Supplementary Materials

Study on the Redox Behavior and Reactive Oxygen Site of Reducible A2B2O7 Composite Oxides

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S1. Supplementary Experimental Information

Analysis of the sample through Raman spectroscopy was carried out utilizing a Renishaw in Via instrument, employing an excitation wavelength of 532 nm. In situ Raman experiments were executed with the same apparatus, integrating a Linkam TS 1500 micro *in situ* cell. The measurements were performed under an atmosphere of either 10% H_2-Ar mixed gas (H_2 purity 99.999%, Ar purity 99.999%) or high-purity Ar (purity 99.999%), with a gas flow rate of 30 mL/min. The temperature was ramped from 25 ºC to 750 ºC at a heating rate of 10 ºC/min.

XRD analysis was conducted utilizing a Bruker AXS D8 Advance diffractometer (Germany), functioning at 40 kV and 30 mA with Cu Kα radiation. The scanning range was established from 10° to 80°, using a step size of 0.02°/min. To accurately ascertain the phase structure of the samples, the lattice parameters of the prepared catalysts were determined using the XRD Rietveld refinement method.

XPS analysis was performed on a Kratos AXIS SUPRA X-ray photoelectron spectrometer (UK) equipped with a monochromatic Al Kα X-ray source. The investigation utilized a standard monochromatic aluminum K-alpha (Al Kα) X-ray source functioning at 300 W, with the analyzer energy configured to 40 eV. Calibration of the elemental binding energies was based on the C 1s peak at 284.8 eV, which was used as a reference.

H_2-TPR experiments utilized a micromeritics Auto Chem 2920 apparatus, typically employing a 100 mg sample. Prior to experimentation, the samples underwent calcination in a 10%O_2-Ar mixed gas flow at 800 ℃ for 30 min to eliminate any potential impurities and carbonates. Following this, the sample was cooled down to 50 ℃ and purged with 99.9% Ar for a duration of 30 min. The H_2-TPR process commenced

at 50 ℃, escalating to 800 °C at a ramp rate of 10 ℃/min, while maintaining a flow of 30 mL/min of a 10% H_2/Ar gas mixture. To track H_2 consumption, a thermal conductivity detector (TCD) was used. The amount of H_2 desorbed from the catalyst was quantified using a CuO standard sample (purity 99.0%), according to the reaction equation: $CuO+H_2 \rightarrow Cu + H_2O$.

The O_2-TPD experiments were carried out using the Micromeritics ASAP2920 apparatus. A 100 mg sample was first heated to 800 ℃ at a flow rate of 10 mL/min with a 3% O_2-He mixture and kept at this temperature for 30 min to remove possible impurities and carbonates. After this process, the sample was cooled down to 50 ℃ and purged with 30 mL/min of 99.99% He for half an hour to eliminate any O_2 that was physically adsorbed. Once the pretreatment was finished, the catalyst was heated from 50 ℃ to 800 ℃ at a rate of 10 ℃/min while maintaining the same gas atmosphere. The thermal conductivity detector (TCD) was used to monitor the O_2 desorption signal. The amount of O_2 desorbed from the catalyst was quantified using a $KMnO_4$ standard sample (purity 99.0%), which completely decomposes at approximately 300 °C, according to the reaction equation: $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2\uparrow$.

The $^{18}O_2$-TPSR-MS experiments were carried out on a FINESORB-3010 instrument equipped with a FINETEC QMS.1800 mass spectrometer and a BelCat II apparatus equipped with a BelMass quadrupole mass spectrometer, with the gas flow rate controlled at 30-60 mL/min. First, 100 mg of the sample was activated at 800 ºC in a 10% O_2-Ar for 30 min, then cooled to 200 ºC and purged under an Ar for 15 min to remove physiosorbed oxygen. Subsequently, the atmosphere was switched to $^{18}O_2$, and the temperature was raised to 800 ºC at a heating rate of 10 ºC/min, while recording the mass spectrometry signals at m/z = 32 ($^{16}O^{16}O$), 34 ($^{16}O^{18}O$), and 36 ($^{18}O1^{8}O$).

S2. Supplementary Results

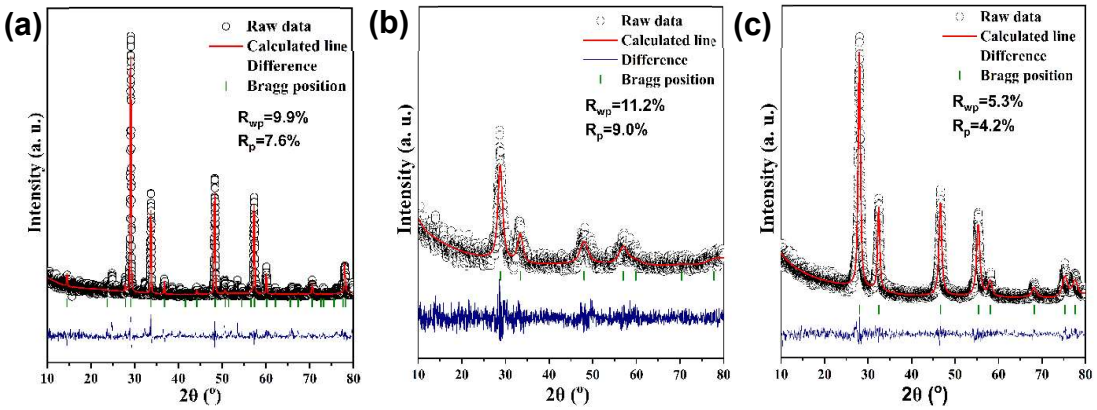


Figure. S1. XRD Rietveld refinement spectra of the Bi-based samples. (a) $Bi_2Sn_2O_7$, (b) $Bi_2Zr_2O_7$ and (c) $Bi_2Ce_2O_7$.

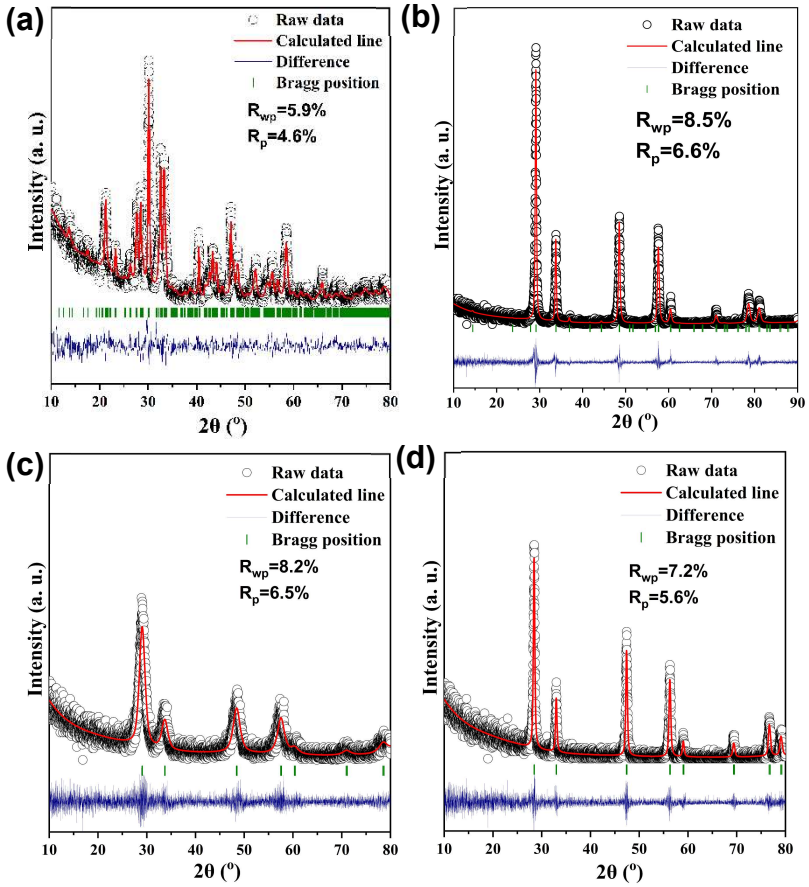


Figure. S2. XRD Rietveld refinement spectra of the Pr-based samples. (a) $Pr_2Ti_2O_7$, (b) $Pr_2Sn_2O_7$, (c) $Pr_2Zr_2O_7$ and (d) $Pr_2Ce_2O_7$.

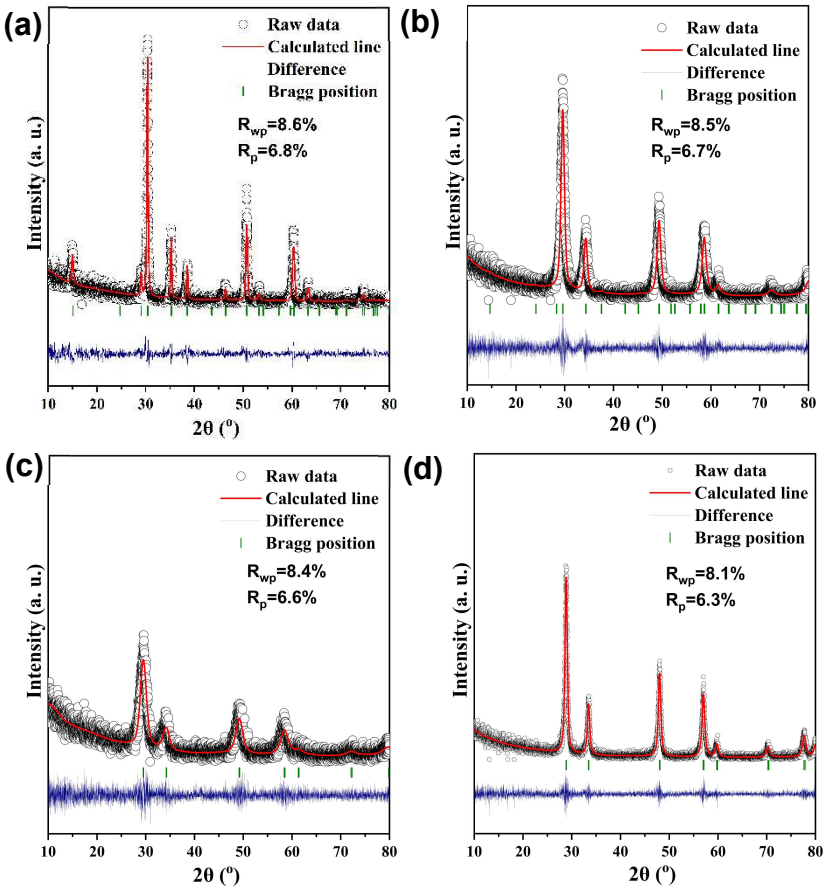


Figure. S3. XRD Rietveld refinement spectra of the Tb-based samples. (a) $Tb_2Ti_2O_7$, (b) $Tb_2Sn_2O_7$, (c) $Tb_2Zr_2O_7$ and (d) $Tb_2Ce_2O_7$.

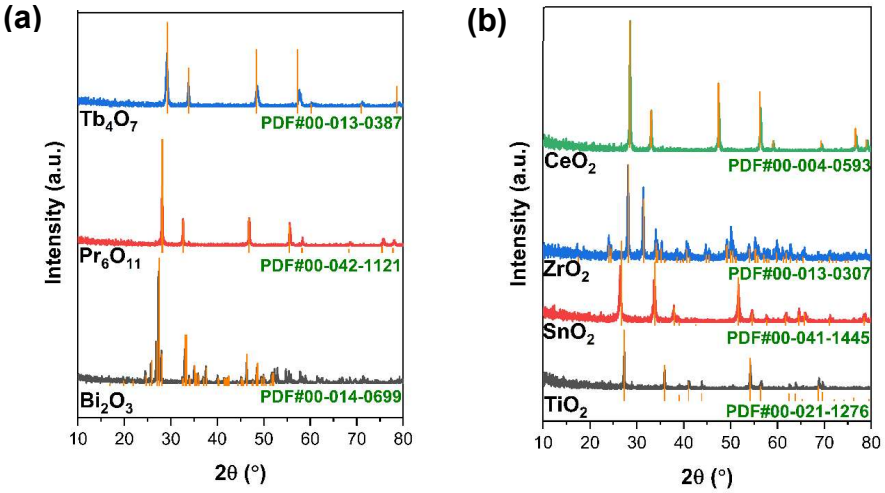


Figure. S4. XRD patterns of the pure metal oxides. (a) A-site metal oxides, (b) B-site metal oxides.

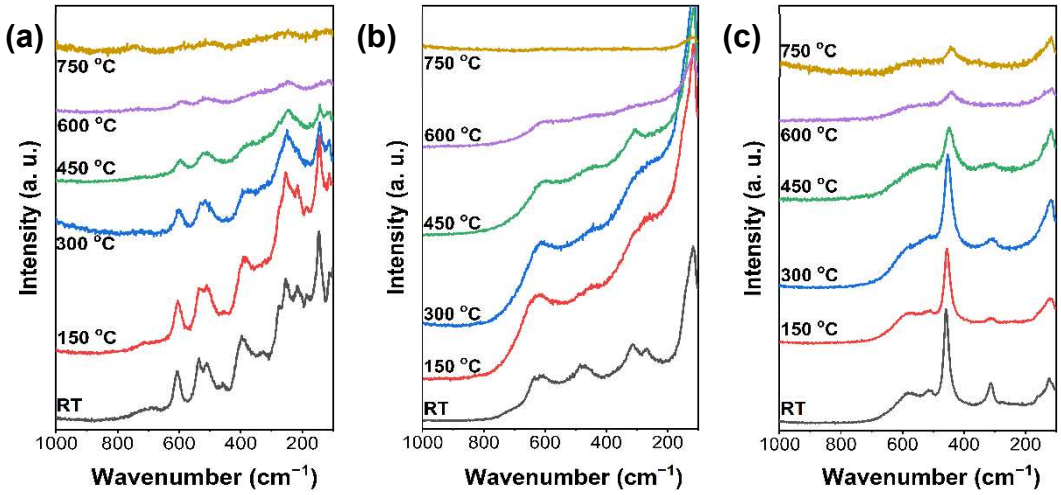


Figure. S5. *In situ* Raman spectra of the Bi-based samples under high-purity Ar atmosphere. (a) $Bi_2Sn_2O_7$, (b) $Bi_2Zr_2O_7$ and (c) $Bi_2Ce_2O_7$.

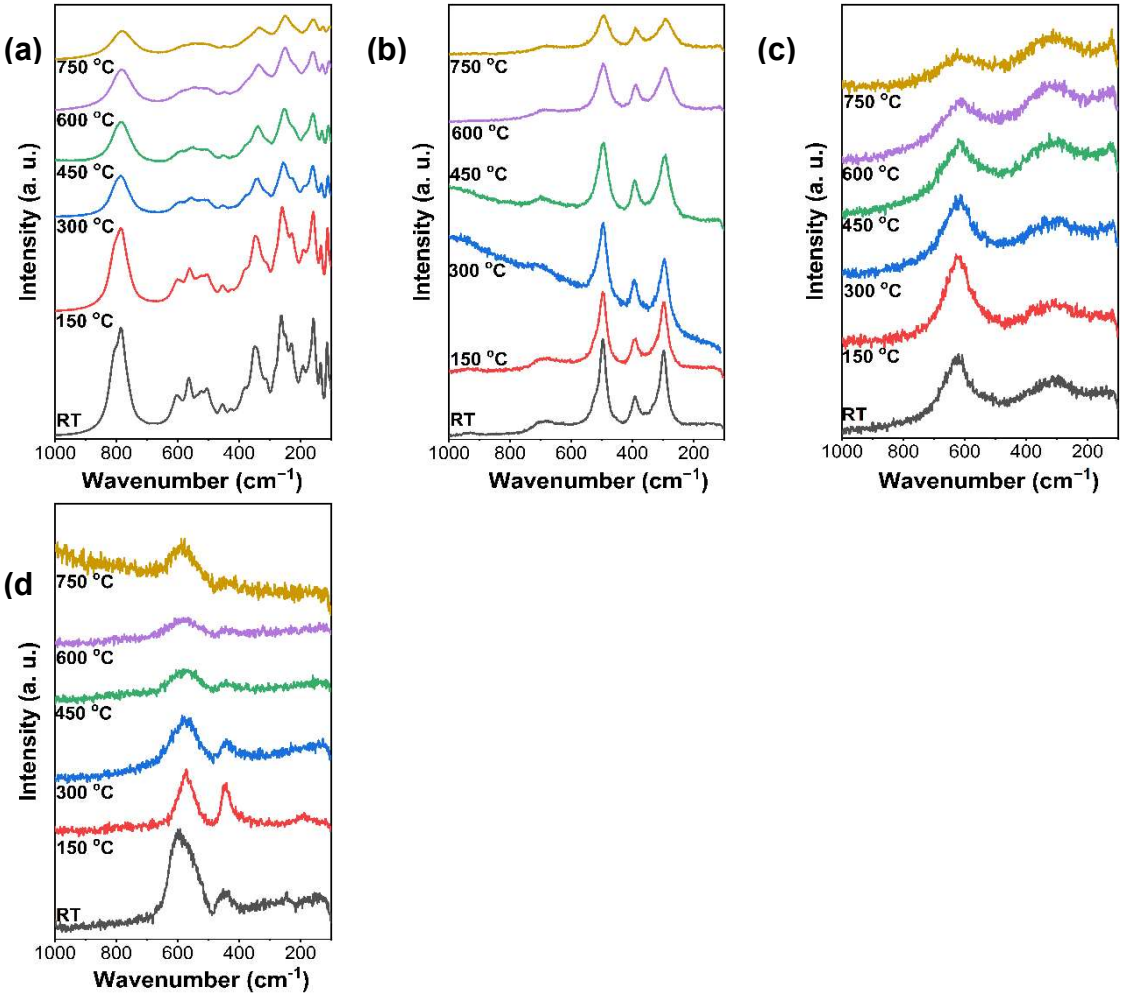


Figure. S6. *In situ* Raman spectra of the Pr-based samples under high-purity Ar atmosphere. (a) $Pr_2Ti_2O_7$, (b) $Pr_2Sn_2O_7$, (c) $Pr_2Zr_2O_7$ and (d) $Pr_2Ce_2O_7$.

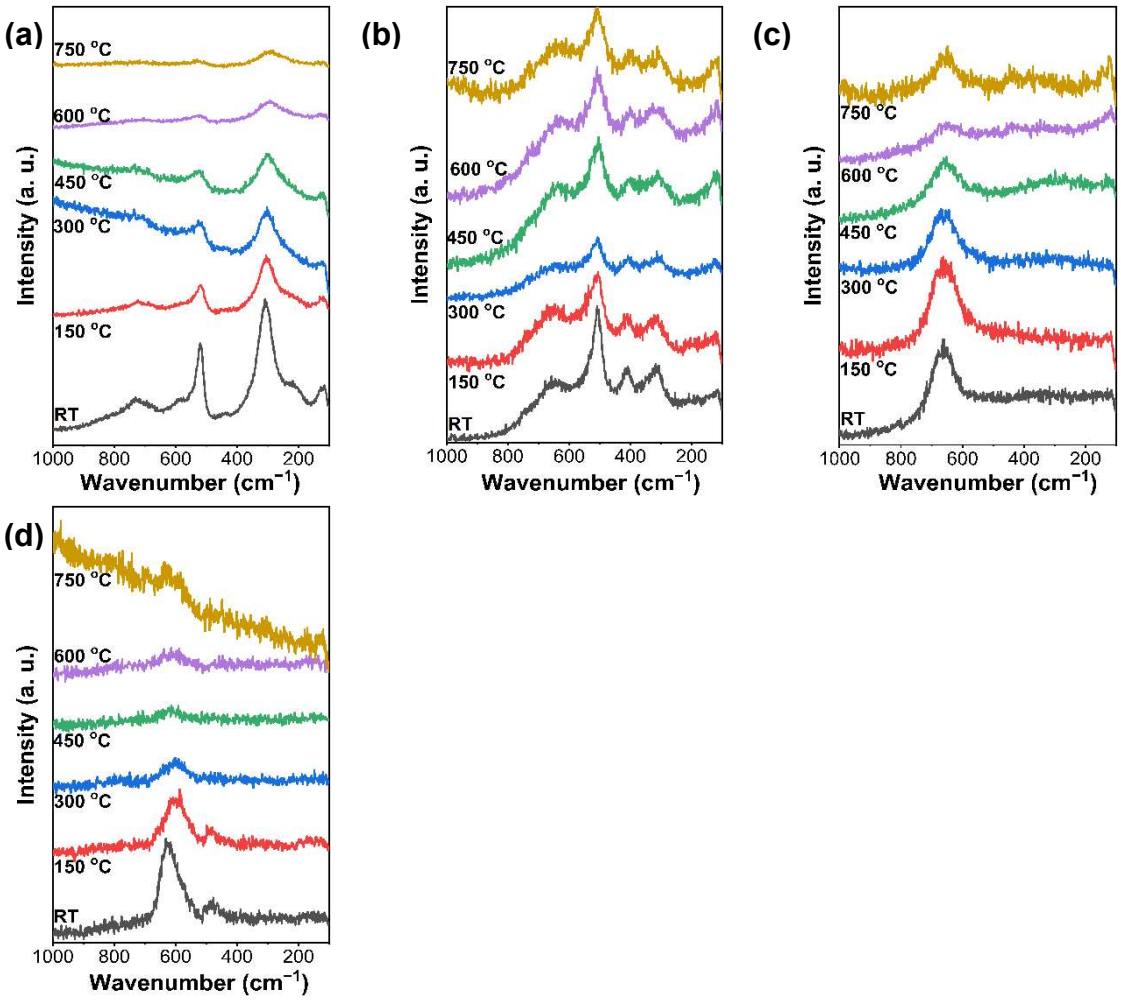


Figure. S7. *In situ* Raman spectra of the Tb-based samples under high-purity Ar atmosphere. (a) $Tb_2Ti_2O_7$, (b) $Tb_2Sn_2O_7$, (c) $Tb_2Zr_2O_7$ and (d) $Tb_2Ce_2O_7$.

Table S1. Quantitative results of H_2-TPR of oxides.

Samples	H_2 Consumption Temperature (°C)	H_2 Consumption Amount (mmol·g^{-1})	Samples	H_2 Consumption Temperature (°C)	H_2 Consumption Amount (mmol·g^{-1})
Bi_2O_3	562	39.6	TiO_2	599	1.3
	693	16.1			
Pr_6O_{11}	473	11.6	SnO_2	622	106.4
Tb_4O_7	452	10.7	ZrO_2	731.7	1.7
-			CeO_2	760	8.8

Table S2. Quantitative results of H_2-TPR of $Bi_2B_2O_7$, $Pr_2B_2O_7$ and $Tb_2B_2O_7$ (B=Ti, Sn, Zr, Ce).

Samples	H_2 Consumption Temperature (°C)	H_2 Consumption Amount (mmol·g^{-1})	Samples	H_2 Consumption Temperature (°C)	H_2 Consumption Amount (mmol·g^{-1})
$Bi_2Sn_2O_7$	550 699	86.8 67.4	$Pr_2Sn_2O_7$	427	2.0
$Bi_2Zr_2O_7$	345	65.9	$Pr_2Zr_2O_7$	385	4.6
$Bi_2Ce_2O_7$	325	55.8	$Pr_2Ce_2O_7$	430	4.8
$Pr_2Ti_2O_7$	-	-	$Tb_2Ti_2O_7$	-	-
$Tb_2Zr_2O_7$	405	9.3	$Tb_2Ce_2O_7$	351/472	3.7
$Tb_2Sn_2O_7$	401	4.5	-	-	-

Table S3. Quantitative results of O_2-TPD.

Samples	Weakly Bound Oxygen Amount (mmol·g^{-1})	Chemisorbed Oxygen Amount (mmol·g^{-1})	Surface Lattice Oxygen Amount (mmol·g^{-1})
Bi_2O_3	-	-	-
Pr_6O_{11}	-	3.9834	-
Tb_4O_7	-	1.6358	3.2745
TiO_2	0.1352	0.0023	-
SnO_2	0.0457	0.1791	-
ZrO_2	-	-	-
CeO_2	0.1206	-	-
$Bi_2Sn_2O_7$	-	0.0185	0.0146
$Bi_2Zr_2O_7$	0.0039	0.0678	0.0381
$Bi_2Ce_2O_7$	0.0061	0.0754	0.0689
$Pr_2Ti_2O_7$	0.0878	-	-
$Pr_2Sn_2O_7$	0.1530	-	0.0542
$Pr_2Zr_2O_7$	0.4681	1.882	-
$Pr_2Ce_2O_7$	0.2189	1.2792	-
$Tb_2Ti_2O_7$	0.0540	0.2716	-
$Tb_2Sn_2O_7$	-	1.3018	0.0834
$Tb_2Zr_2O_7$	0.1005	1.3768	0.0172
$Tb_2Ce_2O_7$	0.3369	2.3655	0.7176