Synopsis of Thesis

Title: "Development of some Cu based p-type transparent conducting oxides through novel doping strategy and investigation of its electrical and optical properties"

Transparent conductive oxides (TCOs) are a unique class of materials exhibiting coexistence of optical transparency in visible region (up to 85%) and high electrical conductivity. Since the advent of 'transparent electronics', TCOs are considered as an important component of multifunctional circuits aimed to use for energy conversion, storage and thermoelectric applications. However, TCOs can be classified into two types: *p*-type and *n*-type. *n*-type TCOs are more common in literature as well as in practical applications because of superior opto-electronic properties than their *p*-type counterparts. Till date, even the best available 'band engineered' *p*-TCO ($CuCrO_2$: Mg) is 100 orders of magnitude behind in conductivity than frequently encountered *n*-TCOs (ZnO, SnO_2, $InSnO_2$ etc.). This is the essence of so called 'bottleneck' of conductivity. At present $CuCrO_2$, is known to be the *p*-TCO with highest reported conductivity upon Mg doping. And it will be good transparency in visible region and highly conductive material. From all the Cu- based delafossites, $CuMO_2$ is particularly large band gaps (direct and indirect) and higher intrinsic conductivity than any other Cu-based TCO. In general optical measurements have found direct band gap in the range 2.95-3.30 eV, which mean $CuCrO_2$ is transparent to visible light. The delafossite structure oxides such as $CuCrO_2$ has a conductivity of the order of 1 scm^{-1} and upon doping with Mg, the conductivity can improved and shows greater electrical conductivity than many other *p*-type TCOs, which have reported. The highest transmittance and conductivity indicate that they can used for visible or near- infrared active devices.

This research will be directed towards the development of some Cu based delafossite materials with wide-band gap particularly $CuMO_2$ TCOs. Current limitations of such materials are its electrical conductivity and optical transparency compared to their *n*-type counterpart. In my first work entitled "Scheme of simultaneous cationic-anionic substitution in CuCrO2 for transparent and superior *p*-type transport". We would like to study in detail both theoretical and experimental aspects of such materials related to above mentioned properties. Structural, electrical and optical properties for pure and co-doped materials with various percentages will be investigated in detail. These materials will be characterized through XRD, UV-VIS, I-V measurement for conductivity analysis in dielectric and transport phenomena. Considering $CuCrO_2$ as a promising *p*-type transparent conducting oxide (TCO), unprecedented simultaneous cationic-anionic doping is carried out for achieving superior transport maintaining its transparency. Magnesium and sulphur are doped at Cr and O-site respectively by solid-state approach ($CuCr_{1-x}Mg_xO_{1-y}S_y$, x, y ranging 0 – 5 atomic %) with significant doping confirmed by Rietveld refinement. UV-Vis spectroscopy is observed to imply optimistic optical properties of engineered materials. DC conductivity of co-doped $CuCr_{0.95}Mg_{0.05}O_{1.9}S_{0.1}$ is observed to be twice as large as $CuCr_{0.95}Mg_{0.05}O_2$ at 300 K which is consistent with the lower frequency shift of negative differential susceptance ($-\Delta B$) and admittance peak indicating higher 'metallicity' for the co-doped samples. Hole mobility of 16.26 $cm^2V^{-1}s^{-1}$ at 300 K is observed for the co-doped material. This strategy culminates established doping scheme at cationic site with our newly developed anionic chalcogen doping aiming to overcome long standing transport bottleneck in the field of semiconductor oxides.

In my next venture entitled "Experimental observation of valence band dispersion and increased hole conductivity in $CuCr_{1-x}Li_xO_{2-y}S_y$". We would like to study in detail both theoretical and experimental aspects of such materials related to above mentioned properties.

Structural, electrical and optical properties for pure and co-doped materials with various percentages will be investigated in detail. These materials will be characterized through XRD, UV-VIS, XPS, I-V measurement for conductivity analysis in dielectric and transport phenomena. Delafossite compounds are layered ternary oxides known for simultaneous exhibition of significant carrier conduction and optical transparency. To survey effect of simultaneous cationic and anionic hole doping in prototype delafossite $CuCrO_2$, we have analysed the structural, optical, impedance and transport mechanism of $CuCr_{1-x}Li_xO_{2-y}S_y$ (x and y ranging 0–2 atomic %) prepared by solid state heating. The substitutional site occupancy of $Li_{Cr}^{\bullet\bullet}$ and $S_O^{\times}$ are confirmed and quantified by Rietveld analysis. Valence band dispersion is demonstrated upon $Li_{Cr}^{\bullet\bullet}$ and $S_O^{\times}$ co-doping by x-ray photoelectron spectroscopy with extended contribution from shallow S 3*p* antibonding states. From diffuse reflectance spectra, the optical gap (~3.5 eV) is evaluated to be wide even upon co-doping. Carrier density and hole mobility for $CCO/(Li_{Cr}^{\bullet\bullet} + S_O^{\times})$ to be 5.32×10^{15} cm^{-3} and 23.50 $cm^2V^{-1}s^{-1}$, respectively. This scheme of band engineering is indicative of a more persuasive alternative to reach the hole conductivity bottleneck threshold.

Also in one of my conference proceedings entitled "En route to the Conductivity Bottleneck in p-type $CuCr_{1-x}M_xO_{2-y}S_y$ (M = Li, Mg)". We extend our material design further aiming to overcome the conductivity bottleneck (1 Scm^{-1}) in *p*-type transparent conducting oxide (TCO). In this work, we execute the strategy of simultaneous cationic-anionic hole doping in the prototype *p*-TCO $CuCrO_2$. $CuCr_{1-x}M_xO_{2-y}S_y$ (M = Li, Mg) is prepared by solid state heating at 1150 °C. Using Rietveld analysis, the presence of $Mg_{Cr}^{\bullet}$, $Li_{Cr}^{\bullet}$ and $S_O^{\times}$ are confirmed and quantified. The diffuse reflectance (DR) spectra are acquired to determine the dominant optical gap (~ 3.5 eV) and found to be affected little upon site selective hole doping. From temperature dependence (80 – 300 K) of DC conductivity (σ_{dc}), $(Li_{Cr}^{\bullet} + S_O^{\times})$ doping can be

identified to be the more plausible alternative to reach the bottleneck threshold compared to ($Mg_{Cr}^{\bullet} + S_O^{\times}$) albeit of smaller σ_{dc} at 300 K.

In my last work entitled "Investigation of the transport and structural properties of nanocrystalline delafossite *p*-$CuAlO_2$". These materials will be characterized through XRD, UV-VIS, HRTEM, FESEM, I-V measurement for conductivity analysis in dielectric and transport phenomena. By using mechanical ball-milling top down approach, we are able to successfully produce *p*-TCOs delafossite $CuAlO_2$ powder that is nanoscale in size. The development of *MICRO* and nanocrystalline $CuAlO_2$ (4−20 h) with a grain size of about 20 nm is demonstrated by the structural, microstructural, optical and transport characterization without any secondary phase generation only delafossite phases with rhombohedral symmetry. It is clear from evaluating the DR spectra that all the doped materials get a wider band gaps in the so-called transparent optical range. The optical gaps are found around 3.77 to 3.79 eV at (4− 20 h) with compared to *MICRO* sample (3.75 eV). The holes become thermally activated around 150 K, and also the VRH method is dominant around 80 to 145 K, according to the temperature dependent electrical conductivity profile (80 - 300 K). The *MICRO*- $CuAlO_2$ (0.41 S-cm^{-1}) seems to have a conductivity that is five times larger than its *NANO* (0.076 S-cm^{-1}) counterpart at room temperature. Due to the fact that ε' and tan δ with in measurement frequency range reduces as frequency rises with constant bias voltage, which exhibiting the semiconducting nature of polycrystalline delafossite $CuAlO_2$. Consequently, in contrast to the *MICRO* $CuAlO_2$, the conductivity reduces consistently at lower frequency while particle size reduces. The cause could be due to an increase mostly in grain density boundaries, which contribute as a centre of holes trapping/recombination. That's because the grain size has a significant impact on electrical conductivity, thermoelectric applications advantage from its characteristics.

In conclusion I have successfully prepared of some Cu based delafossite *p*-TCOs materials with their doping strategy (cationic-anionic) and also wide-band gap particularly $CuMO_2$. Furthermore, by using mechanical ball-milling top down approach, we are able to successfully produce *p*-TCOs delafossite $CuAlO_2$ powder that is nanoscale in size nanostructures and studied the overall structural, microstructural, optical and electrical performances in detail in my PhD work.

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