# SUPPLIMENTARY INFORMATION FOR

## Highly Enhanced Thermal Stability of $Zn_4Sb_3$ Nanocomposites

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### Experimental

### Synthesis.

$Zn_4Sb_3$ samples with ZnO (0.5 and 1 wt %) or $TiO_2$ (0.5 and 1 wt %) nano-inclusions were synthesized. The oxide nano-particles were synthesized in a custom continuous flow supercritical reactor.[1-2] Based on the reports, the resulting particle sizes are 20 ~ 80 nm for ZnO[3] and ~ 9 nm for $TiO_2$ (anatase),[2] and the crystallinities are above 90% and 85%, respectively. For $Zn_4Sb_3$, the elements (99.99% zinc shots, 99.5% antimony powder) were weighed in stoichiometric ratios. Then, the oxide nano-particle powders were added and mixed in plastic vessels under rotation for 1 h. The mixtures were evacuated and sealed in quartz ampoules. After sealing, the ampoules were placed horizontally in a tube furnace, and heated with a 400 K/h ramp to 973 K under continuous rotation. The

samples were held at this temperature for 2 h before quenching in ice water. This resulted in polycrystalline solids, which were ground in an agate mortar to obtain homogeneous powders. To ensure that the samples were single-phase, PXRD data were recorded using CuKα radiation in a 2θ-range of 8-84º with a Stoe STADI P diffractometer.

A homogeneous grain size is important for measuring high quality PXRD data. The present samples were sieved, and only the crystallites smaller than 45 μm were used. The powders were then floated with ethanol in a Petri dish, and left for sedimentation. After one minute, the top layer of the ethanol was removed into a new Petri dish, and left for further sedimentation for three minutes. The top layer was again removed into a new Petri dish and the ethanol was evaporated, leaving a sample fraction of homogeneous grain size. The samples were transferred to 0.2 mm capillaries, and held in an ultra sound bath for about five minutes to obtain a dense packing of the powders.

**Synchrotron PXRD.**

Multi-temperature synchrotron PXRD data were recorded from room temperature to 625 K, using the large Debye-Scherrer camera at beam line BL44B2, SPring8, Japan. The wavelength $\lambda$ = 0.500105(1) Å was determined from Rietveld refinements on a $CeO_2$ standard. Data sets were recorded at 300, 450, 500, 510, 515, 520, 525, 530, 535, 540, and 625 K. Furthermore, three heating cycles (300 K→625 K→300 K→625 K→300 K→625 K→300 K) were performed to investigate the stability in a realistic thermal environment, i.e. heating and cooling of a thermoelectric device. All data sets were Rietveld refined with the program FULLPROF[4] using a pseudo Voigt profile function, and a background modelled with linear interpolation between approximately 60 points.

The structural model of Snyder *et al*. with three interstitial sites[5] was used as starting model for the refinements. Data outside the range $4° < 2\theta < 50°$ were excluded because of a very low signal-background ratio.

**Physical Properties Measurement**

Physical properties were measured on pellets compacted by Spark Plasma Sintering (SPS). A heating ramp of ~125 K/min up to 673 K with five minutes holding period was applied to the samples. Samples were compacted in a graphite die with a diameter of 12.7 mm under a pressure of 100 MPa. Hall coefficient was measured with a 2 T field using the van der Pauw method. Scanning electron microscopy was performed on a FEI NOVA (nano 600) Scanning Electron Microscopy (SEM). High temperature electrical transport properties were measured on a ZEM-3 ULVAC. The high temperature thermal conductivity was measured on a Netszch LFA 457 and obtained as the product of the thermal diffusivity $D_T$, the density and the specific heat capacity $C_p$. The sample densities were measured using the Archimedes technique. The lattice contribution to the thermal conductivity can be obtained by subtracting the electronic component from the total thermal conductivity ($\kappa_L = \kappa - \kappa_e$), where $\kappa_e$ is estimated via the Wiedemann-Franz relationship $\kappa_e = LT/\rho$. With the assumption of transport dominated by acoustic scattering and a single parabolic band, $L$ can be calculated using reduced Fermi energies obtained from experimental Seebeck coefficients.[6]

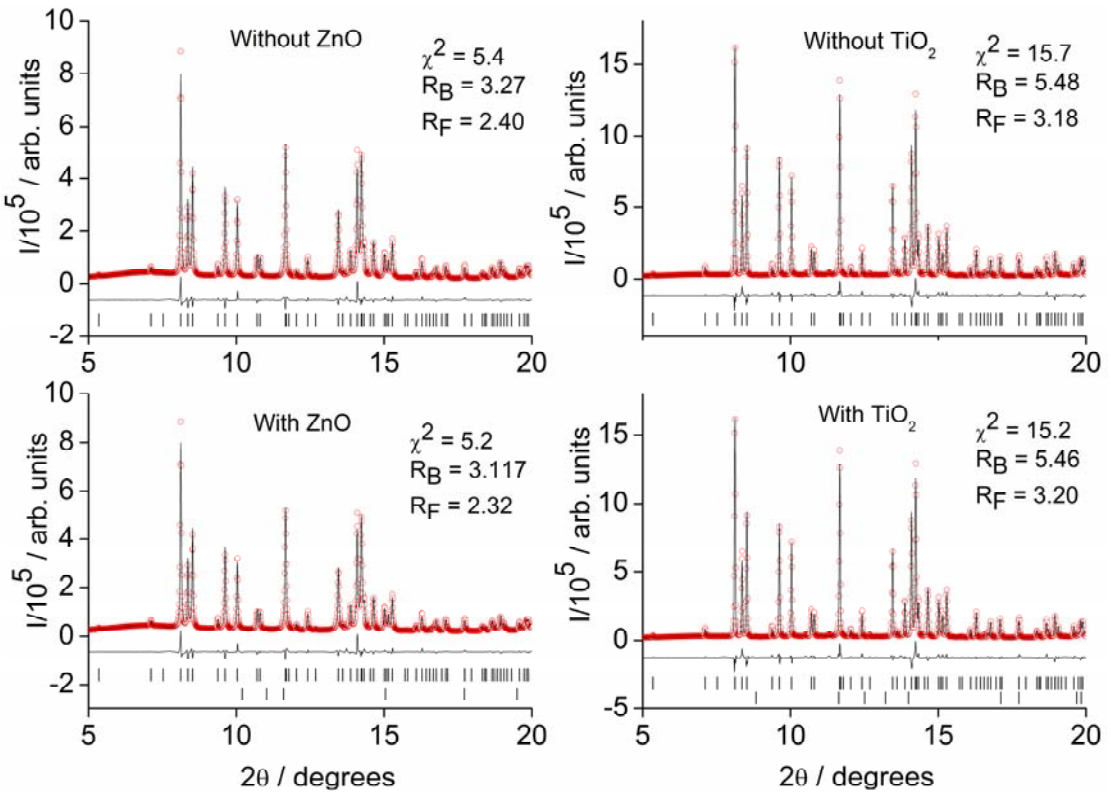


**Figure S1.** Refinement of starting material $Zn_4Sb_3$ at 300 K without (upper) and with (lower) nano-composite phase for 1 % ZnO and 1 % $TiO_2$ samples, respectively.

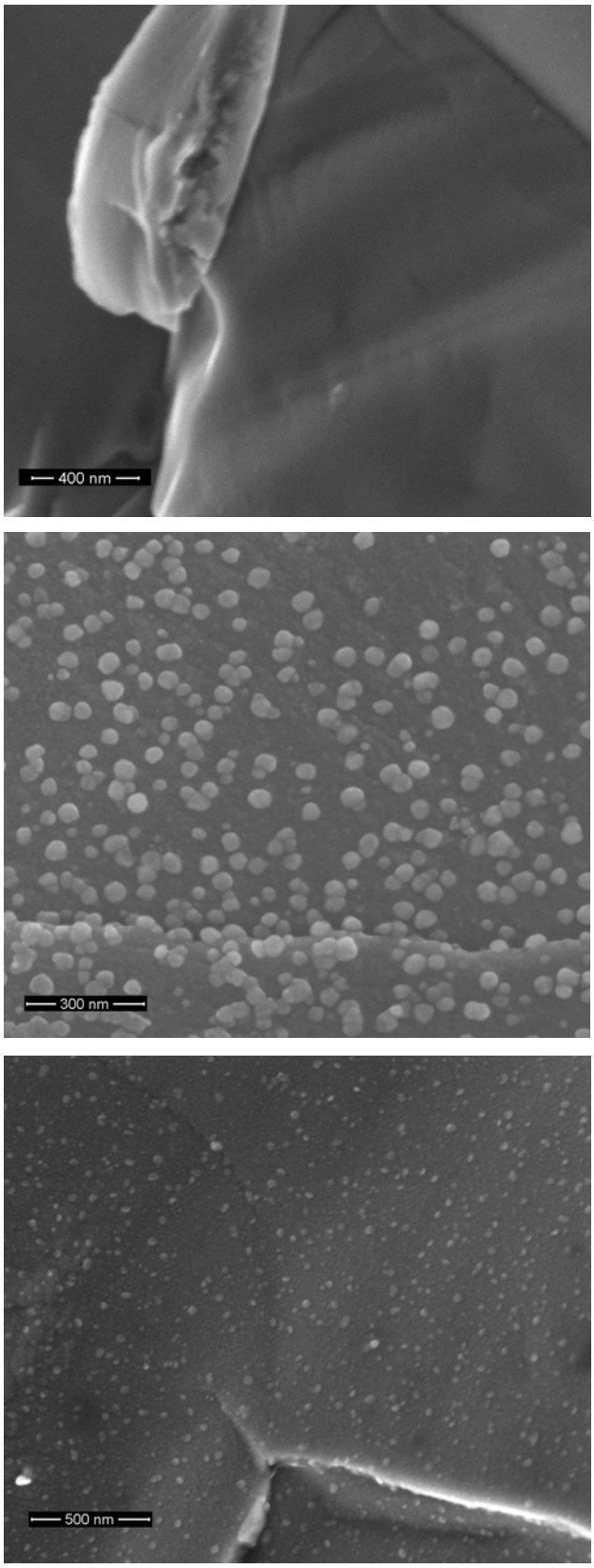


**Figure S2.** SEM images of SPS pressed pellets of pure $Zn_4Sb_3$ (top), 1 wt % ZnO (middle) and 1 wt % $TiO_2$ (bottom).

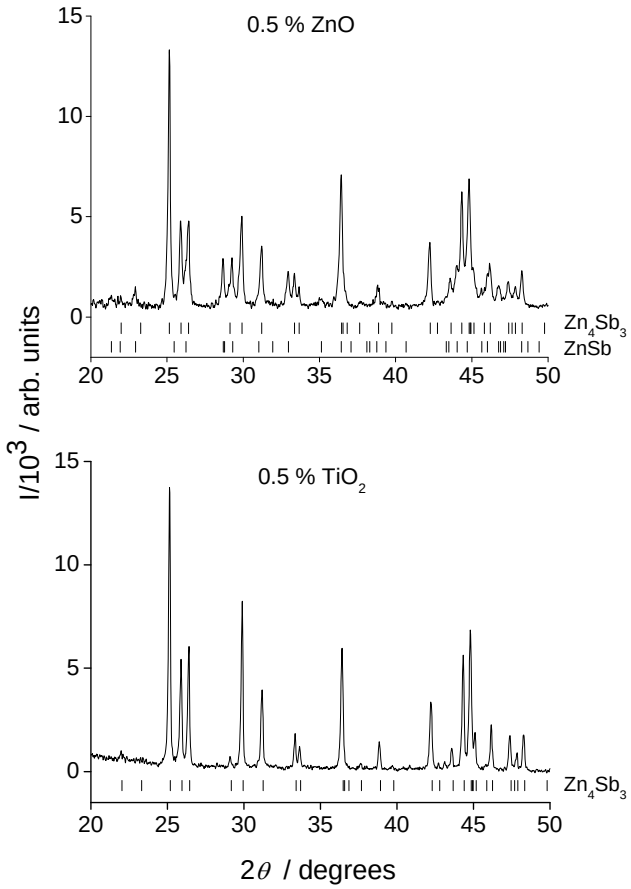


**Figure S3.** Powder X-ray diffraction patterns of 0.5 wt % ZnO sample (upper) and 0.5 wt % TiO2 sample (lower) after heating to 573 K during the electrical properties measurement.

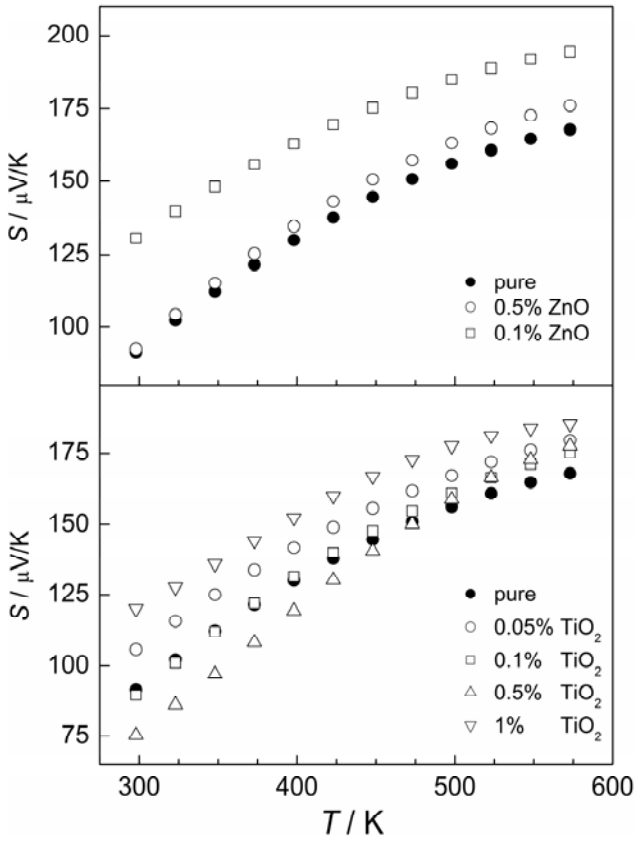


**Figure S4.** Temperature dependence of Seebeck coefficient of pure $Zn_4Sb_3$ and nano-composites.

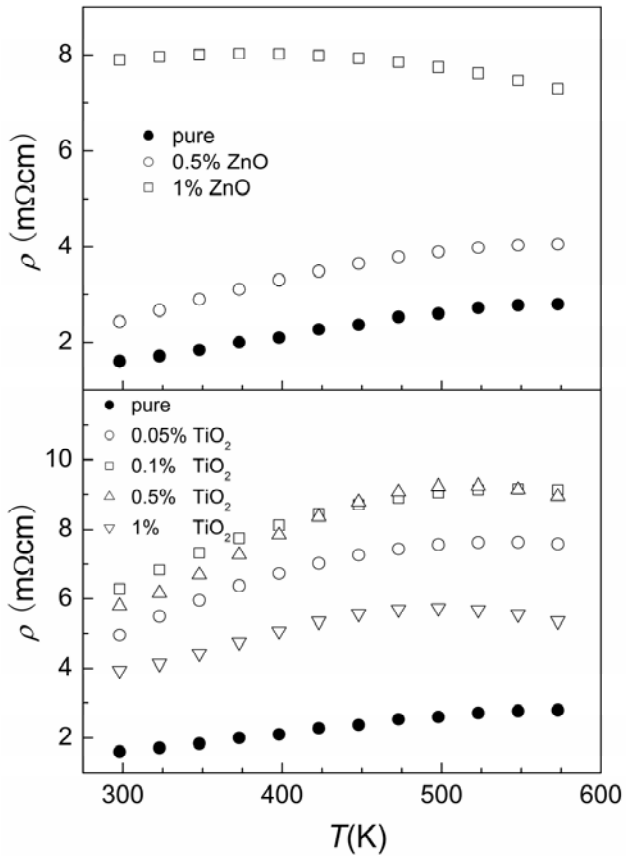


**Figure S5.** Electrical resistivity changes as a function of temperature.

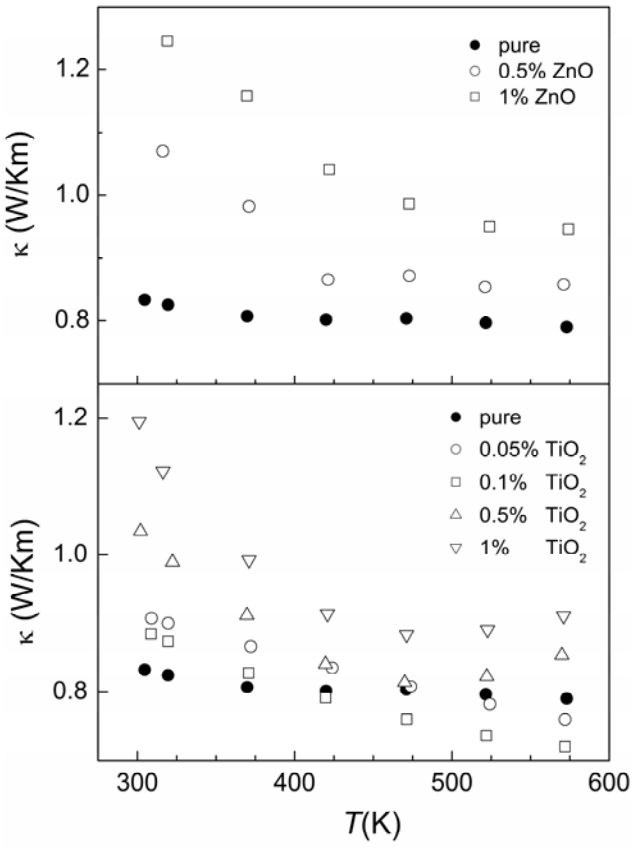


**Figure S6.** Thermal conductivity as a function of temperature.

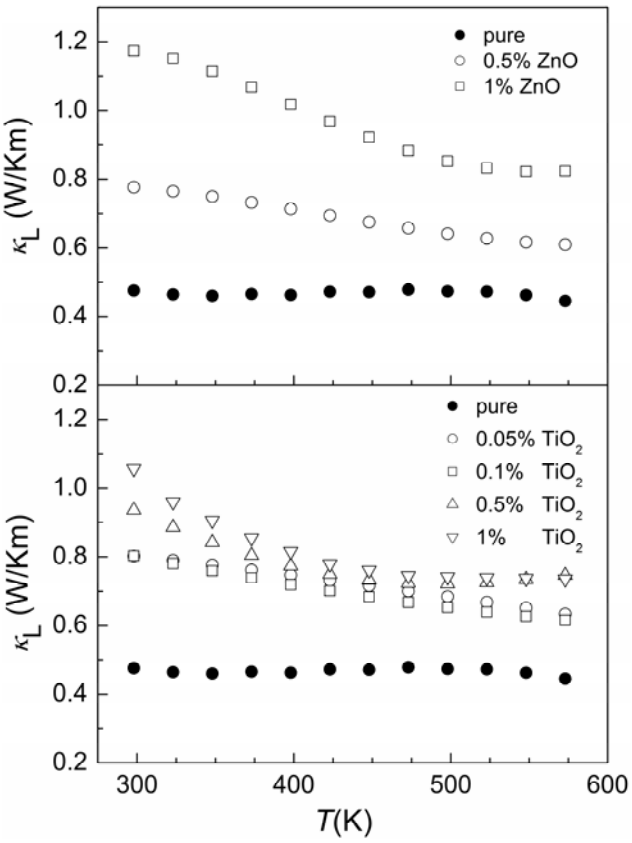


**Figure S7.** The lattice thermal conductivity as a function of temperature.

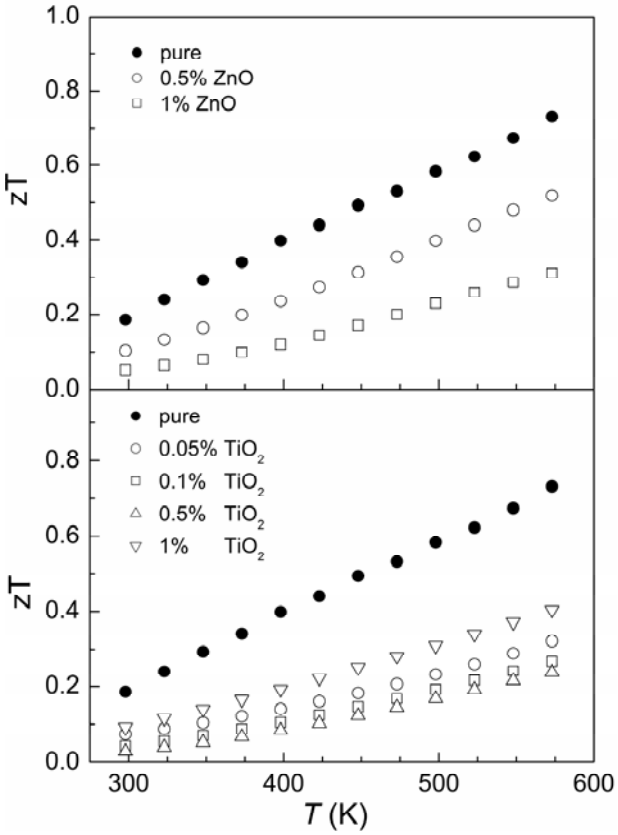


**Figure S8.** Thermoelectric figure of merit zT as a function of temperature for the nano-composites.

**Table ST1.** Crystallographic details and refinement residuals for the nanocomposite samples. "Start" refers to refinements of the data sets recorded before heating, and "after" refers to refinements of the data sets recorded at 300 K after three heating cycles.

| (**a**) | 0.5%ZnO-start | 0.5%ZnO-after | 1%ZnO-start | 1%ZnO-after |
|---|---|---|---|---|
| $T$ (K) | 300 | 300 | 300 | 300 |
| $t_{exp}$ (min) | 5 | 5 | 5 | 5 |
| No. of points | 7797 | 7805 | 7797 | 7805 |
| No. of reflns | 3506 | 7269 | 3152 | 7143 |
| No. of params | 89 | 100 | 90 | 101 |
| $R_F$ (%) | 1.45 | 2.07 | 2.32 | 2.00 |
| $R_{Bragg}$ (%) | 1.41 | 1.96 | 3.11 | 3.02 |
| $R_p$ (%) | 5.65 | 6.07 | 7.64 | 7.03 |
| $R_{wp}$ (%) | 6.20 | 3.88 | 8.39 | 7.97 |
| $\chi^2$ | 2.70 | 4.70 | 5.18 | 6.56 |
| $a = b$ (Å) | 12.2318(1) | 12.2400(1) | 12.2332(1) | 12.2398(1) |
| $c$ (Å) | 12.4211(1) | 12.4333(1) | 12.4275(1) | 12.4356(1) |
| $X$ | 0.298(2) | 0.106(3) | 0.227(4) | 0.0733(5) |
| $Y$ | 0.0187(1) | 0.007(5) | 0.0164(4) | 0.0082(5) |
| $B_{iso}$ Sb1 | 1.00(2) | 0.87(3) | 1.17(3) | 0.98(3) |
| $B_{iso}$ Sb2 | 0.83(2) | 0.77(3) | 0.88(3) | 0.89(3) |
| $B_{iso}$ Zn | 1.71(5) | 1.75(5) | 1.31(5) | 1.69(5) |
| Occ Zn1 | 0.912(3) | 0.934(4) | 0.923(3) | 0.905(4) |
| Occ Zn2 | 0.047(2) | 0.043(3) | 0.054(2) | 0.048(2) |
| Occ Zn3 | 0.047(2) | 0.030(2) | 0.031(2) | 0.049(2) |
| Occ Zn4 | 0.045(2) | 0.037(2) | 0.034(2) | 0.058(2) |
| $V$ (Å$^3$) | 1609.44(2) | 1613.18(1) | 1610.61(2) | 1613.43(1) |
| Wt% ZnSb | 0 | 28.97(13) | 0 | 27.37(35) |
| Wt% ZnO | 2.62(13) | 6.34(19) | 0.95(12) | 3.22(22) |
| Wt% Sb | 0 | 2.59(5) | 0 | 0.12(1) |

| (**b**) | 0.5%$TiO_2$-start | 0.5%$TiO_2$-after | 1%$TiO_2$-start | 1%$TiO_2$-after |
|---|---|---|---|---|
| $T$ (K) | 300 | 300 | 300 | 300 |
| $t_{exp}$ (min) | 5 | 5 | 5 | 5 |
| No. of points | 7795 | 7804 | 7795 | 7806 |
| No. of reflns | 3428 | 7132 | 3425 | 7166 |
| No. of params | 93 | 95 | 95 | 102 |
| $R_F$ (%) | 4.56 | 5.56 | 3.20 | 3.61 |
| $R_{Bragg}$ (%) | 6.69 | 6.82 | 5.46 | 5.92 |
| $R_p$ (%) | 11.0 | 13.9 | 8.83 | 9.91 |
| $R_{wp}$ (%) | 13.2 | 14.4 | 9.91 | 11.3 |
| $\chi^2$ | 12.52 | 18.75 | 15.23 | 22.89 |
| $a = b$ (Å) | 12.2286(1) | 12.2327(1) | 12.2285(1) | 12.2325(1) |
| $c$ (Å) | 12.4208(1) | 12.4272(1) | 12.4240(1) | 12.4280(1) |
| $X$ | 0.078(7) | 0.036(5) | 0.078(5) | 0.033(5) |
| $Y$ | 0.008(1) | 0.008(1) | 0.009(1) | 0.009(5) |
| $B_{iso}$ Sb1 | 1.00(3) | 0.89(3) | 0.88(3) | 0.83(3) |
| $B_{iso}$ Sb2 | 0.80(3) | 0.80(4) | 0.83(3) | 0.82(3) |
| $B_{iso}$ Zn | 1.91(7) | 1.95(6) | 1.66(5) | 1.59(5) |
| Occ Zn1 | 0.897(4) | 0.909(5) | 0.932(3) | 0.926(4) |
| Occ Zn2 | 0.055(3) | 0.033(3) | 0.080(2) | 0.071(3) |
| Occ Zn3 | 0.094(3) | 0.097(3) | 0.035(2) | 0.035(3) |
| Occ Zn4 | 0.078(3) | 0.075(3) | 0.044(2) | 0.030(2) |
| $V$ (Å$^3$) | 1608.54(5) | 1610.45(11) | 1608.94(32) | 1610.50(11) |
| Wt% ZnSb | 0 | 0 | 0 | 2.5(11) |
| Wt% Sb | 0 | 0.21(4) | 0 | 1.44(21) |
| Wt% $TiO_2$ | 0.75(14) | 1.27(31) | 1.27(19) | 0.08(3) |

**Table ST2**. Carrier concentration and Hall mobility of the all samples.

| Sample | pure | ZnO | | $TiO_2$ | |
|---|---|---|---|---|---|
| | | 0.5% | 1% | 0.5% | 1% |
| $n$ ($10^{19}$ $cm^{-3}$) | 5.2 | 3.1 | 1.0 | 4.42 | 6.03 |
| $\mu$ ($cm^2$ $V^{-1}$ $s^{-1}$) | 30.4 | 72 | 134 | 112 | 31.3 |

**Table ST3:** Selected crystallographic details and weight fractions of impurity phases from high temperature Rietveld refinement of the 0.5 wt % ZnO composite

| T(K) | 300 | 450 | 500 | 510 | 515 | 520 |
|---|---|---|---|---|---|---|
| $t_{exp}$ (min) | 5 | 5 | 5 | 5 | 5 | 5 |
| # points | 7797 | 7797 | 7797 | 7797 | 7797 | 7797 |
| # refl | 3506 | 3504 | 3183 | 3176 | 3161 | 3156 |
| # par | 89 | 89 | 98 | 98 | 98 | 98 |
| $R_F$ (%) | 1.45 | 1.60 | 1.75 | 1.87 | 2.01 | 1.97 |
| $R_{Bragg}$ (%) | 1.41 | 1.41 | 1.50 | 1.57 | 1.66 | 1.65 |
| $R_p$ (%) | 5.65 | 5.63 | 5.16 | 5.40 | 5.46 | 5.52 |
| $R_{wp}$ (%) | 6.20 | 6.12 | 5.52 | 5.82 | 5.85 | 5.97 |
| $\chi^2$ | 2.70 | 2.37 | 1.96 | 2.23 | 2.252 | 2.35 |
| $a = b$ (Å) | 12.2318(1) | 12.2618(1) | 12.2724(1) | 12.2754(1) | 12.2769(1) | 12.2782(1) |
| $c$ (Å) | 12.4211(1) | 12.4538(1) | 12.4662(1) | 12.4696(1) | 12.4714(1) | 12.4729(1) |
| X | 0.298(2) | 0.289(3) | 0.243(3) | 0.215(2) | 0.196(2) | 0.187(2) |
| Y | 0.0187(1) | 0.0124(1) | 0.007(1) | 0.006(1) | 0.006(1) | 0.006(1) |
| Biso Sb1 | 1.00(2) | 1.37(2) | 1.51(2) | 1.52(2) | 1.57(2) | 1.59(2) |
| Biso Sb2 | 0.83(2) | 1.18(2) | 1.29(2) | 1.32(2) | 1.36(2) | 1.38(2) |
| Biso Zn | 1.71(5) | 2.72(5) | 3.08(5) | 3.19(5) | 3.24(5) | 3.31(5) |
| Occ. Zn1 | 0.912(3) | 0.932(3) | 0.935(3) | 0.938(3) | 0.934(3) | 0.937(3) |
| Occ. Zn2 | 0.047(2) | 0.053(2) | 0.055(2) | 0.056(2) | 0.059(2) | 0.059(2) |
| Occ. Zn3 | 0.047(2) | 0.034(2) | 0.032(2) | 0.030(2) | 0.029(2) | 0.030(2) |
| Occ. Zn4 | 0.045(2) | 0.042(2) | 0.044(1) | 0.045(1) | 0.047(1) | 0.049(2) |
| $V$ (Å$^3$) | 1609.44(2) | 1621.59(2) | 1626.02(1) | 1627.25(1) | 1627.87(1) | 1628.44(1) |
| Wt% ZnSb | 0 | 0 | 5.55(8) | 7.25(8) | 7.99(8) | 8.44(8) |
| Wt% ZnO | 2.62(13) | 3.31(14) | 3.22(12) | 3.23(12) | 3.27(12) | 3.31(12) |
| Wt% Sb | 0 | 0 | 1.75(5) | 2.40(5) | 2.71(4) | 2.87(4) |

**Table ST3 continued:** Selected crystallographic details and weight fractions of impurity phases from high temperature Rietveld refinement of the 0.5 wt % ZnO composite

| T(K) | 525 | 530 | 535 | 540 | 625 |
|---|---|---|---|---|---|
| $t_{exp}$ (min) | 5 | 5 | 5 | 5 | 5 |
| # points | 7799 | 7799 | 7800 | 7800 | 7801 |
| # refl | 3152 | 3152 | 3152 | 3152 | 3143 |
| # par | 98 | 98 | 98 | 98 | 98 |
| $R_F$ (%) | 1.95 | 2.02 | 2.07 | 2.03 | 2.78 |
| $R_{Bragg}$ (%) | 1.68 | 1.66 | 1.70 | 1.73 | 2.06 |
| $R_p$ (%) | 5.79 | 5.90 | 5.99 | 6.03 | 6.56 |
| $R_{wp}$ (%) | 6.22 | 6.40 | 6.49 | 6.47 | 6.93 |
| $\chi^2$ | 2.58 | 2.74 | 2.83 | 2.83 | 3.18 |
| $a = b$ (Å) | 12.2796(1) | 12.2812(1) | 12.2828(1) | 12.2841(1) | 12.3007(1) |
| $c$ (Å) | 12.4744(1) | 12.4762(1) | 12.4779(1) | 12.4794(1) | 12.5001(1) |
| X | 0.178(2) | 0.173(2) | 0.168(2) | 0.163(2) | 0.113(2) |
| Y | 0.007(1) | 0.006(1) | 0.006(1) | 0.006(1) | 0.007(1) |
| Biso Sb1 | 1.63(3) | 1.63(3) | 1.64(3) | 1.67(2) | 2.05(3) |
| Biso Sb2 | 1.41(2) | 1.41(3) | 1.43(3) | 1.46(3) | 1.79(3) |
| Biso Zn | 3.39(6) | 3.40(4) | 3.44(6) | 3.36(6) | 4.03(8) |
| Occ. Zn1 | 0.937(3) | 0.935(3) | 0.935(3) | 0.933(3) | 0.920(4) |
| Occ. Zn2 | 0.060(2) | 0.061(2) | 0.062(2) | 0.060(2) | 0.073(2) |
| Occ. Zn3 | 0.029(2) | 0.030(2) | 0.031(2) | 0.030(2) | 0.031(2) |
| Occ. Zn4 | 0.049(2) | 0.049(2) | 0.048(2) | 0.047(2) | 0.049(2) |
| $V$ (Å$^3$) | 1628.99(1) | 1629.65(1) | 1630.30(1) | 1630.83(1) | 1637.96(1) |
| Wt% ZnSb | 8.79(8) | 9.14(9) | 9.46(9) | 9.85(9) | 18.48(10) |
| Wt% ZnO | 3.27(12) | 3.33(12) | 3.34(12) | 3.37(12) | 3.96(13) |
| Wt% Sb | 3.01(5) | 3.12(5) | 3.20(5) | 3.27(4) | 2.68(4) |

**Table ST4:** Selected crystallographic details and weight fractions of impurity phases from high temperature Rietveld refinement of the 1 wt % ZnO composite

| T(K) | 300 | 450 | 500 | 510 | 515 | 520 |
|---|---|---|---|---|---|---|
| $t_{exp}$ (min) | 5 | 5 | 5 | 5 | 5 | 5 |
| # points | 7797 | 7797 | 7798 | 7798 | 7798 | 7799 |
| # refl | 3152 | 3159 | 3152 | 3152 | 3152 | 3149 |
| # par | 90 | 90 | 99 | 99 | 99 | 99 |
| $R_F$ (%) | 2.32 | 2.58 | 2.56 | 2.42 | 2.45 | 2.30 |
| $R_{Bragg}$ (%) | 3.11 | 2.89 | 2.33 | 2.68 | 2.74 | 2.65 |
| $R_p$ (%) | 7.64 | 7.62 | 7.19 | 7.10 | 7.02 | 7.10 |
| $R_{wp}$ (%) | 8.39 | 8.16 | 7.71 | 7.60 | 7.52 | 7.60 |
| $\chi^2$ | 5.18 | 4.60 | 4.04 | 4.00 | 3.91 | 3.96 |
| $a = b$ (Å) | 12.2332(1) | 12.2603(1) | 12.2711(1) | 12.2739(1) | 12.2753(1) | 12.2765(1) |
| $c$ (Å) | 12.4275(1) | 12.4530(1) | 12.4657(1) | 12.4692(1) | 12.4708(1) | 12.4722(1) |
| X | 0.227(4) | 0.208(3) | 0.189(3) | 0.180(3) | 0.173(3) | 0.163(3) |
| Y | 0.016(1) | 0.011(1) | 0.007(1) | 0.005(1) | 0.005(1) | 0.005(1) |
| Biso Sb1 | 1.17(3) | 1.56(3) | 1.64(3) | 1.69(3) | 1.71(3) | 1.72(3) |
| Biso Sb2 | 0.89(3) | 1.24(3) | 1.36(3) | 1.37(3) | 1.36(3) | 1.42(3) |
| Biso Zn | 1.31(6) | 2.33(7) | 2.68(7) | 2.68(6) | 2.84(6) | 2.92(6) |
| Occ. Zn1 | 0.833(5) | 0.860(5) | 0.870(5) | 0.875(5) | 0.876(5) | 0.884(4) |
| Occ. Zn2 | 0.055(2) | 0.056(2) | 0.061(2) | 0.061(2) | 0.061(2) | 0.062(2) |
| Occ. Zn3 | 0.099(4) | 0.082(4) | 0.073(3) | 0.069(3) | 0.068(3) | 0.064(3) |
| Occ. Zn4 | 0.071(2) | 0.065(2) | 0.065(2) | 0.064(2) | 0.065(2) | 0.065(2) |
| $V$ (Å$^3$) | 1610.61(2) | 1621.09(2) | 1625.60(1) | 1626.79(1) | 1627.38(1) | 1627.90(1) |
| Wt% ZnSb | 0 | 0 | 2.62(12) | 3.55(11) | 4.08(10) | 4.51(10) |
| Wt% ZnO | 0.95(12) | 0.97(12) | 1.31(16) | 1.06(12) | 1.08(13) | 1.05(12) |
| Wt% Sb | 0 | 0 | 0.37(7)) | 0.56(6) | 0.67(6) | 0.72(5) |

**Table ST4 continued:** Selected crystallographic details and weight fractions of impurity phases from high temperature Rietveld refinement of the 1 wt % ZnO composite

| T(K) | 525 | 530 | 535 | 540 | 625 |
|---|---|---|---|---|---|
| $t_{exp}$ (min) | 5 | 5 | 5 | 5 | 5 |
| # points | 7799 | 7799 | 7800 | 7801 | 7801 |
| # refl | 3148 | 3146 | 3146 | 3147 | 3150 |
| # par | 99 | 99 | 99 | 99 | 100 |
| $R_F$ (%) | 2.44 | 2.40 | 2.52 | 2.50 | 3.59 |
| $R_{Bragg}$ (%) | 2.72 | 2.76 | 2.80 | 2.80 | 3.13 |
| $R_p$ (%) | 7.20 | 7.21 | 7.12 | 7.13 | 8.10 |
| $R_{wp}$ (%) | 7.76 | 7.76 | 7.70 | 7.68 | 8.36 |
| $\chi^2$ | 4.19 | 4.20 | 4.17 | 4.15 | 4.68 |
| *a* = *b* (Å) | 12.2782(1) | 12.2796(1) | 12.2810(1) | 12.2824(1) | 12.2988(1) |
| *c* (Å) | 12.4740(1) | 12.4757(6) | 12.4773(1) | 12.4789(1) | 12.4992(1) |
| X | 0.160(3) | 0.156(3) | 0.152(2) | 0.149(2) | 0.066(6) |
| Y | 0.005(1) | 0.005(1) | 0.004(1) | 0.005(1) | 0.009(1) |
| Biso Sb1 | 1.75(3) | 1.77(3) | 1.76(3) | 1.78(3) | 2.26(4) |
| Biso Sb2 | 1.44(3) | 1.45(3) | 1.46(3) | 1.48(3) | 1.88(4) |
| Biso Zn | 3.08(7) | 3.10(7) | 3.10(7) | 3.13(7) | 3.93(8) |
| Occ. Zn1 | 0.891(4) | 0.891(4) | 0.888(4) | 0.888(4) | 0.882(5) |
| Occ. Zn2 | 0.063(2) | 0.064(2) | 0.064(2) | 0.063(2) | 0.070(3) |
| Occ. Zn3 | 0.061(2) | 0.061(2) | 0.063(3) | 0.061(2) | 0.057(2) |
| Occ. Zn4 | 0.067(2) | 0.066(2) | 0.066(2) | 0.066(2) | 0.070(2) |
| *V* (Å$^3$) | 1628.56(1) | 1629.16(1) | 1629.74(1) | 1630.33(1) | 1637.34(1) |
| Wt% ZnSb | 4.86(10) | 5.24(10) | 5.60(9) | 5.98(9) | 13.68(8) |
| Wt% ZnO | 0.96(11) | 0.95(10) | 1.03(11) | 1.00(10) | 1.08(11) |
| Wt% Sb | 0.82(5) | 0.91(5) | 0.96(5) | 1.00(5) | 0.59(6) |

**Table ST5:** Selected crystallographic details and weight fractions of impurity phases from high temperature Rietveld refinement of the 0.5 wt % $TiO_2$ composite

| T(K) | 300 | 450 | 500 | 510 | 515 | 520 |
|---|---|---|---|---|---|---|
| $t_{exp}$ (min) | 5 | 5 | 5 | 5 | 5 | 5 |
| # points | 7795 | 7795 | 7795 | 7796 | 7796 | 7795 |
| # refl | 3109 | 3121 | 3130 | 3131 | 3131 | 7797 |
| # par | 93 | 88 | 90 | 90 | 87 | 90 |
| $R_F$ (%) | 4.56 | 4.45 | 4.58 | 4.74 | 4.76 | 4.73 |
| $R_{Bragg}$ (%) | 6.69 | 5.53 | 5.73 | 5.82 | 5.74 | 5.85 |
| $R_p$ (%) | 11.9 | 11.8 | 11.9 | 12.0 | 12.0 | 12.3 |
| $R_{wp}$ (%) | 13.2 | 12.4 | 12.4 | 12.4 | 12.5 | 12.6 |
| $\chi^2$ | 12.52 | 10.11 | 9.77 | 9.89 | 10.01 | 10.22 |
| $a = b$ (Å) | 12.2286(1) | 12.2581(1) | 12.2684(1) | 12.2706(1) | 12.2715(1) | 12.2726(1) |
| $c$ (Å) | 12.4208(1) | 12.4516(1) | 12.4621(1) | 12.4657(1) | 12.4669(1) | 12.4680(1) |
| X | 0.078(7) | 0.148(2) | 0.136(2) | 0.128(2) | 0.125(2) | 0.124(2) |
| Y | 0.008(1) | 0.0001(1) | 0.0001(1) | 0.0001(1) | 0.0001(1) | 0.0001(1) |
| Biso Sb1 | 1.00(3) | 1.01(3) | 1.26(3) | 1.28(3) | 1.31(3) | 1.34(4) |
| Biso Sb2 | 0.80(3) | 0.92(4) | 1.05(4) | 1.08(4) | 1.12(4) | 1.11(4) |
| Biso Zn | 1.91(7) | 2.67(7) | 3.01(7) | 3.07(8) | 3.10(8) | 3.08(8) |
| Occ. Zn1 | 0.897(4) | 0.918(4) | 0.920(5) | 0.918(5) | 0.918(5) | 0.913(5) |
| Occ. Zn2 | 0.055(3) | 0.042(3) | 0.045(3) | 0.047(3) | 0.045(3) | 0.046(3) |
| Occ. Zn3 | 0.094(3) | 0.098(3) | 0.096(3) | 0.098(3) | 0.099(3) | 0.098(2) |
| Occ. Zn4 | 0.078(3) | 0.079(3) | 0.078(3) | 0.078(3) | 0.079(3) | 0.081(3) |
| $V$ (Å$^3$) | 1608.54(5) | 1620.33(1) | 1624.54(1) | 1625.46(1) | 1625.86(1) | 1626.30(1) |
| Wt% ZnSb | 0 | 0 | 0 | 0 | 0 | 0 |
| Wt% Sb | 0 | 0 | 0 | 0 | 0 | 0.35(7) |
| Wt% $TiO_2$ | 0.75(14) | 0.80(22) | 0.85(34) | 0.31(26) | 0.73(13) | 0.91(35) |

**Table ST5 continued:** Selected crystallographic details and weight fractions of impurity phases from high temperature Rietveld refinement of the 0.5 wt % $TiO_2$ composite

| T(K) | 525 | 530 | 535 | 540 | 625 |
|---|---|---|---|---|---|
| $t_{exp}$ (min) | 5 | 5 | 5 | 5 | 5 |
| # points | 7797 | 7798 | 7798 | 7799 | 7800 |
| # refl | 3131 | 3132 | 3132 | 3135 | 3135 |
| # par | 94 | 94 | 94 | 94 | 93 |
| $R_F$ (%) | 4.81 | 4.75 | 4.96 | 4.87 | 6.41 |
| $R_{Bragg}$ (%) | 5.91 | 5.90 | 5.96 | 5.93 | 6.33 |
| $R_p$ (%) | 12.7 | 12.8 | 12.9 | 12.8 | 13.4 |
| $R_{wp}$ (%) | 13.2 | 13.2 | 13.3 | 13.2 | 13.2 |
| $\chi^2$ | 11.15 | 11.25 | 11.59 | 11.41 | 10.57 |
| *a* = *b* (Å) | 12.2736(1) | 12.2749(1) | 12.2763(1) | 12.2774(1) | 12.2934(1) |
| *c* (Å) | 12.4692(1) | 12.4707(1) | 12.4723(1) | 12.4735(1) | 12.4937(1) |
| X | 0.123(2) | 0.121(2) | 0.121(2) | 0.119(2) | 0.026(6) |
| Y | 0.0001(1) | 0.0001(1) | 0.0001(1) | 0.0001(1) | 0.009(1) |
| Biso Sb1 | 1.34(4) | 1.36(4) | 1.35(4) | 1.42(4) | 2.01(5) |
| Biso Sb2 | 1.11(4) | 1.14(4) | 1.14(4) | 1.17(4) | 1.70(5) |
| Biso Zn | 3.09(8) | 3.09(8) | 3.21(8) | 3.15(8) | 4.13(9) |
| Occ. Zn1 | 0.911(5) | 0.907(5) | 0.920(5) | 0.903(5) | 0.903(5) |
| Occ. Zn2 | 0.044(3) | 0.046(3) | 0.047(3) | 0.048(3) | 0.055(4) |
| Occ. Zn3 | 0.096(3) | 0.098(3) | 0.096(3) | 0.098(3) | 0.097(3) |
| Occ. Zn4 | 0.079(3) | 0.081(3) | 0.078(3) | 0.081(3) | 0.084(3) |
| *V* (Å$^3$) | 1626.73(1) | 1627.27(1) | 1627.85(1) | 1628.29(1) | 1635.18(1) |
| Wt% ZnSb | 0 | 0 | 0 | 0 | 0.14(4) |
| Wt% Sb | 0.34(7) | 0.36(6) | 0.34(6) | 0.38(6) | 0.28(5) |
| Wt% $TiO_2$ | 0.91(37) | 1.15(41) | 1.02(45) | 1.02(20) | 0.80(14) |

**Table ST6:** Selected crystallographic details and weight fractions of impurity phases from high temperature Rietveld refinement of the 1 wt % $TiO_2$ composite

| T(K) | 300 | 450 | 500 | 510 | 515 | 520 |
|---|---|---|---|---|---|---|
| $t_{exp}$ (min) | 5 | 5 | 5 | 5 | 5 | 5 |
| # points | 7795 | 7795 | 7795 | 7796 | 7797 | 7797 |
| # refl | 3094 | 3119 | 3130 | 3132 | 3132 | 3132 |
| # par | 95 | 91 | 91 | 97 | 96 | 97 |
| $R_F$ (%) | 3.20 | 3.62 | 3.73 | 3.74 | 3.84 | 3.87 |
| $R_{Bragg}$ (%) | 5.46 | 5.49 | 5.66 | 5.56 | 5.48 | 5.61 |
| $R_p$ (%) | 8.83 | 9.39 | 9.55 | 9.55 | 9.42 | 9.67 |
| $R_{wp}$ (%) | 9.91 | 10.3 | 10.4 | 10.4 | 10.2 | 10.5 |
| $\chi^2$ | 15.23 | 14.57 | 14.42 | 14.43 | 14.01 | 14.59 |
| $a = b$ (Å) | 12.2285(1) | 12.2564(1) | 12.2665(1) | 12.2690(1) | 12.2705(1) | 12.2718(1) |
| $c$ (Å) | 12.4240(1) | 12.4514(1) | 12.4625(1) | 12.4652(1) | 12.4670(1) | 12.4685(1) |
| X | 0.078(5) | 0.143(1) | 0.132(1) | 0.126(2) | 0.122(2) | 0.123(2) |
| Y | 0.009(1) | 0.0001(1) | 0.0001(1) | 0.0001(1) | 0.0001(1) | 0.0001(1) |
| Biso Sb1 | 0.88(3) | 1.12(3) | 1.27(3) | 1.31(3) | 1.34(3) | 1.36(3) |
| Biso Sb2 | 0.83(3) | 1.01(3) | 1.14(3) | 1.17(3) | 1.18(3) | 1.21(3) |
| Biso Zn | 1.66(5) | 2.00(6) | 2.23(7) | 2.17(7) | 2.27(7) | 2.28(7) |
| Occ. Zn1 | 0.932(3) | 0.904(5) | 0.893(6) | 0.881(6) | 0.882(6) | 0.884(6) |
| Occ. Zn2 | 0.080(2) | 0.090(2) | 0.095(2) | 0.093(2) | 0.094(2) | 0.094(2) |
| Occ. Zn3 | 0.035(2) | 0.041(3) | 0.048(4) | 0.049(4) | 0.051(5) | 0.047(4) |
| Occ. Zn4 | 0.044(2) | 0.041(2) | 0.041(2) | 0.038(2) | 0.040(2) | 0.040(2) |
| $V$ (Å$^3$) | 1608.94(32) | 1619.86(1) | 1623.97(1) | 1624.99(1) | 1625.61(1) | 1626.16(1) |
| Wt% ZnSb | 0 | 0 | 0 | 0.49(10) | 0.55(11) | 0.80(12) |
| Wt% Sb | 0 | 0 | 0 | 0 | 0 | 0 |
| Wt% $TiO_2$ | 1.27(19) | 1.06(16) | 0.98(15) | 1.00(15) | 0.92(14) | 0.96(14) |

**Table ST6 continued:** Selected crystallographic details and weight fractions of impurity phases from high temperature Rietveld refinement of the 1 wt % $TiO_2$ composite

| T(K) | 525 | 530 | 535 | 540 | 625 |
|---|---|---|---|---|---|
| $t_{exp}$ (min) | 5 | 5 | 5 | 5 | 5 |
| # points | 7798 | 7799 | 7799 | 7800 | 7801 |
| # refl | 3135 | 3137 | 3138 | 3139 | 3148 |
| # par | 93 | 92 | 97 | 93 | 99 |
| $R_F$ (%) | 3.75 | 3.72 | 3.94 | 3.75 | 4.32 |
| $R_{Bragg}$ (%) | 5.53 | 5.55 | 5.74 | 5.56 | 5.75 |
| $R_p$ (%) | 9.71 | 9.74 | 10.0 | 9.82 | 10.4 |
| $R_{wp}$ (%) | 10.7 | 10.6 | 11.0 | 10.8 | 11.2 |
| $\chi^2$ | 15.26 | 14.89 | 16.30 | 15.80 | 15.81 |
| $a = b$ (Å) | 12.2732(1) | 12.2750(1) | 12.2761(1) | 12.2776(1) | 12.2939(1) |
| $c$ (Å) | 12.4700(1) | 12.4720(1) | 12.4732(1) | 12.4748(1) | 12.4952(1) |
| X | 0.121(2) | 0.120(2) | 0.117(2) | 0.117(2) | 0.115(2) |
| Y | 0.0001(1) | 0.0001(1) | 0.0001(1) | 0.0001(1) | 0.0001(1) |
| Biso Sb1 | 1.37(3) | 1.38(3) | 1.42(3) | 1.43(3) | 1.72(3) |
| Biso Sb2 | 1.23(3) | 1.24(3) | 1.28(3) | 1.30(3) | 1.56(3) |
| Biso Zn | 2.35(7) | 2.37(7) | 2.41(7) | 2.45(7) | 2.92(9) |
| Occ. Zn1 | 0.883(6) | 0.882(6) | 0.881(7) | 0.877(7) | 0.863(7) |
| Occ. Zn2 | 0.095(3) | 0.097(2) | 0.099(3) | 0.099(3) | 0.109(3) |
| Occ. Zn3 | 0.047(4) | 0.047(4) | 0.050(5) | 0.052(5) | 0.053(5) |
| Occ. Zn4 | 0.041(2) | 0.040(2) | 0.039(2) | 0.040(2) | 0.042(2) |
| $V$ (Å$^3$) | 1626.71(1) | 1627.46(1) | 1627.91(1) | 1628.50(1) | 1635.51(1) |
| Wt% ZnSb | 0.90(13) | 0.81(10) | 0.79(14) | 0.88(16) | 0.85(1) |
| Wt% Sb | 0 | 0.02(1) | 0.02(3) | 0.06(0) | 0.14(4) |
| Wt% $TiO_2$ | 0.95(14) | 0.90(11) | 1.02(15) | 0.94(14) | 1.02(15) |

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