Influence of vacancies on ultra-low thermal conductivity in scheelite materials

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Outline

- Introduction
- Do scheelite materials have a low thermal conductivity?

  case: $BaMoO_4$ & $BaWO_4$
- Can A-site vacancies in scheelites reduce thermal conductivity even more?

  case: $La_{2/3}\square_{1/3}MoO_4$, $Ce_{2/3}\square_{1/3}WO_4$ and $La_{2/3}\square_{1/3}WO_4$
- What is the minimum vacancy content in scheelites to reduce thermal conductivity?

  case: $xBi_{2/3}\square_{1/3}MoO_4 - (1-x)BiVO_4$
- Conclusions

Applications

Intrinsic low thermal conductivity can be a key property for different applications such as:

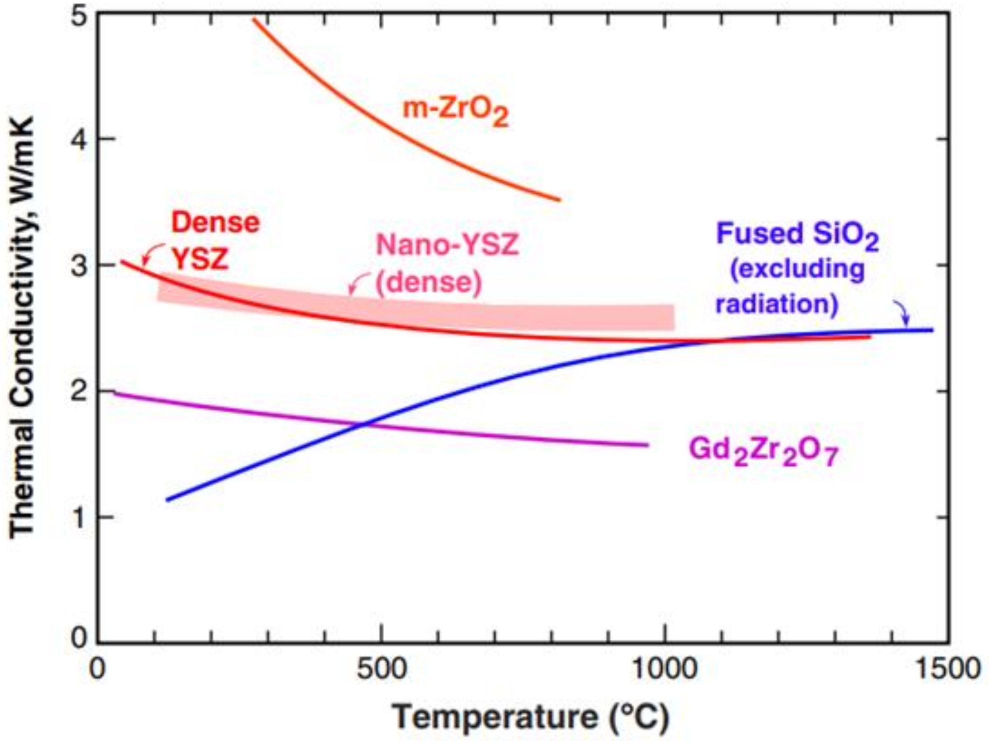
- Thermal Barrier Coatings (TBCs)
- Thermoelectric materials

Thermal Barrier Coatings

Coatings should allow combustors, gas turbine engines, … to operate at higher temperatures

It requires materials with :

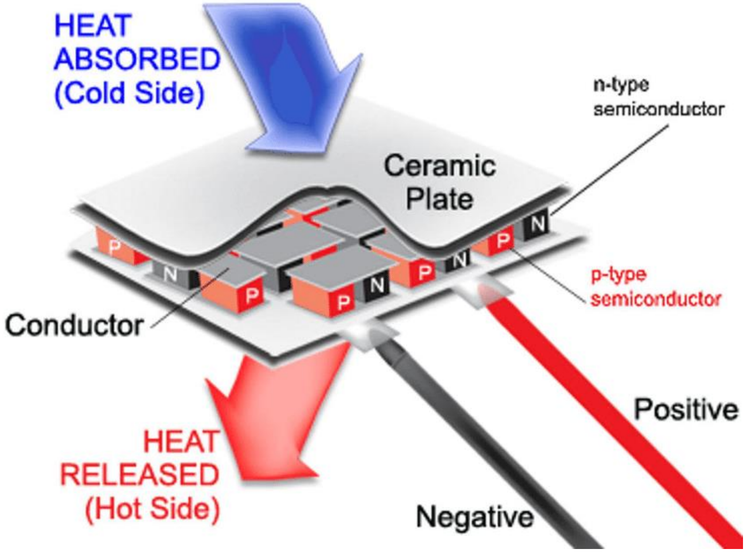
- Low thermal conductivity
- High temperature stability



Winter & Clarke (2007) J. Am. Ceram. Soc. 90, 533

Thermoelectrics

A thermoelectric device is composed of 2 materials (p and n) + junctions



Heat ➡ **Electricity**

Figure of Merit:

$$ZT = T\,S^2\sigma/\kappa$$

S = Seebeck coefficient ($\mu V.K^{-1}$)
σ = Electrical conductivity ($S.m^{-1}$)
κ = Thermal conductivity ($W.m^{-1}.K^{-1}$)

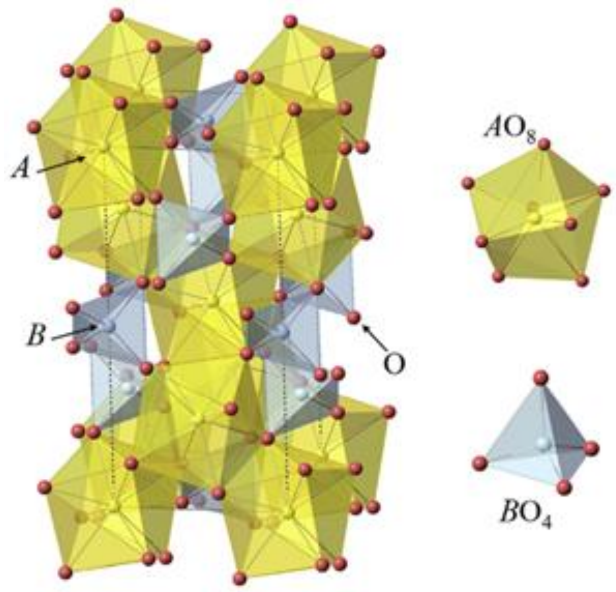
$$\kappa = \kappa_e + \kappa_l$$

- **High** Seebeck coefficient
- **High** Electrical conductivity
- **Low** Thermal conductivity

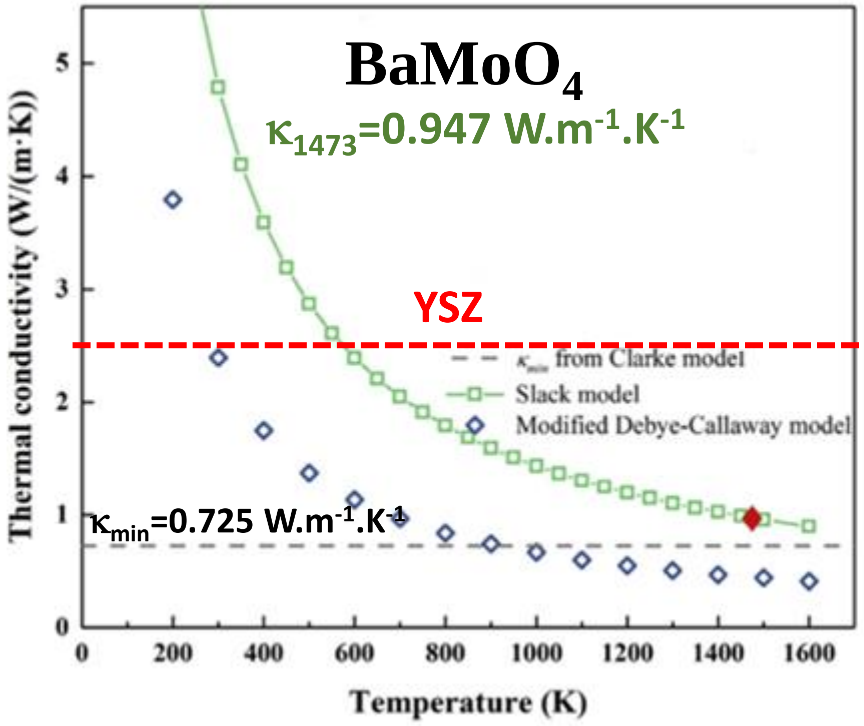
Predicted thermal conductivities of scheelites

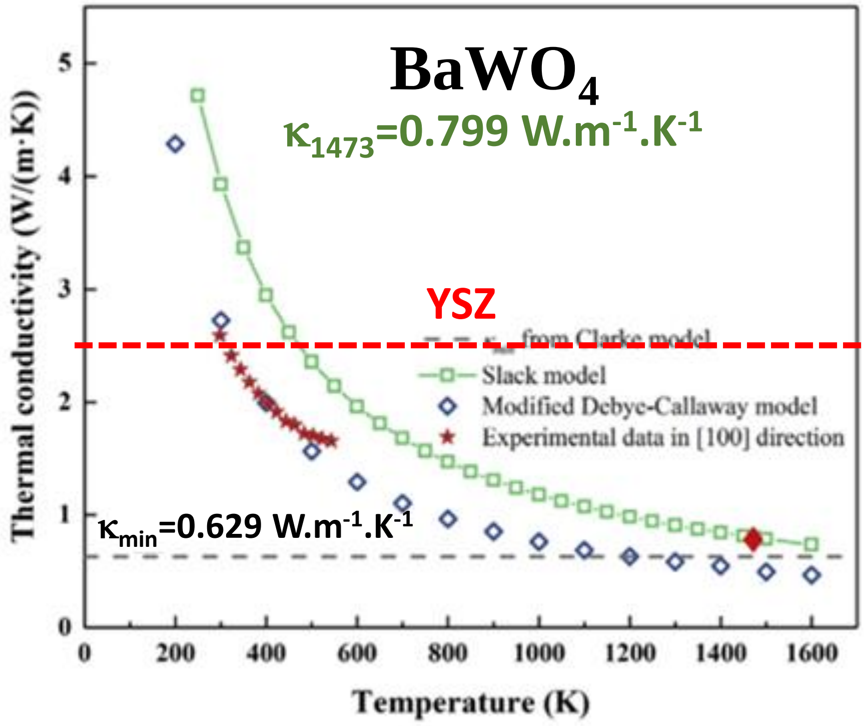
Searching a material presenting a thermal conductivity lower than **2 W.m^{-1}.K^{-1}**

Recently, Liu et al. have proposed ABO_4 scheelite compounds as low thermal conductivity materials from first principles calculations



Scheelite ABO_4





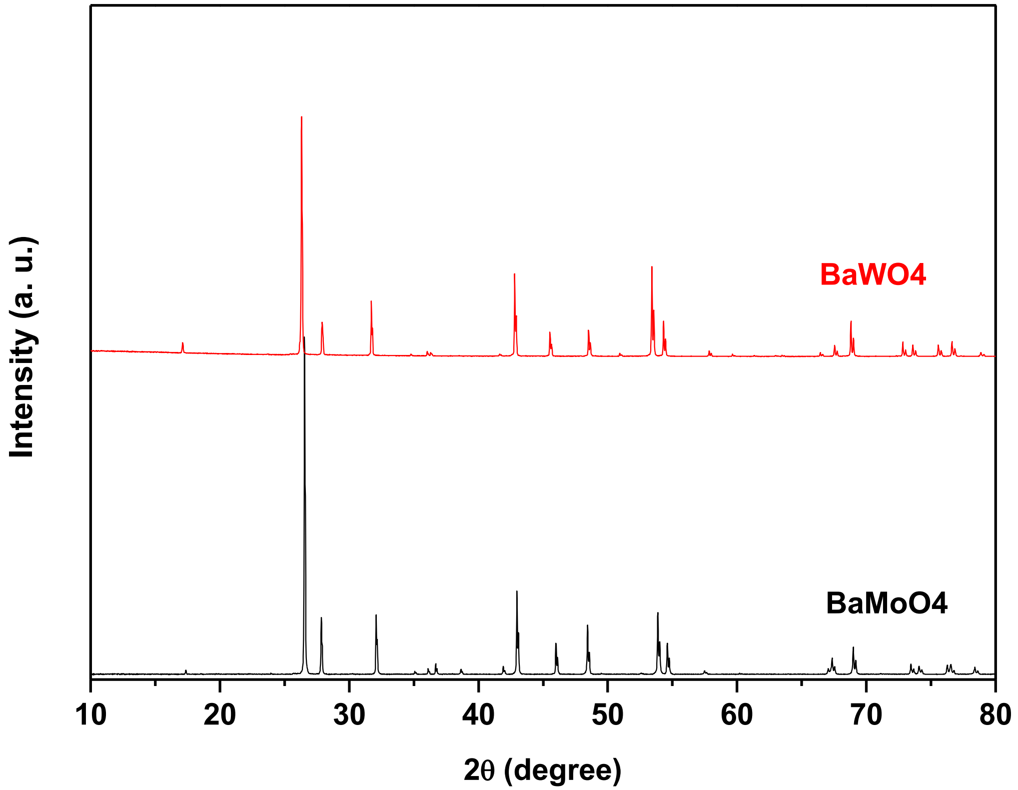
Liu et al. (2020) Journal of Materiomics 6, 702

Do scheelite materials have a low thermal conductivity ?

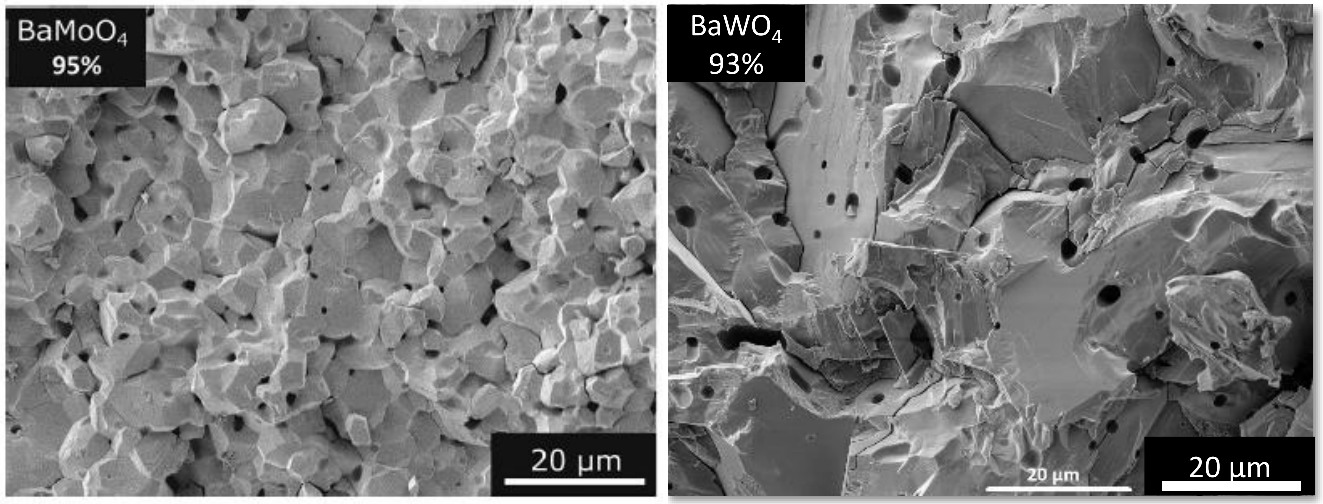
$BaMoO_4$ & $BaWO_4$

Structural and microstructural study of $BaMoO_4$ and $BaWO_4$ scheelites

- Synthesis: Solid-state reaction method (ball milling at 300 rpm)
- Conventional sintering

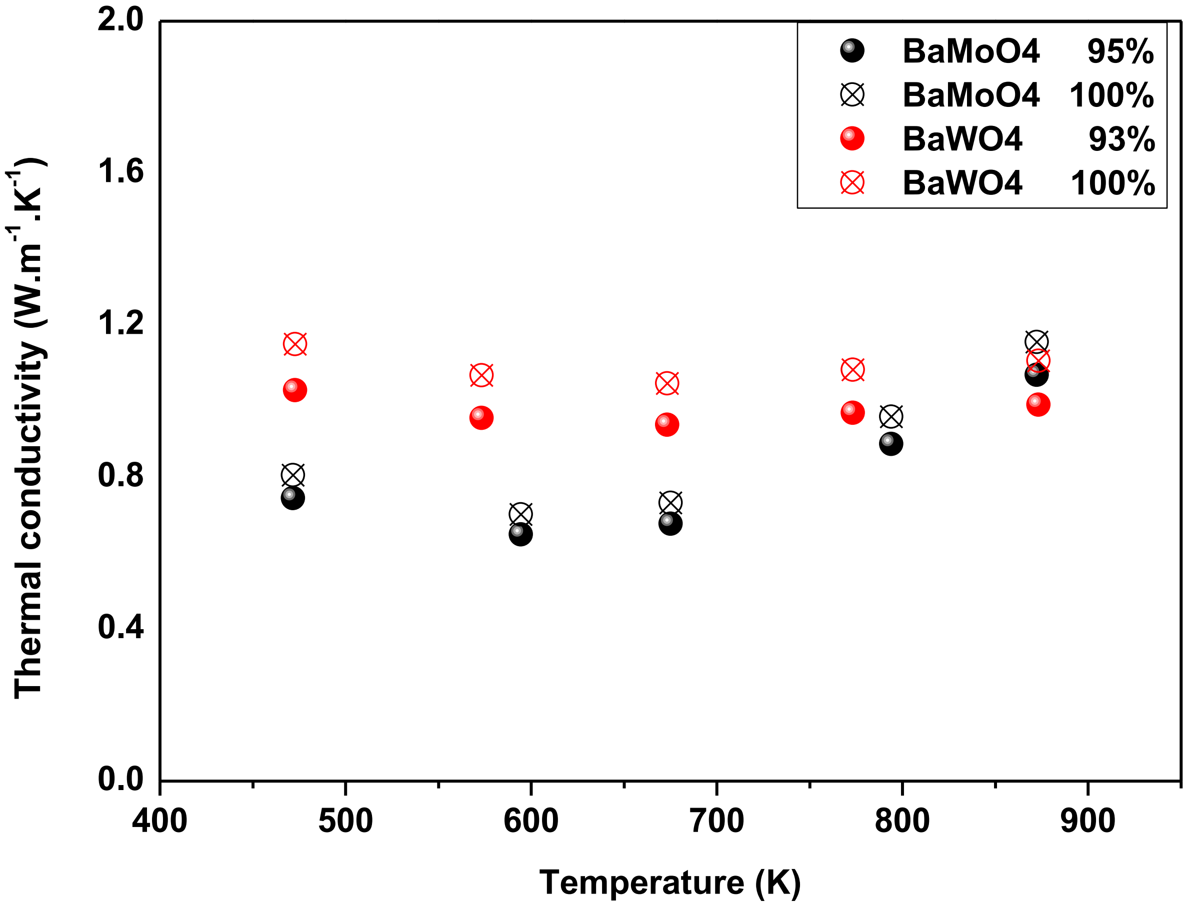


- Pure phase for $BaMoO_4$ and $BaWO_4$



- $BaMoO_4$, relative density = 95 %
  $BaWO_4$, relative density = 93 %

Thermal conductivity of $BaMoO_4$ and $BaWO_4$ scheelite ceramics



$$\kappa = D.\ \rho.\ C_p$$

D: Thermal diffusivity

ρ : Density

C_p: Specific heat capacity

$$\kappa_{dense} = \kappa_{measured} \frac{1}{(1 - 1.5\phi)}$$

Φ: Porosity

Winter & Clarke (2007) J. Am. Ceram. Soc. 90, 533

➡ **0.9-1.2** $W.m^{-1}.K^{-1}$ for 100 % dense $BaMoO_4$ *(Bsaibess et al. (2021) Scripta Materialia 201, 113950)*

1.1-1 $W.m^{-1}.K^{-1}$ for 100 % dense $BaWO_4$

Do scheelite materials have a low thermal conductivity ?

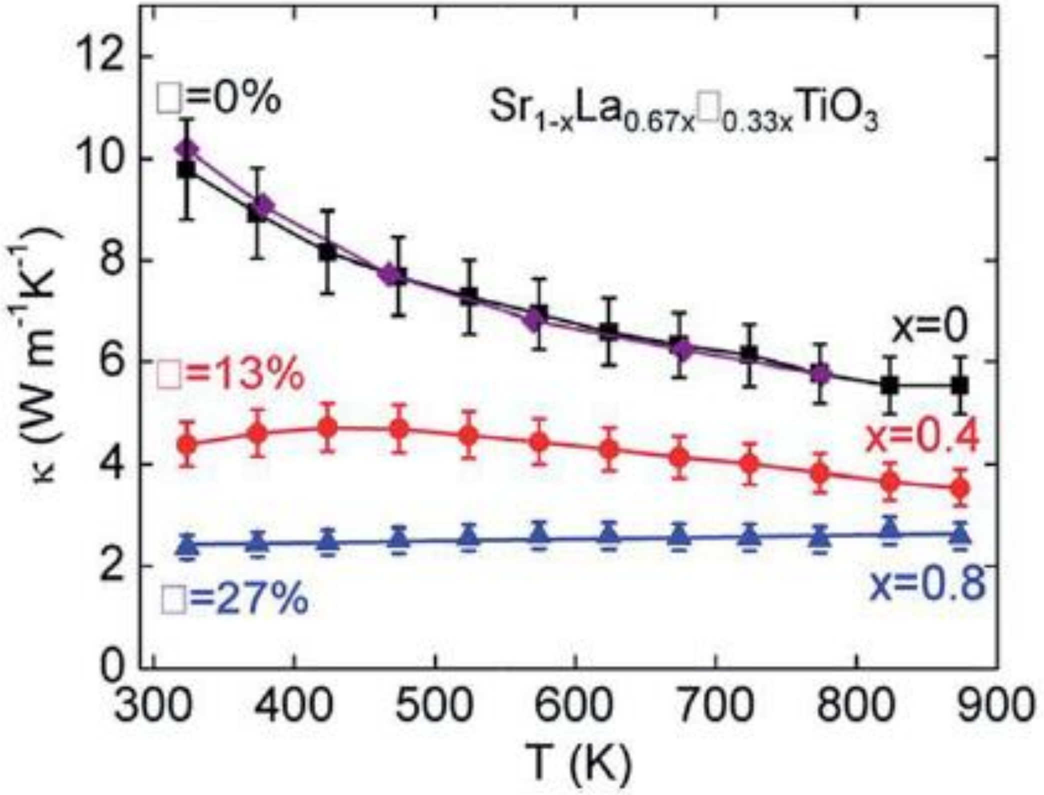
$BaMoO_4$ and $BaWO_4$ ceramics reveal a low thermal conductivity (**close to 1 $W.m^{-1}.K^{-1}$**)

Can A-site vacancies in scheelites reduce thermal conductivity even more?

$La_{2/3}\square_{1/3}MoO_4$, $Ce_{2/3}\square_{1/3}WO_4$ and $La_{2/3}\square_{1/3}WO_4$

Influence of vacancies on thermal conductivity

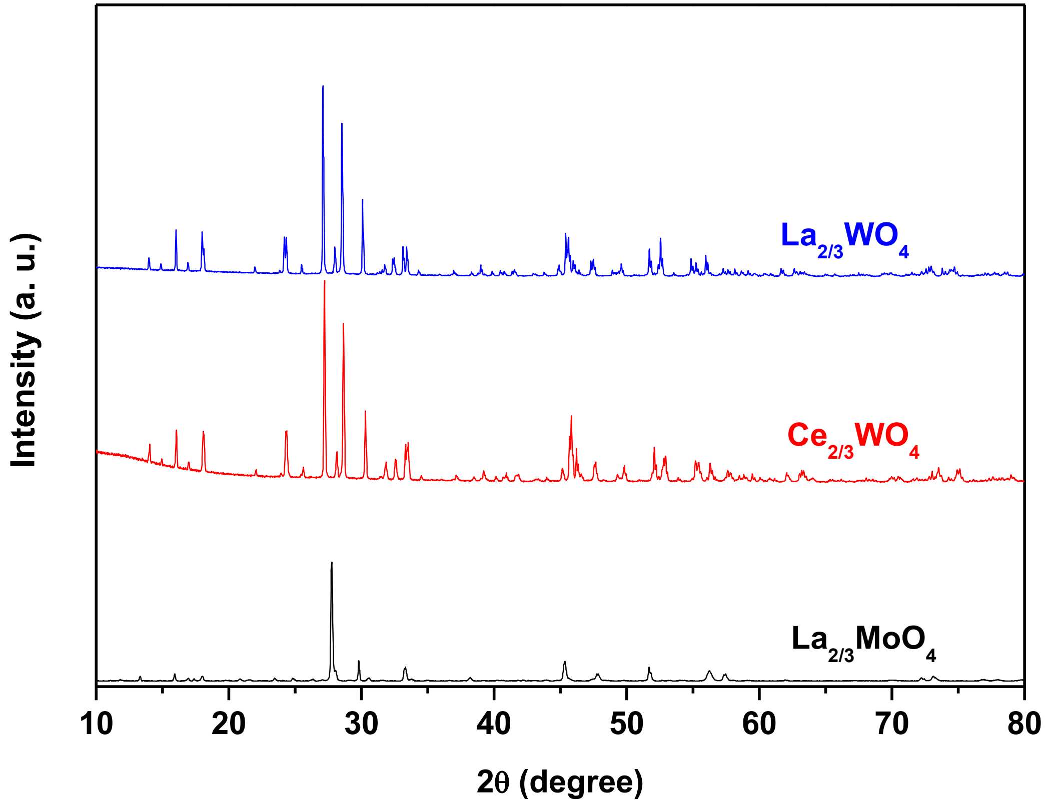
Popuri et al. have shown that A-deficient $SrTiO_3$ (**Perovskites**) exhibits lower thermal conductivity.

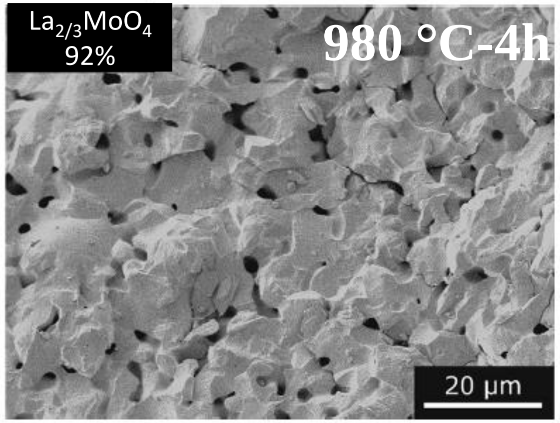


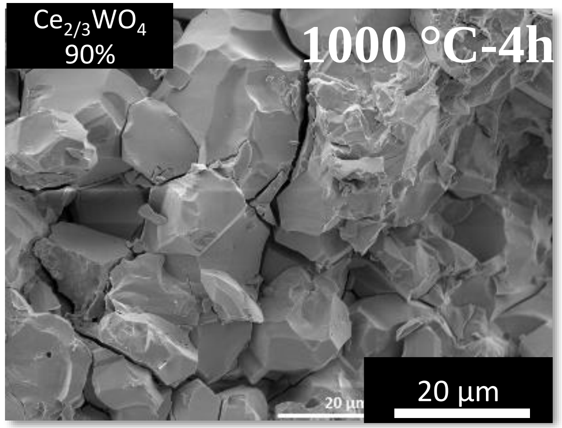
Popuri et al. (2014) RSC Adv. 4, 33720

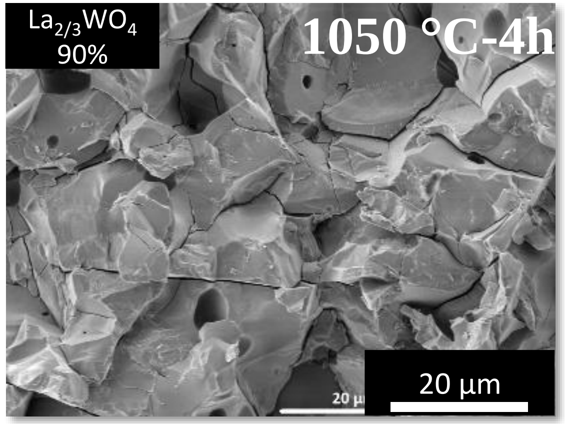
Structural and microstructural study of A-deficient scheelites

$La_{\frac{2}{3}}\square_{\frac{1}{3}}MoO_4$, $Ce_{\frac{2}{3}}\square_{\frac{1}{3}}WO_4$ and $La_{\frac{2}{3}}\square_{\frac{1}{3}}WO_4$







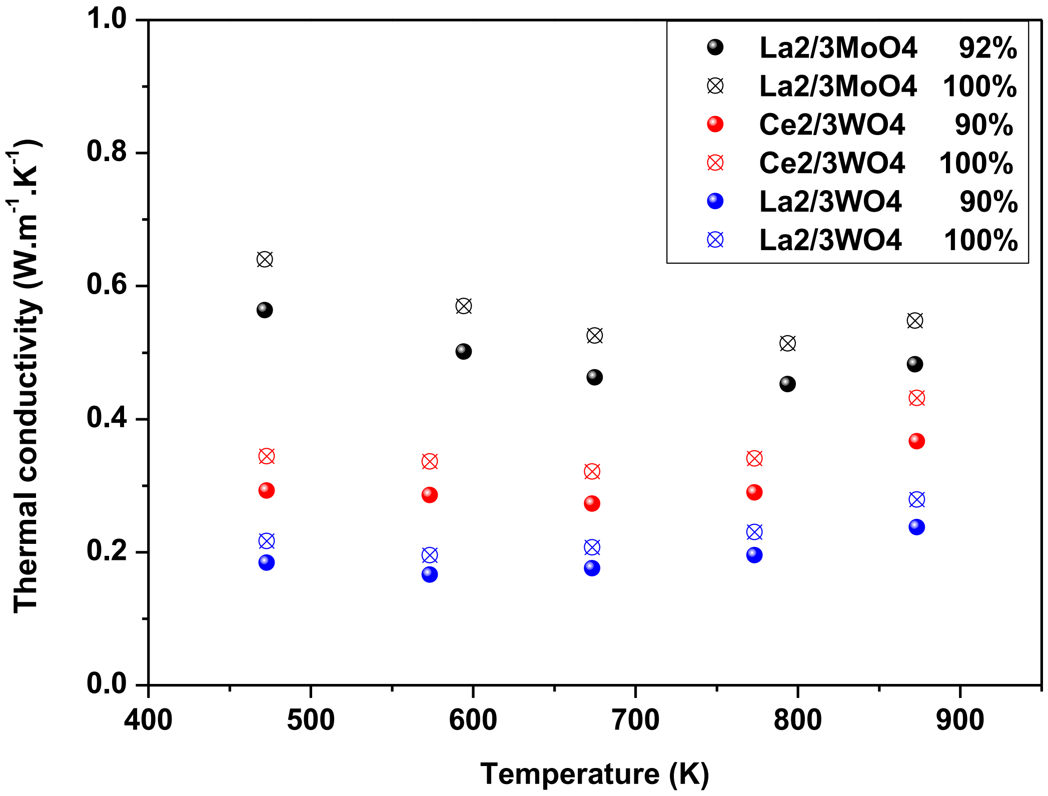


- Pure scheelite-phase for $La_{2/3}MoO_4$, $Ce_{2/3}WO_4$ and $La_{2/3}WO_4$

- $La_{2/3}MoO_4$, relative density = 92 %
  $Ce_{2/3}WO_4$, relative density = 90 %
  $La_{2/3}WO_4$, relative density = 90 %

Thermal conductivity of A-deficient scheelite ceramics

$La_{\frac{2}{3}}\square_{\frac{1}{3}}MoO_4$, $Ce_{\frac{2}{3}}\square_{\frac{1}{3}}WO_4$ and $La_{\frac{2}{3}}\square_{\frac{1}{3}}WO_4$



- **0.6-0.5** W.m^{-1}.K-1 for 100 % dense $La_{2/3}MoO_4$
  ~**0.3** W.m^{-1}.K^{-1} at **675 K** for 100% $Ce_{2/3}WO_4$
  ~**0.2** W.m^{-1}.K^{-1} at **675 K** for 100 % dense $La_{2/3}WO_4$

Lowest thermal conductivity value : **$La_{2/3}WO_4$**

Can A-site vacancies in scheelites reduce thermal conductivity even more?

Presence of 33% of vacancies in scheelite structure decreases the thermal conductivity

(lower than 1 $W.m^{-1}.K^{-1}$)

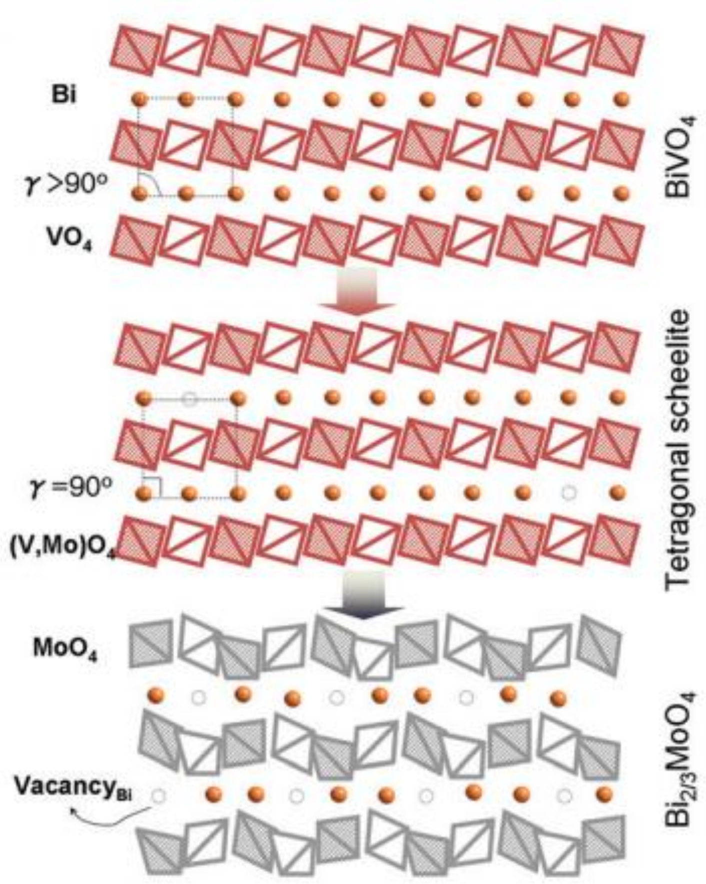
What is the minimum vacancy content in scheelites to reduce thermal conductivity?

$$xBi_{2/3}\square_{1/3}MoO_4 - (1-x)BiVO_4$$

$$xBi_{\frac{2}{3}}\square_{\frac{1}{3}}Mo_xO_4 - (1-x)BiVO_4$$

Vacancy

$BiVO_4$ ⟷ $Bi_{2/3}\square_{1/3}MoO_4$



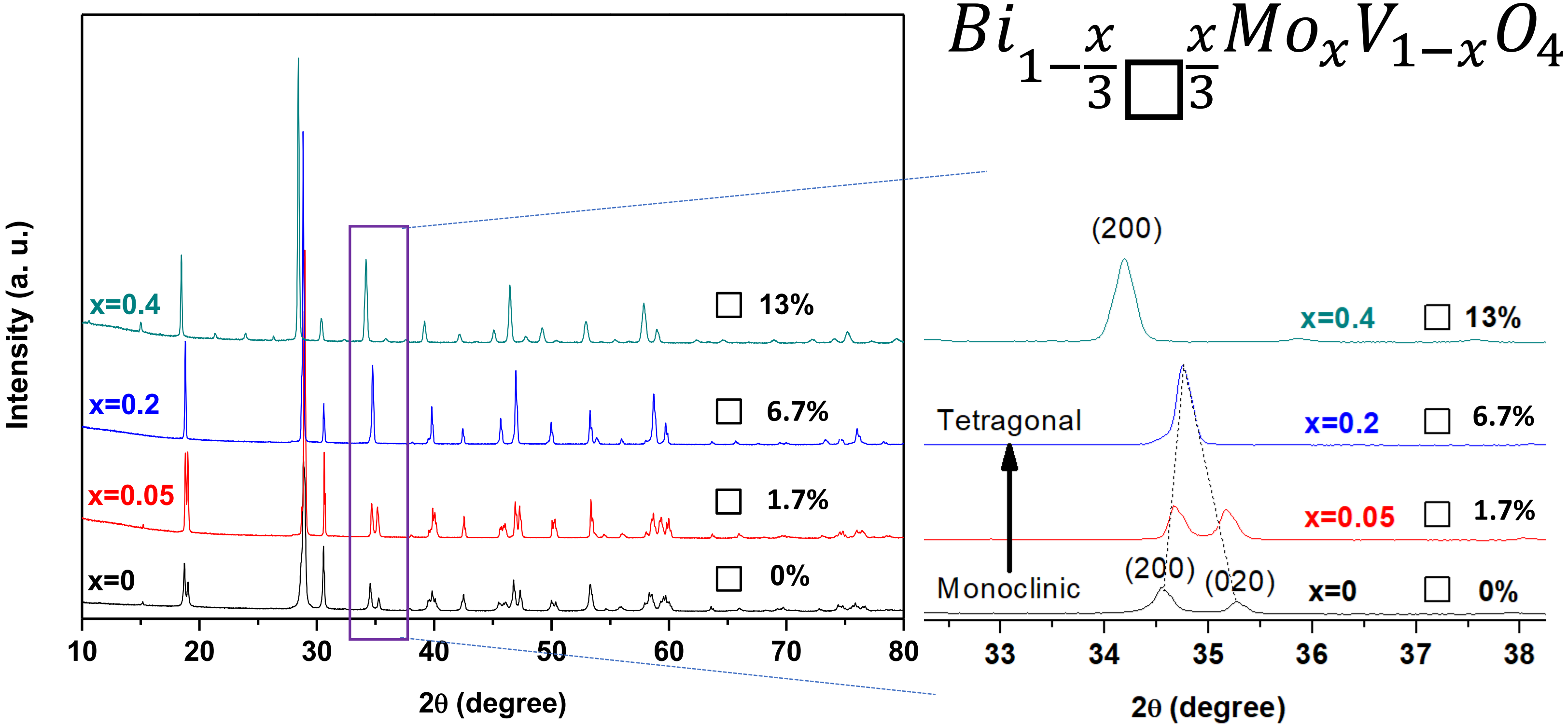
$$Bi_{1-\frac{x}{3}}\square_{\frac{x}{3}}Mo_xV_{1-x}O_4$$

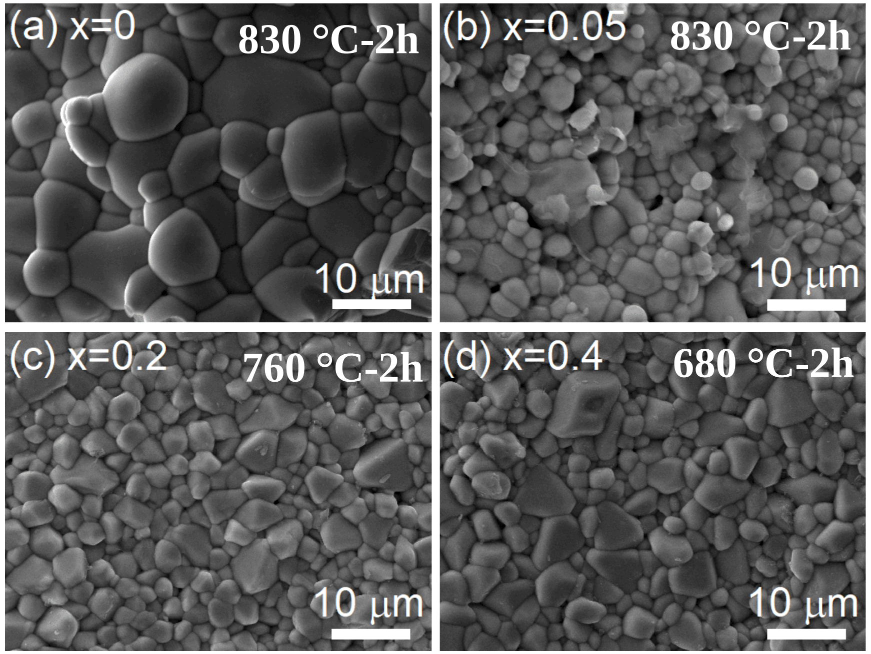
D. Zhou et al. (2014) Dalton Trans. 43, 7290

Structural and microstructural study of A-deficient scheelites

$$xBi_{\frac{2}{3}}\square_{\frac{1}{3}}Mo_xO_4 - (1-x)BiVO_4$$

$$Bi_{1-\frac{x}{3}}\square_{\frac{x}{3}}Mo_xV_{1-x}O_4$$





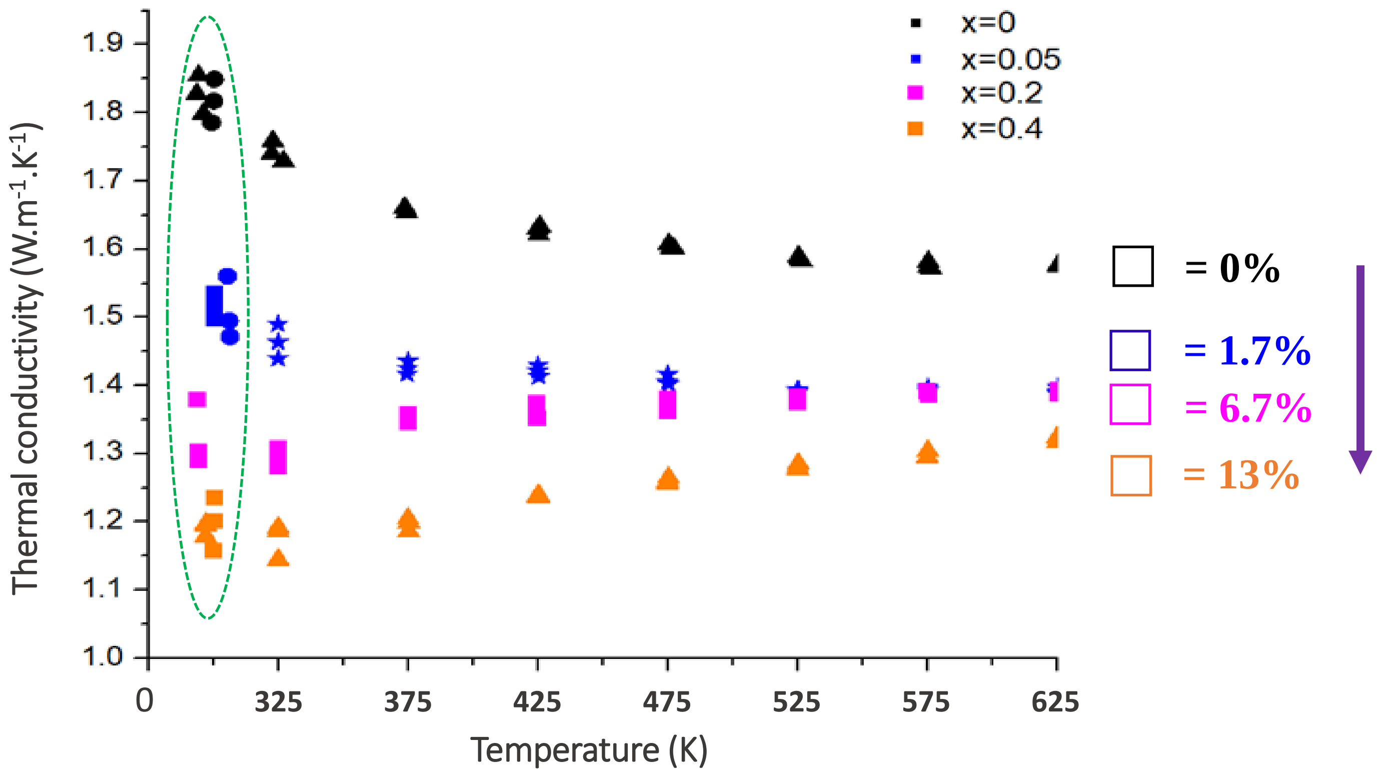
Pure scheelite-phase for $xBi_{2/3}MoO_4$-(1-x)$BiVO_4$ where x= 0, 0.05, 0.2 and 0.4

The monoclinic scheelite structure changes to a tetragonal structure at x=0.2

x=0, relative density = 96 %
x=0.05, relative density = 97 %
x=0.2, relative density = 91 %
x=0.4, relative density = 92 %

Thermal conductivity study of A-deficient scheelite ceramics

$$\mathbf{xBi_{\frac{2}{3}}\square_{\frac{1}{3}}Mo_xO_4-(1-x)BiVO_4} \quad (Bi_{1-\frac{x}{3}}\square_{\frac{x}{3}}Mo_xV_{1-x}O_4)$$



➡ The thermal conductivity decreases with vacancies content from **1.8** W.m^{-1}.k^{-1} for □ = **0%** to **1.5**, **1.3** and **1.2** W.m^{-1}.k^{-1} for □=**1.7%**, **6.7%** and **13%**, respectively at 300 K

What is the minimum vacancy number in scheelites to reduce thermal conductivity?

Thermal conductivity in A-site deficiency scheelite structure can be decreased by

20% for 1.7% of vacancies

Conclusions

- Pure scheelite ceramics were obtained by conventional sintering method

- Scheelite materials show a low thermal conductivity: $BaMoO_4$ & $BaWO_4$

- A-site vacancies in scheelites decrease thermal conductivity (< 1 $W.m^{-1}.K^{-1}$)

⬇

$La_{2/3}WO_4$ scheelite exhibits an ultra-low thermal conductity value (0.2 $W.m^{-1}.K^{-1}$)

- 1.7 % of A-site vacancies can reduce by up to 20% the thermal conductivity in solid solution scheelite

THANK YOU FOR YOUR ATTENTION !