

First PAC experiments in MAX-phases

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Abstract MAX-phases are hexagonal ternary carbides and nitrides with the general formula: $M_{n+1}AX_n$ and $n = 1$ to 3. ^{111}In was implanted into the two MAX compounds Ti_2InC and Zr_2InC . Based on the general knowledge of previous ^{111}In implantations one expects to find the probes on the indium lattice-site in these compounds. First experiments on the annealing behaviour and the thermal stability of the indium-containing MAX-phases are reported. The observed EFGs are interpreted and first PAC-measurements under compressive stress are shown.

Keywords Perturbed angular correlation (PAC) · MAX-phase · Ti_2InC · Zr_2InC · Static pressure

1 Introduction

MAX-phases are layered, hexagonal ternary carbides and nitrides (general formula: $M_{n+1}AX_n$ where n varies from 1 to 3). M stands for an early transition metal, A for an A-group (mostly IIIA and IVA) element and X represents either C and/or N. They belong to space group D_{6h}^4 , $P6_3/mmc$, with two formula units per unit cell (see Fig. 1). X -ions sit in the centre of an M -octahedron. The 211 MAX-phases

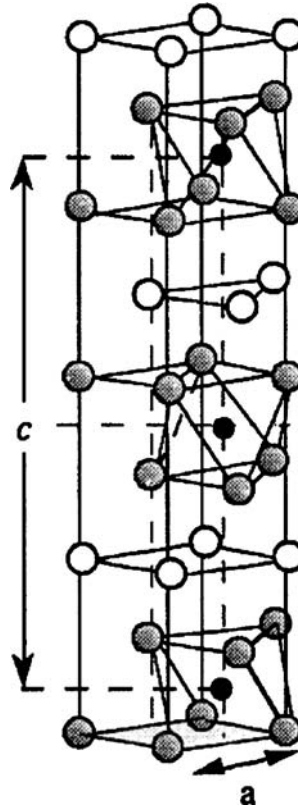
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Fig. 1 Structure of M_2AX_1 ($=211$): M gray, A white, X black

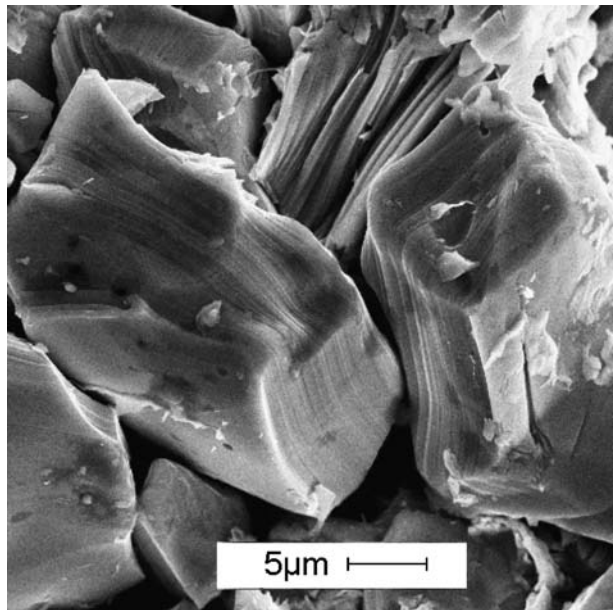


($n = 1$) show in the direction of the c -axis the layer-sequence $AMXMA\dots$, the 312 phases ($n = 2$) show $AMXMXMA\dots$ and the 413 phases ($n = 3$) come with $AMXMXMXMA\dots$

These compounds combine some of the best properties of metals and ceramics. Like metals, they are electrically and thermally conductive, most readily *machinable*, not susceptible to thermal shock, plastic at high temperatures, and exceptionally damage tolerant. Like ceramics, they are elastically rigid, lightweight, and maintain their strengths to high temperatures. The ternaries Ti_3SiC_2 and Ti_2AlC are creep, fatigue and oxidation resistant [1]. At present the explanation of this extraordinary behavior is assumed to be in the microstructure of the layered material: kinking bands and delamination seem to play a central role [2].

Using perturbed $\gamma\gamma$ -angular correlations (PAC) with ^{111}In probe nuclei, changes of MAX-phase properties during elastic deformations can be observed on an atomic scale. PAC experiments in complex compounds with different crystallographic sites often suffer from the problem to find the position of the probes. In the two MAX compounds Ti_2InC and Zr_2InC the probe ^{111}In is a constituting element of the compounds. Therefore, one expects to find the probes on the indium lattice-site, which should establish a PAC fingerprint, typically for the In-site in MAX phases, or more general for the A -site in the MAX compounds. In complete analogy, the M -site fingerprint can be discovered using the ^{181}Hf probe. Such studies will provide

Fig. 2 Pressed Ti_2InC —seen with an electron raster microscope. The typical nanolaminate structure of a MAX-phase clearly shows up



the key information to investigate by PAC the microstructure of the full class of MAX phases (about 50 compounds) which do not necessarily contain In-ions on the *A*-site or Hf-ions on the *M*-site of the structure. Knowing the “fingerprints” the technical important MAX-phases can be investigated.

2 Experimental details

The Ti_2InC and Zr_2InC samples have been provided by M. Barsoum. The fabrication is described in Ref. [3]: Elemental powders of Zr, Ti, In and graphite have been mixed in the proper stoichiometric ratios and cold pressed at 630 MPa. The resulting cylindrical pellets were sealed in borosilicate glass tubes under vacuum, placed in a hot isostatic press (HIP), heated at $20^\circ\text{C}/\text{min}$ to 973 K and held at that temperature for 30 min, before Ar was introduced to the chamber. The HIP was then heated at the same rate to 1573 K, where it was held for 7 h before cooling. The pressure at 1573 K was ~ 50 MPa. Finally the glass was removed mechanically. Predominantly single phase, fully dense samples were obtained. They were cut by a diamond saw into 20 mm^2 large slices of about 1 mm thickness.

About 10^{12} of $^{111}\text{In}^+$ ions were implanted at 400 keV into such samples, using the Göttingen implanter IONAS [4]. The radiation damage after the implantation was annealed out by heating the samples above $T_a = 700$ K in vacuum, which caused some problems (see Section 3.1). PAC-spectra were taken at different measuring temperatures T_m , with the help of a standard setup of four NaI-detectors in 90° geometry. Details on the data analysis can be found in [5]. The static pressure was applied by placing a sample between two DURAL-pistons, which were screwed against each other (Fig. 2). A pressure of about 1 GPa could be estimated from the “engrammes” made by the sample in the Al.

3 Results

3.1 Indium loss

In first studies it was reported, that Ti_2InC evaporates indium, when heated in vacuum at 1,173 K for ~ 2 h. XRD showed the emergence of peaks corresponding to TiC_x . Also a weight loss was found. It was assumed that Ti_2InC dissociates peritectically into the A-group element and the MX_2 phase [3]. Some light on the final dissociation product came from FPLAPW-calculations of ordered titanium carbide (Ti_2C)-phases. The trigonal phase was found to be more stable than the cubic one, but all calculated Ti_2C phases were found to be stable against segregation into TiC and metallic Ti [6]. The observation of In-whisker formation on Zr_2InC samples can be seen in the same context: The samples contained some unreacted indium in the grain boundaries. The In-content, determined from differential scanning calorimetric analysis, was 4 vol. %. The majority of the grains ranged in the size between 3–5 μm [7].

Heating Ti_2InC for 1 day at 473 K and for 1 day at 573 K in vacuum (PAC-tempering sequence) caused a loss of about of 30% of the implanted ^{111}In probes. Less pronounced was this loss for Zr_2InC under similar conditions, and for Ti_2InC it could be lowered by a vacuum annealing for only 10 min at 873 K.

3.2 The MAX-phase Ti_2InC

PAC spectra after the implantation (Fig. 3, top) show the need for an annealing step, although some ^{111}In -loss can be expected (Section 3.1). Afterwards a fraction $f_{\text{In}} \sim 50\%$ of the probes were found at the substitutional site in In-metal precipitates, identified by the well known frequency of 17 MHz with $\eta = 0$ [8]. When heating the sample above the melting point of indium (430 K), the precipitates transform into liquids, which have no EFG. Consequently, a PAC measurement at $T_{\text{m}} = 436$ K shows now the fraction $f_{\text{In}} \sim 50\%$ with $\nu_{\text{Q}} = 0$ MHz. This process is reversible and proves the existence of In-precipitates, un-reacted indium or decomposed MAX-phase. The rest of the probes has a well defined EFG, fitted with the parameters $\nu_{\text{Q}} = 290$ MHz and $\eta = 0$. Spectra are given in Fig. 3, the temperature and annealing conditions are given in the same figure. XRD analyses before and after the PAC cycle showed the compound still intact and gave no hints of disintegration phases. Therefore, this high frequency is attributed to probes at the In-lattice site (A-site) of Ti_2InC .

3.3 The MAX-phase Zr_2InC

The necessary vacuum annealing step after the ^{111}In -implantation caused—as expected—also in this MAX-compound a loss of indium. The contaminated container/envelope was removed and also this compound showed 65% of the probes with the typical parameters of the substitutional site in In-metal ($\nu_{\text{Q}} = 17$ MHz, $\eta = 0$). Above the indium melting point we found $f_{\text{In}} = 65\%$ with $\nu_{\text{Q}} = 0$ MHz, a clear proof, that the ^{111}In is located in metallic indium. The rest of the probes showed two

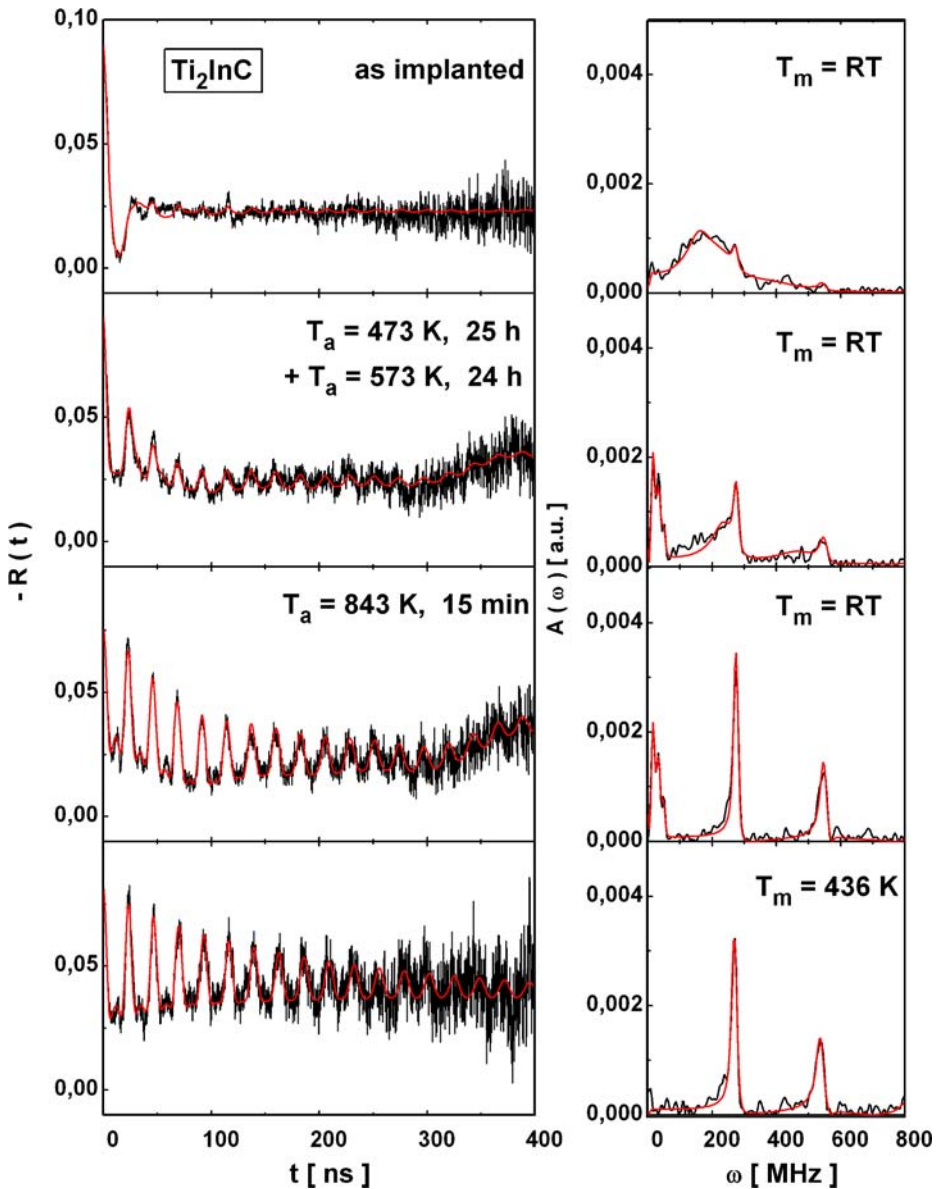


Fig. 3 PAC-spectra and their Fourier transforms for Ti_2InC

well defined EFGs of similar magnitude, fitted with the parameters $\nu_{Q1} = 348$ MHz, $\nu_{Q2} = 328$ MHz and $\eta_1 = \eta_2 = 0$ (see Table 1). The PAC-spectra are given in Fig. 4. The temperature and annealing conditions are included in the same figure. Similarly to the case of Ti_2InC we attribute this high frequency to probes on the In-lattice site of Zr_2InC .

Table 1 PAC parameters of the A-site EFG (measured at RT) in different MAX-phases: ν_Q and η describe the strength and symmetry of the EFG, δ is the distribution-width around ν_Q and the fraction gives the percentage of probes on this A-site

Compound	ν_Q [MHz]	η	δ [MHz]	Fraction [%]
Ti ₂ InC	290 (3)	0	6 (1)	43–65
Zr ₂ InC	348 (3)	0	2 (0.3)	25
	328 (9)	0	5 (1)	12.5
Ti ₃ SiC ₂	348 (3)	0	2 (0.3)	68

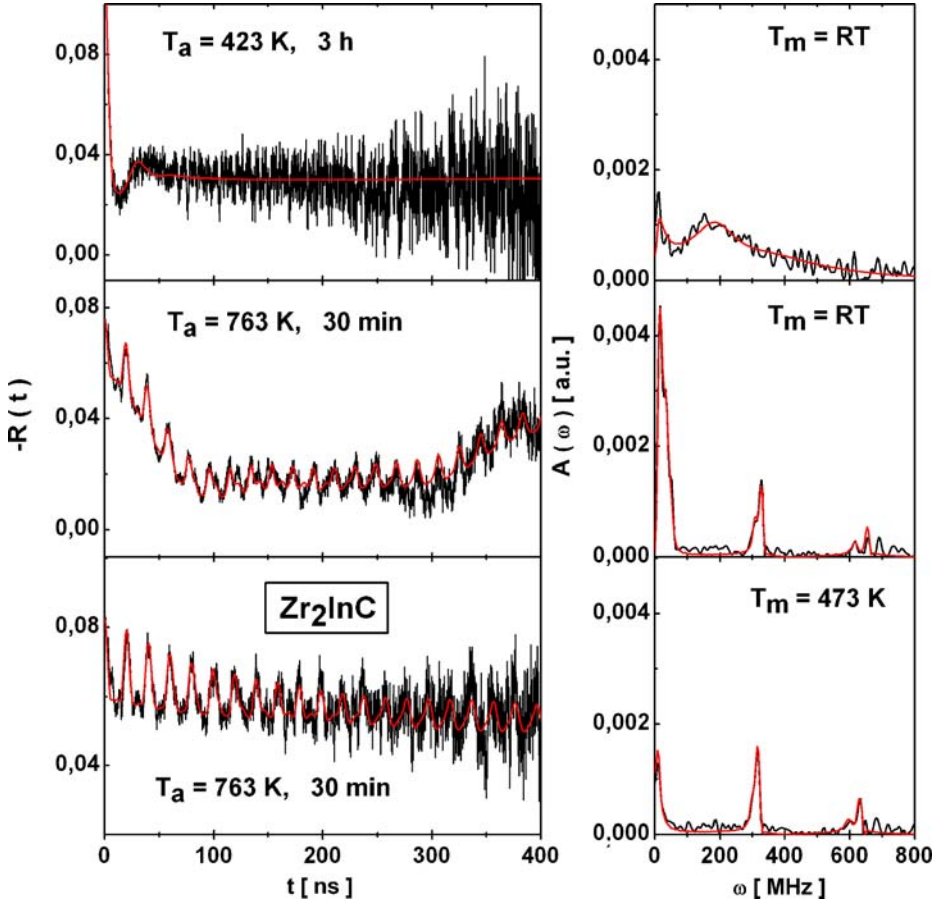


Fig. 4 PAC-Spectra and their Fourier transforms for Zr₂InC

3.4 Compressive stress on Ti₂InC

After all annealing steps, which prepared a maximum of the A-site EFG (Fig. 5, upper part), the Ti₂InC sample of Fig. 3 was placed between two Al-pistons. The sample's position was flat in the detector plane. Under compressive stress, the PAC

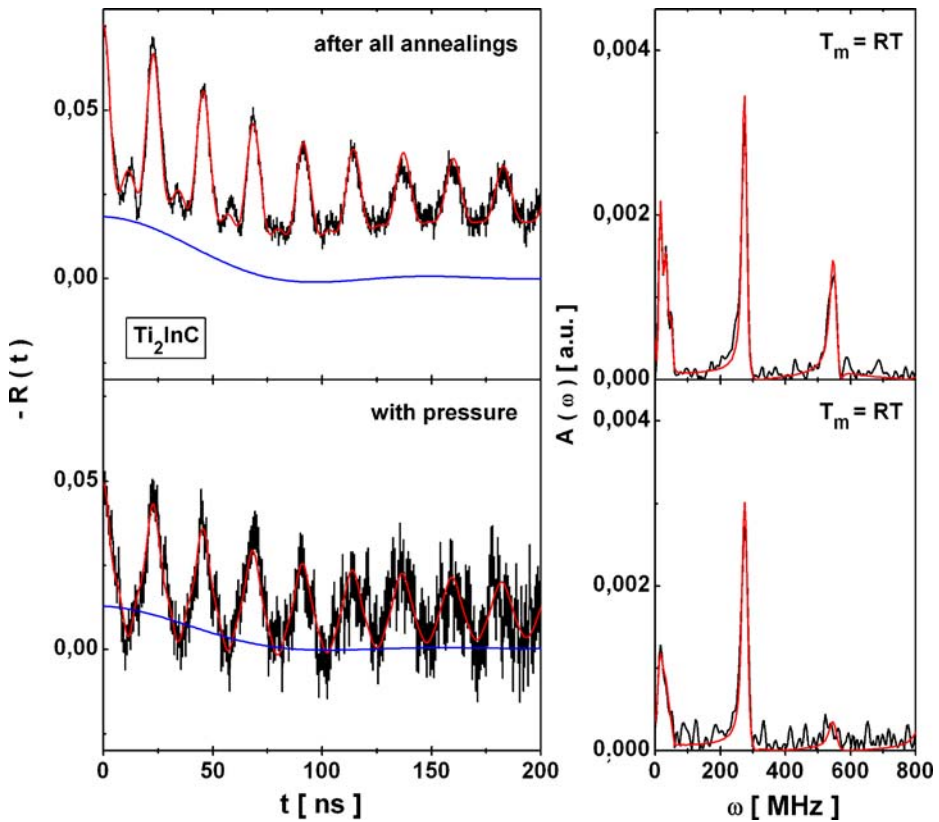


Fig. 5 Ti_2InC well annealed (*upper panel*), under pressure (*lower panel*). The line shows the part of the $R(t)$ -function, which is caused by probes in metallic indium

spectrum (Fig. 5, lower part) showed a clear texture with the EFG pointing into the detector plane, i.e. vertically to the direction of the pressure.

4 Discussion

The idea to find a “fingerprint EFG” of the A-site in MAX phases seems to work. In Table 1 the observed high frequencies are collected, including a first result on Ti_3SiC_2 , probably the technologically most important MAX-phase, which is stable to high temperatures and contains no indium in the structure. In all three of them we observed high EFGs in the range between 290 and 350 MHz. As demonstrated in the oxides [9] different compounds of the same lattice structures (as an example bixbyite class: In_2O_3 , Y_2O_3 , ...) show similar EFGs for a probe on a specific site in that structure. Despite the problematic question of a disintegration of the In-containing MAX phases, we assume that these new high EFGs are typical for probes on the A-site in the MAX phases.

All three compounds show a different result, therefore carbon-precipitates can be excluded, as they should give the same frequency in all three cases. Nevertheless,

the identical frequency $\nu_Q = 348$ MHz is observed in two different compounds. The strength of the observed EFGs is similar to impurity-In pairs in semiconductors [10]. We propose, that the ^{111}In probe—sitting on the A-site—catches an interstitial carbon atom. The small distance within this pair causes the high EFG. A trapping in slightly different geometries might explain, why in Zr_2InC two very similar high EFGs are observed. Unfortunately, this hypothesis can not yet be proven, but has to be solved in the future.

One of the extraordinary features of the MAX-phases is the elastic behavior of these ceramics. Our first simple compression experiment shows, that the PAC technique is sensitive to this question. Having the probe on a well known site, we will be able to learn more about the microscopic changes during application and release of pressure in these layered structures.

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