Supporting Information

Synthesis and Characterization of the Rare-Earth Dion-Jacobson Layered Perovskites, APrNb$_2$O$_7$ (A = Rb, Cs and CuCl)

Dariush Montasserasadi,[a,b] Mark Granier,[a,b] Leonard Spinu,[b,c] Satish Chandra Rai,[c] Weilie Zhou,[c] and John B. Wiley[a,b],*

[a]Department of Chemistry, [b]Advanced Materials Research Institute, [c]Department of Physics
University of New Orleans, New Orleans, LA 70148-2820, United States

Fig. S1: XRDs of RbPrNb$_2$O$_7$ prepared from molten salt RbCl and from Pr$_2$O$_3$ and O$_2$. (a-c) ½ Rb$_2$CO$_3$: 1/6 Pr$_6$O$_{11}$: Nb$_2$O$_5$: 5 RbCl -temperature 1050 °C 2hrs -temperature 1060 °C 2 hrs -temperature 1200°C 2 hrs (d) ½ Rb$_2$CO$_3$: ½ Pr$_2$O$_3$: Nb$_2$O$_5$ + O$_2$ temperature 1000 °C 6.5hrs (e)½ Rb$_2$CO$_3$: 1/6 Pr$_6$O$_{11}$: Nb$_2$O$_5$ temperature 1100 °C 2 days.
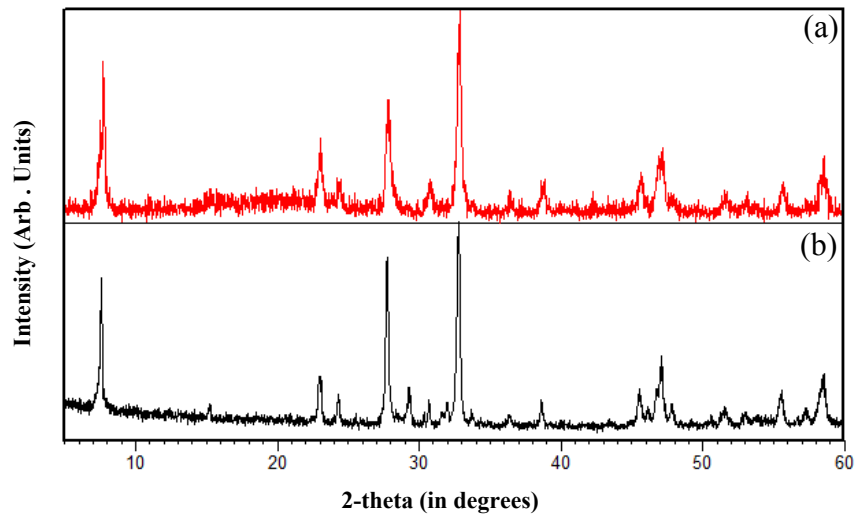
Fig. S2: The XRD pattern of (CuCl)PrNb$_2$O$_7$ which has been prepared from (a) RbPrNb$_2$O$_7$ at 325 °C over 7days and (b) CsPrNb$_2$O$_7$ 340 °C over 7 days.
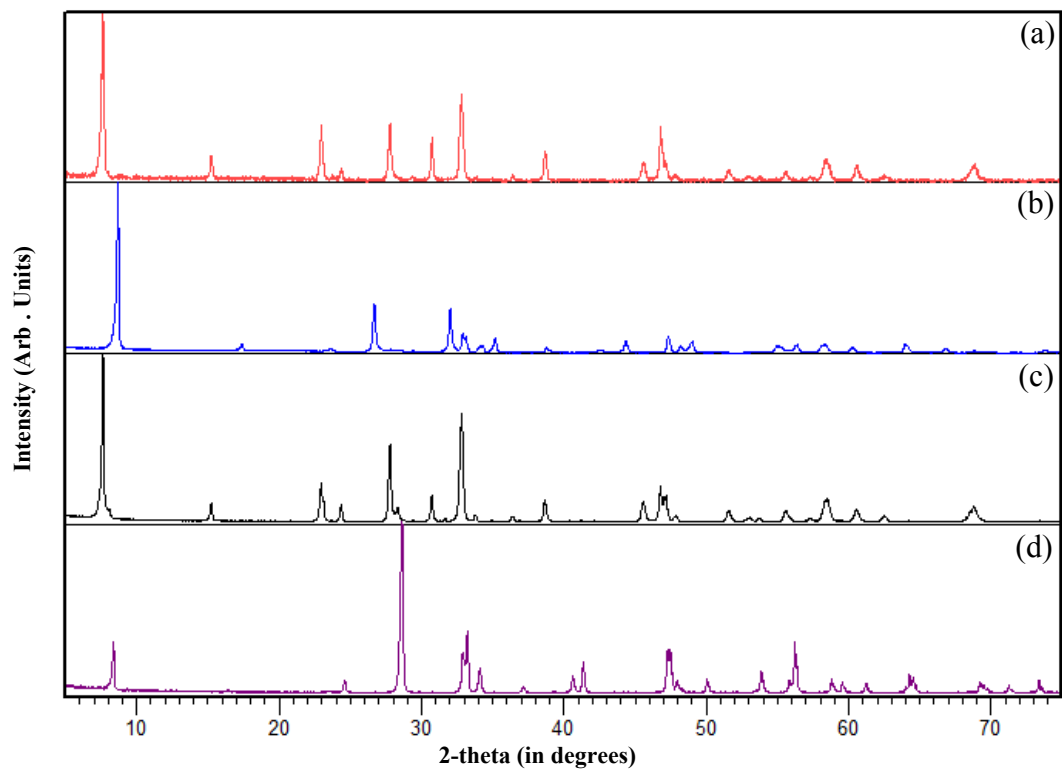
Fig. S3: XRD (CuCl)PrNb$_2$O$_7$ prepared from LiPrNb$_2$O$_7$ and CuCl$_2$. (a) (CuCl)PrNb$_2$O$_7$ (LiPrNb$_2$O$_7$:CuCl$_2$ 1:2) at 300 °C, 4 days. (b) LiPrNb$_2$O$_7$, (c) (CuCl)PrNb$_2$O$_7$ prepared from RbPrNb$_2$O$_7$ 355 °C 7 days, and (d) RbPrNb$_2$O$_7$.
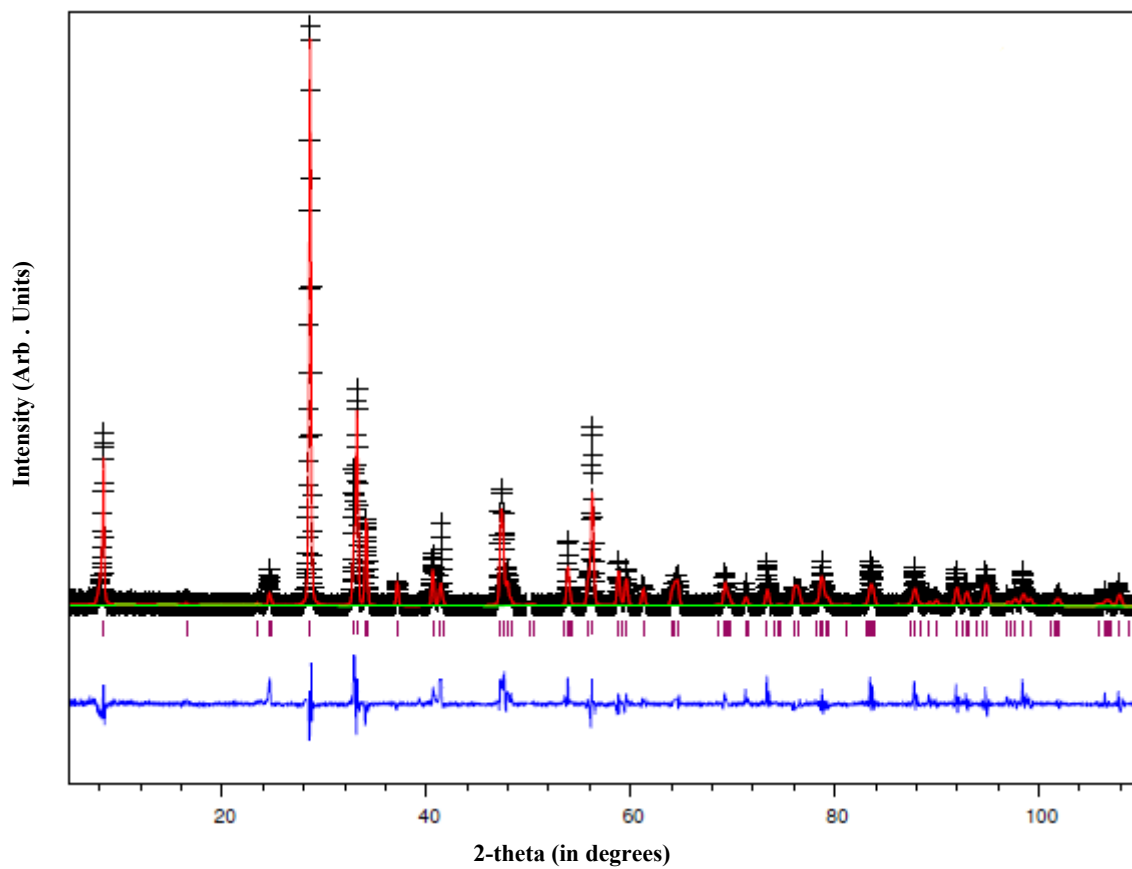
Fig. S4: Refinement of $RbPrNb_2O_7$ in *P4/mmm* space group ($R_p = 37.1\%$, $R_{wp} = 27.9\%$, and $\chi^2 = 4.946$). Orthorhombic model in *Imma* space group was found to be superior.

Fig. S5: Observed and calculated data for the Rietveld refinement of $CsPrNb_2O_7$ in *P*4/*mmm* space group. Observed data is indicated by crosses, calculated pattern by a (red) solid line, and the bottom (blue) curve is the difference plot. Peak positions are presented as black tic marks. (Z=1; R_p=13.17% R_{wp}= 12.26%; χ^2 = 1.837.)

Table S1: Crystallographic Data for $CsPrNb_2O_7$.

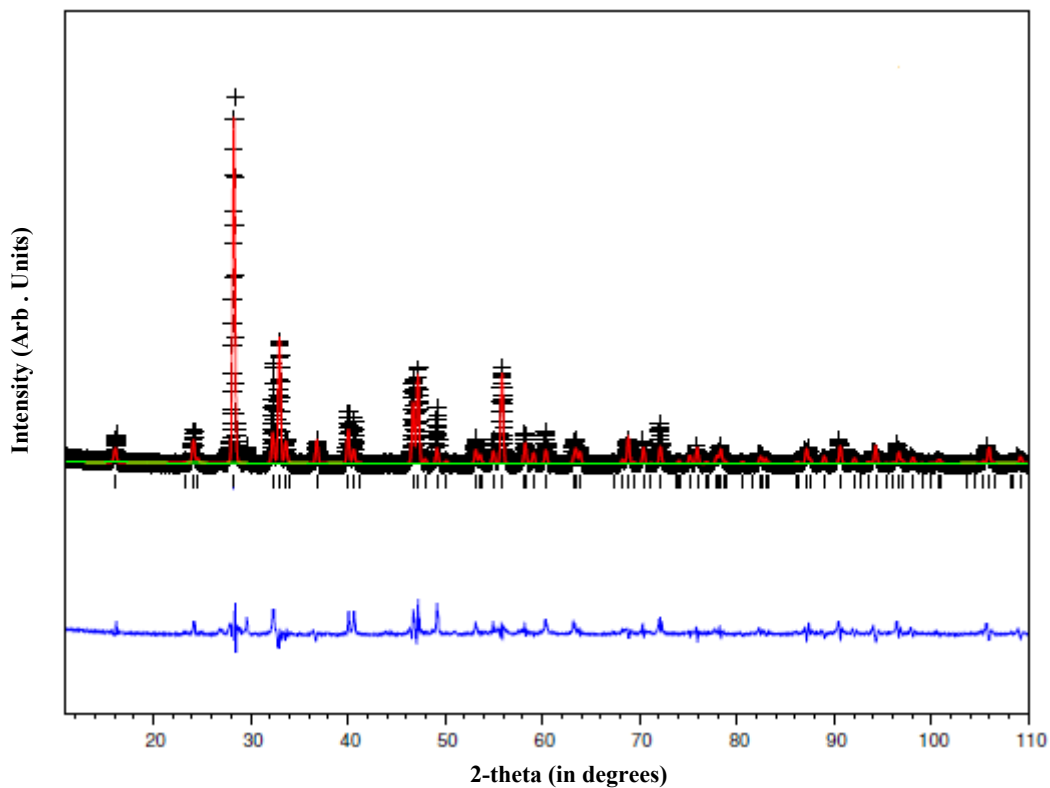| Atom	Site	x	y	z	g	U_{iso} (Å^2)
Cs	1b	0	0	0.5	1.09(8)	0.023(1)
Pr	1a	0	0	0	1.01(9)	0.012(1)
Nb	2h	0.5	0.5	0.2014(1)	1.03(9)	0.011(3)
O$_1$	4i	0	0.5	0.1671	1	0.005(5)
O$_2$	2h	0.5	0.5	0.3692	1	0.01(2)
O$_3$	1c	0.5	0.5	0	1	0.08(2)

Z=1; R_p=13.17% R_{wp}= 12.26% and χ^2 = 1.837
Space group $P4/mmm$ a = 3.8668(2), c = 11.163(1) V = 166.92(2) Å^3

Table S2: Bond valence sum results for $CsLaNb_2O_7$ and $CsPrNb_2O_7$.

$CsLaNb_2O_7$		$CsPrNb_2O_7$	
Cs	0.9876	Cs	1.0529
La	2.8808	Pr	3.0805
Nb	5.2305	Nb	5.2374

Table S3: Selected Bond Lengths Extracted from the Refined Structure of $CsPrNb_2O_7$ versus $CsLaNb_2O_7$.

$CsLaNb_2O_7$		$CsPrNb_2O_7$	
Bond Type	**Length (Å)**	**Bond Type**	**Length (Å)**
Cs-O2 x 8	3.191(4)	Cs-O2 x 8	3.1673(9)
La-O1 x 8	2.672(4)	Pr-O1 x 8	2.6021(1)
La-O3 x 4	2.763(1)	Pr-O3 x 4	2.73427(1)
Nb-O1 x 4	1.999(1)	Nb-O1 x 4	1.9987(6)
Nb-O2 x 1	1.736(7)	Nb-O2 x 1	1.7350(1)
Nb-O3 x 1	2.248(1)	Nb-O3 x 1	2.2481(1)
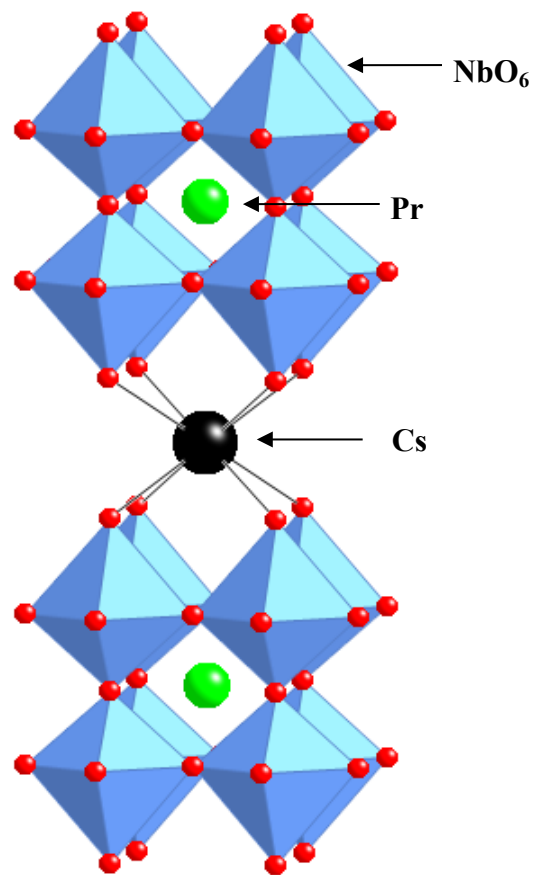
Fig. S6: Crystal structure for CsPrNb$_2$O$_7$.
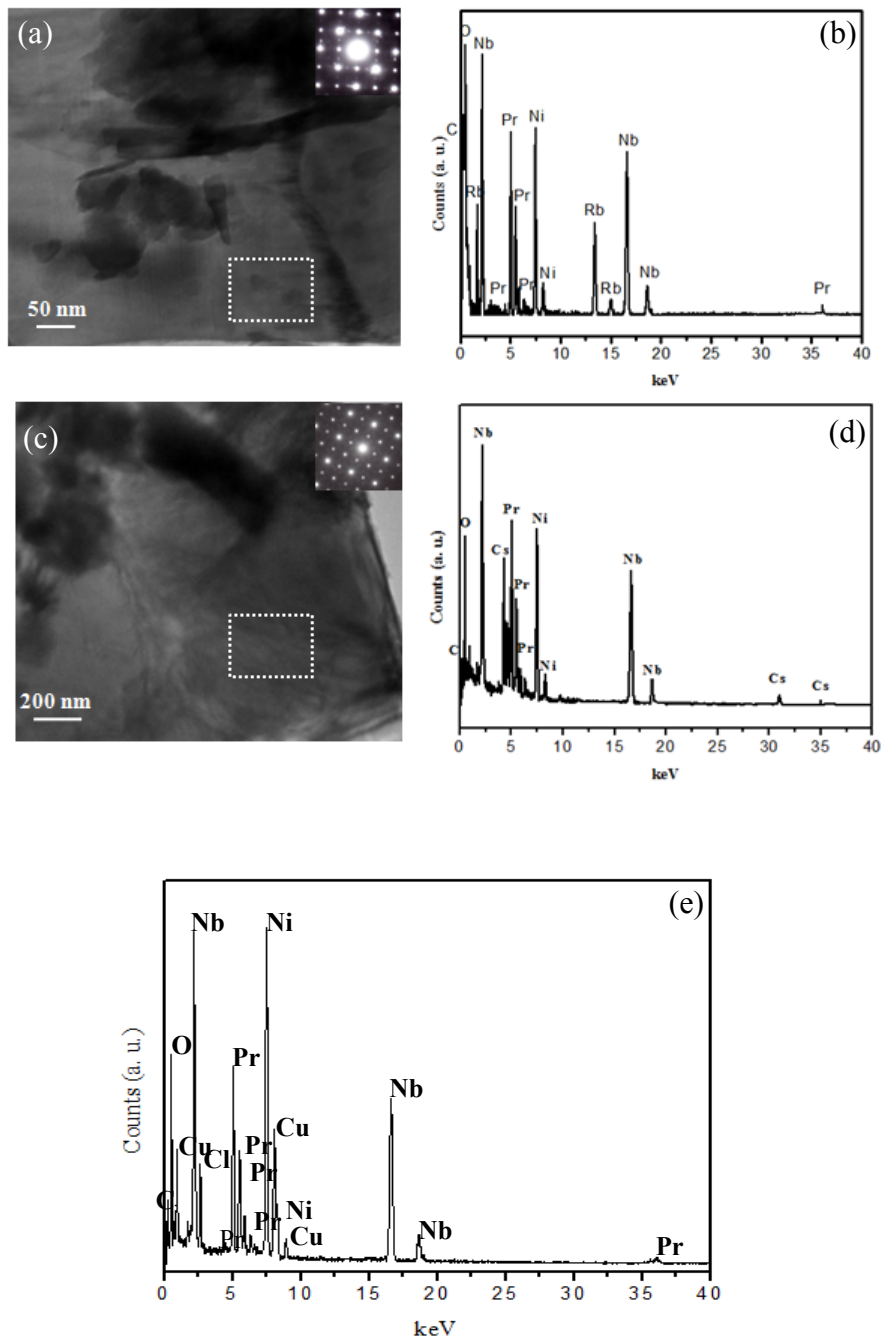
Fig. S7: TEM image, SAED and elemental analysis of (a,b) $CsPrNb_2O_7$, (c,d) $RbPrNb_2O_7$, and (e) elemental analysis of $(CuCl)PrNb_2O_7$.
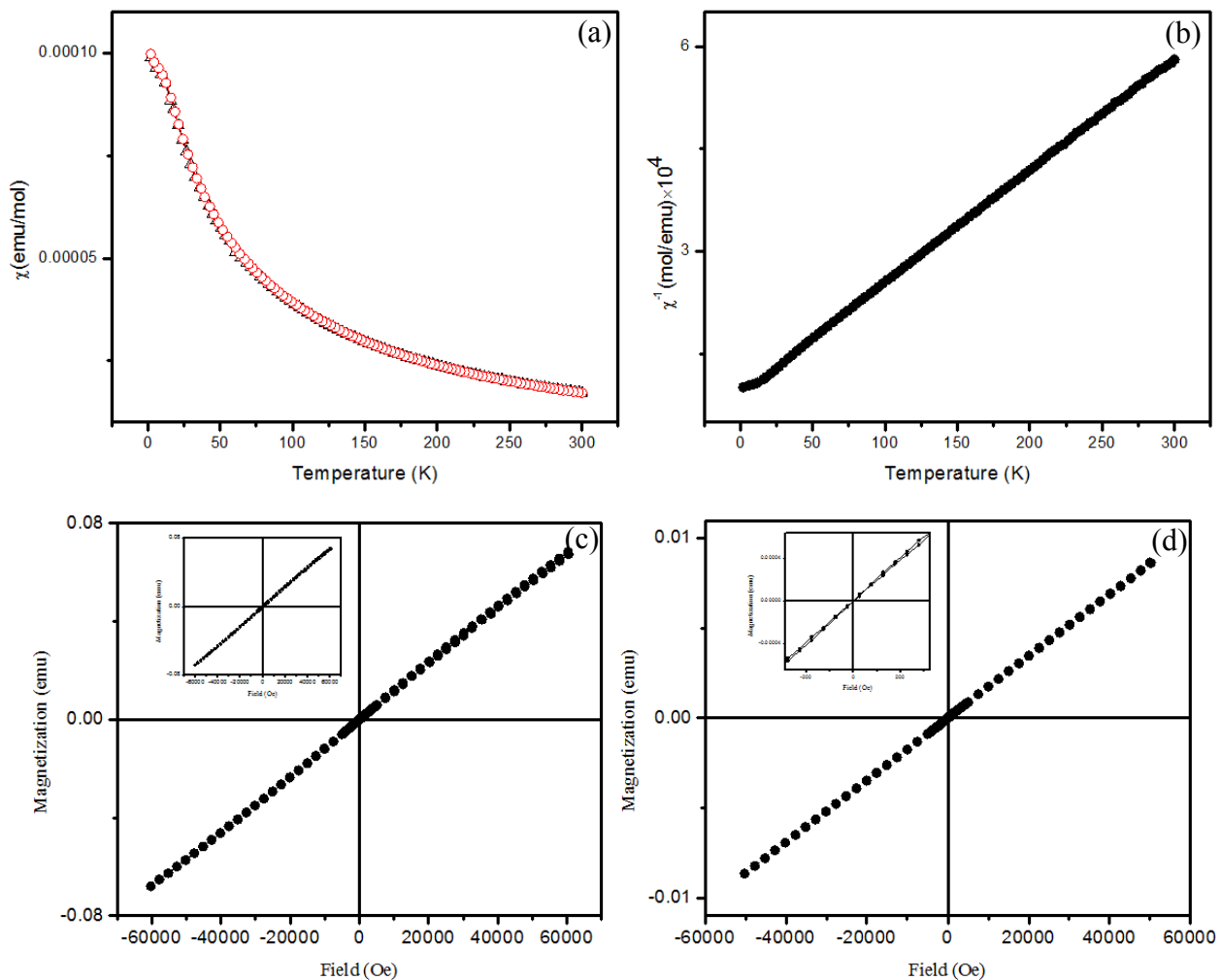
Fig. S8: (a) Temperature dependence of magnetic susceptibility and (b) reverse susceptibility of $CsPrNb_2O_7$. Measurments were carried out on cooling at a constant field of 100 Oe. (red circle shows FC and occluded black triangle shows ZFC). The magnetization vs the magnetic field for $CsPrNb_2O_7$ at (c) 2 K and (d) 300 K.
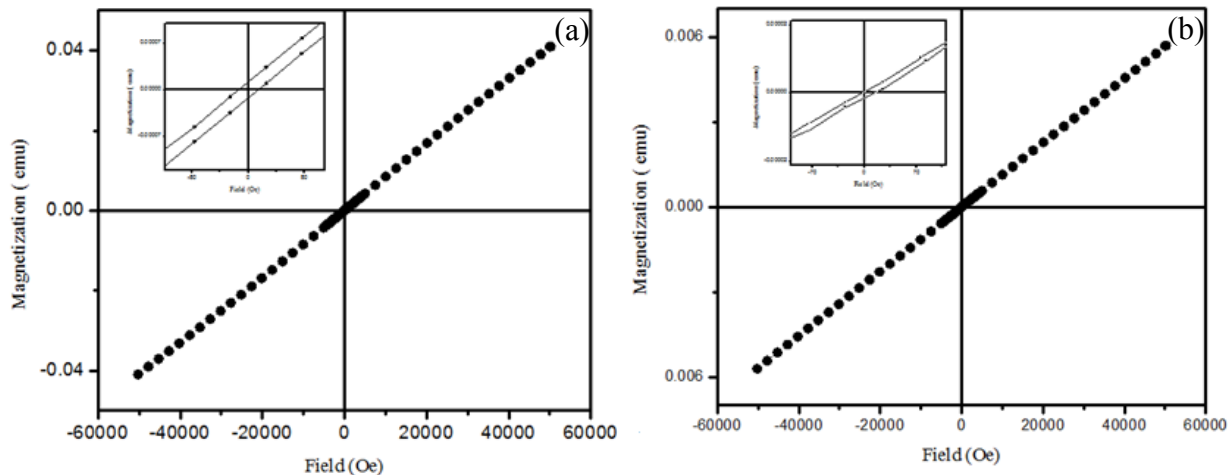
Fig. S9: The magnetization vs the magnetic field for $RbPrNb_2O_7$ at (a) 4K and (b) 300 K.
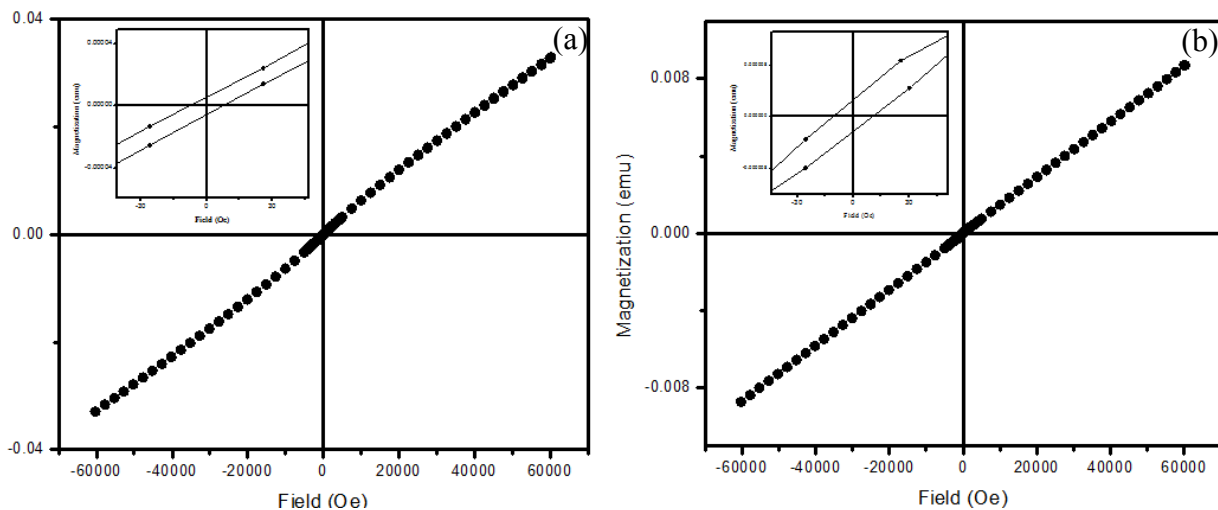

Fig. S10: The magnetization versus magnetic field for $(CuCl)PrNb_2O_7$ at (a) 2 K (inset shows slight hysteresis of 15 Oe) and (b) 300 K (inset, hysteresis of 40 Oe).
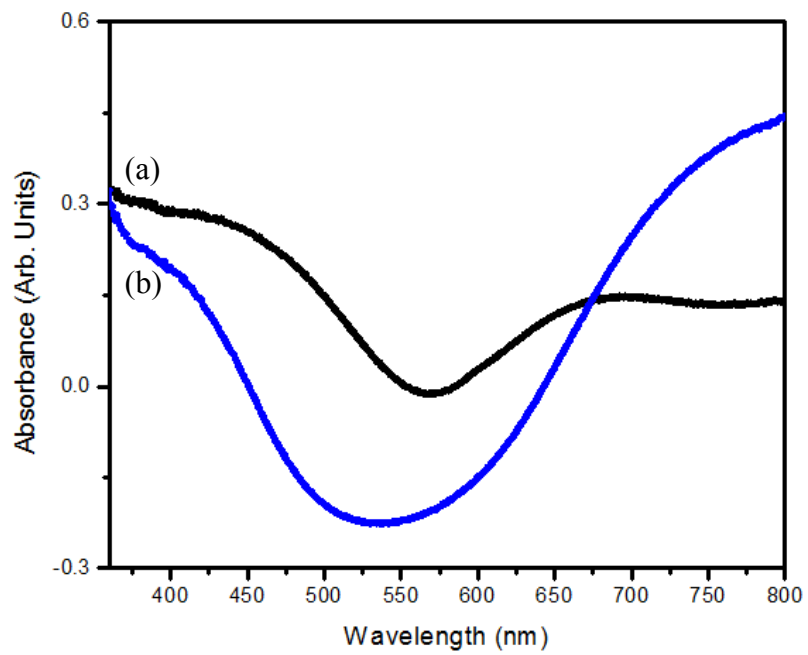
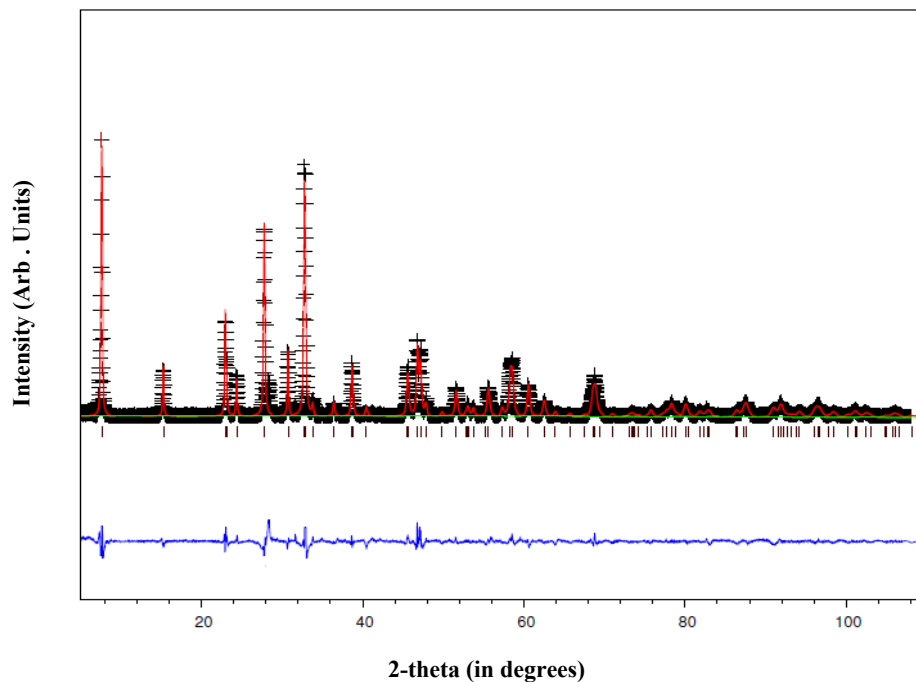**Fig. S11:** UV-Vis spectra of the (a) $CuCl_2 \cdot 2H_2O$ and (b) $(CuCl)PrNb_2O_7$.

Fig. S12: Refinement of $(CuCl)PrNb_2O_7$ in *P4/mmm* space group. Observed and calculated data for the Rietveld refinement of $(CuCl)PrNb_2O_7$. Observed data are indicated by crosses, calculated pattern by a red solid line, and the bottom blue curve is the difference plot. Peak positions are presented by black dot color. (Z=1; a=3.86421(9) Å, c=11.6782(2) Å V= 174.381(8) Å³; R_p=11.52% R_{wp}= 8.64% and χ^2= 6.172.) Orthorhombic model in *Pbam* space group was superior.

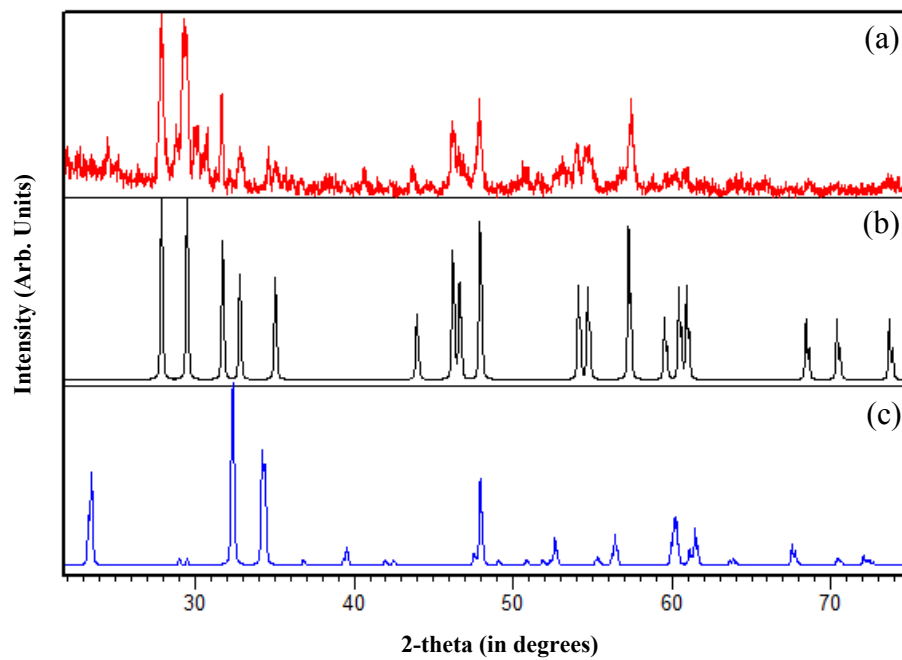**Fig. S13:** XRD of (CuCl)PrNb$_2$O$_7$ after TGA/DTA (a) at 1000 °C, (b) PrNbO$_4$ and (c) CuNbO$_3$.