SUPPORTING INFORMATION

Sol-gel foam based Cr(III)-Sn(IV) doped indium oxide: characterizations of morphological, structural and magnetic properties

Nilanjana Das, Sunirmal Jana and Prasanta Kumar Biswas*

Sol-Gel Division, CSIR-Central Glass & Ceramic Research Institute
196 Raja S.C. Mullick Road, Jadavpur, Kolkata-700 032, India
E-mail: prasantabiswascgcri@gmail.com, pkbiswas@cgcri.res.in  *Author for correspondence
Tel.: +91-33-2483 8082, Fax: +91-33-2473 0957

Calculation of Thermodynamic parameters using Coats and Redfern equation

The Coats and Redfern equation can be represented as:

\[
\ln \left[ \frac{-\ln (1-\alpha)}{T^2} \right] = -\frac{E}{R} + \ln \frac{AR}{\beta E} \]

(considering n=1, i.e, 1\textsuperscript{st} order reaction)

where,

‘\(\alpha\)’ - fraction of decomposition at temperature ‘\(T\)’(obtained from TG curve of the TG-DSC analysis),

‘\(\beta\)’ - heating rate during the TG-DSC experiment,

‘\(R\)’ - universal gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)),

‘\(A\)’ - pre-exponential factor,

‘\(E\)’ - activation energy [calculated from eqn (ii) based on DSC experiment]

‘\(T\)’ - decomposition temperature.

The values of the activation enthalpy (\(\Delta H\)) and heat capacity (\(\Delta C_p\)) are obtained from the DSC measurement. Utilizing the \(\Delta H\) value, the energy of activation (\(E\)) is calculated at temperature ‘\(T\)’ using eqn (ii), where ‘\(R\)’ is the universal gas constant.

\[
\Delta H = E - RT \]

(\(\Delta C_p\) = \(\frac{\Delta H}{T}\))

(\(\frac{\Delta C_p}{T}\)) = \(\frac{E}{R}\)
The pre-exponential factor \( A \) is calculated using the values of the parameters of eqn (i) from DSC experiment.

The activation entropy \( \Delta S^\# \) and the free energy of activation \( \Delta G^\# \) are calculated using the following equations:

\[
\Delta S^\# = 2.303 \left[ \log \frac{A h}{k T} \right] R \quad \text{......................... (iii)}
\]

\[
\Delta G^\# = \Delta H - T \Delta S^\# \quad \text{.......................... (iv)}
\]

where,

\( h \) - Planck constant \((6.626 \times 10^{-34} \text{ J sec})\) and

\( k \) - Boltzmann constant \((1.380 \times 10^{-23} \text{ J K}^{-1})\).

The calculated thermodynamic parameters values are given in Table 2 of the main manuscript.

**Shifting and broadening of the x-ray peaks**

It has been observed that all the x-ray diffraction peaks are shifted by \(0.1^\circ - 0.2^\circ\) in the foam based Cr(III) doped ITO specimens. The shifting of the peaks are understood from the expanded regions of the respective peaks from the x-ray diffractogram (Fig. S1). This peak shifting may be due to a change in the peak broadening which results due to a change in the crystallite size and lattice strain or lattice constant due to change in baking temperature.

According to the work of G. K. Williamson and his student, W. H. Hall, the total peak broadening \( \beta \) is due to the contributions of size broadening \( \beta_L \) and strain broadening \( \beta_E \). The respective equations are given by:

\[
(\beta_L) = K \lambda / D \cos \theta \quad \text{........... (v)}
\]

where, \( D \) = crystallite size, \( K \) = shape factor \((0.9)\), and \( \lambda \) = wavelength of CuK\(\alpha\) radiation.

\[
(\beta_E) = 4E \tan \theta \quad \text{...........(vi)}
\]

where, \( E \) = lattice strain.
Therefore, the total broadening $(\beta)$ may be written as

\[
(\beta) = (\beta_L) + (\beta_E) = \frac{K\lambda}{D \cos \theta} + 4E \tan \theta \quad \text{………… (vii)}
\]

Rearranging equation (xxvii) we get,

\[
\beta \cos \theta / \lambda = \frac{K}{d} + 4E \sin \theta / \lambda \quad \text{………… (viii)}
\]
The above equation (viii) is Williamson-Hall equation.

If a plot of \((4\sin\theta/\lambda)\) vs \((\beta \cos\theta/\lambda)\) is drawn [as per eqn. (viii)], then the crystallite size could be estimated from the y-intercept of the linear fit, and the strain \(E\), from the slope of the fit.

These graphs are plotted for all the specimens (Fig. S2) and accordingly the crystallite sizes and lattice strains are evaluated (Table 3 of main manuscript).

**Figure S2**: Williamson-Hall plot for the Cr(III) doped ITO foam product heated at (a) 400°C (CrI-400), (b) 600°C (CrI-600) and (c) 800°C (CrI-800)
Reitveld Analysis

Reitveld analysis for the foam based Cr(III) doped ITO system from XRD patterns were performed by X’pert high score plus software (PANalytical). For this purpose, X-ray diffraction patterns of the samples were recorded in X’pert Pro MPD diffractometer (PANalytical) using X’Celerator operating at 45kV and 35 mA using Ni-filtered CuKα radiation. The XRD data were recorded in continuous mode with step size 0.05° (2θ) and time 25 sec from 18° to 90°. A specially prepared NIST 660a was taken as the instrumental standard to encompass the effect of instrumental broadening of the diffractometer.

Figure S3: X-ray diffraction pattern of CrI-400 along with difference plot as obtained by Rietveld refinement
**Figure S4:** X-ray diffraction pattern of CrI-600 along with difference plot as obtained by Rietveld refinement

**Figure S5:** X-ray diffraction pattern of CrI-600 along with difference plot as obtained by Rietveld refinement