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Electronic Supporting Information

Cadmium-Rare Earth Oxyborates $Cd_4ReO(BO_3)_3$ (Re = Y, Gd, Lu) : Congruently Melting Compounds with Large SHG Responses

Guohong Zou, Zuju Ma, Kechen Wu, and Ning Ye*

Fujian Institute of Research on the Structure of Matter,
Key Laboratory of Optoelectronic Materials Chemistry and Physics,
Chinese Academy of Sciences, Fuzhou, Fujian, 350002, P. R. China
Email: nye@fjirsm.ac.cn

Table S1. Atomic coordinates and equivalent isotropic displacement parameters for $Cd_4YO(BO_3)_3$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	$U_{eq}(Å^2)$
Cd(1)	0.3842(1)	0.1120(1)	0.2218(2)	0.009(1)
Cd(2)	1.0005(2)	-0.1786(1)	-0.4741(3)	0.013(1)
Y(1)	0.7380(2)	0	-0.1131(5)	0.003(1)
O(1)	0.5610(17)	0	0.3100(40)	0.003(3)
O(2)	0.9411(19)	0	-0.5240(40)	0.009(3)
O(3)	0.5262(18)	0.1792(8)	0.7720(40)	0.021(3)
O(4)	0.1993(12)	0.0764(7)	0.6500(30)	0.005(2)
O(5)	0.8226(13)	-0.1422(7)	-0.0370(30)	0.006(2)
O(6)	0.2110(20)	0.2305(9)	0.01860(40)	0.032(3)
B(1)	1.1120(30)	0	-0.4120(60)	0.006(4)
B(2)	0.6880(20)	0.1976(13)	0.9600(50)	0.011(3)

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for $Cd_4GdO(BO_3)_3$

atom	x	y	z	$U_{eq}(Å^2)$
Gd(1)	0.1150(2)	0.5000	0.1531(3)	0.019(1)
Cd(1)	0.4660(1)	0.3878(1)	-0.1851(2)	0.009(1)
Cd(2)	-0.1517(2)	0.6782(1)	0.5088(3)	0.011(1)
O(1)	0.2900(20)	0.5000	-0.2610(50)	0.010(3)
O(2)	-0.3485(16)	0.5774(8)	0.3930(30)	0.015(3)
O(3)	0.0200(15)	0.6474(9)	0.0730(40)	0.019(3)
O(4)	0.6400(20)	0.2699(9)	-0.1450(40)	0.032(4)
O(5)	0.3206(19)	0.3212(10)	0.2690(40)	0.031(4)
O(6)	-0.0960(20)	0.5000	0.5550(50)	0.028(5)
B(1)	-0.2660(30)	0.5000	0.4470(80)	0.008(4)
B(2)	0.1600(20)	0.3014(12)	0.0630(50)	0.006(3)

Table S3. Atomic coordinates and equivalent isotropic displacement parameters for $Cd_4LuO(BO_3)_3$.

atom	x	y	z	$U_{eq}(Å^2)$
Cd(1)	0.0624(2)	0.1121(1)	0.9295(3)	0.001(1)
Cd(2)	0.4479(2)	0.1779(1)	0.6265(4)	0.010(1)
Lu(1)	-0.2946(2)	0	1.2627(4)	0.015(1)
O(1)	-0.1190(30)	0	0.8480(80)	0.011(5)
O(2)	-0.0800(30)	0.1781(12)	1.3850(60)	0.015(4)
O(3)	0.2490(20)	0.0768(13)	0.5090(50)	0.010(4)
O(4)	-0.3770(20)	-0.1413(13)	1.1860(50)	0.013(4)
O(5)	0.2340(30)	0.2282(13)	0.9620(60)	0.021(4)
O(6)	-0.4860(50)	0	1.6840(100)	0.031(8)
B(1)	-0.2420(30)	0.1998(18)	1.1870(80)	0.006(5)
B(2)	0.3190(50)	0	0.5490(100)	0.002(6)

Table S4. Bond lengths (Å) for $Cd_4YO(BO_3)_3$.

Cd(1)-O(1)	2.249(8)	Y(1)-Y(1)#1	3.4706(4)
Cd(1)-O(3)	2.301(13)	Y(1)-Y(1)#2	3.4706(4)
Cd(1)-O(6)	2.316(15)	Y(1)-Cd(1)#5	3.6834(18)
Cd(1)-O(4)#1	2.323(9)	Y(1)-Cd(1)#6	3.7575(17)
Cd(1)-O(3)#1	2.336(14)	Y(1)-Cd(1)#1	3.7575(17)
Cd(1)-O(4)	2.337(10)	O(1)-Y(1)#2	2.238(13)
Cd(1)-Cd(1)#1	3.4706(4)	O(1)-Cd(1)#5	2.249(8)
Cd(1)-Cd(1)#2	3.4706(4)	O(2)-B(1)	1.35(3)
Cd(1)-Y(1)	3.6834(18)	O(2)-Y(1)#1	2.374(14)
Cd(1)-Y(1)#2	3.7575(17)	O(3)-B(2)	1.37(2)
Cd(2)-O(4)#3	2.249(11)	O(3)-Cd(1)#2	2.336(14)
Cd(2)-O(5)#1	2.276(10)	O(3)-Cd(2)#7	2.400(13)
Cd(2)-O(5)	2.323(10)	O(4)-B(1)#8	1.391(16)
Cd(2)-O(6)#3	2.357(16)	O(4)-Cd(2)#9	2.249(11)
Cd(2)-O(3)#4	2.400(13)	O(4)-Cd(1)#2	2.323(9)
Cd(2)-B(2)#4	2.744(19)	O(5)-B(2)#6	1.39(2)
Cd(2)-Cd(2)#1	3.4706(4)	O(5)-Cd(2)#2	2.276(10)
Cd(2)-Cd(2)#2	3.4706(4)	O(6)-B(2)#10	1.37(2)
Y(1)-O(1)	2.206(14)	O(6)-Cd(2)#9	2.357(16)
Y(1)-O(1)#1	2.238(13)	B(1)-O(4)#3	1.391(16)
Y(1)-O(2)	2.336(14)	B(1)-O(4)#11	1.391(16)
Y(1)-O(5)#5	2.346(11)	B(2)-O(6)#12	1.37(2)
Y(1)-O(5)	2.346(11)	B(2)-O(5)#13	1.39(2)
Y(1)-O(2)#2	2.374(14)	B(2)-Cd(2)#7	2.744(19)

Symmetry transformations used to generate equivalent atoms:
#1 x,y,z-1 #2 x,y,z+1 #3 x+1,-y,z-1
#4 x+1/2,y-1/2,z-1 #5 x,-y,z #6 x,-y,z-1
#7 x-1/2,y+1/2,z+1 #8 x-1,y,z+1 #9 x-1,-y,z+1
#10 x-1/2,-y+1/2,z-1 #11 x+1,y,z-1
#12 x+1/2,-y+1/2,z+1 #13 x,-y,z+1

Table S5. Bond lengths (Å) for $Cd_4GdO(BO_3)_3$.

Gd(1)-O(1)	2.182(15)	Cd(2)-O(3)	2.275(12)
Gd(1)-O(1)#1	2.263(17)	Cd(2)-O(4)#7	2.374(13)
Gd(1)-O(6)	2.380(19)	Cd(2)-O(5)#8	2.404(15)
Gd(1)-O(3)#2	2.447(15)	Cd(2)-B(2)#8	2.765(18)
Gd(1)-O(3)	2.447(15)	O(1)-Cd(1)#2	2.249(10)
Gd(1)-O(6)#3	2.444(18)	O(1)-Gd(1)#3	2.263(17)
Gd(1)-Gd(1)#1	3.494(4)	O(2)-B(1)	1.386(18)
Gd(1)-Gd(1)#3	3.494(4)	O(2)-Cd(1)#7	2.333(11)
Gd(1)-Cd(1)#2	3.685(3)	O(2)-Cd(1)#9	2.349(12)
Gd(1)-Cd(1)	3.685(3)	O(3)-B(2)#2	1.38(2)
Gd(1)-Cd(1)#4	3.748(3)	O(3)-Cd(2)#3	2.247(14)
Gd(1)-Cd(1)#1	3.748(3)	O(4)-B(2)#10	1.33(2)
Cd(1)-O(1)	2.249(10)	O(4)-Cd(2)#5	2.374(13)
Cd(1)-O(5)#3	2.303(13)	O(5)-B(2)	1.39(2)
Cd(1)-O(4)	2.311(13)	O(5)-Cd(1)#1	2.303(13)
Cd(1)-O(2)#5	2.333(11)	O(5)-Cd(2)#11	2.404(15)
Cd(1)-O(2)#6	2.349(12)	O(6)-B(1)	1.34(4)
Cd(1)-O(5)	2.373(13)	O(6)-Gd(1)#1	2.444(18)
Cd(1)-Gd(1)#3	3.748(3)	B(1)-O(2)#2	1.386(18)
Cd(2)-O(2)	2.222(13)	B(2)-O(4)#12	1.33(2)
Cd(2)-O(3)#1	2.247(14)	B(2)-O(3)#2	1.38(2)

Symmetry transformations used to generate equivalent atoms:
#1 x,y,z+1 #2 x,-y+1,z #3 x,y,z-1
#4 x,-y+1,z+1 #5 x+1,-y+1,z-1 #6 x+1,-y+1,z
#7 x-1,-y+1,z+1 #8 x-1/2,y+1/2,z
#9 x-1,-y+1,z #10 x+1/2,-y+1/2,z
#11 x+1/2,y-1/2,z #12 x-1/2,-y+1/2,z

Table S6. Bond lengths (Å) for $Cd_4LuO(BO_3)_3$.

Cd(1)-O(2)#1	2.27(2)	Lu(2)-O(4)#6	2.33(2)
Cd(1)-O(1)	2.268(17)	Lu(2)-Lu(2)#1	3.436(2)
Cd(1)-O(5)	2.27(2)	Lu(2)-Lu(2)#2	3.436(2)
Cd(1)-O(3)	2.309(16)	Lu(2)-Cd(1)#6	3.686(2)
Cd(1)-O(2)	2.33(2)	O(1)-Lu(2)#1	2.24(3)
Cd(1)-O(3)#2	2.334(18)	O(1)-Cd(1)#6	2.268(16)
Cd(1)-Cd(1)#2	3.436(2)	O(2)-B(1)	1.39(3)
Cd(1)-Cd(1)#1	3.436(2)	O(2)-Cd(1)#2	2.27(2)
Cd(1)-Lu(2)	3.686(2)	O(2)-Cd(2)#7	2.416(19)
Cd(2)-O(3)	2.23(2)	O(3)-B(2)	1.33(3)
Cd(2)-O(4)#3	2.24(2)	O(3)-Cd(1)#1	2.334(18)
Cd(2)-O(4)#4	2.297(18)	O(4)-B(1)#6	1.42(3)
Cd(2)-O(5)	2.349(19)	O(4)-Cd(2)#8	2.24(2)
Cd(2)-O(2)#5	2.416(19)	O(4)-Cd(2)#9	2.297(18)
Cd(2)-B(1)#5	2.74(3)	O(5)-B(1)#10	1.37(3)
Cd(2)-Cd(2)#1	3.436(2)	O(6)-B(2)#11	1.54(5)
Cd(2)-Cd(2)#2	3.436(2)	O(6)-Lu(2)#2	2.28(4)
Lu(2)-O(1)	2.16(2)	B(1)-O(5)#12	1.37(3)
Lu(2)-O(1)#2	2.24(3)	B(1)-O(4)#6	1.42(3)
Lu(2)-O(6)	2.27(3)	B(1)-Cd(2)#7	2.74(3)
Lu(2)-O(6)#1	2.28(4)	B(2)-O(3)#6	1.33(3)
Lu(2)-O(4)	2.33(2)	B(2)-O(6)#13	1.54(5)

Symmetry transformations used to generate equivalent atoms:
#1 x,y,z-1 #2 x,y,z+1 #3 x+1,-y,z
#4 x+1,-y,z-1 #5 x+1/2,-y+1/2,z-1
#6 x,-y,z #7 x-1/2,-y+1/2,z+1 #8 x-1,-y,z
#9 x-1,-y,z+1 #10 x+1/2,-y+1/2,z
#11 x-1,y,z+1 #12 x-1/2,-y+1/2,z
#13 x+1,y,z-1

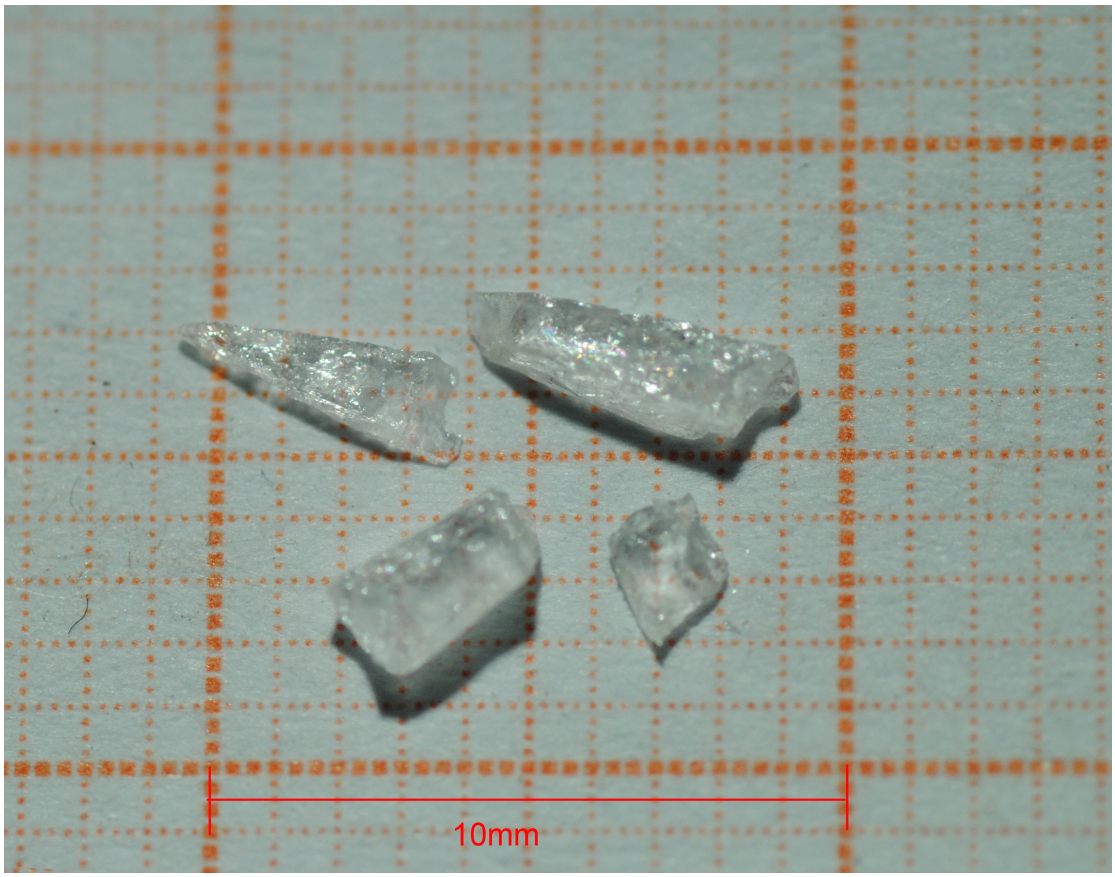

Figure S1. Photograph of $Cd_4ReO(BO_3)_3$ (Re=Y, Gd, Lu) crystals

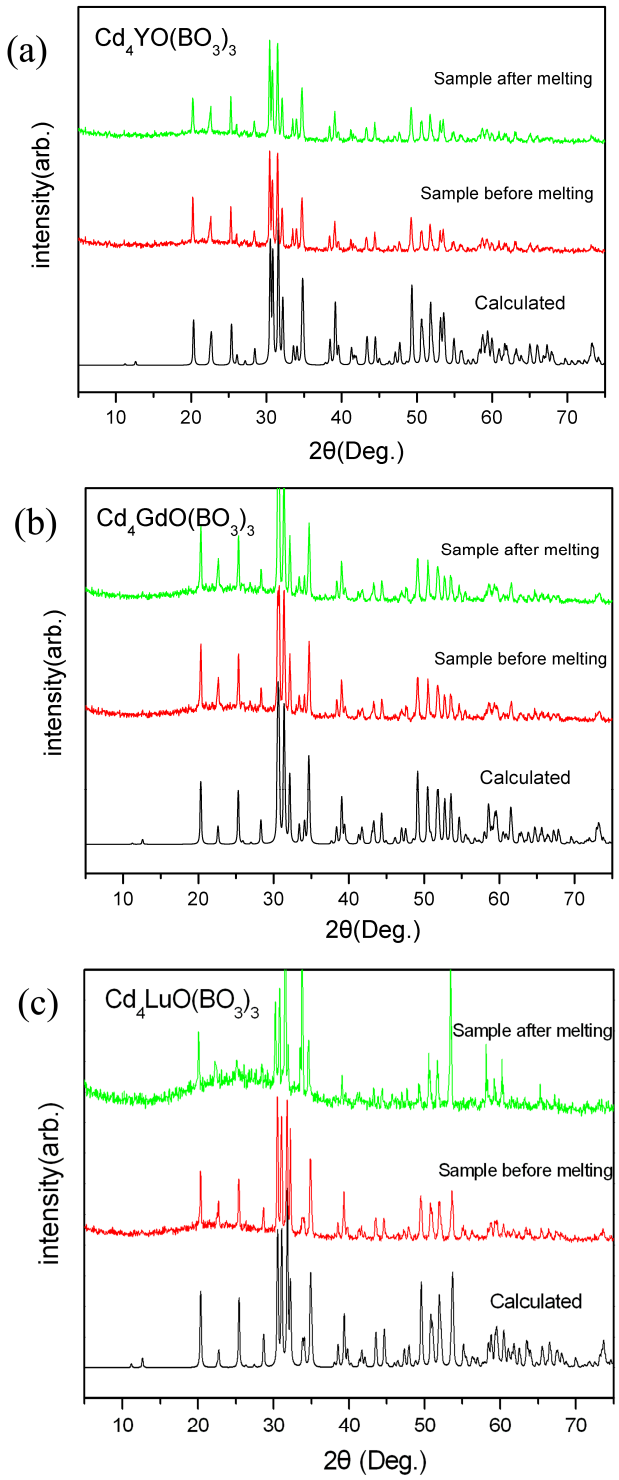

Figure S2. Experimental and calculated XRD patterns for $Cd_4YO(BO_3)_3$ (a), $Cd_4GdO(BO_3)_3$ (b), $Cd_4LuO(BO_3)_3$ (c). The black curves are the calculated ones, the red are the patterns of samples before melting and the green are the patterns of samples after melting.

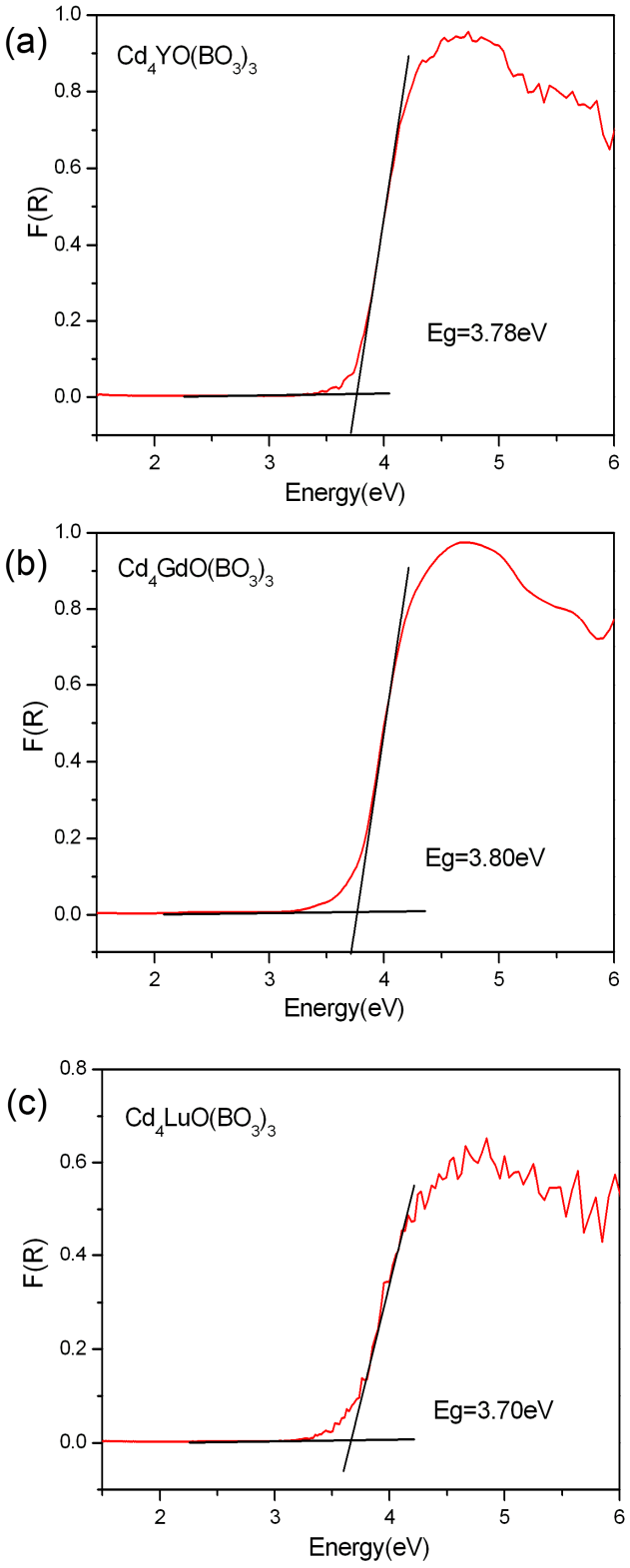

Figure S3. Optical diffuse reflectance spectra for $Cd_4YO(BO_3)_3$ (a), $Cd_4GdO(BO_3)_3$ (b), and $Cd_4LuO(BO_3)_3$ (c).

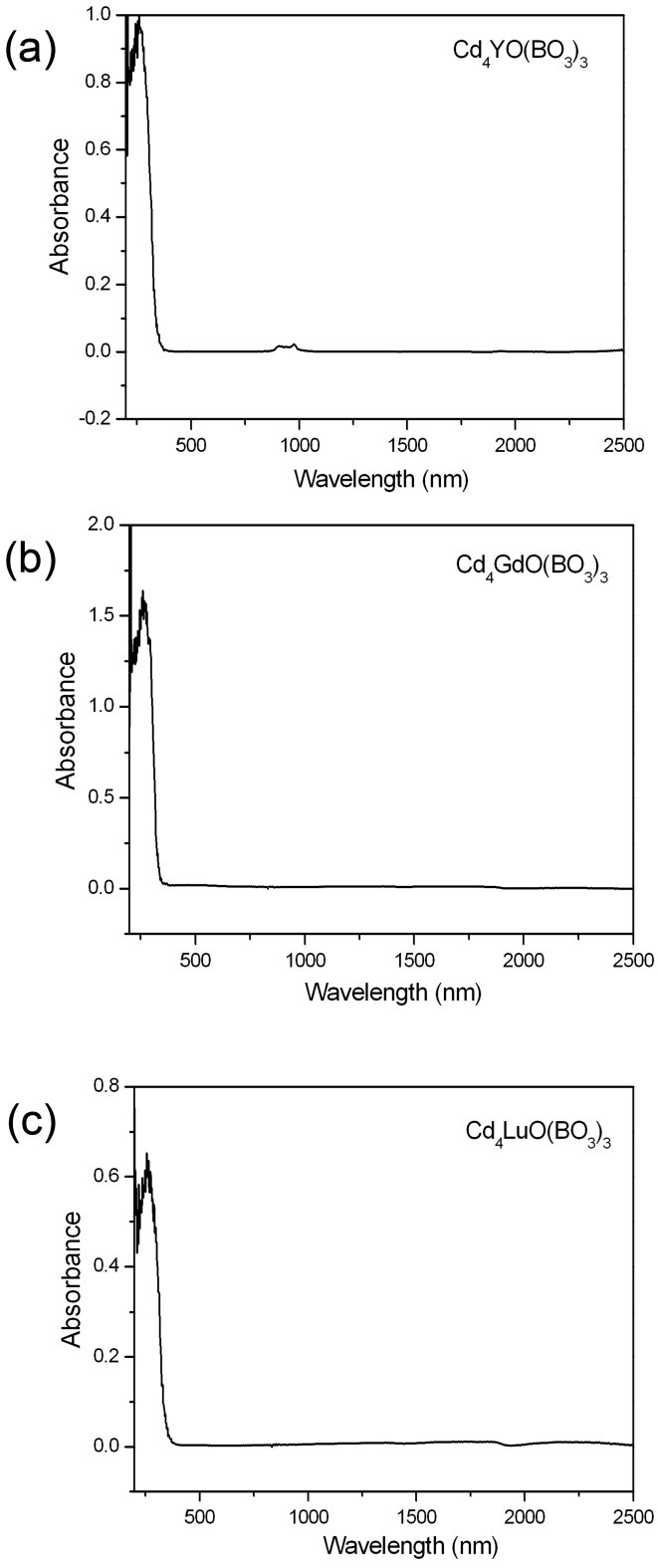

Figure S4. UV absorption spectra of $Cd_4YO(BO_3)_3$ (a), $Cd_4GdO(BO_3)_3$ (b) and $Cd_4LuO(BO_3)_3$ (c).

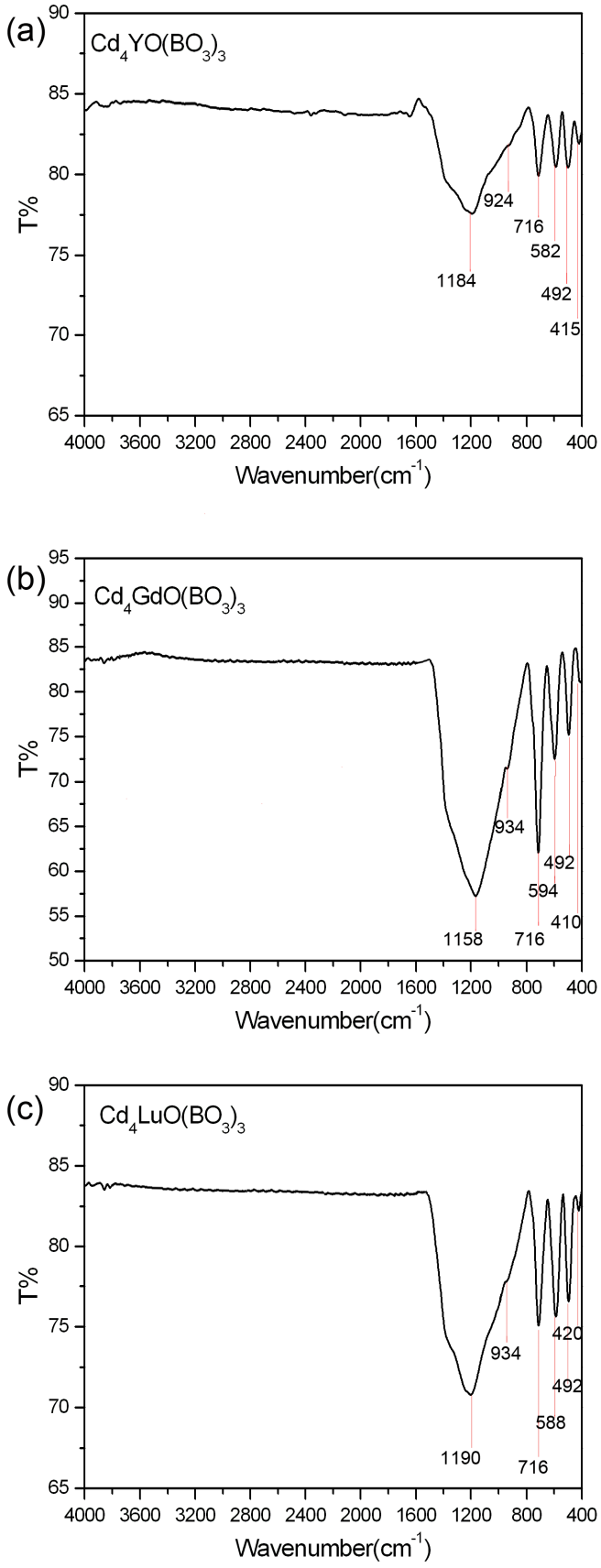

Figure S5. IR spectra for $Cd_4YO(BO_3)_3$ (a),$Cd_4GdO(BO_3)_3$ (b) and $Cd_4LuO(BO_3)_3$ (c).

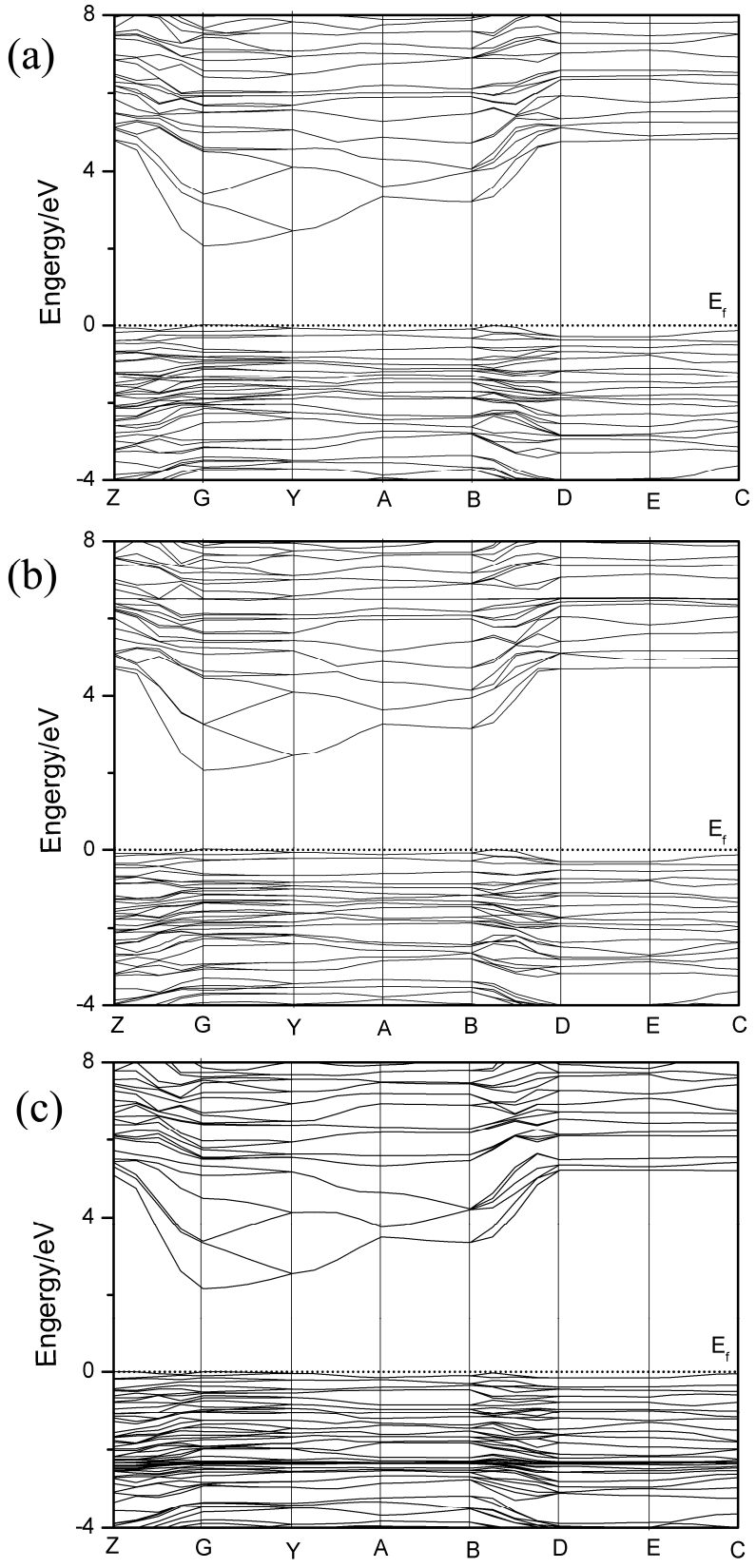

Figure S6. Band structures for $Cd_4YO(BO_3)_3$ (a), $Cd_4GdO(BO_3)_3$ (b) and $Cd_4LuO(BO_3)_3$ (c).

Optical Properties Calculations.

In calculation of the static $\chi^{(2)}$ coefficients, the so-called length-gauge formalism derived by Aversa and Sipe[1,2] and modified by Rashkeev *et al* is adopted. The imaginary part of the static second-order optical susceptibility can be expressed as:

$$\chi^{abc} = \frac{e^3}{\hbar^2\Omega}\sum_{nml,k}\frac{r^a_{nm}(r^b_{ml}r^c_{ln}+r^c_{ml}r^b_{ln})}{2\omega_{nm}\omega_{ml}\omega_{ln}}[\omega_n f_{ml}+\omega_m f_{ln}+\omega_l f_{nm}] + \frac{ie^3}{4\hbar^2\Omega}\sum_{nm,k}\frac{f_{nm}}{\omega^2_{mn}}[r^a_{nm}(r^b_{mn;c}+r^c_{mn;b})+r^b_{nm}(r^a_{mn;c}+r^c_{mn;a})+r^c_{nm}(r^a_{mn;b}+r^b_{mn;a})] \quad (1)$$

where r is the position operator, m and n are the valence and conduction bands, respectively, $\hbar\omega_{nm} = \hbar\omega_n - \hbar\omega_m$ is the energy difference for the bands m and n. In order to better understand the contribution of different states to the susceptibility, the value of m and n could be tuned in our program to include some special bands.

Complete reference.

reference 1: C. Aversa, J. E. Sipe, *Phys. Rev. B*, 1995, **52**, 14636.

reference 2: S. N. Rashkeev, W. R. L. Lambrecht, B. Segall, *Phys. Rev. B*, 1998, **57**, 3905.