Appendix A

Rietveld Refinement of X-ray Diffraction Data
The detailed crystal structure of rare-earth tungsten bronzes of the form $\text{M}_0.1\text{WO}_3$ (where M is a rare-earth) has not been hitherto reported in literature. The only information on the lattice parameters is presently available. X-ray diffraction patterns of these bronzes have been recorded by Ostertag [1] by using 114-mm Debye-Scherrer camera in the year 1966, and by Ganguly et al [2] in 1986 by using JEOL diffractometer. These authors obtained only the lattice parameters, interplanar distances and miller indices. The exact intensities and atomic positions of tungsten and oxygen atoms and space group have not been determined. In the year 1993, JCPDS-ICDD published the update of the earlier JCPDS cards with intensities for different Bragg reflections in these compounds. However, no data on atomic coordinates of tungsten and oxygen atoms, crystal angles and space groups for these compounds have been given. In the present work, we thought it interesting to study and analyse in detail the X-ray diffraction patterns of the polycrystalline samples of a few representative rare-earth tungsten oxide bronzes and to obtain all the structural parameters by using recent methods [3, 4] for the analysis of X-ray diffraction patterns.

In the present investigation, X-ray diffraction patterns of two representative compounds of rare-earth tungsten oxide bronzes, namely, $\text{La}_{0.1}\text{WO}_3$ and $\text{Eu}_{0.1}\text{WO}_3$ were recorded on a Rigaku X-ray diffractometer (Model D/Max II-C) using monochromatized Cu $K_{\alpha}$ as well as Fe $K_{\alpha}$ radiation and a NaI:Tl scintillation detector. This diffractometer is equipped with a curved-crystal graphite monochromator for elimination of undesired $K_{\beta}$ radiation. The measurements were carried out in the $2\theta$ range 20°-140°. The powder diffraction pattern was scanned in steps of 0.02 ($2\theta$) and fixed time counting was employed. At the end of data collection the stability of the intensity of the incident beam was checked by recording first few lines of pattern. The whole procedure was repeated three times using different samples prepared from the two bronzes. The diffractograms for these two bronzes are given in Figs. A.1 and A.2. Before giving the details of the analysis, we shall describe in brief the objectives and methods of the Rietveld refinement.
Fig.A.1: The observed, calculated and difference profiles for lanthanum tungsten bronze.
The object of the Rietveld method is to produce refined values of crystal structure parameters from powder diffraction data. Many materials of great interest cannot be made available for study in the single crystal form. This may be because it is not possible to prepare single crystal form at all or because the single crystal form differ from the polycrystalline form with the properties of interest or due to unavailability of single crystal X-ray diffractometer. Thus, our basic understanding of the atomic scale mechanism is limited on the structural side by the information that can be deduced from the powder diffraction patterns. The Rietveld method has greatly extended the amount of structural details that can be obtained routinely from powder diffraction patterns. In this method, structural parameters such as atom coordinates, thermal motion and site occupancy parameters are adjusted in a least-squares refinement procedure until a best fit is obtained between entire calculated and observed powder diffraction patterns, as a whole. This method of pattern fitting has now been successfully applied to X-ray and Neutron diffraction data by several groups all over the world.

The program developed by Young and coworkers [5] to perform Rietveld analysis of X-ray or Neutron powder diffraction data collected with a $\theta$-2$\theta$ diffractometer operated in a step scan mode (equal steps in 2$\theta$) and either one or two (for e.g., Ka doublet) wavelengths. It basically uses Newton-Raphson algorithm to minimize the quantity:

$$S_y = \sum_i w_i [Y_i - Y_{ci}]^2 \tag{A.1}$$

where $w_i = 1/(Y_i)$, $Y_i$ is observed (gross) intensity at $i^{th}$ step, $Y_{ci}$ is calculated intensity at the $i^{th}$ step and the sum is over all data points.

The calculated count $Y_{ci}$ are determined by summing the contribution from the neighbouring Bragg reflections, K, plus the background, $y_{bi}$;

$$Y_{ci} = sSRA \sum_K [L_F K^2 \Phi (2\theta_i - 2\theta_K) L_P K] + y_{bi} \tag{A.2}$$

where $s$ is a scale factor, $S_R$ is a function to model the effects of surface roughness, $A$ is an absorption factor, $F_K$ is the structure factor, $\Phi$ is a reflection profile function which approximates the effects of both instrumental and, possibly, specimen features. $L_K$ contains the Lorentz, polarization and multiplicity factors, $P_K$ is a preferred orientation function and $y_{bi}$ is the background contribution.
Fig.A.2: The observed, calculated and difference profiles for europium tungsten bronze.
The ratio of intensities for the two $\alpha$ wavelengths is observed in the calculation of $|F_K|^2$, so that only a single scale factor is required. The program uses different profile functions viz. Gaussian, Lorentzian, modified Lorentzian, Split Pearson, Pseudo-Voigt function, etc. depending on the diffraction patterns. At the end of the refinement, the structural parameters are then derived from the best fit. With this brief description about refinement method, we shall now discuss its application to our compounds.

X-ray examination of the samples of bronzes showed that single phase compounds were formed. The patterns of both the bronzes showed sharp diffraction lines corresponding to a simple cubic structure. Indexing of the power pattern was done using the computer program PDP11 (version 1.1) written by Calligaris [6]. From the result of this indexing, lattice parameters were calculated. The estimated values are 3.8245 Å and 3.8088 Å for $\text{La}_{0.1}\text{WO}_3$ and $\text{Eu}_{0.1}\text{WO}_3$ respectively. Since the single crystal analysis has not been done on these systems, it was assumed in the present work that the bronze system $M_x\text{WO}_3$ is isostructural with $\text{Li}_{0.1}\text{WO}_3$. It may be interesting to note that Ostertag [1] also assumed this kind of similarity of bronzes with the structure of $\text{Li}_{0.1}\text{WO}_3$.

$\text{Li}_{0.1}\text{WO}_3$ crystallizes in a simple cubic structure with the lattice parameter 3.729 Å and space group $\text{Pm}3\text{m}$ [7]. For Rietveld analysis of our compounds, we have used [7] the structural parameters viz., space group, atomic coordinates, lattice parameter and thermal parameters of $\text{Li}_{0.1}\text{WO}_3$ as a starting model for the refinement. The Rietveld refinement were carried out with the help of revised program DBWS 3.2 (Distribution package : DBWS/9411) for Rietveld Analysis of X-ray and Neutron Powder Diffraction Pattern written by Young and coworkers from Georgia Institute of Technology, Atlanta, U.S.A.

A modified Lorentzian function (Mod 2 Lorentzian in the program of Young et al) was used for representation of the individual reflection profiles and the angular dependence of the peak FWHM (full width at half maximum), $H_K$, described by the usual quadratic form in $\tan(\theta)$:

$$
\text{Mod 2 Lorentzian} = \frac{\sqrt{C_3}}{2H_K} \left[ 1 + C_3(2\theta_i - 2\theta_K)^2 / H_K^2 \right]^{-3/2}
$$

(A.3)
where $C_3 = 4 \left( \sqrt{2^{2/3}} + 1 \right)$ and

$$H_k^2 = U \tan^2 \theta + V \tan \theta + W$$  \hspace{1cm} (A.4)

where $U$, $V$ and $W$ are parameters whose values are refined in the program. The background intensity was evaluated by refining a background function $y_{bi}$:

$$y_{bi} = \sum_{m=0}^{5} B_m [(2\theta_i / BKPOS) - 1]^m$$  \hspace{1cm} (A.5)

where $B_m$ are refined and $BKPOS$ is the origin of polynomial for background in $2\theta$ and the background refinements were effected through $90^\circ$. It is observed that the inclusion of the lower angle region for the background refinement made the refinements slightly unstable.

Refinement started with the guessing value of scale factor and then followed by the scale factor and lattice parameter. After these had stabilized, the zero correction, the halfwidth and the asymmetry parameters were refined separately (three cycles for each group of parameters). Finally all the profile parameters and the scale factor were refined together followed by the refinement of overall isotropic thermal parameter. Reflections collected beyond $110^\circ 2\theta$ were broad and weak and contributed very little to the refinement and therefore the data beyond $125^\circ 2\theta$ were eliminated. The quantities used to estimate the agreement between the observations and the model during the course of Rietveld refinement can be written as

The profile $R_p$

$$R_p = \frac{\sum |y_i(\text{obs}) - (1/c)y_i(\text{calc})|}{\sum y_i(\text{obs})}$$ \hspace{1cm} (A.6)

The weighted profile $R_{wp}$

$$R_{wp} = \left[ \frac{\sum w_i[y_i(\text{obs}) - (1/c)y_i(\text{calc})]^2}{\sum w_i[y_i(\text{obs})]^2} \right]^{1/2}$$ \hspace{1cm} (A.7)

The Bragg $R_B$

$$R_I = \frac{\sum |I(\text{obs}) - I(\text{calc})|}{\sum I(\text{obs})}$$ \hspace{1cm} (A.8)

The structure factor

$$R_F = \frac{\sum |I(\text{obs})(1/2) - I(\text{calc})(1/2)|}{\sum I(\text{obs})(1/2)}$$ \hspace{1cm} (A.9)
The expected $R_{\text{exp}}$

$$R_G = \left[ \frac{N - P}{\sum w_i [y_i(\text{obs})]^2} \right]^{1/2}$$  \hspace{1cm} (A.10)

The goodness of fit $GF$

$$GF = \left[ \frac{R_{\text{wp}}}{R_{\text{exp}}} \right]^2$$  \hspace{1cm} (A.11)

The values of various $R$ factors mentioned above are used to judge the quality of the fitted profiles and the quality of structure determination.

The observed, calculated and difference patterns for tungsten oxide bronzes, $\text{La}_{0.1}\text{WO}_3$ and $\text{Eu}_{0.1}\text{WO}_3$ are presented in Figs. A.1 and A.2. The observed $\theta$ values, Miller indices, relative intensities and the interplanar distances calculated are presented in Tables A.1(a) and (b) respectively for $\text{La}_{0.1}\text{WO}_3$ and $\text{Eu}_{0.1}\text{WO}_3$. As mentioned above, both the compounds crystallize in simple cubic structure. The application of Rietveld Analysis has fully revealed the details of the structure of the tungsten oxide bronzes studied in this investigation. The atomic coordinates, positional parameters, sites and symmetries for each tungsten and oxygen atoms are given in Table A.2. In Table A.3 are given the summary of Rietveld refined data for $\text{La}_{0.1}\text{WO}_3$ and $\text{Eu}_{0.1}\text{WO}_3$.

The similarity between the calculated and the observed profile for $\text{La}_{0.1}\text{WO}_3$ and $\text{Eu}_{0.1}\text{WO}_3$ implies that the space group, atomic parameters, thermal parameters and the asymmetry parameters of the model $\text{Li}_{0.1}\text{WO}_3$ are also valid in the case of bronzes studied.

The refined lattice parameter value for $\text{Eu}_{0.1}\text{WO}_3$ matches very well with that reported by Ostertag [1] and in JCPDS card No. 19-465. For comparison of the lattice parameter of $\text{La}_{0.1}\text{WO}_3$ lattice parameter data is not available in the literature.

It may be noted that in $\text{Li}_{0.1}\text{WO}_3$, as shown by Zhong [7], the lithium atoms occupies unknown interstitial sites in the lattice. In rare-earth tungsten oxide bronzes also, the rare-earth ions may possibly go into the interstitial sites. However, it is difficult to confirm the location of the rare-earth ion from the present study. It requires some other experimental techniques to find out such interstitial site occupancy.
The various R factors obtained in the present analysis are consistent with those reported for X-ray Rietveld refinements [8, 9] thereby indicating the correctness of the structure refined. It may be interesting to note that even with less than optimum X-ray diffraction data, the Rietveld method allows a definitive structural solution to be achieved.