Data Article

X-ray diffraction data and analysis to support phase identification in FeSe and \( \text{Fe}_7\text{Se}_8 \) epitaxial thin films

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1. Data

The complex binary phase diagram of the Fe–Se system poses several challenges for researchers in the fields of single crystal and thin film growth of FeSe and related compounds. The crystal phase of...
In the related research article [1], epitaxial thin films were grown by pulsed laser deposition (PLD) using a target formed of a mixture of \( \beta \)-FeSe (22%) and 3c-\( \text{Fe}_7\text{Se}_8 \) (78%) whose X-ray diffraction (XRD) is shown in Fig. 1. All observed diffraction peaks in Fig. 1 index to either \( \beta \)-FeSe or 3c-\( \text{Fe}_7\text{Se}_8 \). 3c-\( \text{Fe}_7\text{Se}_8 \) is easily identified in the PLD target, instead of 4c-\( \text{Fe}_7\text{Se}_8 \), by the 3c-(115) peak at \( 2\theta = 35.41^\circ \). The (115) reflection is due to the iron vacancy ordering so it is not present in the fundamental NiAs structure (\( \delta \)-FeSe) and there are no possible 4c reflections near the same location. During certain growth conditions, the resulting films took on a doubly epitaxial configuration in which both \( \beta \)-FeSe and \( \text{Fe}_7\text{Se}_8 \) grew epitaxially oriented. \( \beta \)-FeSe was \( c \)-axis oriented, with the (001) plane oriented parallel to the substrate surface. Rocking curve analysis (Fig. 2) of the (001) reflection indicates mosaic structure in this phase, with a FWHM = 1.30° that is much larger than the instrumental resolution of 0.08°.
It cannot be assumed that 3\textit{c}-\textit{Fe}_7\textit{Se}_8 formed during PLD growth because the specific structure of \textit{Fe}_7\textit{Se}_8 is highly dependent on growth conditions. Because 3\textit{c}- and 4\textit{c}-\textit{Fe}_7\textit{Se}_8 share the same fundamental NiAs-type structure, their powder XRD patterns differ only in vacancy superstructure diffraction peaks. Standard $\theta$-$2\theta$ scans do not provide enough information to differentiate between the two structures when they are epitaxially oriented because the orientation makes many reflections geometrically unavailable. Based on the $\theta$-$2\theta$ XRD scans in Fig. 1 of [1], the orientation of the \textit{Fe}_7\textit{Se}_8

![Fig. 1. Undoped FeSe target XRD shows a mixture of 22% $\beta$-FeSe and 78% 3\textit{c}-\textit{Fe}_7\textit{Se}_8.](image)

![Fig. 2. Rocking curve of $\beta$-FeSe (001) peak for film grown at 500 °C and 3.4 J/cm².](image)
phase was found to take on two different orientations with (101) and (001) planes oriented parallel to the substrate surface, using Miller indices referred to the setting of the fundamental NiAs-type structure of Fe$_7$Se$_8$. This convention of indexing the Fe$_7$Se$_8$ lattice planes and reflections with respect to its fundamental NiAs-type structure is adopted throughout this paper, unless otherwise noted, and is necessary whenever it is not possible to specify which Fe vacancy superstructure (3c or 4c) is present, which is our case.

In order to verify the (001) orientation of Fe$_7$Se$_8$, powder diffraction patterns were generated to compare with the $\theta$-2$\theta$ scan of a thin film grown with a substrate temperature of 550 °C and laser fluence of 3.4 J/cm$^2$, in which the c-axis diffraction peaks were more intense than in any other sample. Fig. 3 shows a detailed view of each of the Fe$_7$Se$_8$ (00l) peaks for this film, overlaid with the calculated diffraction patterns. At the lowest angle, the (001) Fe$_7$Se$_8$ reflection is observed at 2$\theta$ = 15.13° and is equivalent to the 3c-(003) and 4c-(004) reflections in the settings of the 3c and 4c structures, respectively. The observation of this peak rules out $\delta$-FeSe for the c-axis orientation because the (001) reflection does not exist without the presence of ordered Fe vacancies. The next two peaks at 2$\theta$ = 30.54° and 2$\theta$ = 63.56° confirm the c-axis orientation, matching to the (002) and (004) Fe$_7$Se$_8$ reflections. The equivalent peak indices in the setting of their own crystal structures are (006) and (0012) for 3c-Fe$_7$Se$_8$, and (008) and (0016) for 4c-Fe$_7$Se$_8$. It should be noted that further information is required to differentiate between 3c and 4c.

2$\theta$ scans with $\omega = 2\gamma$ were employed to search for additional diffraction peaks that could be used to verify the Fe$_7$Se$_8$ (101) orientation for films grown with substrate temperatures in the 350–450 °C range at a fixed laser fluence of 3.4 J/cm$^2$. The relative fraction of $\beta$-FeSe to Fe$_7$Se$_8$ in these films changed from majority $\beta$-FeSe at 350 °C to majority Fe$_7$Se$_8$ at 450 °C. In 2$\theta$ scans, observed diffraction peaks correspond to crystal planes that are tilted with respect to the surface normal with an angle given by $\varphi = \theta - \omega$, where $\theta$ is the Bragg angle and $\omega$ is the incident angle of the x-rays. The angle between the crystal orientation and other diffraction planes, the interplanar angle, can be calculated to determine what angle $\omega$ is required to detect other diffraction planes in 2$\theta$ scans.

In Fig. 4, the 2$\theta$ scans predominantly feature two major reflections, one near 2$\theta$ = 42.5° and the other near 2$\theta$ = 55.5°. The peak near 2$\theta$ = 42.5° is the (102) reflection of Fe$_7$Se$_8$, which is equivalent to either 3c-(206) or 4c-(408). The angle of this measured plane with respect to the substrate surface is 19.2° which is a good match to the 18.8° interplanar angle between Fe$_7$Se$_8$ (101) and (102), confirming the (101) orientation of Fe$_7$Se$_8$. The second major peak near 2$\theta$ = 55.5° is consistent with the $\beta$-FeSe
Reflection, having an interplanar angle between \( b\)-FeSe (001) and (103) of 26.6°, which is a close match to the observed 25.8° with respect to the substrate surface. Additionally, the Fe\(_7\)Se\(_8\) (103) reflection is expected at 55.5° and will be convoluted with \( b\)-(103). The interplanar angle for Fe\(_7\)Se\(_8\) (103) with respect to (101) is 29.9° which is several degrees beyond what the \( 2\theta \) scan should detect. This means that the majority, if not all, of the intensity measured near \( 2\theta = 55.5° \) is due to the \( b\)-FeSe (103) reflection. Discrepancies between interplanar angles and \( 2\theta \) positions are due to differences in the theoretical lattice constants used for calculations and the lattice constants of the actual thin film. The choice of \( \omega = 2° \) is a compromise that enables both Fe\(_7\)Se\(_8\) (102) and \( b\)-FeSe (103) to be visualized on the same XRD scan. Since mosaicity is confirmed in the films, the peaks observed in the \( 2\theta \) scans are actually observable over a range of \( \omega \) with the true peak intensity existing at some optimized \( \omega \) value for each phase, which is unlikely to be exactly 2°. Therefore, the presented \( 2\theta \) scans should not be used to calculate lattice constants because the peak \( 2\theta \) value may be false. Reciprocal space mapping would enable the identification of the true peak intensity and correct lattice constants could be calculated.

The raw data for all of the XRD scans that were discussed have been uploaded alongside the article to be made available for download.

2. Experimental design, materials, and methods

Rocking curve and \( 2\theta \) XRD scans were carried out on a Philips X'Pert-MPD with Cu K\( \alpha \) radiation. Incident and diffracted optics, as well as scan parameters were the same in each case. A 1/8° divergence slit and 10 mm mask were used on the incident side and the diffracted x-rays were passed through a parallel plate collimator and detected with a proportional counter. The step size was 0.05° with a time per step of 0.5 s. The incident angle for the \( 2\theta \) scans was fixed at \( \omega = 2° \) and \( 2\theta \) was fixed at 16.064° for the rocking curve scan. PLD target composition was calculated using the Rietveld refinement function in Powder Cell [6].

The powder diffraction patterns for \( \delta\)-FeSe, 3c-, and 4c-Fe\(_7\)Se\(_8\) were generated using the VESTA software [7]. The 4c unit cell was defined in VESTA based on the crystal structure given by Okazaki [5] and the 3c structure was adapted from Parise [8] to have the lattice parameters \( a = 7.2631 \) Å and \( c = 17.550 \) Å. The 4c structure was made orthorhombic with lattice parameters \( a = 12.580 \) Å,
b = 7.263 Å, and c = 23.400 Å. The 3c and 4c lattice parameters correspond to a fundamental NiAs-type structure with a = 3.632 Å and c = 5.850 Å. Lattice constants used for β-FeSe are a = 3.672 Å and c = 5.513 Å. Interplanar angles were calculated for Fe7Se8 with equation (1) and for β-FeSe with equation (2) [9].

\[
\cos \varphi = \frac{h_1 h_2 + k_1 k_2 + \frac{1}{2} (h_1 k_2 + h_2 k_1) + \frac{3}{4} \frac{a_1^2 l_1 l_2}{a^2 c^2}}{\sqrt{\left(\frac{h_1^2 + k_1^2 + h_1 k_1}{a^2} + \frac{3}{4} \frac{a_1^2 l_1^2}{a^2 c^2}\right) \left(\frac{h_2^2 + k_2^2 + h_2 k_2}{c^2} + \frac{3}{4} \frac{a_2^2 l_2^2}{a^2 c^2}\right) + \frac{l_1^2}{c^2}}}
\] (1)

\[
\cos \varphi = \frac{h_1 h_2 + k_1 k_2 + \frac{1}{2} (h_1 k_2 + h_2 k_1) + \frac{3}{4} \frac{a_1^2 l_1 l_2}{a^2 c^2}}{\sqrt{\left(\frac{h_1^2 + k_1^2 + h_1 k_1}{a^2} + \frac{3}{4} \frac{a_1^2 l_1^2}{a^2 c^2}\right) \left(\frac{h_2^2 + k_2^2 + h_2 k_2}{c^2} + \frac{3}{4} \frac{a_2^2 l_2^2}{a^2 c^2}\right) + \frac{l_1^2}{c^2}}}
\] (2)

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dib.2019.104778.

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