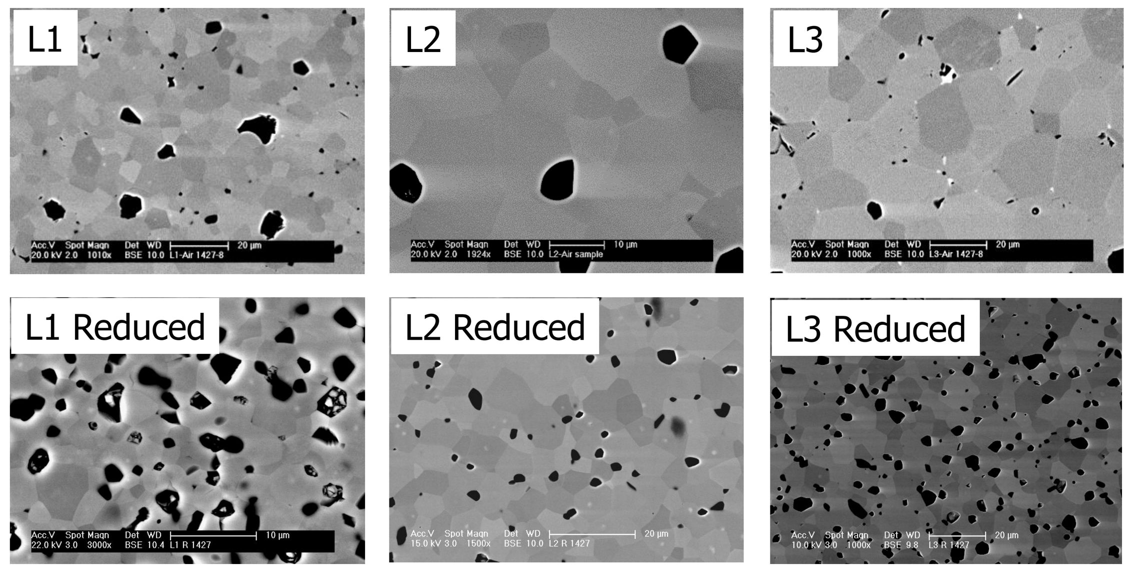
Email : Deepanshu.Srivastava@manchester.ac.uk

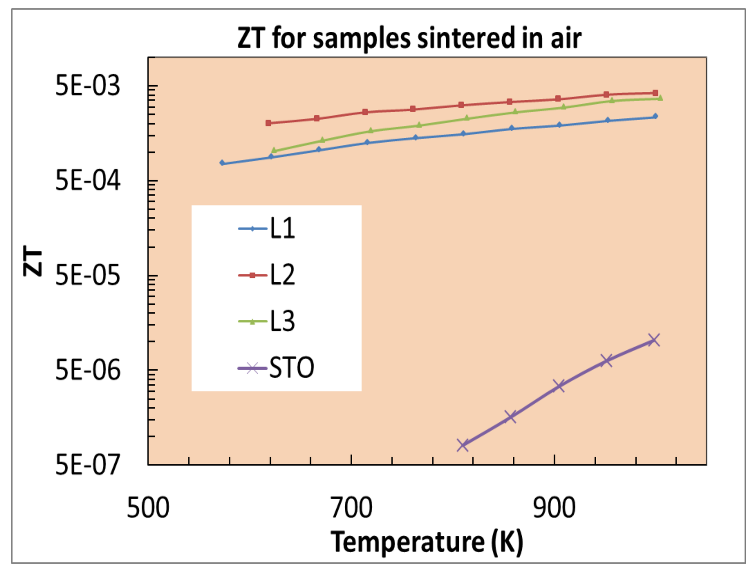
Phone No : +44 – 0161 306 2264

RESULTS

L(x) were prepared by conventional mixed oxide route for x = 0 to 1 in steps of 0.1. XRD characterisation showed that predominant single phase structure were obtained for x= 0.1, 0.2, 0.3. All compositions were stabilised in cubic symmetry (Pm3m). The lattice parameter increases as shown in inset below.

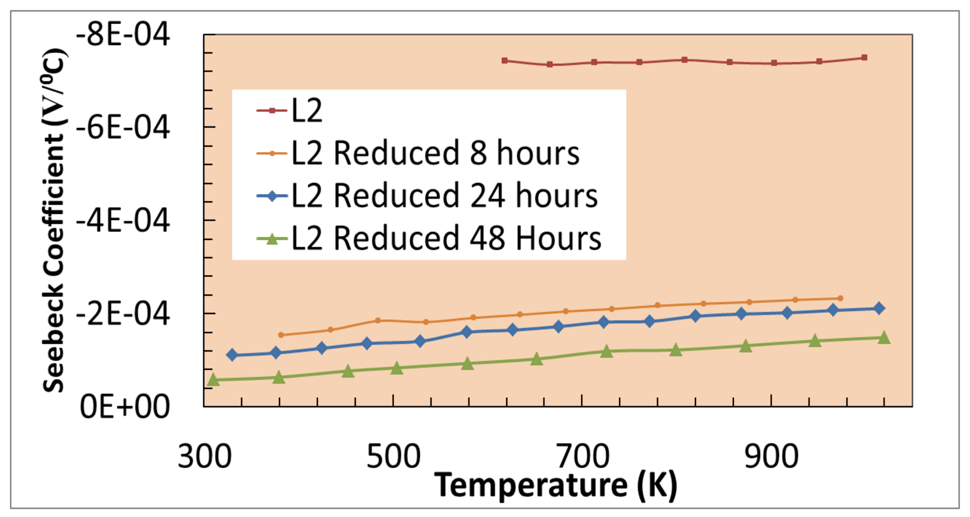


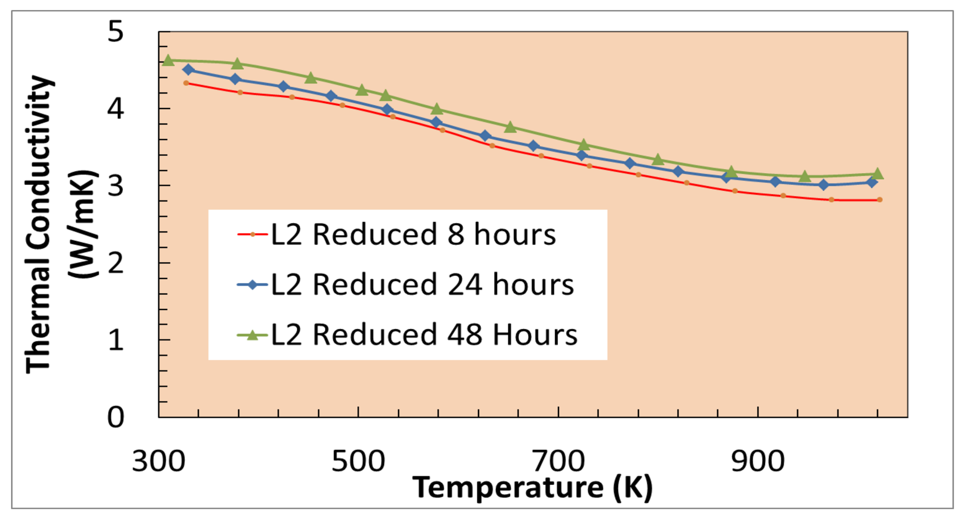


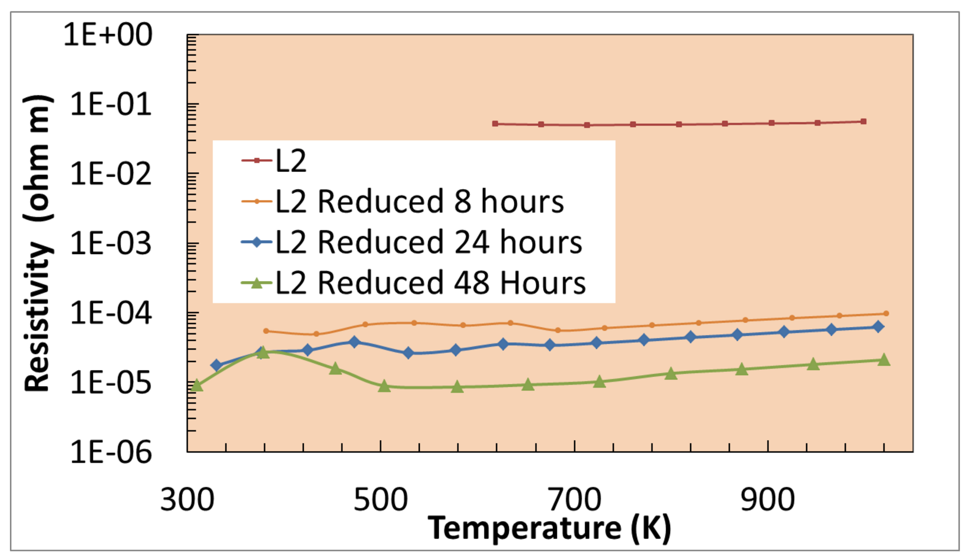


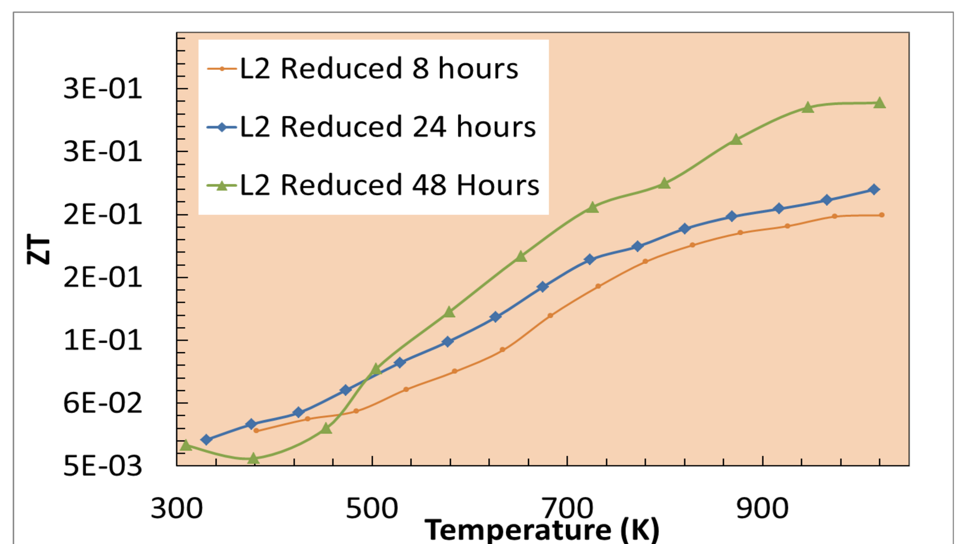
Based on optimum microstructure - crystal structure, improved density and higher TE values among **x**=0,0.1,**0.2**,0.3; L2 was selected for further detailed study.

THERMOELECTRIC PROPERTIES vs SINTERING TIME





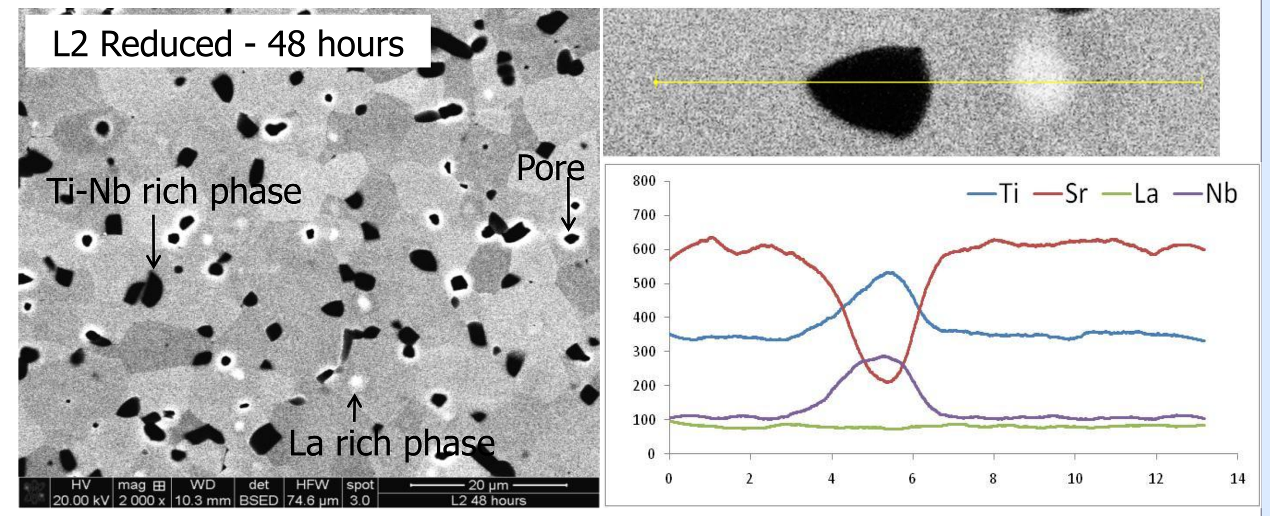




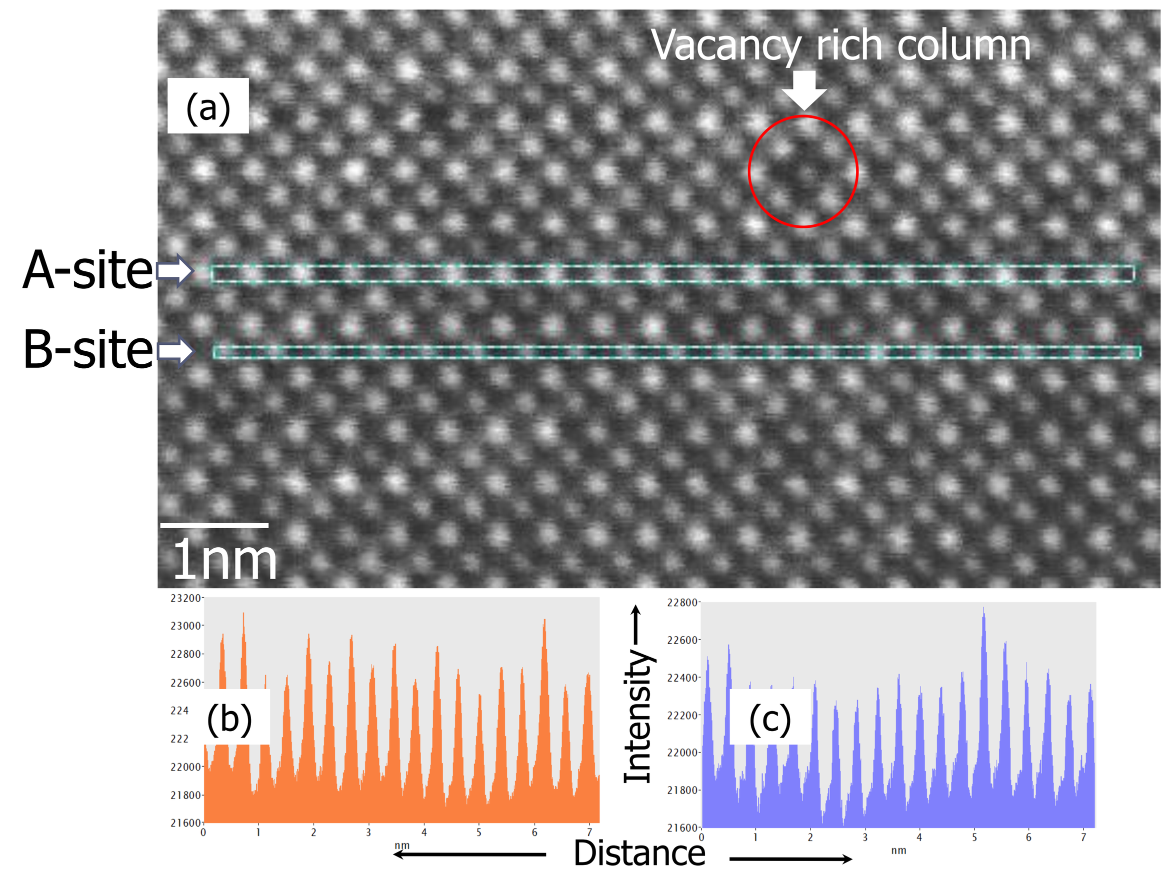
Sintering Time ↑ Electrical Resistivity ↓ Seebeck Coefficient ↑ Thermal Conductivity ↑ ZT ↑

L2 composition was sintered directly in Ar/H2 for different sintering times to study the effect on TE properties as shown above.

MICROSTRUCTURE



A second phase develops with increasing sintering time. Line EDS scan on the microstructure reveals Ti-Nb rich phase and La-rich core in the grains. Grain size gradually increases with sintering time.



(a)-TITAN (ChemiStem) HAADF image for L3 showing both A-site and B-site atomic columns. Variation in the intensity indicates random distribution of Sr, La and vacancies in A-site and Ti and Nb in B-sites.

(b)-Intensity along A-sites.

(c)-Intensity along B-sites.

CONCLUSIONS

- $Sr_{1-x}La_{x/3}Ti_{1-x}Nb_xO_3$, where x=0.2, sintered for 48 hours (Ar/H_2) has optimized TE properties with a maximum ZT = 0.29 at 1000 K.
- TE properties have been shown to improve by control on sintering conditions.
- Critical areas are to determine oxygen vacancies, Ti^{4+} reduction and effective mechanism of second phases.

Acknowledgements

The University of Manchester Engineering and Physical Sciences

Armourers & Brasiers' Trust

IOP Institute of Physics