Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for:

Optimum in the thermoelectric efficiency of nanostructured Nb-doped TiO_2 ceramics: from polarons to Nb-Nb dimers

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Supporting Information Available

Determination of the amount of dimer.

When the niobium content in the material is lower than the limiting concentration before the appearance of the dimers ($x \leq c_{Nb}^{L}$), a linear relationship is observed between the lattice parameters of the crystalline structure and the concentrations of its constituent elements (Vegard's Law). The evolution of the lattice parameter c can be described according to equation 1.

$$c = xc_{Nb2O5} + (1 - x)c_{TiO2} \qquad (1)$$

In this case, x represents the concentration in Nb, $c_{Nb_2O_5}$ the lattice parameter c of Nb_2O_5 assuming that it crystallizes in the space group $P4_2/mnm$ (this parameter is determined by a simple linear refinement and is equal to 0.313 nm) and c_{TiO_2} the lattice parameter c of TiO_2 (0.2959 nm) in the space group $P4_2/mnm$ (rutile).

When the Nb concentration exceeds the c_{Nb}^{L} limit but does not exceed the Nb solubility limit in the rutile lattice (7.5 mol% of Nb), we observe a deviation from Vegard's Law. To take into account the influence of the Nb-Nb dimers, we describe the evolution of the parameter c by the following law (equation 2).

$$c = x[2\alpha c_{Nb-Nb} + (1 - 2\alpha)c_{Nb2O5}] + (1 - x)c_{TiO2} \qquad (2)$$

In this case, x represents the concentration in Nb, α the dimer fraction, $c_{Nb_2O_5}$ the lattice parameter c of Nb_2O_5 assuming that it crystallizes in the space group $P4_2/mnm$, c_{TiO_2} the lattice parameter c of TiO_2 (0.2959 nm) in the space group $P4_2/mnm$ (rutile) and c_{Nb-Nb} the lattice parameter c of the material during the formation of dimers (0.280 nm[S1]).

Copy of the pcr file that was used for the Rietveld refinement.

```
COMM AVC-B-076-03
! Current global Chi2 (Bragg contrib.) =      2.954
! Files => DAT-file: AVC-B-076-03.dat,  PCR-file: AVC-B-076-03
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
   0   7   1   0   1   0   0   0   0   0   0   1   0   0   0   0   0   0   1
!
!  Resolution file for Pattern#   1
/Users/averchere/ownCloud/Othello/FullProf/AVC-B-076-03/LaB6_D8-t3_Soller2,5.irf
!Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 NLI Prf Ins Rpa Sym Hkl Fou Sho Ana
   0   0   1   0   1   0   4   0   0  -3  10  -1   0   1   0   0   0
!
! Lambda1  Lambda2    Ratio    Bkpos    Wdt    Cthm     muR   AsyLim   Rpolarz  2nd-muR -
> Patt# 1
 1.540560 1.544390  0.50000   42.000 20.0000  1.0000  0.0000   60.00    0.0000  0.0000
!
!NCY  Eps  R_at  R_an  R_pr  R_gl     Thmin       Step       Thmax    PSD    Sent0
 60  0.10  1.00  1.00  1.00  1.00      4.1229   0.020475    80.0052   0.000   0.000
!
! Excluded regions (LowT  HighT) for Pattern#  1
        0.00       20.00
!
!
      12    !Number of refined parameters
!
!  Zero    Code    SyCos    Code   SySin    Code  Lambda     Code MORE ->Patt# 1
  0.00000    0.0  0.01032   61.0  0.00000    0.0 0.000000    0.00   0
!   Background coefficients/codes  for Pattern#  1  (Polynomial of 6th degree)
      76.366     -65.933      89.968     -57.978       0.000       0.000
       21.00       51.00       81.00       71.00        0.00        0.00
!------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:     5.50
!------------------------------------------------------------------------------
Rutile
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ    Nvk Npr More
   2   0   0 0.0 0.0 1.0   0   0   0   0   0        255.676   0   7   0
!
!
P 42/m n m               <--Space group symbol
!Atom   Typ       X         Y         Z      Biso       Occ     In Fin N_t Spc /Codes
Ti     TI      0.00000  0.00000  0.00000  0.31359   0.15549   0   0   0    0
                  0.00     0.00     0.00     0.00    111.00
O      O       0.30524  0.30524  0.00000  0.64888   0.33772   0   0   0    0
                 91.00    91.00     0.00     0.00    121.00
!-------> Profile Parameters for Pattern #  1
!  Scale        Shape1      Bov       Str1      Str2      Str3   Strain-Model
 0.71755E-02   0.00000   0.00000   0.00000   0.00000   0.00000       0
    11.00000     0.000     0.000     0.000     0.000     0.000
!       U         V          W          X          Y        GauSiz   LorSiz Size-Model
   0.004503   0.000000   0.000000   0.000000   0.105902   0.001131   0.000000    0
      0.000      0.000      0.000      0.000    101.000      0.000      0.000
!     a          b         c        alpha      beta       gamma      #Cell Info
   4.594127   4.594127   2.961263  90.000000  90.000000  90.000000
   31.00000   31.00000   41.00000    0.00000    0.00000    0.00000
!  Pref1    Pref2      Asy1      Asy2      Asy3      Asy4       S_L       D_L
  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.04286  0.00000
     0.00     0.00     0.00     0.00     0.00     0.00     0.00     0.00
!  2Th1/TOF1    2Th2/TOF2  Pattern to plot
      20.000      80.005       1
```

Copy of the irf file that was used for the Rietveld refinement.

```
! LaB6_D8-t3_soller_2.5
!    U         V          W          X          Y        Z
 0.001971  -0.001543   0.000864   0.007410   0.022966     0.0
 0.001971  -0.001543   0.000864   0.007410   0.022966     0.0
```

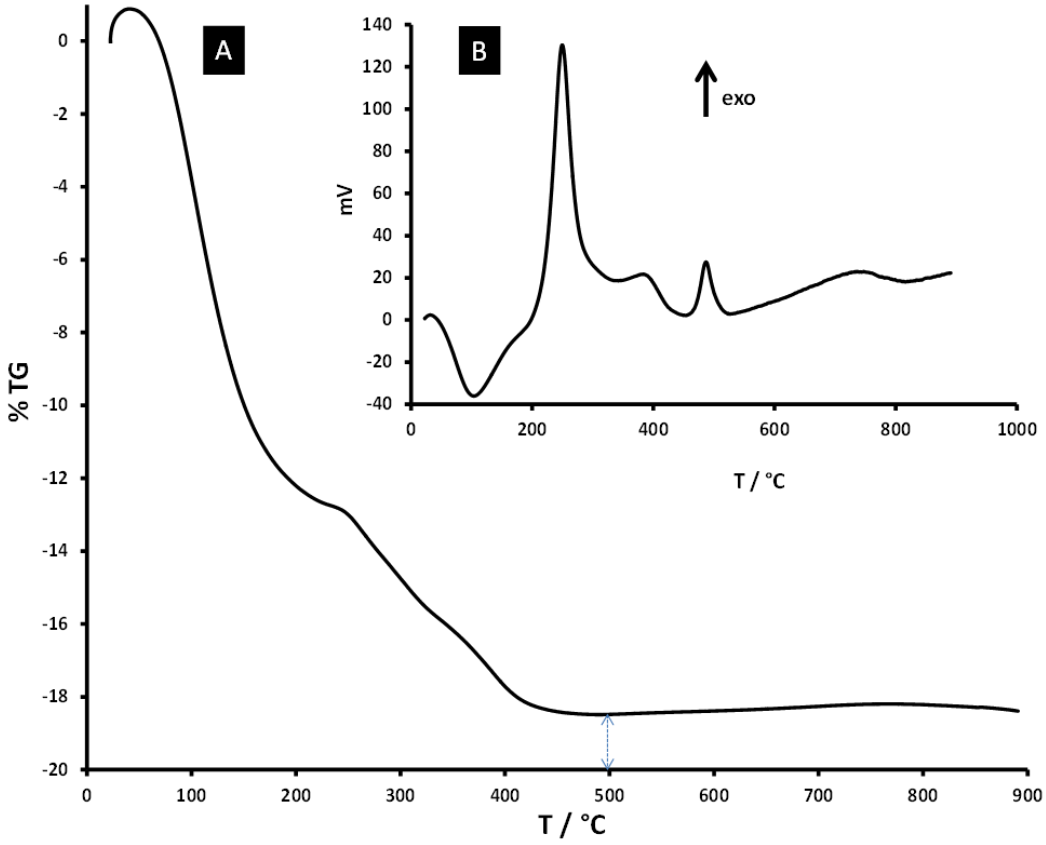

Fig. S1 (A) TGA and (B) TDA curves of the TiO_2:Nb obtained from $Ti(OEt)_4$ + x $[Nb(OEt)_5]_2$.

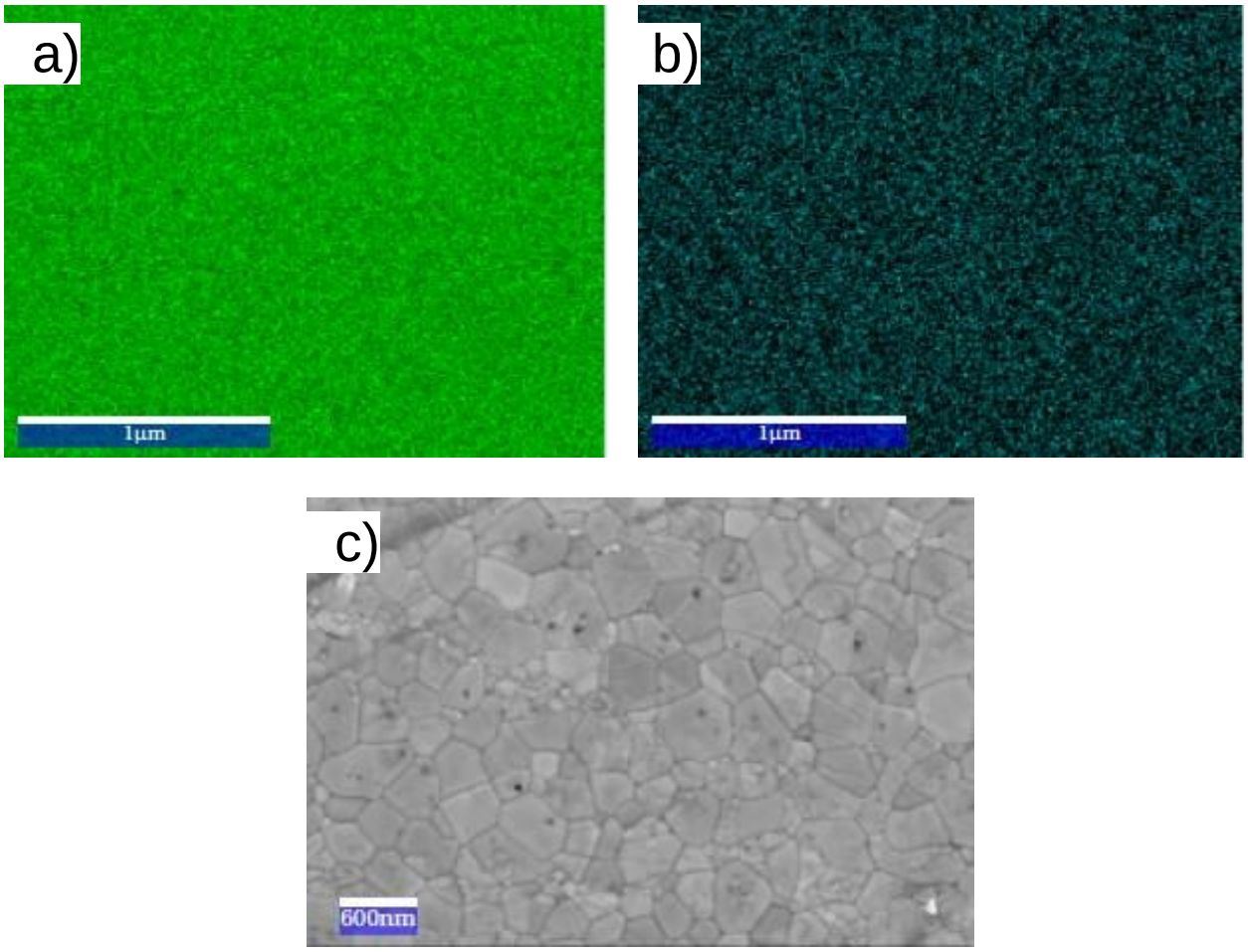

Fig. S2 SEM images and elemental mapping of a TiO_2 pellet doped with 2 mol% of niobium after sintering at 1233 K. The mapping of elements Ti-K (panel **a)**) and Nb-L (panel **b)**) shows that niobium is uniformly distributed in the TiO_2 lattice and creates a solid solution. SEM image of the mapping area of the sintered pellet at 1233 K (panel **c)**).

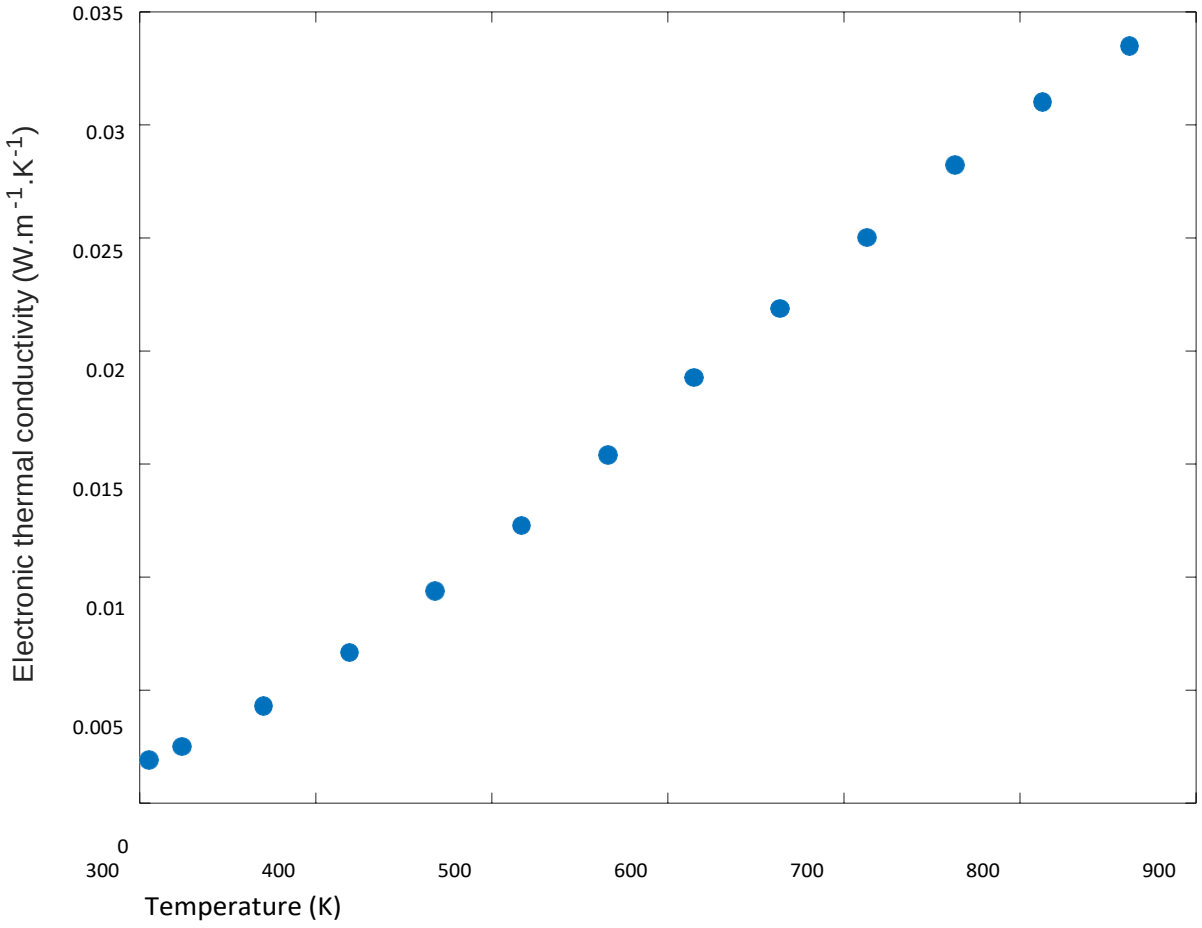

Fig. S3 Electronic thermal conductivities of the $Ti_{0.972}Nb_{0.028}O_2$ pellet sintered at 1123 K according to the Wiedemann-Franz law. The electronic thermal conductivity of our materials constitutes about 2% of total thermal conductivities (• : $Ti_{0.972}Nb_{0.028}O_2$).

References

(S1) K. Sakata, *J. Phys. Soc. Jpn.*, 1969, **26**, 1067–1067.