

A.7: Studies on structural and optical gap tunability in α -(Ga_xCr_{1-x})₂O₃ solid solutions

Transparent conducting oxides (TCOs) are a class of materials displaying a combination of a close-to 'metallic' and almost transparency (>80%) in the visible light range. Generally, most of these wide band gap oxide materials, where the valence band (VB) predominantly consist of O 2p states, suffer from the formation of polaronic holes localized by lattice distortions on oxygen sites. It hinders p-type conductivity in these materials. Most of p-type conducting oxides show conductivity due to mixing of d state of cations and O 2p states in the valence band. α -Cr₂O₃ crystallizes in corundum structure (R-3c space group) with an optical gap of 3.4 eV. P-type conductivity in Cr₂O₃ is explained in term of Cr 3d and O 2p states mixing which reduce polaronic localization on the O sites. It is also well established that the Cr³⁺ 3d³ electron configuration, with good dopability, high density of 3d near the valence band maximum (VBM) and covalent combination between Cr and O, plays a critical role in enhancing the p-type conductivity. Therefore, it attracts scientific community as a p-type TCO. Along with the p-type conductivity, band gap tuning in the higher energy side is also desirable for Cr based oxide materials to open up the possibility of its uses in the UV based transparent electronic and photovoltaic applications. Optical band gap tuning from 3.41 to 3.60 eV in Ni substituted Cr₂O₃ have been reported. Due to significant difference in the ionic radii of Ni²⁺ and Cr³⁺, only up to 10% Ni substitution is possible. In this direction, α -Ga₂O₃ is an important semiconductor material with a band gap of ~5 eV and Ga atom can easily be replaced by Cr atom as the ionic radius of Ga³⁺ (0.62 Å) is close to that of Cr³⁺ (0.615 Å). Therefore, synthesis of ternary α -(Ga_xCr_{1-x})₂O₃ material system has been carried out and its optical properties have been studied in detail.

Room temperature powder synchrotron x-ray diffraction (SXRD), using BL-11 of Indus-2 synchrotron source, with $\lambda \sim 0.6318$ Å, has been carried out to examine the structural properties. SXRD measurements reveal that Ga atom can be substituted for Cr atom up to gallium composition of $x = 0.45$ in R-3c space group. The variation in the lattice parameters as a function of concentration (x) shows a clear deviation from the Vegard's law with the bowing parameter of -0.0510 Å and 0.0305 Å in in-plane (a) and out of plane (c) lattice parameters respectively (Figure A.7.1). The optical gap of ternary α -(Ga_xCr_{1-x})₂O₃ solid solutions has been determined using diffuse reflection spectroscopy (DRS). The observed room temperature DRS spectrum of the samples is converted to equivalent absorption using Kubelka–Munk (KM) treatment. The absorption (α) versus $h\nu$ plots for α -Cr₂O₃ has been plotted as a representation in Figure A.7.2(a). Several absorption peaks have been observed which are related to the

various transitions of α -Cr₂O₃. The absorption peaks observed at ~2.058 eV, ~2.68 eV, ~3.45 eV, and ~4.96 eV are assigned to the transitions originating from $4A_{2g} \rightarrow 4T_{2g}$, $4A_{2g} \rightarrow 4T_{1g}$, $Cr t_{2g} \rightarrow e_g^*$ and $O2p \rightarrow Cr d^*$ states respectively. It is well established that the d–d splitting ($Cr t_{2g} \rightarrow e_g^*$) gives rise to the optical band gap (~3.4 eV) in α -Cr₂O₃. Optical band gap with Ga compositions (x) is plotted in Figure A.7.2(b).

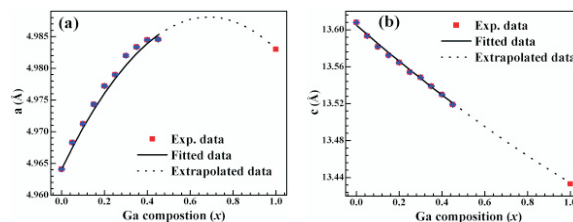


Fig. A.7.1: Variation of in-plane and out of plane lattice parameter (a) and (c) of ternary α -(Ga_xCr_{1-x})₂O₃ solid solution as a function of Ga composition deduced from Rietveld refinement of XRD data. The data is extrapolated to lattice parameter of α -Ga₂O₃.

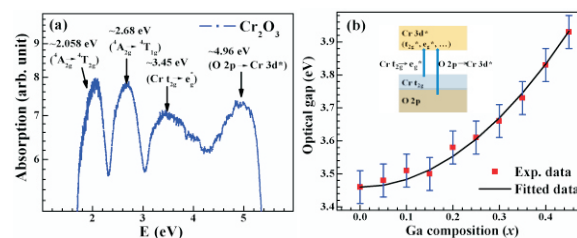


Fig. A.7.2: (a) Variation of the K-M function with energy for α -Cr₂O₃ and (b) Variation of optical band gap as a function of Ga composition (x) in ternary α -(Ga_xCr_{1-x})₂O₃ solid solutions.

Optical band gap blue shifts systematically with Ga composition (x) and the variation is fitted with the quadratic equation:

$$E_{Optical\ gap}(eV) = 3.45 + 0.2578x + 0.2365x^2$$

The results show that optical band gap of α -Cr₂O₃ can be tuned from 3.45 eV to 3.95 eV by Ga doping, which is the largest reported tunability in the Cr based material systems. It has also observed that Cr 3d level shifts towards the O 2p level in the valence band, which has been reconfirmed by photo electron spectroscopy (not shown here). The observed shift indicates enhancement of mixing between these levels which leads to further delocalization of hole states in the valence band or improvement in the hole conductivity in the α -Cr₂O₃. These results suggest that ternary α -(Ga_xCr_{1-x})₂O₃ ($0 \leq x \leq 0.45$), with large band gap tunability and improved Cr 3d and O 2p mixing, is a useful material system in the field of UV transparent electronics and photo detectors. For more details, please see *J. Alloys and Compounds*, 766, 876-885 (2018).

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