(†ESI) Electronic Supplementary Information for

Optical and dielectric properties of Sillén $Bi_2Y_{1-x}M_xO_4Cl$ (M = Cu, Cd)

Meena Sheokand[§], Shivangi Rao[§], Neetu Yadav and Rajamani Nagarajan*

Materials Chemistry Group, Department of Chemistry

University of Delhi, Delhi-110007 INDIA

*Corresponding Author: rnagarajan@chemistry.du.ac.in

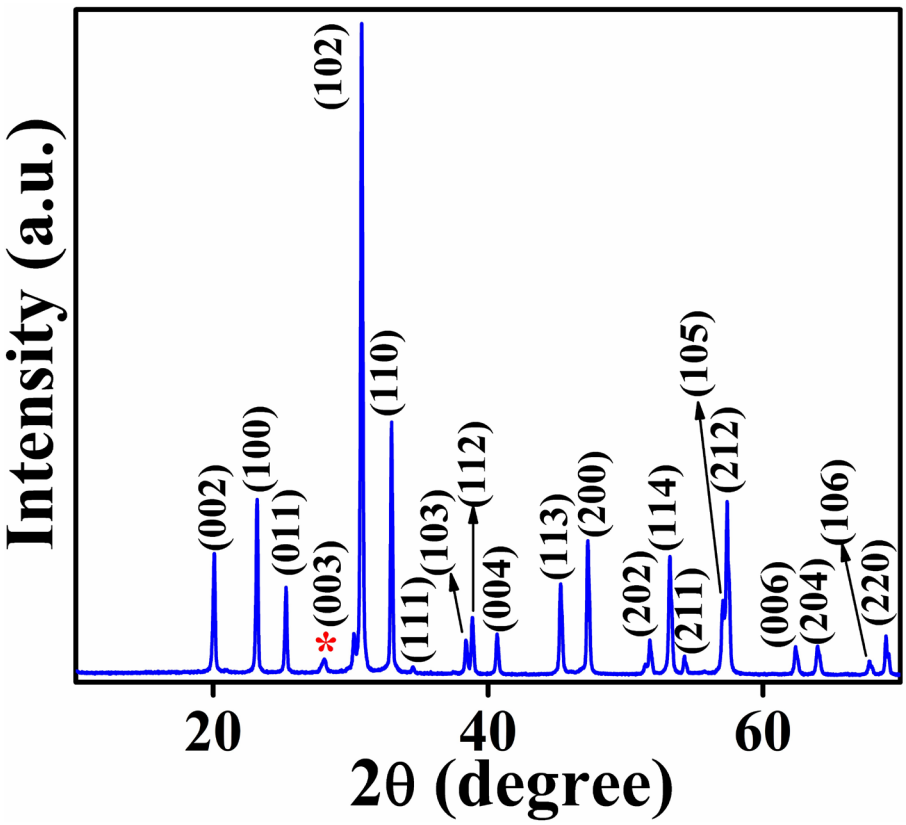

Fig. S1 PXRD pattern of $Bi_2Y_{0.70}Cu_{0.30}O_4Cl$ sample. The diffraction peak marked with '*' corresponds to β-Bi_2O_3 (ICSD No: 98-002-7157).

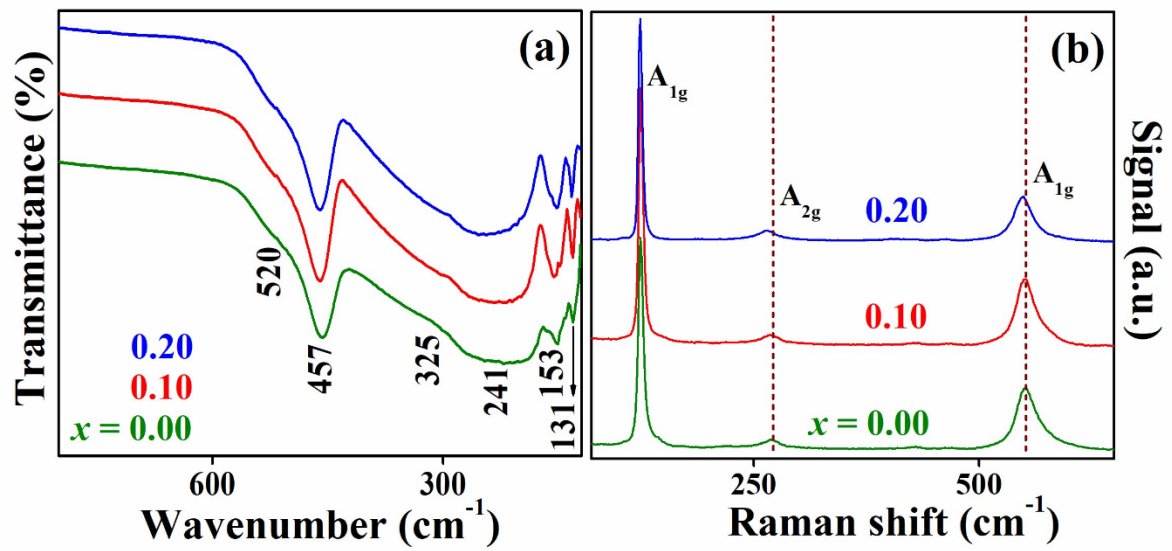

Fig. S2(a) FTIR, and (b) Micro-Raman spectra of $Bi_2Y_{1-x}Cu_xO_4Cl$ (x = 0.00, 0.10, and 0.20) samples.

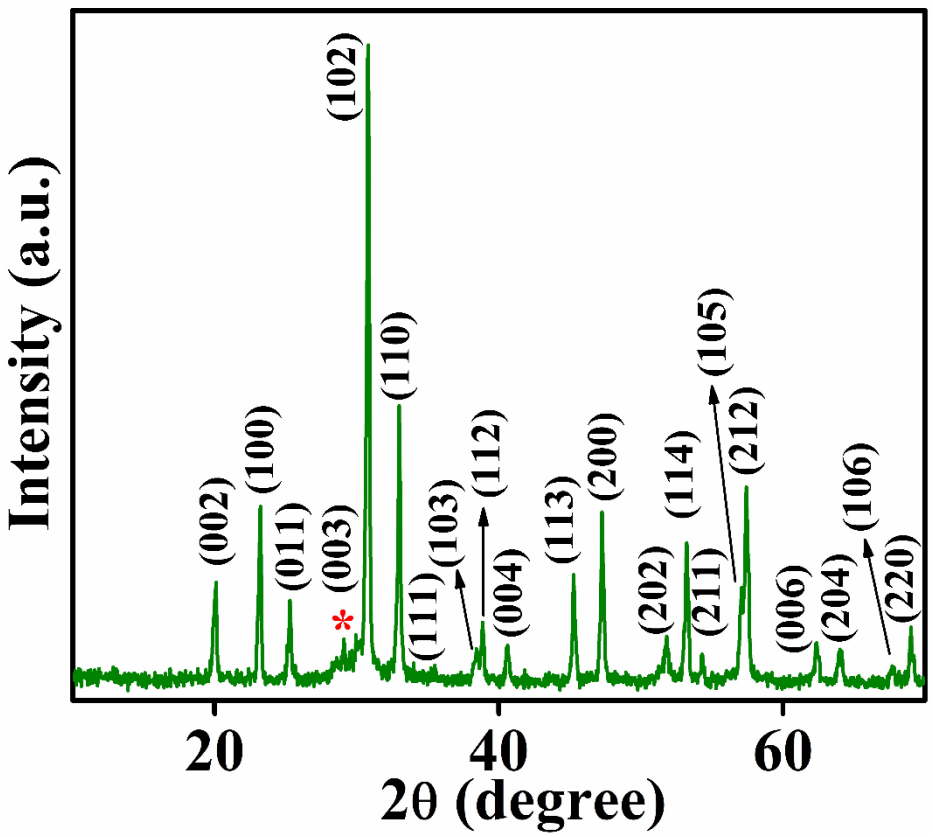

Fig. S3 PXRD pattern of $Bi_2Y_{0.70}Cd_{0.30}O_4Cl$ sample. The diffraction peak marked with '*' corresponds to β-Bi_2O_3 (ICSD No: 98-0041764).

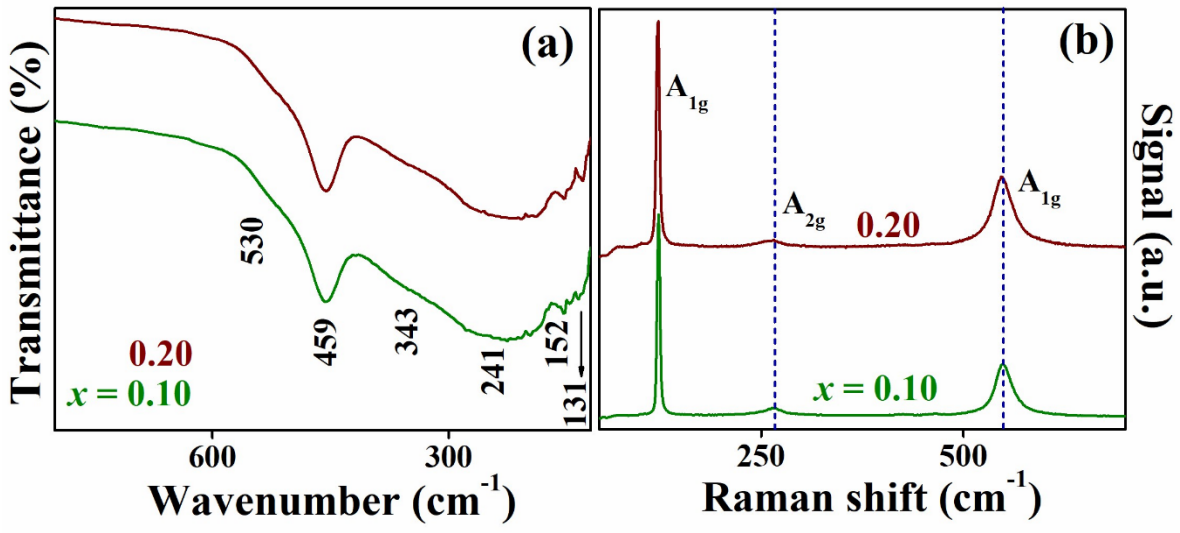

Fig. S4 (a) FTIR spectra, and (b) Micro-Raman of $Bi_2Y_{1-x}Cd_xO_4Cl$ (x = 0.10 and 0.20) samples.

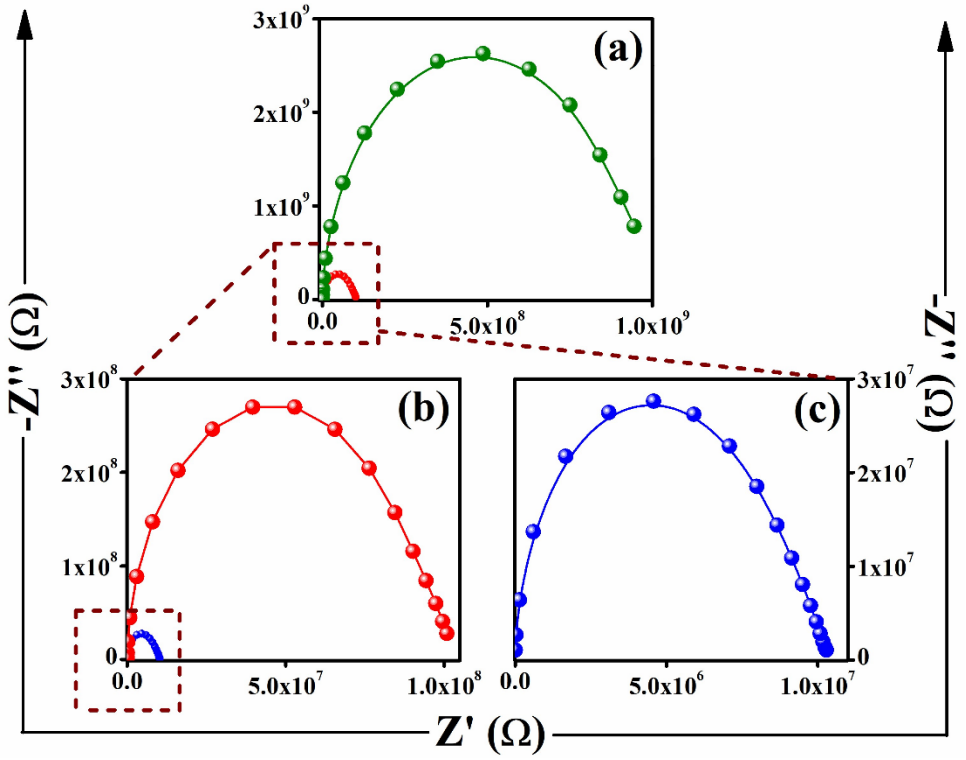

Fig. S5 Complex impedance variation plots as a function of temperature for the $Bi_2Y_{0.80}Cu_{0.20}O_4Cl$ sample recorded at different frequencies: (a) 1 Hz, (b) 10 Hz, and (c) 100 Hz.

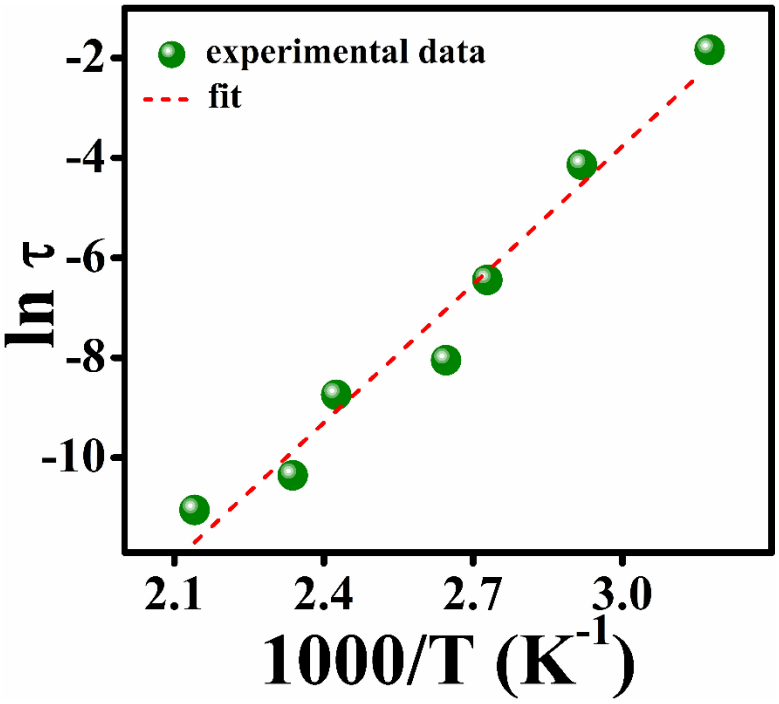

Fig. S6 Plot of ln τ vs. 1000/T for $Bi_2Y_{0.80}Cd_{0.20}O_4Cl$ sample.

Table S1 Details dealing with the amounts of reactants used to synthesize Cu- and Cd-substituted Bi_2YO_4Cl samples.

$Bi_2Y_{1-x}Cu_xO_4Cl$			
Composition	**$YCl_3.6H_2O$ (mmol)**	**$Cu(NO_3)_2$ (mmol)**	**Citric Acid (mmol)**
$x = 0.00$	0.3033 g (1.00)	--	0.5187 g (2.70)
$x = 0.10$	0.2730 g (0.90)	0.0241 g (0.10)	0.5129 g (2.67)
$x = 0.20$	0.2427 g (0.80)	0.0483 g (0.20)	0.5073 g (2.64)
$x = 0.30$	0.2123 g (0.70)	0.0724 g (0.30)	0.5013 g (2.61)
$Bi_2Y_{1-x}Cd_xO_4Cl$			
Composition	**$YCl_3.6H_2O$ (mmol)**	**$CdCO_3$ (mmol)**	**Citric Acid (mmol)**
$x = 0.10$	0.2730 g (0.90)	0.0172 g (0.10)	0.5129 g (2.67)
$x = 0.20$	0.2427 g (0.80)	0.0344 g (0.20)	0.5073 g (2.64)
$x = 0.30$	0.2123 g (0.70)	0.0517 g (0.3)	0.5013 g (2.61)
One mmol (0.4659 g) of Bi_2O_3 was reacted in all the above reactions. $Bi_2Y_{1-x}Cu_xO_4Cl$ and $Bi_2Y_{1-x}Cd_xO_4Cl$ compositions were calcined at 800 °C for three hours in air.			

Table S2 Interplanar distances (*d*) of the Bi_2YO_4Cl and $Bi_2Y_{0.80}M_{0.20}O_4Cl$ (M = Cu and Cd) samples.

Composition	$d_{(002)}$ (Å)	$d_{(004)}$ (Å)	$d_{(101)}$ (Å)	$d_{(102)}$ (Å)
Bi_2YO_4Cl	4.3823	3.8044	2.2119	1.9163
$Bi_2Y_{0.80}Cu_{0.20}O_4Cl$	4.4075	3.8299	2.2163	1.9204
$Bi_2Y_{0.80}Cd_{0.20}O_4Cl$	4.4556	3.8603	2.2268	1.9270

Table S3 Selected bond distances of Bi_2YO_4Cl, $Bi_2Y_{0.80}Cu_{0.20}O_4Cl$, and $Bi_2Y_{0.80}Cd_{0.20}O_4Cl$ samples obtained from the Rietveld refinements.

Sample	**Interatomic distances (Å)**		
	Y–O	**Bi–O**	**Bi–Cl**
Bi_2YO_4Cl	8 × 2.3662(3)	4 × 2.2236(2)	4 × 3.3483(3)
$Bi_2Y_{0.80}Cu_{0.20}O_4Cl$	8 × 2.3554(2)	4 × 2.2245(3)	4 × 2.3494(3)
$Bi_2Y_{0.80}Cd_{0.20}O_4Cl$	8 × 2.3729(2)	4 × 2.2251(2)	4 × 3.3501(2)

Table S4 Summary of binding energies (B.E.) and spin-orbit splitting energies (ΔE) of constituents in $Bi_2Y_{0.80}M_{0.20}O_2Cl$ (M = Cu and Cd) after deconvoluting their core-level XPS.

Constituent elements and B.E. (eV)		$Bi_2Y_{0.80}Cu_{0.20}O_4Cl$	$Bi_2Y_{0.80}Cd_{0.20}O_4Cl$
Bi(III) 4*f*	$4f_{7/2}$	158.4	158.8
	$4f_{5/2}$	163.8	164.1
Bi(V) 4*f*	$4f_{7/2}$	159.3	160.2
	$4f_{5/2}$	164.5	165.5
	ΔE	5.5	5.3
Y	$3p_{3/2}$	300.1	299.2
	$3p_{1/2}$	312.2	311.9
	ΔE	12.1	12.7
Cu 2*p*	$2p_{3/2}$	931.9	-
	$2p_{1/2}$	951.6	-
	s	939.7	-
	ΔE	19.7	-
Cd 3*d*	$3d_{5/2}$	-	404.9
	$3d_{3/2}$	-	411.7
	ΔE	-	6.8
O 1*s*	M–O	528	529.5
	O–H ads.	529.6	531.4
Cl 2*p*	$2p_{3/2}$	198.2	197 .6
	$2p_{1/2}$	199.8	199.3