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Determination of atomic positions and polar direction in the half-Heusler $\text{Sb}_{1-x}\text{Sn}_x\text{Ti}_{1-y-z}\text{Hf}_y\text{Zr}_z\text{Co}$ using Electron channeling

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Abstract

The variation of the electron induced x-ray emission with crystal direction of an incoming electron beam (channeling) was used to study the crystal site preference of the different elements in a promising thermoelectric half-Heusler material with Sb, Co and Ti as the majority elements, and with lower contents of Hf, Zr and Sn. We confirm experimentally, in accordance with previous assumptions, that Sb and Sn occupy one of the octahedral sites, $4a(0,0,0)$, Ti, Zr and Hf the other octahedral site, $4b(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and that Co-atoms occupy the tetrahedral site, $4c(\frac{1}{4},\frac{1}{4},\frac{1}{4})$. We furthermore observe a strong asymmetry along the polar directions as it should be in a half-Heusler when the Co atoms have a strong preference for one of the two sets of tetrahedral sites. Such asymmetries can not be observed by kinematical diffraction according to Friedel's law, demonstrating that the observation of element characteristic signals under channeling conditions is a unique technique for determining the sense of polar directions and distinguishing crystal symmetry alternatives in small crystal grains and nanocrystals.

Introduction

The search for materials with low thermal conductivity is a central issue within several fields of materials science. An example is thermoelectric materials where atomic disorder may contribute to reduced thermal conductivity, and may thus result in a higher energy efficiency of the material used in thermoelectric heat-pumps and electricity generators. To better understand the lattice (phonon) contribution to the thermal conductivity [1], the crystal site preference for the different elements and the spatial variations in compositions are useful knowledge. In this study we have used the variation in the electron induced element characteristic x-ray emission under electron channeling conditions [2] to address the site occupancy on the three different crystal sites for the six different elements in the half-Heusler $\text{Sb}_{1-x}\text{Sn}_x\text{Ti}_{1-y-z}\text{Hf}_y\text{Zr}_z\text{Co}$ which for certain x-, y- and z-values is an excellent p-type thermoelectric material [3,4]. We pay particular attention to the practical use of this electron channeling technique (also referred to as ALCHEMI [5]) to determine the site preferences as well as addressing the lack of inversion symmetry in half-Heuslers.

Specimen preparation and electron microscope equipment

The material was fabricated by arc-melting powders of the different elements in the proportions expressed by the chemical formula $\text{Sb}_{0.8}\text{Sn}_{0.2}\text{Ti}_{0.5}\text{Hf}_{0.25}\text{Zr}_{0.25}\text{Co}$ with subsequent ball milling followed by spark plasma sintering. Fig. 1 shows a typical electron induced x-emission spectrum obtained by using a scanning electron microscope (SEM) equipped with an EDAX energy dispersive x-ray spectrometer, and table 1 the composition in different regions as determined from x-ray spectra. Fig 2a shows a SEM image obtained by detecting backscattered electrons, and fig. 2 b-g show SEM images obtained by mapping using characteristic x-rays from the six

different elements. The inhomogeneity in Ti, Zr and Hf-content is in agreement with previous studies [6, 7]

Crushed fragments of the material were used for the channeling studies in a JEOL 2100 transmission electron microscope with a LaB₆ electron source, operating at 200 kV. The x-ray emission spectra under electron channeling conditions were collected with an energy dispersive spectrometer, also of type EDAX.

The channeling technique

Electron channeling experiments to obtain crystallographic information from the electron induced x-ray emission are performed with a convergent beam of electrons focused on the specimen [8]. In planar channeling experiments, which are more frequently used than axial channeling, one tries to avoid all reflections except those along a certain reciprocal lattice row. The convergence of the electron beam should be small enough to avoid overlap between the diffraction disks, and the electron probe on the specimen so small as to cover only a thin area at the edge of the specimen. In many cases thicknesses above 50 nm are too large. If the material is brittle, a good way of preparing the specimen is by grinding small pieces of the material submerged in ethanol in a mortar. A drop of the mixture of ethanol and the tiny fragments of material is then placed on a holey carbon film. (Ion milling may produce a relatively large volume fraction of disordered or amorphous material on the thin areas of the crystal foil).

Let us now look specifically at procedures to obtain information about the site occupancy. Fig. 3 shows the half-Heusler structure projected down the 001 and 1 -10 direction together with the sequence of atomic planes along the directions 100, 110, 111 and 311.

We notice in fig. 3 that along the 110 direction all atom planes contain the chemical composition of the crystal, while across the 100 planes we have alternating planes with different crystal sites, two of the three sites in a half Heusler on one of the planes and one site on the plane halfway between. As an analogy to the NaCl structure we refer to the plane with two sites as the plane with octahedral C sites, $4a(0,0,0)$, and octahedral N sites, $4b(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and the plane in between with one site as the T plane, $4c(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, (T for tetrahedral position in the NaCl structure). Across the 111 and 311 planes we see that there are three separate planes, one containing the C-

sites, one containing the N sites and one plane containing the T sites. Furthermore, we notice the lack of inversion symmetry across the 111- and the 311-planes.

As an alternative to rely on drawings of the projected structure to find useful conditions for performing channeling experiments, we may consider the expression for the structure factors [8] which may be particularly convenient for more complicated structures. For the half-Heuslers we have three types of reflections:

$$\text{Reflections with } h+k+l = 4n \text{ such as } 220, 400 \text{ etc. where } F_{hkl} = 4(f_C + f_N + f_T) \quad (1)$$

$$\text{Reflections with } h+k+l = 4n+2 \text{ such as } 200, 222 \text{ etc. where } F_{hkl} = 4(f_C + f_N - f_T) \quad (2)$$

Reflections with h, k and l all odd numbers give two alternatives as a consequence of the lack of inversion symmetry:

$$F_{hkl} = 4(f_C - f_N + f_T \exp i\left(2\pi m + \frac{\pi}{2}\right)) \text{ or } F_{hkl} = 4(f_C - f_N + f_T \exp i\left(2\pi m + \frac{3\pi}{2}\right)) \quad (3)$$

We see that the sequence of planes in fig. 3 can be expressed as phase factors for the different crystal sites.

Experimental results

Fig. 4 shows observation of how the normalized x-ray emission varies as a function of the angle between the incident beam and the lattice planes when the incident beam forms small angles with the 200 planes in fig. 4a, and with the 111 planes in fig. 4b. We notice the symmetry around the 200 planes and the deviation from symmetry around the 111-planes in agreement with what is the case in a half-Heusler as seen in fig. 3. In table 2 we present several measurements of the ratio between the normalized x-ray emission with the pairs of spectra with the 311 and -3-1-1 reflection at the Bragg position. The consistency in the deviation from unity for this ratio (either above one or below one for a given element) demonstrates that the sensitivity to lack of inversion symmetry is highly reproducible. Fig. 5 shows measurements along the 100-row with longer acquisition time and thus better counting statistics.

Discussions

Qualitatively the observations can be explained by considerations from classical physics. At the atomic planes the incident electrons see wells in the Coulomb potential and is thus attracted to the atoms if they enter parallel to the planes, and more so to the deep wells caused by the presence of elements with high atomic numbers as is the case for the 100 plane with the C and the N sites. The uppermost part of the atomic planes may thus be looked upon as cylindrical lenses that focus the electrons as illustrated in fig.6. If the beam is slightly tilted the intensity of the wave field tends to be on one side of the planes for a very thin crystal. Now, if the crystal lacks inversion symmetry across a plane there may be an asymmetry in the x-ray yield for the same amount of tilting in opposite directions relative the lattice planes. This is what we observe for the 111 planes in fig 4b and for the 311-planes in table 2.

Many beam Bloch wave calculations are powerful for a detailed study of the electron wave field within the crystal for a given thickness and direction of the incident beam. However, it is a challenge to accurately determine the experimental conditions for the small crystal volumes and the small tilts of the incident beam we are dealing with. Thus, for our purpose, which is to extract crystallographic information, it has hardly any purpose to move beyond two-beam Bloch-wave calculations that can be performed analytically. Fig. 7 shows qualitatively two-beam Bloch wave calculations of the thickness integrated wave field modulations for thin crystals for three incident beam directions. We notice that exactly at the Bragg position there is a uniform wave-field intensity over the crystal unit cell. However, for a very thin crystal the thickness integrated wave field exhibits a considerable variation across the unit cell when we disregard what is often referred to as absorption, which is rather diffuse scattering out of the incident and Bragg reflected beams. The wave field at thickness z and position x across the repetition unit with the reflection g at Bragg position, is given by:

$$I(x, z) = 1 - \sin(2\pi gx) \sin(2\pi(\gamma_1 - \gamma_2)z) \quad (4)$$

Here $(\gamma_1 - \gamma_2)$ is the inverse of the period of the thickness oscillation. We see that for a very thin crystal there is an asymmetry in the thickness integrated wave field intensity across the crystal unit cell when the g -reflection is at the Bragg position, and the asymmetry is inverted with the $-g$ reflection at the Bragg position [9]. Thus, the ratio between the wave field intensities for the two two-beam conditions is expected from eq. 4 to be:

$$\frac{I_{\bar{1}\bar{1}\bar{1}}}{I_{111}} = \frac{1 - D \sin 2\pi x}{1 + D \sin 2\pi x} \quad (5)$$

where the factor D is much smaller than unity due to the averaging over thickness and the diffuse scattering out of the Bragg beams (absorption). Eq. 5 applies also to the 311 row by replacing 111 by 311. In fig. 8 we use the experimental data of table 2. Here we have considered Ti, Zr and Hf as one entity by presenting the average of their ratios weighed by their atomic content. By trial and error fitting of the D-value and the position of the origin of x, the agreement with observation is reasonable. In the two-beam approximation the origin of x would be at the position where the structure factor assumes a real and positive value [8, 9]. In this study the exact position of the origin of x is difficult to assess due to the coupling with other reflections along the reciprocal row and the inaccuracies in calculating the structure factor of the 311 reflection due to the many elements involved and the compositional inhomogeneities. Our best estimate suggests that the origin should be a small fraction of the unit cell further to the left in fig. 8.

The variation of the x-ray emission with incident beam direction shown in fig. 5 is consistent with the Co atoms being on the tetrahedral sites and the other five elements on the octahedral sites. The variation in normalized x-ray counts with incident beam direction is much larger for Co than for the other elements. This is attributed to strong diffuse scattering of the fast electrons when the electron wavefield is confined to the plane containing the majority of atoms with high atomic number.

We can not distinguish between C- and N- sites based on observations along the 200 reciprocal lattice row, however. For that purpose the data shown in table 2 and fig. 8 provide further information. These observations suggest that the Ti atoms are on the N-sites and Sb and Sn on the C-sites. For Zr and Hf the observations are less conclusive which may be caused by an unintentionally shift in position of the electron probe on the specimen when collecting the two spectra within a pair. Thus, because the Ti, Zr and Hf content changes over small distances on the specimen, see fig. 2, their x-ray counts may change more based on small position changes on the specimen than based on site preference.

An interesting observation from the SEM data in table 1 is that the amount of Co tends to be slightly higher than 33 %, around 36 %, while the sum of Sb and Sn as well as the sum of Ti, Zr and Hf tends to be 32 %. The excess of Co relative to the other groups of elements may suggest that some 10 % of the Co atoms occupy the other tetrahedral site, 4d ($\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$). The asymmetry

across the 111 and 311 planes leaves little doubt that the great majority of the Co atoms occupy one of the tetrahedral positions, however.

In this study the challenges have been greater than in previous channeling studies involving oxide minerals [10] for two major reasons: The quite high atomic number of the elements causing much diffuse scattering (absorption) with the requirement of very thin crystal regions for the channeling experiments, and furthermore, composition inhomogeneities caused partly by phase separation. These difficulties are to a certain degree compensated by the possibility of studying different reciprocal lattice rows including rows that give information about lack of centrosymmetry, and about the sense of polar axes.

The channeling technique used here is complementary to traditional crystallographic procedures based on Rietveld refinement of neutron or x-ray synchrotron data [11]. Those diffraction techniques are highly quantitative involving a large number of parameters, and their achievements are impressive considering that only one quality is directly available from the diffraction data: In the case of x-ray diffraction this is the electron density. The channeling technique used in this study is more qualitative and limited to address crystal site occupancies (including polarity and thus absolute position). For that purpose the technique is robust and provides a useful supplement for crystals containing many different elements.

Conclusion

We have studied the compositional inhomogeneity and crystal site preference in a half-Heusler of composition $\text{Sb}_{0.8}\text{Sn}_{0.2}\text{Ti}_{0.5}\text{Hf}_{0.25}\text{Zr}_{0.25}\text{Co}$, a promising p-type thermoelectric material.

The spatial distribution of the elements was studied at a resolution around 100 nm by chemical mapping through detecting the element characteristic x-ray emission by using a scanning electron microscope. The content of Co was rather uniform, while the other five elements showed a considerable spatial variation. On the other hand, locally the sum of the content of Sb and Sn, and the sum of the content of Ti and Zr and Hf, was nearly constant. Typically the local content of Sb plus Sn, as well as the local content of Ti plus Zr plus Hf, was 32 %, while the content of Co was around 36 %

By detecting the x-ray emission under channeling conditions in a transmission electron microscope we find that the Sb and Sn atoms occupy the 4a (0, 0, 0) position and the Ti, Zr and Hf occupy the 4b ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) position. The polarity observations in the channeling experiments

allow us to conclude that the majority of the Co atoms occupy the tetrahedral position 4c ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$). However, the higher content of Co than of the other groups of elements suggest that around 10 % of the Co atoms occupy the other tetrahedral position 4d ($\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$).

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Figure captions

Fig 1. A typical x-ray spectrum collected using the scanning electron microscope (SEM). Lines used for the mapping are marked with their respective element.

Fig. 2 SEM images, all from the same area: a) using backscattered electrons, b –f) Images showing the distribution of the elements mapped using element characteristic x-ray signals from Sb, Sn, Ti, Zr, Hf and Co respectively. Bright areas represent heavy atoms in a), and high x-ray emission in b) – g). g) and b) show dark areas which are bright in c) suggesting areas with very high Sn concentration. Similarly, rather bright regions in g) correlates with bright region in c), suggesting a phase with high content of Co and Sn. These phases were avoided in the channeling measurements by judging the diffraction pattern as well as the EDS spectrum. (Note in column 6 in table 1 the high content of Co and Sn suggesting in the SEM measurement contribution from the phase with much Co and Sn).

Table 1 Compositions in different regions as determined from the x-ray spectra in SEM

Fig. 3 Projected structure of a half-Heusler along the (010) direction and the (1-10) direction with sequences of planes along (100), (110), (111) and (311)- directions. The illustrated sequences of

the planes are those encountered in planar channeling by tilting around the appropriate axis away from the main projections.

Fig. 4 Normalized x-ray yield as we tilt away from symmetrical orientation

a) (100)-row

b) (111)-row

Table 2 Ratio between normalized x-ray counts with the 311 and $-3 -1 -1$ reflection at the Bragg positions.

Fig. 5 Variation in the x-ray emission along the 100 row for the six elements in the case of longer acquisition time and thus better statistics

Fig. 6 An illustration, based on classical physics considerations, of how the wave field is channeled (or rather focused in the case of the negative electrons) in a crystal for incident electrons entering the crystal along the crystal planes. a) and c) slightly tilted in opposite directions and b) parallel to the planes.

Figure 7. Two beam Bloch wave calculations of the thickness averaged wave field modulation between the atomic planes for different directions of the incident beam. Left: the incident beam angle smaller than the Bragg angle. In the middle: exactly at the Bragg position. Right: larger than the Bragg angle. The modulation varies with thickness, at the Bragg position according to eq. 4.

Fig. 8 Ratio between the normalized x-ray counts when the 311 and the $-3-1-1$ reflections are at the Bragg position together with theoretical calculation of the modulation based on eq. 5.

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