

# Conductivity enhancement of Apatite-Type Doped Lanthanum Silicates

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# Solid Oxide Fuel Cell (SOFC)

Fuel Cell = power generator using  $O_2$  and  $H_2$



## Solid Oxide Fuel Cell(SOFC)

- High total efficiency (~87%)
- High output power
- Easy gas reforming



<http://www.chuden.co.jp/hekinan-pr/guide/facilities/thermalpower.html>

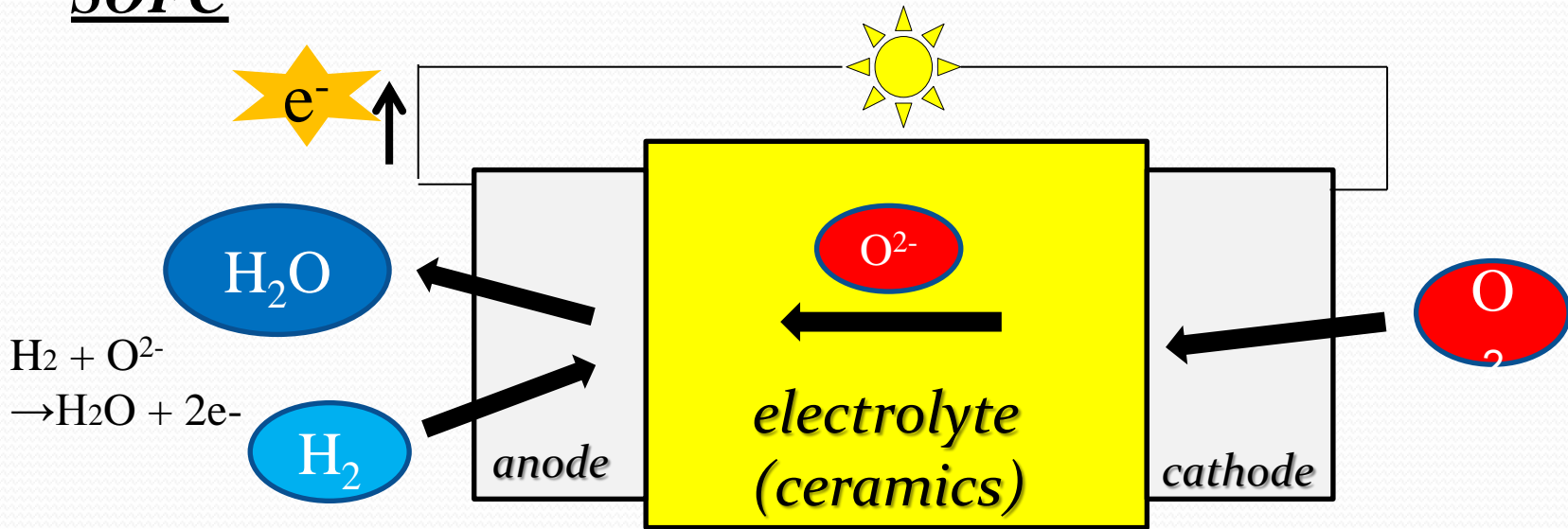
<http://techon.nikkeibp.co.jp/article/WORD/20060418/116213/>

[http://www.osakagas.co.jp/company/press/pr\\_2010/1190846\\_2408.html](http://www.osakagas.co.jp/company/press/pr_2010/1190846_2408.html)



# Solid Oxide Fuel Cell (SOFC)

## SOFC



## Electrolyte performance

= oxygen ion conductivity

$$\sigma = qn\mu$$

$\sigma$ : conductivity  $q$ : charge  
 $n$ : carrier concentration  
 $\mu$ : carrier mobility



Higher temperature  
(700~1000°C)  
is necessary



**Degradation**  
**Limited material**

# Apatite-type lanthanum silicate

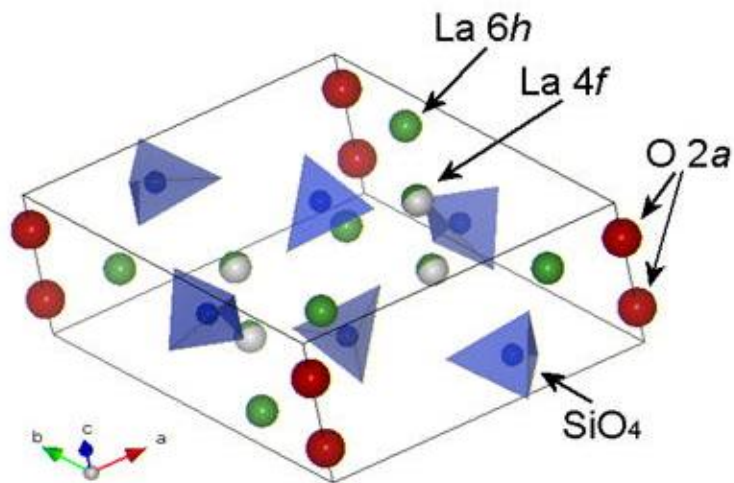


Fig. crystal structure of  $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$  showing a unit cell[1]

Reference:  
Welcome to  
Apatite Ionic  
Conductivity  
Home Page

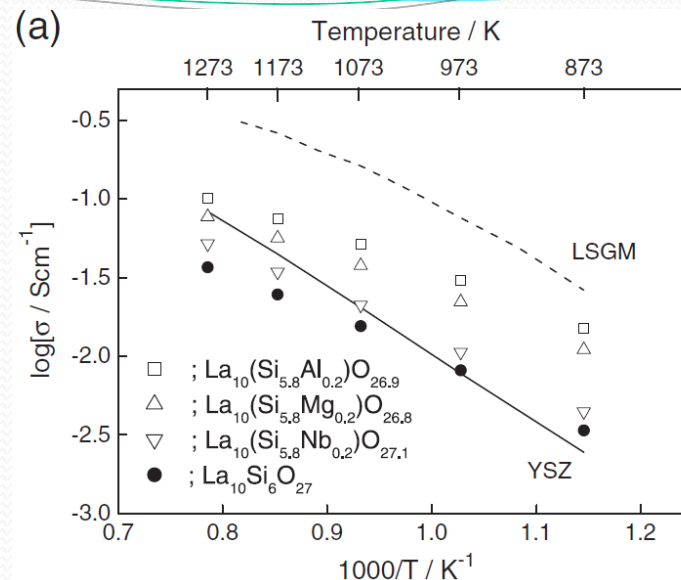


Fig. conductivities of electrolyte[2]

[YSZ:  $(\text{ZrO}_2)_{0.91}(\text{Y}_2\text{O}_3)_{0.09}$  LSGM:  $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Ga}_{0.8}\text{Mg}_{0.2})\text{O}_{3-\alpha}$ ]



- structure  $\equiv$  apatite  $[\text{Ca}_{10}(\text{PO}_4)_6\text{O}_2]$
- conductor : interstitial oxygen ion
- conduction path : c-axis

advantage

1. Higher ion conductivity
2. Lower temperature dependency



**SOFC can be used  
at lower temperature**

# Purpose

Improvement of oxygen ion conductivity

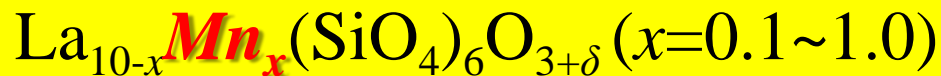
$$\sigma = qn\mu$$

$\sigma$ : conductivity  $q$ : charge

$n$ : carrier concentration  $\mu$ : carrier mobility



Sample:



Mn<sup>+2</sup>

Mn<sup>+3</sup>

Mn<sup>+4</sup>

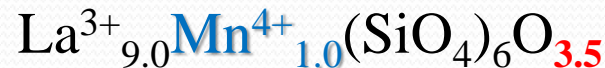
Mn<sup>+6</sup>

Mn<sup>+7</sup>

Ex.)



Mn<sup>4+</sup>



*How does Mn influence the conductivity?*

# Solid state reaction method

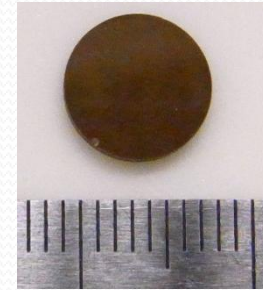
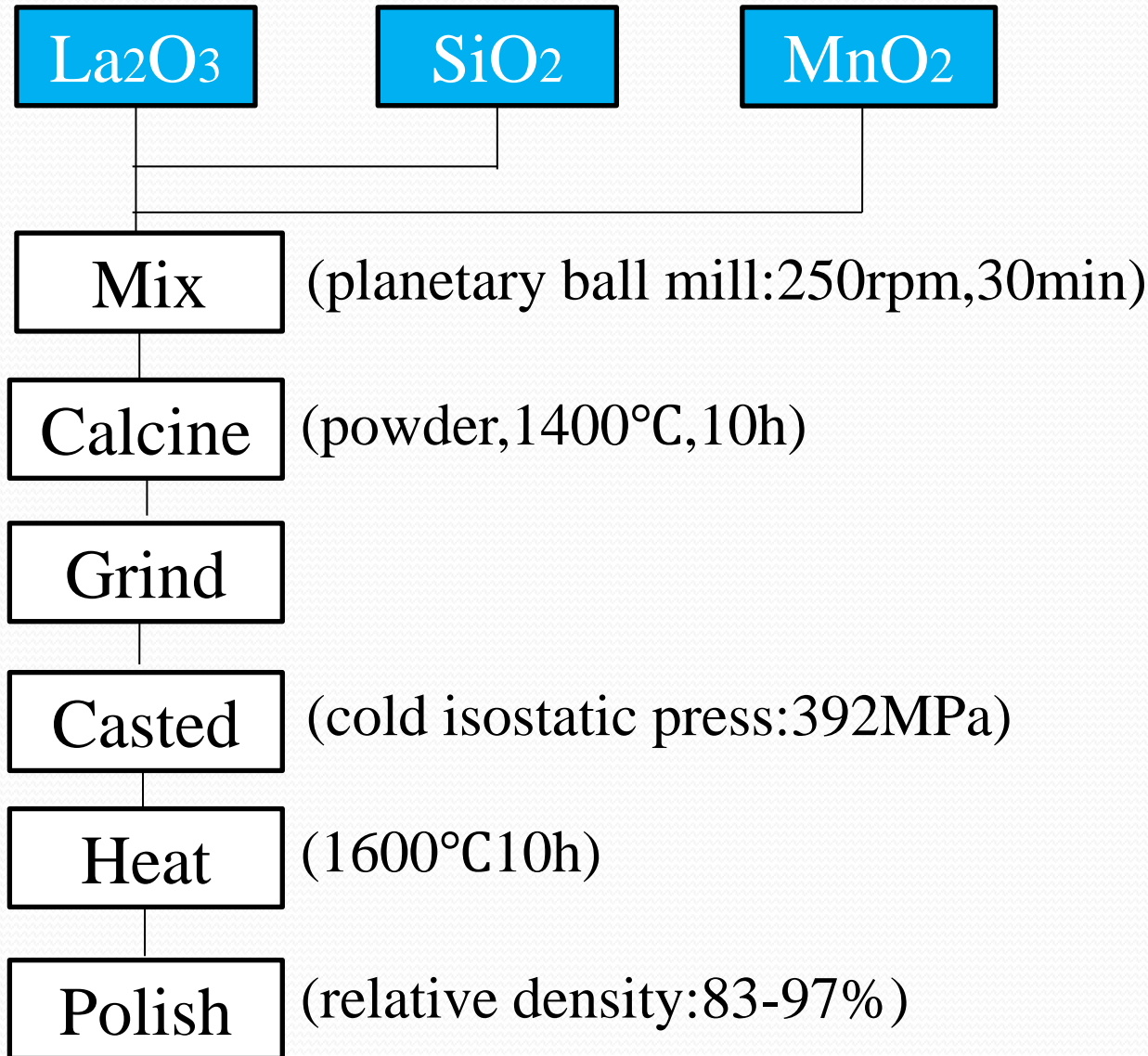


Fig. obtained pellet

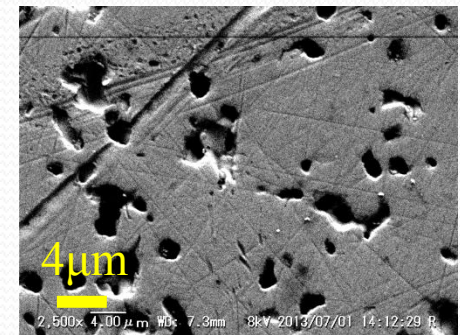
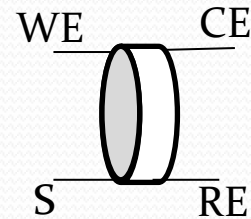
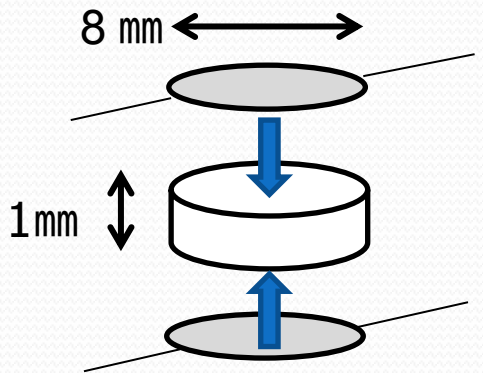


Fig. SEM image of pellet's surface

# Measurement method

## AC · Two-terminal method

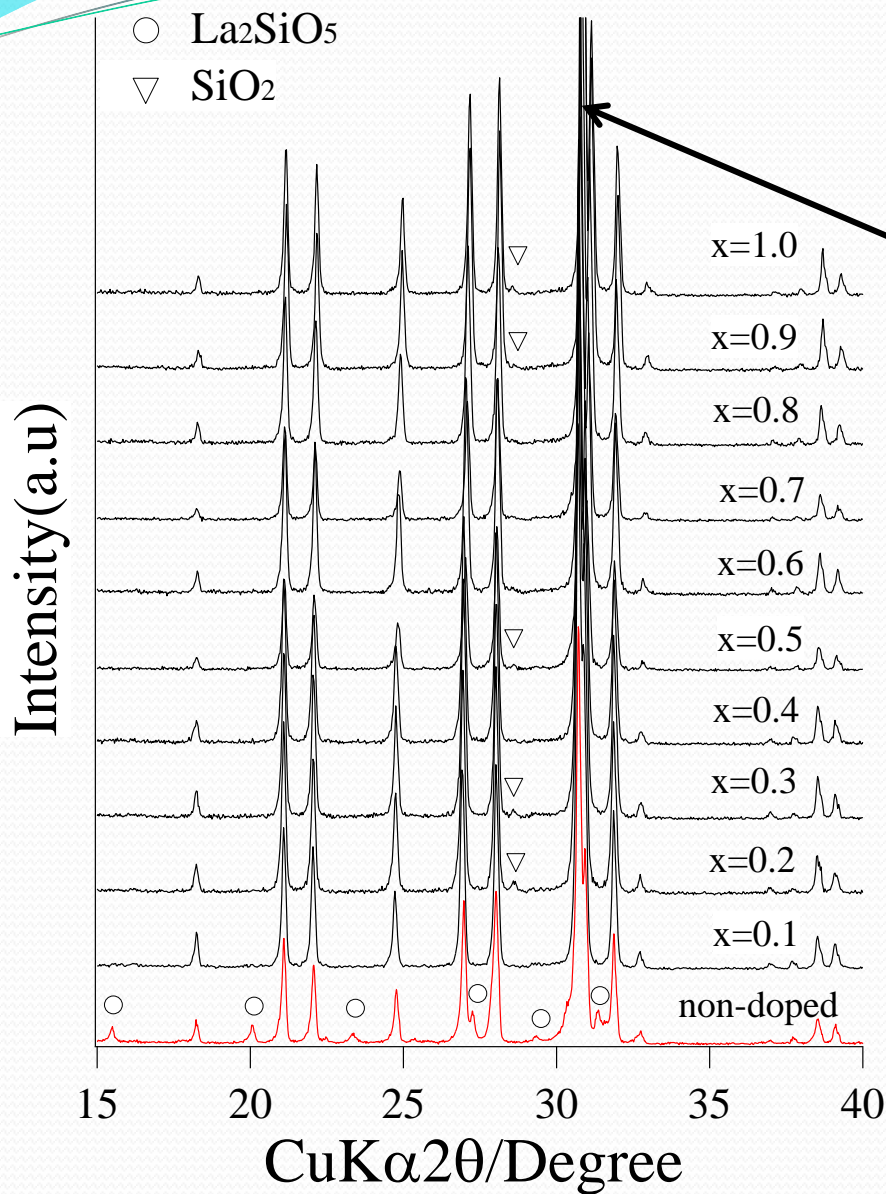


① Pellets attached with Pt mesh by Pt paste. Heated at 1000°C for 2h

② Connect with the electric wire

③ Measure in the temperature 500 ~ 1000°C ( in Air )

# Phase identification by XRD



sample:  $\text{La}_{10-x}\text{Mn}_x(\text{SiO}_4)_6\text{O}_{3+\delta}$

**No mark : apatite**

Non-doped

➔  $\text{La}_2\text{SiO}_5$  appear

**Mn doping**

➔  $\text{La}_2\text{SiO}_5$  disappear

Fig. XRD results of  $\text{La}_{10-x}\text{Mn}_x(\text{SiO}_4)_6\text{O}_{3+\delta}$

# Lattice constants change

## Shannon's ionic radius(Å)

**La**  $>$  **Mn**  $>$  **Si**  
(1.03-) (0.67-0.90) (0.26-0.40)

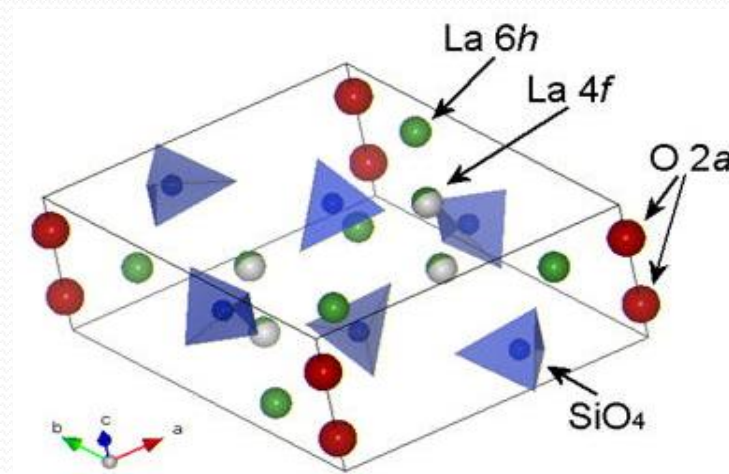
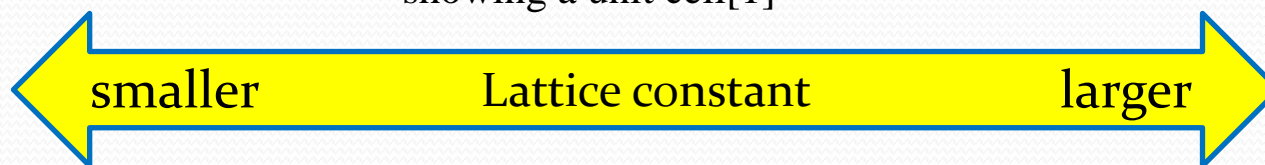


Fig. crystal structure of  $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$  showing a unit cell[1]



# Lattice constants change

Sample:  $\text{La}_{10-x}\text{Mn}_x(\text{SiO}_4)_6\text{O}_{3+\delta}$

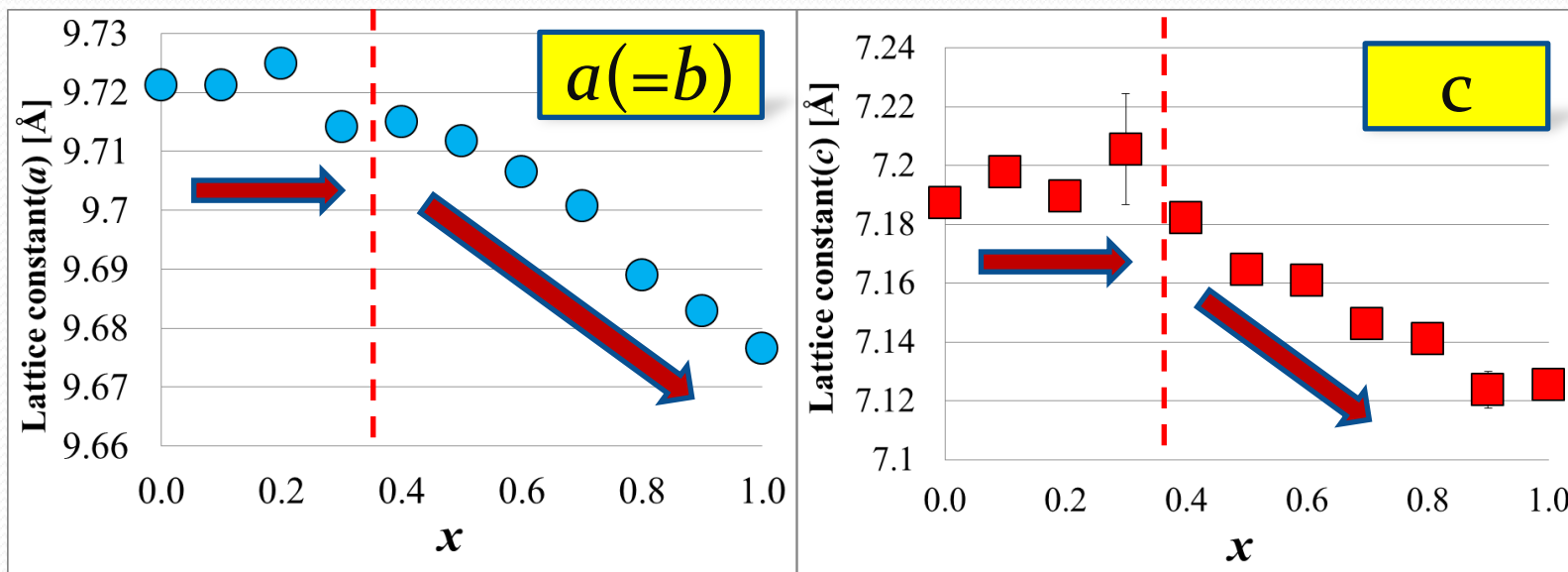
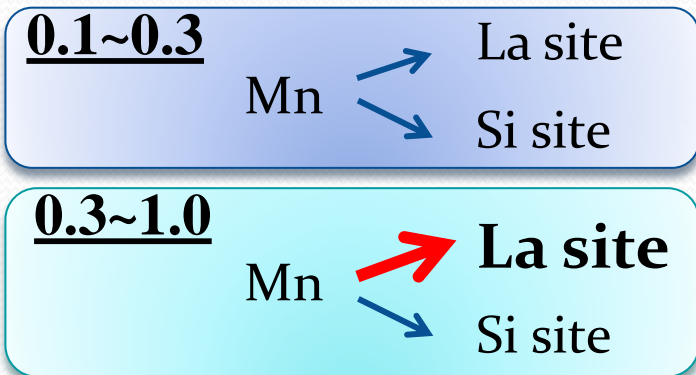


Fig. lattice constant  $a$  and  $c$  to the amount of Mn doped into La site



# Conductivity

Sample :  $\text{La}_{10-x}\text{Mn}_x(\text{SiO}_4)_6\text{O}_{3+\delta}$

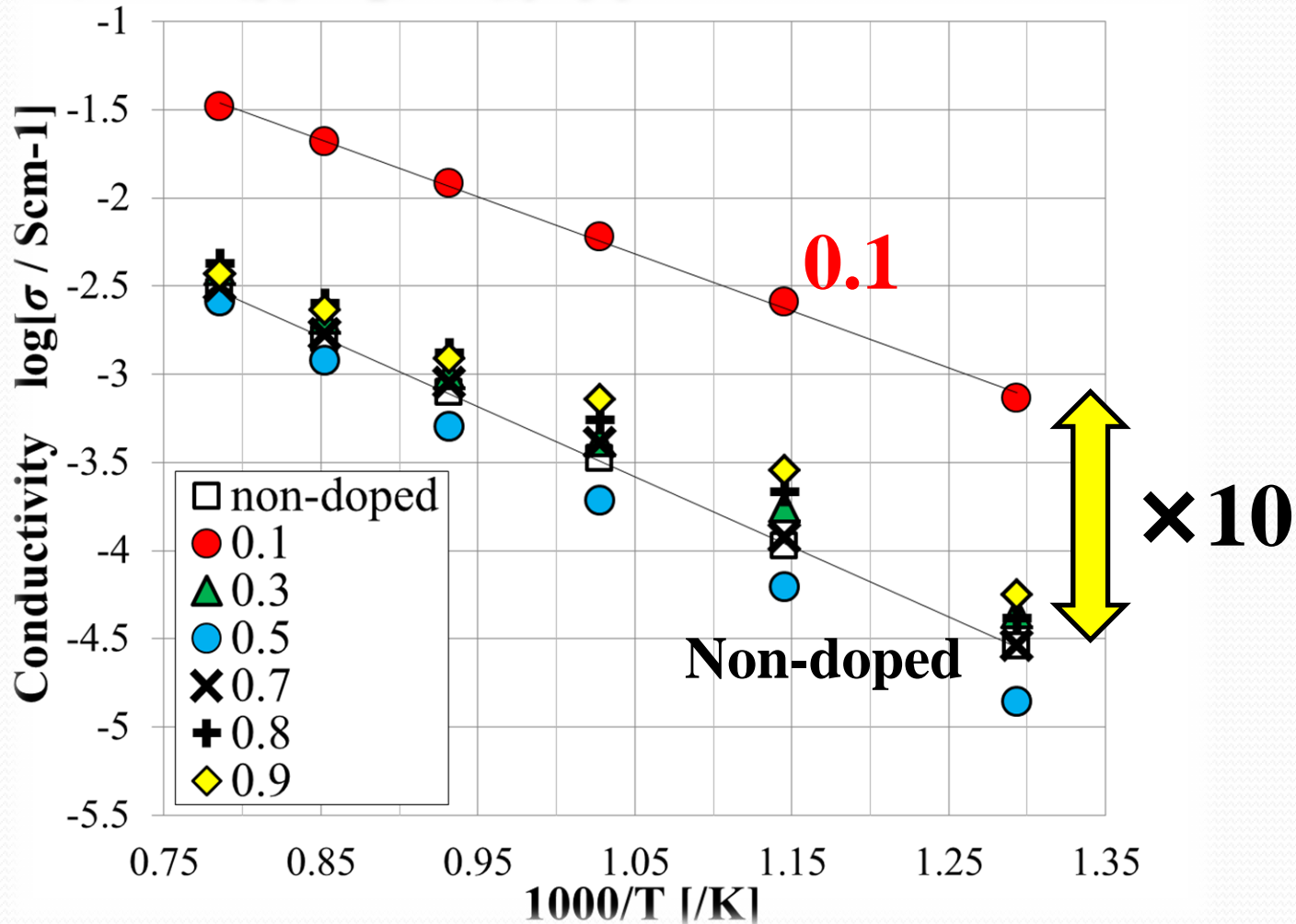


Fig. Arrhenius plot of  $\text{La}_{10-x}\text{Mn}_x(\text{SiO}_4)_6\text{O}_{3+\delta}$

# Discussion

$$\sigma = qn\mu$$

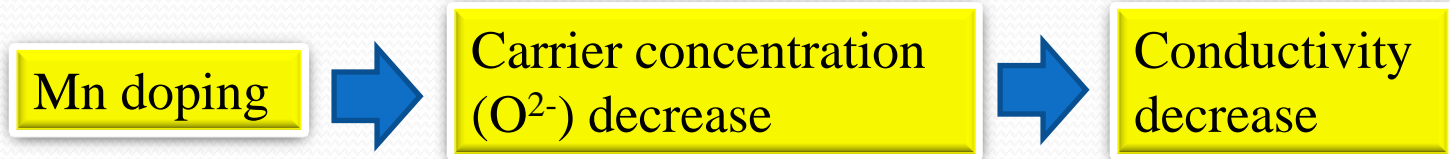
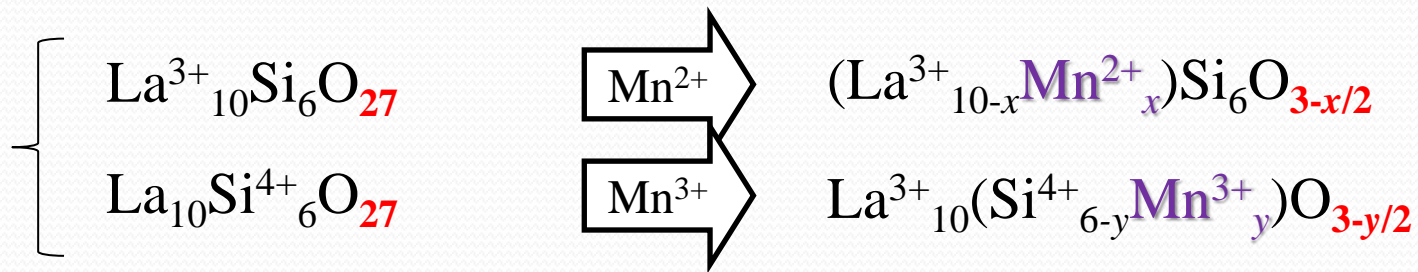
Carrier (O<sup>2-</sup>) mobility

The number of Carrier ( O<sup>2-</sup> )

Phase purity

[  $\sigma$ : conductivity  $q$ : charge  
 $n$ : carrier concentration  $\mu$ : carrier mobility ]

La site : Mn<sup>2+</sup> Si site: Mn<sup>3+</sup> [2]



[2] Julian R. Tolchard, Peter R. Slater, and M. Saiful Islam (2007), Insight into Doping Effects in Apatite Silicate Ionic Conductors, *Adv.Funct.Mater*, 2007, Vol.17, pp.2564-2571

# Discussion

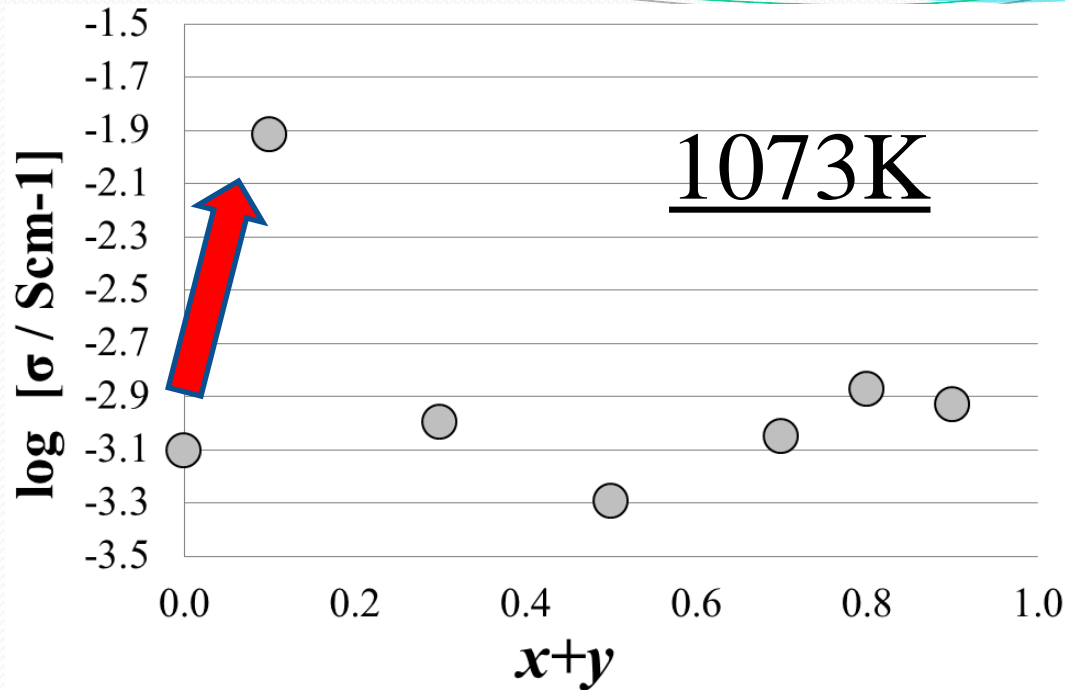


Fig. conductivities as the function of  $x+y$  at 1073K



□ Si substitution  
 ⇒ carrier mobility improved  
 ⇒ conductivity improved  
 Ex)  $\text{La}_{9.83}(\text{Si}_{4.5}\text{Al}_{1.5})\text{O}_{26}$  [3]



Carrier mobility ↑

Phase purity ↑  
 ( $\text{La}_2\text{SiO}_5$  disappeared)



Conductivity enhanced

[3] E. J. Abram, D.C. Sinclair and A. R. West (2001), A novel enhancement of ionic conductivity in the cation-deficient apatite  $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ , *J. Mater. Chem.*, 2001, Vol.11, 1978–1979

# Discussion

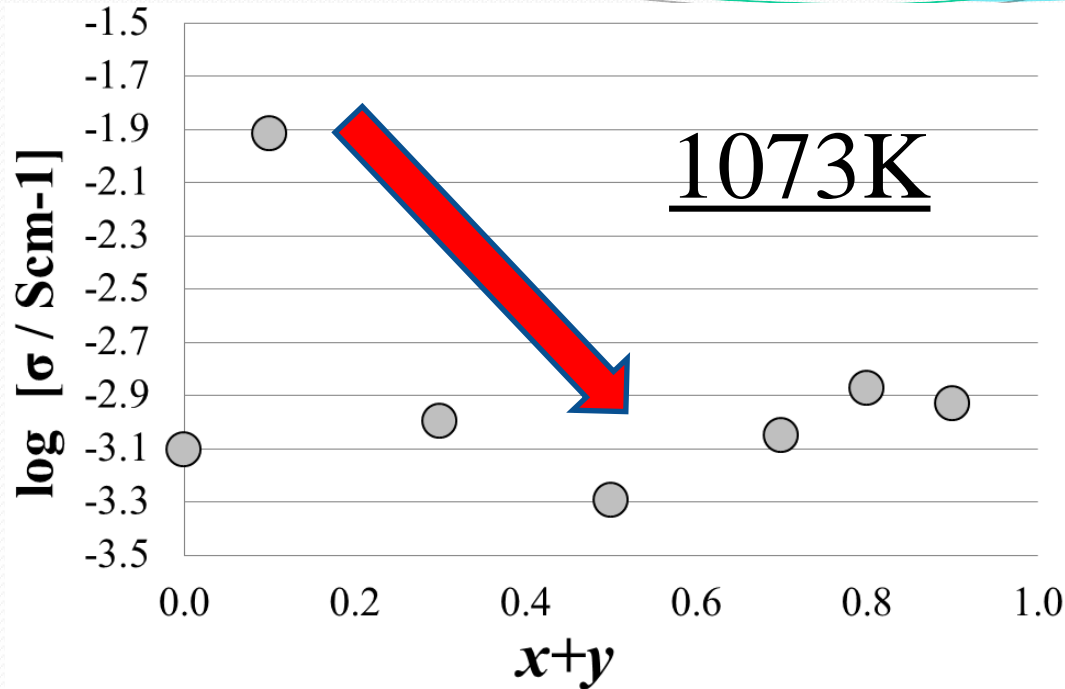
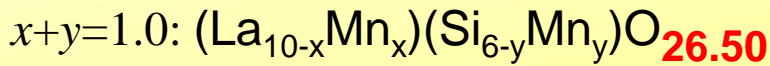
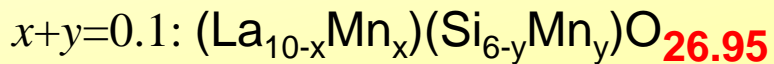


Fig. conductivities as the function of  $x+y$  at 1073K



Carrier( $\text{O}^{2-}$ )  
concentration



Conductivity  
decreased

# Conclusion

- ① Co-exist phases like  $\text{La}_2\text{SiO}_5$  which appeared in  $\text{La}_{10}\text{Si}_6\text{O}_{26+\delta}$  were not observed in  $\text{La}_{10-x}\text{Mn}_x\text{Si}_6\text{O}_{26+\delta}$ .
- ② The structure formula of Mn-doped lanthanum silicate was  $(\text{La}_{10-x}\text{Mn}_x)[\text{Si}_{6-y}\text{Mn}_y]\text{O}_{26+\delta}$ .
- ③ The sample of  $x = 0.1$  showed the highest conductivity in this examine.
- ④ Conductivity of Mn-doped lanthanum silicate is affected by the amount and distribution of Mn.