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Growth, Optical, Electrical, Dielectric Properties and V-I Characteristics of Cobalt mixed Cadmium Oxalate Crystal

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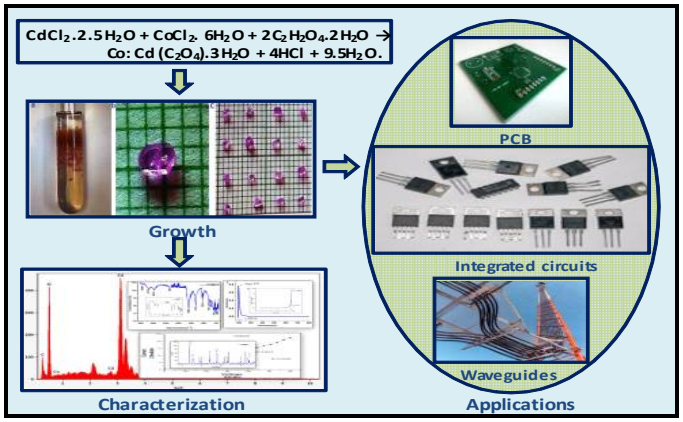
ABSTRACT

Cobalt mixed Cadmium oxalate crystal (COMCO) was grown by gel diffusion reaction method. Optimum condition for crystal growth was established by varying gel parameters and chemical composition of reactants. Occupation of Co^{2+} ions in the vacancies of parental Cd^{2+}ions caused the change in morphology of intrinsic Cadmium oxalate crystal (ICO). This resulted in the formation of pink colored, hard and transparent COMCO crystals. Elemental analysis using energy dispersive X-ray spectroscopy (EDX) confirmed the presence of Cd^{2+} and Co^{2+} ions in the lattice of COMCO crystal. Thermo-gravimetric analysis (TGA) of the crystal elucidated the thermal stability up to 950°C. Fourier transform infrared (FT-IR) spectral studies identified water of crystallization, carboxyl and metal–oxygen bonding. Powder X-ray diffraction (P-XRD) studies showed well defined peaks for different 2θ values and established high crystalline nature of COMCO crystal. UV-Visible spectroscopic studies measured the band gap energy of the crystal. Electrical conductivity measurements showed moderate conductivity in COMCO crystal. Dielectric studies of the mixed crystal measured capacitance and ϵ_r. V-I characteristics emphasized linear variation and analyzed leakage resistance of COMCO crystal.

Graphical Abstract



Keywords: Mixed crystal, spectra, optical, conductivity, dielectric, characteristics

INTRODUCTION

In this day and age production of high quality crystals is essential in the field of material science [1]. Growth of crystals in low specific gravity, keeping unidirectional transport of ions and a controlled growth in porous network are the essential conditions for optimizing growth process. These conditions of crystallization are most promisingly attainable by adopting gel method [2-4]. Crystal growth in gel is an inexpensive and simple technique and generally used to grow water insoluble crystals. Growth of pure and bulk crystals is the additional feature of gel method [6].

Studies on Oxalate crystals show wide spectrum for the researchers and require deep involvement of both chemist and solid state physicist [5-7]. Review of literature showed the adoption of gel method for growing alkaline earth metal oxalates and transition metal oxalate crystals due to their low solubility in water. Most rare earth oxalates and molybdates are used as electro and acousto optical devices [4]. Few Oxalate crystals possess insulating behavior with high dielectric constants and used as optoelectronic devices, in printed circuit boards, in capacitor industries and high temperature electronics applications [5].

Recently we have published detailed studies of Cr^{3+}, Ca^{2+} and Sr^{2+} ions mixed Cadmium oxalate crystals with silica hydro gel as growth media [5]. Our present study mainly focused on growing Co^{2+} mixed Cadmium oxalate crystals (COMCO) in silica gel adopting single test tube gel diffusion technique. The grown COMCO crystals were characterized and their optical, electrical, dielectric properties and V-I characteristics were discussed.

MATERIALS AND METHODS

Mixed Cadmium oxalate crystals can be grown using gel diffusion reaction method. Reaction method consists of U - tube, Ψ – tube, double tube and single tube gel diffusion techniques [6, 7]. All these methods adopt common chemical reaction expressed as

$$AX + BY \longrightarrow AY + BX$$

Where A, B are cations and X, Y are the anions [4]. Various gels used by the researchers are silica, agar, gelatin, soft soaps, pectin, oleates and stearates [8, 9] to grow crystals. COMCO crystals were grown using single test tube gel diffusion technique with silica hydro gel as growth media. Chemicals used for growing COMCO crystals were Sodium meta silicate (Na_2SiO_3), Oxalic acid ($C_2H_2O_4.2H_2O$), Cobalt chloride ($CoCl_2.6H_2O$) and Cadmium chloride ($CdCl_2.2.5H_2O$) of AR grade.

Growth of Co^{+2} mixed cadmium oxalate crystals: Silica hydro gel was prepared by mixing oxalic acid (0.5 M) with Na_2SiO_3 (SMS) solution of specific gravity 1.04. SMS solution is added drop-wise to a beaker containing 0.5 M oxalic acid in the ratio 5:4 to attain gel pH of 4.25. Continuous stirring is needed to avoid excessive local ion concentration, which may cause premature local gelling and make final solution inhomogeneous [6-9]. The solution is transferred to several glass tubes. The gel found to set in 30 min to several days, depending upon its pH and the environmental temperature. Once the gel is set, mixture solution of aqueous cadmium chloride (0.5 M) and Cobalt chloride (0.5 M) in the ratio 4:2 was carefully poured over the gel with the help of a pipette to overcome surface damage and breakage of the gel [9-11]. The Cd^{2+} ions diffuse slowly through narrow pores of the gel and react with the oxalate ions to form nucleation centers. Co^{2+} ions also diffuse through the gel and occupy the vacancies of Cd^{2+} ions resulted in the growth of COMCO mixed crystals. The following reaction scheme is involved in the formation of mixed crystals.

$$CdCl_2 2.5H_2O + CoCl_2\ 6H_2O + 2\ C_2H_2O_4 2H_2O \rightarrow Co{:}\ Cd(C_2O_4)3H_2O + 4HCl + 9.5H_2O.$$

The diffusion of cations into the gel continued for few days and gets saturated. For COMCO crystals, growth accomplished till 20 days and attained the size of $(l \times b \times h)$ $=3.8\times3\times2.5 (mm^3)$. The mixed crystals were extracted from the gel and subjected to further characterization processes. Optimum condition for growth of the mixed crystal is recorded in table 1. Figure 1 illustrates the growth and extraction of COMCO crystals.

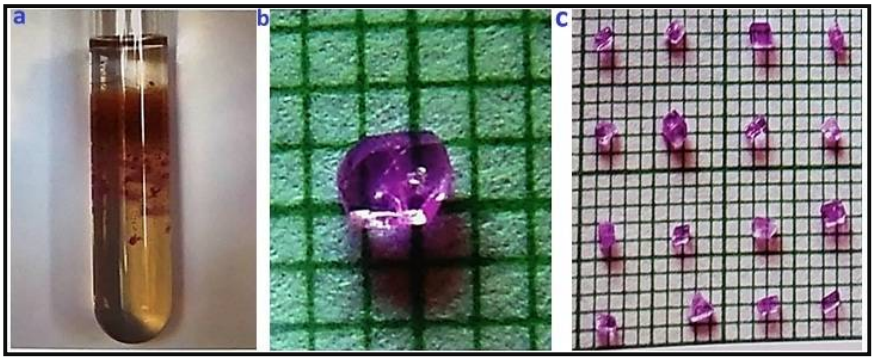


Figure 1. (a) Growth of COMCO crystals, (b) and (c) extracted COMCO crystals.

Table 1. Optimum growth aspects of COMCO crystals.

Parameter	COMCO crystal
Sp. gravity	1.0375
Gel pH	04.25
SMS: Oxalic acid	5:4
Mixture ratio	4:2
Growth period	20 days
Chemical formula	Co: $Cd(C_2O_4)3H_2O$
Size; $l \times b \times h$ (mm^3)	3.8×3×2.5
Colour	Pink
Physical appearance	Hard, transparent

Characterization: Elemental analysis, presence of Cd^{2+} ions and Co^{2+} ions in the sample crystals were determined using energy dispersive X-ray spectrum (EDX). The EDX spectrum was performed using the instrument CARL ZIESS FESEM attached with EDS [12-14]. Thermal stability and decomposition behavior of the COMCO crystals were measured using Perkin Elmer Pyris TGA instrument [15-18]. Temperature was recorded at heating rate of 10°C min^{-1} under N_2 atmosphere. FTIR spectra of the mixed crystal were recorded per wavelength range of 450 to 4000 cm^{-1} using IR Prestige-21 SHIMADZU instrument calibrated in attenuated total reflectance [19]. Structural characterization of mixed oxalate crystals was performed using powder X-ray diffractometer Minflex 600 Rigaku having X-ray Cu-K alpha radiation of wavelength 1.54 Å with a scan speed of 1°C min^{-1}. Forbidden energy gap associated with the COMCO crystals was determined using UV-Vis spectrophotometer (UV-1800 SCHIMADZU) for the spectral range of 200-1200 nm followed by tauc plot. Further, electrical conductivity measurements and V-I characteristics of the mixed crystals were carried out in the range 0-1000 mMho cm^{-1} using Mittal instruments and Keithley source measuring instrument 2450 series respectively. Dielectric studies of mixed crystals were performed using Mittal instruments 2151/T-7C calibrated to generate sine wave for frequency 253.88 KHz in DSO.

RESULTS AND DISCUSSION

Quantitative and elemental analysis of COMCO crystals were performed using EDAX measurements. Figure 2 provide the EDAX spectra, which exhibits prominent peaks of Cd, Co, O and C elements associated in the mixed crystal. This confirms the formation of COMCO crystal. The weight [%] and

atomic [%] constituent elements of mixed crystal were recorded in table 2. Figure 3 illuminates the electron image of COMCO crystal.

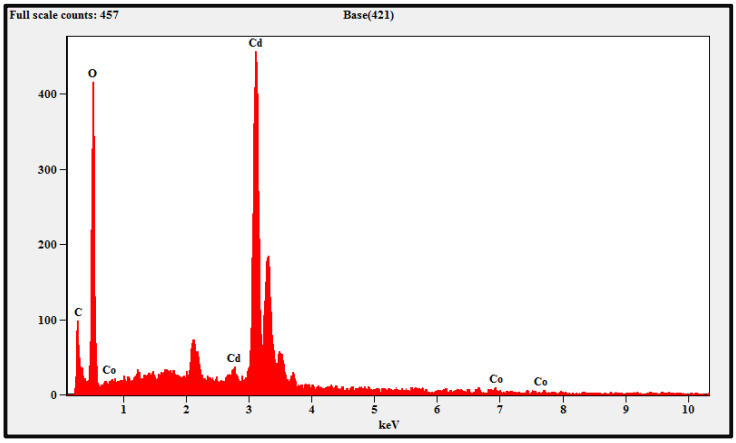


Figure 2. EDAX spectra of COMCO crystal.

Table 2. EDAX results of COMCO crystal.

Crystal	Elements present	Weight %	Atomic %
COMCO	Cd	49.41	11.40
	Co	00.39	00.12
	O	36.46	58.99
	C	13.74	29.49
	Total	100	100

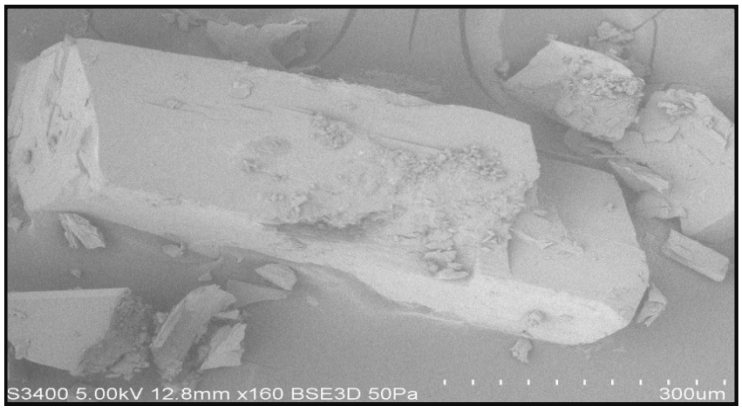


Figure 3. SEM image of COMCO crystal.

Thermo gravimetric analysis of COMCO crystal elucidated that, the decomposition to occur in two stages between the temperature ranges of 29°C-320°C (Figure 4). The crystal [Co:Cd(C_2O_4)3H_2O] loses its three water molecules in the first stage of decomposition with measured weight loss of 21.82% (calculated loss: 21.273%). This occurs in the temperature range of 29°C-118°C. The dehydrated COMCO crystal undergone second decomposition phase between the temperature range 230°C-336°C subjected to a weight loss of 27.32% (calculated loss: 28.347%) loosing CO and CO_2 simultaneously. On heating above 336°C the crystal exhibited thermal stability in the oxide state [Co:CdO] until 950°C [19]. The decomposition behavior of COMCO crystal is recorded in table 3.

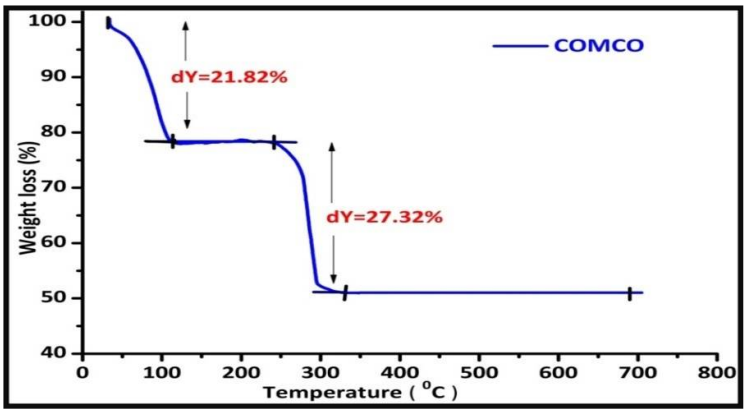


Figure 4. TG plot of COMCO crystal

Table 3. TGA results of COMCO crystals

Crystal: COMCO					
Decomposition stage	**Calculated weight loss (%)**	**Observed weight loss (%)**	**Decomposition temperature (°C)**	**Decomposition process involved**	**Molecule decomposed**
First	21.273	21.82	29–118	$Co:Cd(C_2O_4).3H_2O \rightarrow Co:Cd(C_2O_4) + 3H_2O$	$3H_2O$
Second	28.347	27.32	230-336	$Co:Cd(C_2O_4) \rightarrow Co:CdO + CO + CO_2$	CO and CO_2

Figure 5 illuminates the FTIR spectra of COMCO crystal. Inner graph elucidates the functional groups associated with parent intrinsic Cadmium oxalate crystal [ICO]. COMCO crystal possesses similar functional groups as one exists with its parent crystal. However, there exists a shift in wave numbers of absorption bands. Fingerprint region identifies the presence of M – O bond (where, M represents Cd and Co) in COMCO crystal. Table 4 lists the FTIR results of mixed crystal.

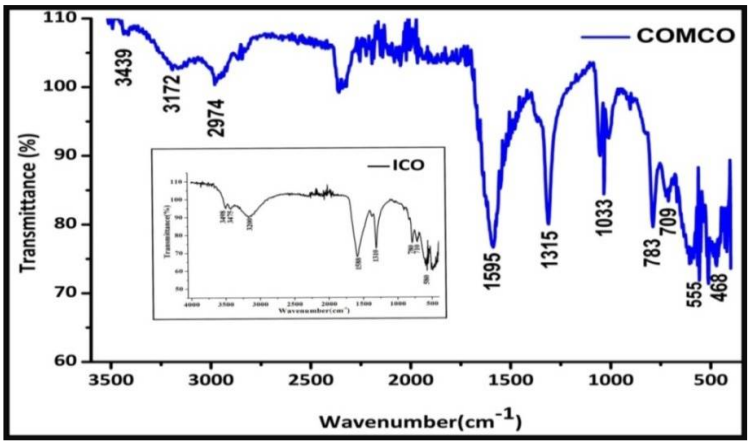


Figure 5. FTIR spectra of COMCO crystal

Mixed crystal exhibits intense broad band (3439 cm^{-1} to 2974 cm^{-1}) are due to symmetric and asymmetric stretching of O-H group represents water of crystallization [19, 20]. Strong asymmetrical band around 1595 cm^{-1} indicates C=O stretching in carboxylate ion [21]. The sharp absorption peaks at 1315 cm^{-1} are due to C-C vibrations and C-O stretching [22]. Absorption peak at 1033 cm^{-1} represents C-O absorption band. The absorption bands at 783–709 cm^{-1} are due to O-H out of plane bending and metal oxygen (M-O) bonding. Absorption peaks around 555-468 cm^{-1} corresponds to O-M stretching of COMCO crystal.

Table 4. FTIR results of COMCO crystals

S. No.	Band assignments	Wave number cm^{-1}
01	Symmetric and asymmetric stretching of OH group and water of crystallization	3439 3172 2974
02	C=O stretching, O-H bending	1595
03	C-C vibrations, C-O stretching	1315
04	C- O absorptions	1033
05	O-H out of plane bending	783, 709
06	O-M stretching	555, 468

COMCO crystals in powder form were subjected to PXRD analysis, which showed well defined Bragg's diffraction peaks indicating high crystalline nature of the grown crystals (Figure 6). Diffraction patterns were indexed using N-TREOR09 program. Resulted *d*-spacing and the Miller indices are in agreement with the standard values (JCPDS data) [26]. Unit cell parameters of COMCO crystals were recorded in table 5.

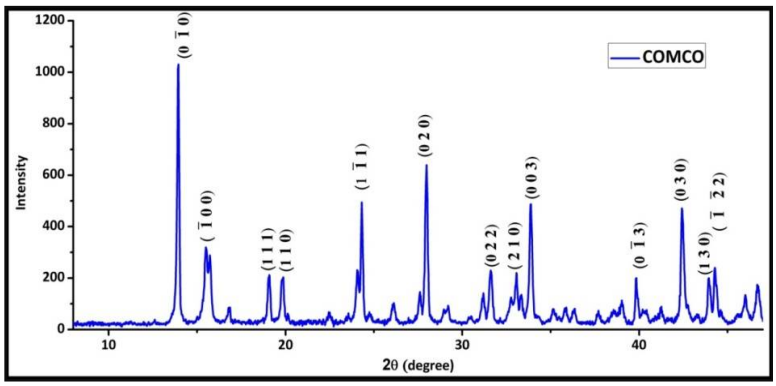


Figure 6. Powder XRD pattern of COMCO crystal.

Table 5. Cell parameters of COMCO crystal

Cell parameters	COMCO
*a*Å	5.9563
b Å	6.6479
*c*Å	8.4566
α (^{0})	74.78
β (^{0})	74.52
Υ (^{0})	81.00

Optimizing the growth parameters, COMCO crystals were successfully grown adopting single test tube gel diffusion technique with silica hydro gel as media of growth. Elemental analysis using EDAX, thermal studies, FTIR results and powder XRD measurements confirmed the presence of Co^{+2} ions and Cd^{2+} ions in the lattices of COMCO crystal. The studies also emphasized the existence of three water molecules in the lattices of mixed crystal. PXRD pattern enumerated high crystalline nature of the mixed crystal and its existence in triclinic system.

Optical properties of the mixed oxalate crystals were investigated using UV-Visible spectroscopy [23, 24]. Figure 7(a) elucidates UV-Visible spectra of COMCO crystal, which reveals that the crystal is highly transparent to visible light and showed absorption in the UV region. Mixed crystal possesses maximum absorption at 196nm with A_{max} = 0.78. Figure 7(b) illuminates the tauc plot used to

investigate band gap energy (Eg) associated with the mixed crystal [23, 24]. COMCO crystal exhibits band gap energy of 5.60 eV and behaves as insulator.

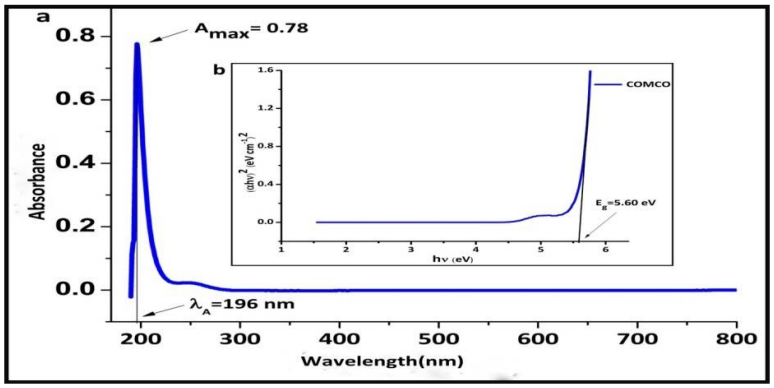


Figure 7(a). UV- Visible spectra of COMCO and (b). Tauc plot for measuring energy gap.

Electrical conductivity measurements of COMCO crystal were carried out by dissolving in suitable solvents. About 10 mg of mixed oxalate crystals were dissolved in 1.5 N sulphuric acid heated at uniform temperature bath of 80°C for 20 min and cooled to lab temperature. The instrument is calibrated to neutralize the conductivity of sulphuric acid [25, 26]. The measured electrical conductivity of COMCO crystal is shown in Table 6. The crystal possesses lower electrical conductivity due to larger band gap energy. Electrical conductivity measurements confirmed the insulating behavior of COMCO crystal.

Table 6. Electrical aspects of COMCO crystal

Electrical conductivity (m℧/cm)	03.68
Dielectric constant	80.71
Refractive index	08.98
Capacitance (pF)	57.63
Leakage resistance (KΩ.)	02.83

Dielectric properties of COMCO crystal were measured by forming circular crystal pellets of thickness approximately 1mm and area equals to the dimension of gold plated dielectric cell [27, 28]. Measuring capacitance (C) of the crystal pellet and approximating capacitance (C_o) of air to the dimension of crystal pellet, the dielectric constant ϵ_r of the mixed crystal is measured as

$$\epsilon_r = \frac{C}{C_o} = \frac{57.63\times10^{-12}}{0.714\times10^{-12}} = 80.71 \qquad (1)$$

Refractive index (n) of the transparent COMCO crystal is estimated as

$$n = \sqrt{\epsilon_r} = \sqrt{80.71} = 8.98 \qquad (2)$$

Higher ϵ_r and n values indicate that the mixed crystal has higher dielectric strength and the crystal is suitable in wave guides, printed circuit boards, capacitors, opto-electronic and micro-electronics applications.

Complete electrical behavior of the COMCO crystal are elucidated by studying its volt-ampere (V-I) characteristics (Figure 8). Using Keithley source measuring unit high dc voltage of 60V is applied across the mixed crystal and measured the current. Mixed crystal exhibited linear variation of current with voltage and recorded leakage resistance of 2.83kΩ.

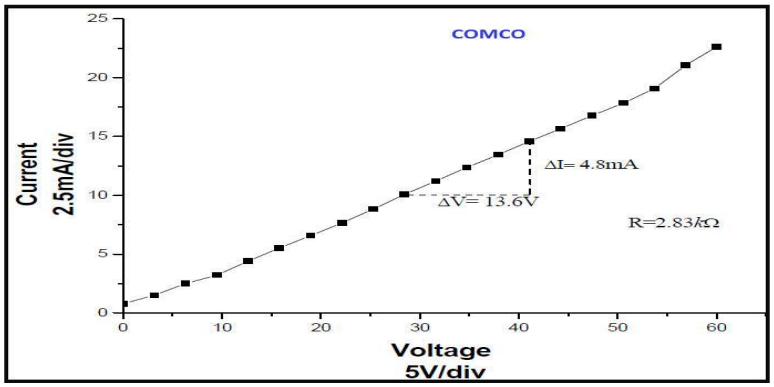


Figure 8. V-I characteristics of COMCO crystal

APPLICATION

The studies on properties of COMCO crystal revealed that the mixed crystal is thermally stable up to 950°C and associated with high dielectric constant, refractive index, large band gap energy and insulating behaviour. These results support wide applications for COMCO crystal. The mixed crystal can be used as dielectrics in printed circuit boards and capacitors, in optoelectronic and microelectronic devices. The mixed crystals are also suitable for transmission line and microwave applications.

CONCLUSIONS

COMCO crystals are grown efficiently by adopting single test tube gel diffusion reaction method. Optimum condition for growth is established by varying gel parameters and composition of reactants. EDAX measurements confirmed the presence of transitional metal ions Co^{2+} and Cd^{2+} in the lattice of COMCO crystal. The mixed crystal exhibits thermal stability until 950°C in the oxide state. FTIR results of the mixed crystals confirm the association of water molecules, carboxyl and the metal-oxygen bonds. PXRD analysis predicted the existence of mixed crystal in triclinic system. UV-Visible spectroscopic studies measured band gap energy of 5.61*eV* for COMCO crystal and thus the crystal behaves as insulator. Mixed crystal exhibits lower electrical conductivity, dielectric constant of 80.71 and refractive index of 8.98.V-I characteristics of COMCO crystal showed linear variation and measured leakage resistance of 2.83kΩ.

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