Perturbed angular correlation studies of the MAX phases Ti$_2$AlN and Cr$_2$GeC using ion implanted $^{111}$In as probe nuclei

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A R T I C L E   I N F O

Article history:
Available online 26 February 2010

Keywords:
MAX phases
Radioactive ion implantation
Hyperfine interactions
Perturbed angular correlation (PAC)

A B S T R A C T

PAC measurements were done for the first time on the 211-MAX phases Ti$_2$AlN and Cr$_2$GeC which do not have indium as a constituent material. Radioactive $^{111}$In ions were implanted at 400 keV into the MAX bulk-samples. The radiation damage was annealed under vacuum up to temperatures of 1373 K. During each heating cycle the samples were sealed in new quartz tubes, as a loss of the $^{111}$In probes out of the samples was observed at high temperatures. Both MAX phases showed EFGs similar to the ones observed in indium containing MAX phases. In all cases they are attributed to probes residing on the A-site of the 211-structure. After high and long annealing temperatures an additional fraction of probes is observed in Cr$_2$GeC with a different EFG. The corresponding site may be the M-site of the 211-structure, or a site in a Cu$_2$ZnSiS$_4$ phase. The comparison of the X-ray diffraction spectra, taken before the implantation and after the end of the PAC measurements, showed that Cr$_2$GeC partly disintegrates to Cr$_2$C.

1. Introduction

The MAX phases are nanolaminated layered, hexagonal ternary carbides and nitrides with the general formula M$_n$+1AX$_n$ (MAX). Here n goes from one to three, M is an early transition metal, A is an element mostly of the IIIB and IVB groups, formally called A-groups, and X is either C and/or N. The compounds belong to space group D$_6$h, P6$_3$/mmc with two formula units per unit cell. Up to now roughly 60 compounds are known to exist. The vast majority of them have the M$_2$AX structure, henceforth referred as the 211-phases [1,2].

These phases combine some of the best attributes of metals and ceramics. Like metals, they are electrically and thermally conductive, easily machinable, plastic at high temperatures and highly damage tolerant. Like ceramics, they are elastically stiff, lightweight, oxidation and thermal shock resistant and maintain their strengths up to high temperatures [1,2]. The origin of this special set of properties can be found in its microstructure – influenced by kink band formation and microrielding of the nanolaminated configuration [3–5]. Electrical and mechanical characteristics of several phases have been studied extensively in the last few years, but mostly with macroscopic tools [6–8]. To obtain insight on the atomic scale, X-ray diffraction and transmission electron microscopy are routinely used.

A less common technique is the perturbed angular correlation method (PAC). Radioactive isotopes decaying by a $\gamma$-$\gamma$ cascade are utilized as probe nuclei, sensing their local surrounding via hyperfine interactions. All changes in the direct neighborhood of the probe atom (missing or trapped atoms, dislocations, ...) result in different electric or magnetic hyperfine fields. Ion implantation is a successful method to insert these “spies” in materials. In the present study the standard PAC isotope $^{111}$In was used which decays by electron capture to $^{111}$Cd with a half life of 2.83 days. Therefore, PAC measurements can be performed during 2–3 weeks, until most of the probes have decayed.

An important point for any data interpretation in PAC spectroscopy is knowing which lattice site the probe atoms occupy. For some MAX phases this question can easily be answered by choosing the compounds which have indium as a constituent. Owing to that consideration, previous experiments were performed for the key-compounds Ti$_2$InC and Zr$_2$InC [10] since the A-element is chemically identical to the $^{111}$In atoms. One expects that the probes occupy the In-site or more generally the A-site. It has been shown [for example for the delafossites [9]] that within a family of different compounds with the same structure one PAC-probe senses similar EFGs (in strength and symmetry). Simply speaking, one gets a “fingerprint” of a certain lattice site. We found in [10] that these phases show, after long annealings at high temperatures, axially symmetric EFGs with quadrupole coupling constants of $v_{Q1} = 291(1)$ MHz for Ti$_2$InC and $v_{Q1} = 345(2)$ MHz for Zr$_2$InC.

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Using $^{111}$In in other 211-phases which do not contain indium as a constituent, one expects an EFG in the same range of about 300 MHz assuming $^{111}$In atoms at A-sites. The purpose of this work is to characterize the A-site EFG parameters for $^{111}$In incorporated in the compounds Ti$_2$AlN and Cr$_2$GeC and to study the annealing behavior after implantation of In probe atoms.

2. Experimental details

Polycrystalline samples of Ti$_2$AlN and Cr$_2$GeC were fabricated as bulk material. Their synthesis rely on the principle of hot isostatic pressing (HIP) whereas the optimal process parameters for different compounds vary among each other. The starting point is pure elemental powders mixed in the right stoichiometric ratio via dry ball milling and cold pressed afterwards. The resulting pellets were sealed under vacuum in borosilicate ampullae and placed in a HIP working with an applied pressure in the range of 40–100 MPa at temperatures from 800 K to a maximum of 1700 K for several hours. Further details of the phase fabrication are described elsewhere [11,12]. The HIPed samples were cut into 10–15 mm$^2$ slices of about 1 mm thickness using spark erosion.

Into each sample approximately $10^{12}$ $^{111}$In$^+$ ions were implanted at 400 keV using the Göttingen Cockcroft–Walton type implantation IONAS [13]. The radioactive material was obtained from Perkin Elmer as carrier free $^{111}$InCl$_3$ solution. Microlitre droplets were placed on a hollowed tip of a support rod and dried by an infrared heating lamp. After covering the tip with a little tube it was inserted in the S055 ion source of IONAS. The $^{111}$In transmission from source to target is typically 20%, in the best cases 25–30% [14]. For Ti$_2$AlN the ion range calculated with the code stopping and range of ions in matter (SRIM) [15] is about 113 nm having a straggling width of 37 nm. In the case of Cr$_2$GeC, it is 81 nm with 30 nm distribution. The induced radiation damage caused by the implantation was annealed at different temperatures and duration steps in vacuum. Afterwards PAC measurements were performed at room temperature using a standard setup with four NaI(Tl)–detectors in 90° geometry which allows a simultaneous recording of eight 90° and four 180° coincidence spectra. From these twelve spectra the experimental perturbation $R(t)$ can be calculated. Data analysis details are described in Ref. [16].

All annealings were performed in evacuated and sealed quartz ampullae to prevent oxidation. In the course of these procedures we observed in Cr$_2$GeC a strong correlation between the increase of the annealing temperature and the loss of radioactive $^{111}$In from the specimens. Above 1000 K more than 25% of the still present $^{111}$In probes were lost from the samples, reaching a maximum value of 45–65% at 1273 K depending on the annealing duration. Previous studies of indium containing MAX phases have shown that the loss occurred by the precipitation of excessive indium [10].

In the present case, grayish discolorations within the quartz tubes were observed. We suppose that these discolorations resulted from non-reacted germanium or chromium which might coincide with the loss of $^{111}$In. Additionally the indium loss in Cr$_2$GeC might be favored by the porous surface character (see Fig. 1). The large inner surface would enhance the possibility for $^{111}$In to diffuse out, encouraged by the low melting point of indium ($T_{\text{melt}} = 430$ K) compared to the applied annealing temperatures.

To reduce the loss of $^{111}$In during tempering a small piece of inactive $^{115}$In was inserted in one ampulla to create an indium-backpressure. However, after annealing for 2 h at 1273 K more than 90% of the current activity was found in the attached indium piece. In addition a large amount of $^{111}$In$^+$diffused into the sample. This can be concluded, as 80% of the still present probes moved within the sample into the newly present In-metal, proved by the well established EFG of $\nu_0 = 17.3$ MHz [17].

3. Results and discussion

3.1. The 211-system Ti$_2$AlN

Based on previous PAC studies of the indium containing MAX phases, Ti$_2$InC and Zr$_2$InC [10], the indium-free compound Ti$_2$AlN was chosen to look for a similar EFG value according to the “fingerprint approach”. Due to the chemical relationship of aluminium and indium – both are members of the group IIIA in the periodic table – it is reasonable to assume that the implanted $^{111}$In ions occupy the Al-site. Based on the known vacuum annealing parameters of the In-MAX phases an annealing temperature of 1073 K was applied for 1 h. After this treatment all probes sensed the same local surrounding. The PAC spectra showed a sharp axially symmetric EFG fitted with the quadrupole coupling constant $\nu_0 = 259(2)$ MHz and a distribution width $\delta \nu = 1–2\%$ (see Fig. 2). The strength of the EFG in Ti$_2$AlN is comparable to the one found in Ti$_2$InC in which the probes are presumably located on the In-sites. This result confirms that the $^{111}$In probes were integrated on the same lattice sites creating an EFG in the same range of $\nu_0$ as in Ti$_2$InC.

Besides the determination of the probes’ lattice location we note that the shape of the perturbation function $R(t)$ deviates from the one of random polycrystalline samples which show pure electric quadrupole interaction. For the latter the ratio of the transition frequency intensities in Fourier space takes $\omega_1 : \omega_2 : \omega_3 = 3 : 2 : 1$ according to Ref. [16].

In Ti$_2$AlN we observed a ratio of 7:2:1 in horizontal sample alignment which indicates a texture within the
influence on the strength of the EFG.

fore the numbers of valence electrons vary which might have an
tents – Cr and Ge – take other positions in the periodic table. There-

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and Zr are from group IVB, whereas Al and In are from group IIIA

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the following in common: the elements of the M-layers as well

3.2. The 211-system Cr2GeC

Up to now all MAX phases studied with PAC spectroscopy had
the following in common: the elements of the M-layers as well
as the ones of the A-layers belonged to the same groups, e.g. Ti
and Zr are from group IVB, whereas Al and In are from group IIIA
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te the chromium atoms, that means they occupy the M-sites of the

Fig. 3. PAC spectra with Fourier transforms of 111In in Cr2GeC for different
annealing steps measured in air. Labeling according to Table 1.

main plane of the sample, most likely caused by the machining
operation.

As mentioned in Section 2 the removal of the ampullae after
high temperature annealings is of great importance as can be seen
in Fig. 4, where nearly all probe atoms sense the same surrounding
which manifests itself in a sharp axially symmetric EFG, fitted by a
quadrupole coupling constant of $Q_0 = 249(1)$ MHz and a small
distribution width of $\delta Q_1 = 0.4(1)\%$.

The attempt to observe a clear PAC signal like obtained in other
211-phases required now a second annealing cycle in which the
heating period was raised to 5 h, starting at 873 K and ending at
1273 K. Already after $T_{\text{anneal}} = 973$ K the hyperfine parameters
reached nearly constant values, using a fit with three different frac-
tions listed in Table 1. One of these $R(t)$ curves is illustrated in
Fig. 3(c).

Fig. 4. PAC spectrum and its Fourier transform of 111In in Cr2GeC. Sample stayed for
quoted annealing procedure in the same quartz ampulla which was removed for the
shown measurement. Labeling according to Table 1.

Further experiments were performed to reproduce this result
and to look for a recipe to obtain such spectra by varying annealing
temperatures and durations. By choosing long heating cycles at
high temperatures even before implantation, not only the known
A-site EFG appeared but also a fraction of approximately 40% occu-
ding only a small decrease of the present Ti2Al and $\alpha$–TiN0.3

3.3. XRD measurements

In addition to PAC measurements X-ray diffraction spectra were
recorded in $\theta - 2\theta$ geometry to determine the phase composition of Ti2AlN and
Cr2GeC slices before the implantation and later after all PAC measurements. Due to discolorations of some of the heated
quartz tubes XRD was used to check for possible phase transitions
or dissociations. In the case of Ti2AlN the applied annealings

Table 1

<table>
<thead>
<tr>
<th>Site</th>
<th>Fraction (%)</th>
<th>$Q_0$ (MHz)</th>
<th>$\delta Q_1$ (%)</th>
<th>$\eta$</th>
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<td>249–250</td>
<td>0–1</td>
<td>0.0</td>
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<td># 2a</td>
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<td>132–135</td>
<td>5–8</td>
<td>0.76–0.8</td>
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<tr>
<td># 2b</td>
<td>35–39</td>
<td>134–135</td>
<td>0–1</td>
<td>0.0</td>
</tr>
<tr>
<td># 3</td>
<td>37–44</td>
<td>146–149</td>
<td>8–13</td>
<td>0.0</td>
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reflection intensities. Pieces of untreated Cr$_2$GeC included already small amounts of binary phases like Cr$_{11}$Ge$_8$ and Cr$_7$C$_3$. Heating these samples caused different results which are shown in Fig. 6. In part (b) the intensities of all MAX reflections have increased by a factor greater than 3 which implies that the phase synthesis was not totally completed and the additional annealing improved the MAX phase quality (see Fig. 6(b)). The opposite case, that a partial decomposition took place is illustrated in Fig. 6(c) where Cr$_2$C was generated among others. The new EFG of $Q_2 = 135$ MHz which was observed could possibly originate from probes in the Cr$_2$C phase or as discussed above from the M-site in the MAX phase. A systematic PAC investigation of the decomposition products has not taken place yet but is planed for the near future.

4. Conclusion

In Ti$_2$AlN we observed an axially symmetric EFG with $Q_1 = 259(2)$ MHz in agreement with the expectations [10] for

the EFG strength for $^{111}$In atoms on the A-site. The phase Cr$_2$GeC showed a similar EFG of $Q_2 = 249$ MHz confirming the “fingerprint approach” for the A-site. After annealing to 1373 K a second In-site is observed which may be either due to the $^{111}$In residing on the M-site or a site in Cr$_2$C. To achieve a high fraction of $^{111}$In on the A-site in Cr$_2$GeC, high annealing temperatures and long annealing times are required which also causes a significant loss of In-probes.

Acknowledgements

We like to thank Detlef Purschke for successfully performed $^{111}$In implantations, Hans-Gregor Gehrke for providing SEM images as well as Volker Ebrecth for technical help. A part of this work was financially supported by the German Research Foundation (DFG) under Contract No. HO 1125/19-1 and by the National Science Foundation (DMR 0503711).

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