

An assessment of structural enthalpy and crystallisation pathways of $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ bulk metallic glass and amorphous films

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August 30, 2017

ABSTRACT

The structural nature and thermal stability of amorphous alloys is highly dependent on the method by which they are produced, i.e. their relaxation rate upon cooling. Both bulk samples and metallic glass films of $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ were produced by copper mold casting and direct current (DC) magnetron sputtering onto aluminium substrates, respectively. Comparisons between structural enthalpy, crystallisation pathways, relaxation and crystallisation kinetics of the bulk samples and films were examined by elevated temperature XRD and DSC. Compared with equivalent experiments on the bulk alloy, results for the thin films show distinct differences in structural enthalpy and deviations from the expected crystalline phase evolution, displaying minor peak shifts, failure of some phases to evolve, and variations in the evolution rates.

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1 INTRODUCTION

The structural nature and thermal stability of amorphous alloys is highly dependent on the method by which they are produced, i.e. their relaxation rate upon cooling. Both bulk samples and metallic glass films of $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ were produced by copper mold casting and direct current (DC) magnetron sputtering onto aluminium substrates, respectively. Comparisons between structural enthalpy, crystallisation pathways, relaxation and crystallisation kinetics of the bulk samples and films were examined by elevated temperature XRD and DSC. Compared with equivalent experiments on the bulk alloy, results for the thin films show distinct differences in structural enthalpy and deviations from the expected crystalline phase evolution, displaying minor peak shifts, failure of some phases to evolve, and variations in the evolution rates.

2 METHOD

2.1 Master alloy

The master alloy of $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ was produced using high-purity elements of Mg (99.85 wt%), Zn (99.995 wt%), and Ca (99.8 wt%). The alloy was prepared with an in-house induction melting furnace within boron nitride coated graphite crucibles, purged with Ar (99.997 vol.% purity) five times, and protected with a circulating Ar atmosphere. Alloy homogeneity was ensured by heating and cooling through a cycle of 700°C, 385°C, 650°C, 385°C, 650°C to a casting temperature of 500 °C and 450°C for injection and gravity casting respectively. Bulk amorphous $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ rods of nominal 2.5mm diameter sectioned to 2mm thickness, and plates of nominal 1.2mm thickness were produced by copper mold injection casting. The 25.4mm diameter targets were prepared from cylindrical copper mold gravity castings sectioned to nominal thicknesses of 3.25 mm, and polished. All samples and targets were stored under Ar when not being examined or used.

2.2 DC magnetron sputtering

Films were produced from an in-house DC magnetron sputtering facility with Ar working gas (99.997 vol.% purity). The power was 15W, typical voltage of 285 – 325V, nominal chamber pressure of 1 bar, substrate temperature of 25°C, and Ar flow of 3.01 SCCM. Films were deposited directly onto to Al DSC lid substrates. Depositions were for a period of 35 minutes at an estimated deposition rate of 0.8nm/s.

2.3 Stylus profiler analysis

Nominal film thickness was measured by a stylus profiler (Dektak 2A, Bruker, Germany). A glass slide was placed under the substrates within the sputtering chamber, allowing the substrates to act as a mask. Profile measurements were taken by measuring the height difference between the bare glass and the film coated glass. This film thickness was used to estimate the sputter deposition rate.

2.4 EDS analysis

Alloy composition and homogeneity were confirmed by SEM-EDS (S3400-N, Hitachi, Japan; Nova NanoSEM 230/450, FEI, The Netherlands). Hyper-maps were collected with an accelerating voltage of 15 – 20 keV, a probe current of 50 μ A, spot size 4.2, counts of 5000 cps or better, dead time less than 20%, and working distance was 5 mm.

2.5 DSC characterization

Isochronic DSC (204 F1 Phoenix, Netzsch, Selb, Germany) was carried out in Al crucibles under a protective Ar atmosphere (99.997 vol.% purity). Scans were performed at heating rates (β s) of 5 to 100 K/min.

Isothermal relaxation *acrs*hortdsc was performed by heating samples at 20 K/min to the desired annealing temperature, holding for the desired time, and Ar quenching to room temperature.

For annealed XRD the samples were heat treated in the DSC by heating to the desired temperature at 20 K/min followed by Ar quenching to room temperature.

2.6 XRD characterization

Annealing XRD (Empyrean, PANalytical, Cu K_α X-ray source, $\lambda = 1.541 \text{ \AA}$) was performed on heat treated bulk rods and films at room temperature. With a generator voltage 45 kV, tube current 40 mA, scan step size 0.0262606, and time per step of 397.29.

Dynamic XRD (D8, Bruker, Cu K_α X-ray source, $\lambda = 1.541 \text{ \AA}$) was performed on as manufactured bulk plates and films by raising temperature at a rate of 20 K/min and performing scans *in situ*. The first scan was performed at 35°C, then 75°C, after which temperature was raised in 5°C increments until reaching a final temperature at 185°C. The 2θ

scans from $31 - 60^\circ$ were completed within 1092sec (18min , 12sec) to minimise the effects of recrystallisation during the experiment. With a generator voltage 45kV , tube current 100mA , scan step size 0.02 , and time per step of 134.4 .

3 RESULTS

3.1 Alloy composition

From the 35 minute depositions a nominal film thickness of $1.64 \pm 0.48\mu\text{m}$ was obtained, giving a deposition rate of approximately $0.81 \pm 0.22\text{nm/s}$. The substrate temperature within the chamber was found to rise $2.9 - 3.5^\circ\text{C}$, significantly less than the expected 20K suggested by similar setups [1], see Figure 1.

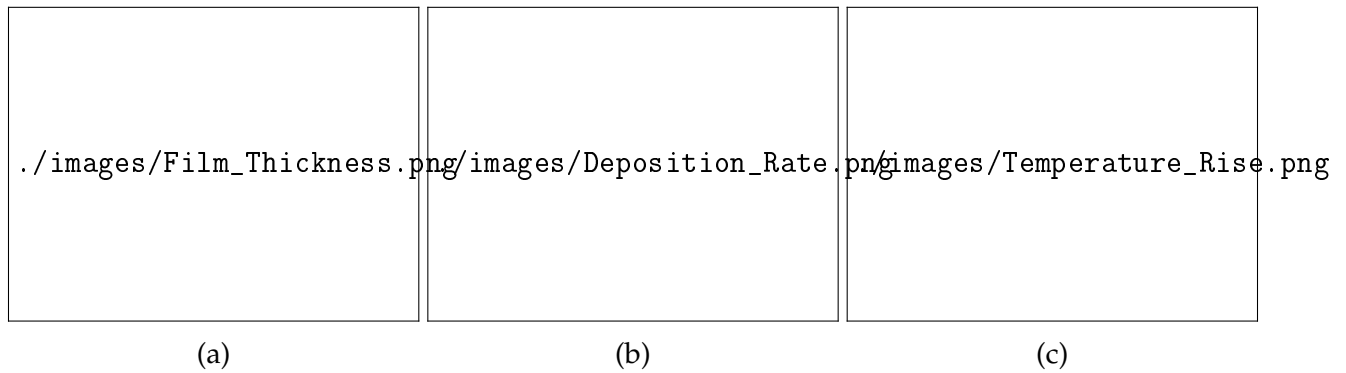


Figure 1: (a) Box and whisker plot of the measured film thicknesses from depositions. (b) Box and whisker plot of the calculated deposition rates achieved. (c) Box and whisker plot of substrate temperature rise.

EDS analysis shows good agreement in the nominal composition for both the bulk and film $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$, see Table 1.

Table 1: EDS composition of bulk and film $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ in atomic weight percent.

EDS Analysis	Bulk (at%)	Film (at%)
Mg	64.92 ± 3.22	63.20 ± 3.28
Zn	29.55 ± 0.84	30.95 ± 0.96
Ca	5.53 ± 0.17	5.85 ± 0.19

3.2 DSC

3.2.1 Isochronic DSC

Isochronic DSC was performed on the bulk and film $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ to examine the thermal properties. The bulk alloy was relaxed at 120°C for 10 minutes before DSC measurements to ensure the glass transition temperature (T_g) was clearly visible. The film was not relaxed as unlike the bulk the loss in free volume from relaxation would be significant and make differences between the samples much more difficult to observe [source needed???].

The bulk $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ was examined at heating rates (β s) of 5, 10, 15, 20, 30, 40, 60, 80, and 100 K/min to observe changes in the T_g and crystallisation temperatures (T_x s) with β . As expected greater β resulted in greater signal strength, exothermic peaks shifting to higher start temperatures, and an increase in thermal lag resulting in later exothermic finish temperatures and curve convolution. With this convolution the T_g and T_{x1} remained clearly visible for all β s, but $T_{x2,4,5}$ were only visible at low β s, and T_{x3} was not clear at any β , see Figure 2.

The film was examined at β s of 15, 20, 30, 40, 60, 80, and 100 K/min . The lower β s of 5 and 10 K/min were not utilised owing to the lower film signal compared to the bulk. The reduced signal was likely from the low mass of the film, about $\frac{1}{10}$ that of the bulk. The film showed the expected variable relationships with increasing β as observed in the bulk. The signal intensity increased at a compatible rate to bulk up until β s of 80 and 100 K/min . These final two β s showed great increases in the signal intensity. The exothermic peaks all convoluted together making many of the thermodynamic events difficult to observe at all β s. It also appeared that all exothermic events shifted to lower temperatures as compared to the bulk. The film T_g and T_{x1} s were less defined than for the bulk, but could still be identified for all β s. For all β s the T_{x2-5} onsets could not be easily identified, see Figure 3.

3.2.2 Fragility

Using the isochronic DSC T_g s the fragility (m) of the $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ system could be established for both the bulk and film. Numerical solutions were used to fit the DSC variant of the Vogel–Fulcher–Tammann (VFT) relationship for β [2].

$$\beta^{-1} = \tau_0 e^{\left(\frac{D^* T_0}{T_g - T_0}\right)} \quad (1)$$

Where τ_0 is a pre-exponential factor, D^* is the liquid fragility parameter, and T_0 is the VFT temperature where the barrier to flow becomes infinite.

The m could then be calculated from Equation 2 [3, 4].

$$D^* = 590/(m - 16) \quad (2)$$

Using these two equations for the bulk it was found $\beta^{-1} = 1.338E - 16e^{5274(\frac{1}{T-T_0})}$ with an Adj. $R^2 = 0.972$. This gave a $D^* = 20.4$, and a $m = 44.9$. The film was fitted to $\beta^{-1} = 5.921E - 11e^{2766(\frac{1}{T-T_0})}$ with a lower confidence of Adj. $R^2 = 0.861$, likely owing to the reduced number of data points. This gave a $D^* = 10.0$, and $m = 75.0$, see Figure 4.

3.3 DSC deconvolution

3.3.1 Onset determination

Numerical solutions were used to deconvolute the isochronic DSC curves so the various T_x onsets could be accurately determined. This numerical fitting utilised a summation of skewed Gaussian curves to fit a target curve corresponding to the original data; as is a common method [5–9]. For simplified, un-skewed peaks this fitting summation takes the form of Equation 3.

$$f(x) = \sum_{n=i}^n h_i e^{-\left(\frac{(x - T_i)^2}{(2c_j)^2}\right)} \quad (3)$$

Where h is the magnitude of the enthalpy peak, T is the temperature at the enthalpy peak centre, and c is the Gaussian RMS width.

The final deconvolved solutions of this fitting for both the bulk and film are shown in Figures 5 and 6 respectively. These results are tabulated in Table 2 for the bulk and Table 3 for the film. Tables 2 and 3 are also plotted together in Figure 7 with the bulk shown in black and the film in red. Note the T_g and T_{x1} are obtained from the original raw data, not the deconvolution.

It is worth noting the deconvolution fitted 5 crystallisation events for the bulk $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$, but only 3 events for the film. This occurred because the bulk had 5 well defined events, whereas the film was largely convoluted together. Thus unique solutions could not be obtained for the lesser T_{x2} and T_{x4} events of the film.

Table 2: Bulk $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ alloy onset temperatures for the various DSC heating rates (β s). All temperatures are in $^{\circ}\text{C}$.

Heating Rate β K/min	T_g $^{\circ}\text{C}$	T_{x1} $^{\circ}\text{C}$	T_{x2} $^{\circ}\text{C}$	T_{x3} $^{\circ}\text{C}$	T_{x4} $^{\circ}\text{C}$	T_{x5} $^{\circ}\text{C}$
100	136.1	164.8	193.4	201.8	240.2	262.4
80	132.0	160.0	194.4	201.9	238.2	260.3
60	129.6	157.7	190.0	197.8	232.9	259.0
40	126.6	155.2	189.0	200.0	226.4	254.7
30	126.2	151.5	187.0	198.4	221.0	251.1
20	125.1	149.8	188.4	197.0	216.0	246.8
15	123.8	148.3	186.2	195.6	212.2	243.9
10	123.5	144.5	183.4	192.9	207.4	239.8
5	120.5	141.1	179.7	187.5	199.8	232.7

Table 3: Film $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ alloy onset temperatures for the various DSC heating rates (β s). All temperatures are in $^{\circ}\text{C}$.

Heating Rate β K/min	T_g $^{\circ}\text{C}$	T_{x1} $^{\circ}\text{C}$	T_{x2} $^{\circ}\text{C}$	T_{x3} $^{\circ}\text{C}$	T_{x4} $^{\circ}\text{C}$	T_{x5} $^{\circ}\text{C}$
100	108.5	128.6		177.3		240.3
80	106.0	121.2		165.6		238.8
60	107.3	134.0		176.1		237.8
40	100.2	119.8		170.7		234.2
30	95.3	110.4		169.5		232.5
20	95.5	115.2		170.5		229.4
15	92.5	113.5		168.8		224.0

3.3.2 Reaction enthalpy

The deconvolution fits were integrated to find the area under each curve. This information provides the specific enthalpy (h) of the crystallisation formation of each phase. These energies are presented in Tables 4 and 5 for the bulk and film respectively. Figure 8 shows the T_x onsets and specific enthalpy (h) for both the bulk and film plotted together.

From Tables 4 and 5, and Figure 8 it can be seen most of the crystallisation formation energy is needed to form the 1st, 3rd, and 5th phases (i.e. $T_{x1,3,5}$). With these three phases accounting for approximately $73 \pm 7\%$ of the bulk crystallisation energy. The total crystallisation energy of these three bulk phases is also similar to the total energy for the films. Demonstrating that the bulk requires more energy to crystallize than the films.

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Table 4: Bulk $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ alloy specific enthalpy (h) of crystallisation formation for T_{x1-5} for the various DSC heating rates (β s); h is in J/g .

Heating Rate β K/min	$h_{T_{x1}}$ J/g	$h_{T_{x2}}$ J/g	$h_{T_{x3}}$ J/g	$h_{T_{x4}}$ J/g	$h_{T_{x5}}$ J/g	h_{Total} J/g
100	59.59	6.97	49.16	22.84	46.08	184.64
80	42.61	6.08	32.33	18.27	31.25	130.54
60	30.02	4.05	25.41	16.76	19.81	96.05
40	16.93	4.36	12.44	11.13	11.68	56.54
30	12.03	3.68	9.32	9.18	9.02	43.23
20	7.18	2.21	4.99	5.67	5.78	25.83
15	5.48	2.01	3.65	4.69	4.43	20.26
10	3.45	1.43	2.28	3.14	2.92	13.22
5	1.65	0.69	1.09	1.47	1.42	6.32

Table 5: Film $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ alloy specific enthalpy (h) of crystallisation formation for T_{x1-5} for the various DSC heating rates (β s); h is in J/g .

Heating Rate β K/min	$h_{T_{x1}}$ J/g	$h_{T_{x2}}$ J/g	$h_{T_{x3}}$ J/g	$h_{T_{x4}}$ J/g	$h_{T_{x5}}$ J/g	h_{Total} J/g
100	48.24		49.85		43.38	141.47
80	43.27		53.56		36.18	133.01
60	15.5		8.78		22.4	46.68
40	16.22		9.13		16.27	41.62
30	13.72		7.16		11.81	32.69
20	6.16		2.3		7.45	15.91
15	6.99		3.66		6.57	17.22

3.3.3 Relaxation enthalpy

For next paper on relaxation / rejuvenation.

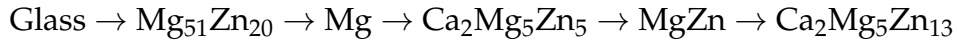
3.4 XRD

3.4.1 Annealing XRD

The crystallisation events observed and deconvoluted from the DSC were further examined with annealing XRD. Both the bulk and film were heat treated by annealing to 120, 140, 145, 170, 200, 250, 290, and 320°C before XRD. This allowed for the location of the T_g and T_x s to be confirmed as well as for the crystallisation phases to be identify.

From these experiments 5 previously observed crystallisation phases of the MgZnCa system [10–14] were characterised in the bulk and film $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$. This allowed the

crystallisation process of $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ from the fully amorphous glass to fully crystalline metal to be identified as;



The annealing XRD results are shown in Figures 9 and 10 for the bulk and film respectively. In these figures each phase is identified with a tracer at the temperature it was most strongly observed. Note the Al substrates peaks have been faceted in Figure 10 as to not dwarf the other peaks.

In Figures 9 and 10 it can be observed that $\text{Mg}_{51}\text{Zn}_{20}$ and Mg come out at a lower temperature in the film compared to the bulk, while the other phases nucleate and grow at similar rates for both the bulk and film. The temperature each phase is first and last observed are tabulated in Table 6.

Note the phases identified in Table 6 have reasonable agreement with the T_g and T_x onset temperatures presented in Tables 2 and 3. With $\text{Mg}_{51}\text{Zn}_{20}$ and Mg corresponding to either T_{x1} or T_{x2} , $\text{Ca}_2\text{Mg}_5\text{Zn}_5$ to T_{x3} , MgZn to T_{x4} , and $\text{Ca}_2\text{Mg}_5\text{Zn}_{13}$ to T_{x5} .

Table 6: Temperatures at which each crystallisation phase is first and last observed in the annealing XRD for both the bulk and film. All temperatures are in $^{\circ}\text{C}$.

Phase	Bulk		Film	
	First Temp	Last Temp	First Temp	Last Temp
Glass	35	200	35	200
$\text{Mg}_{51}\text{Zn}_{20}$ [10, 13]	170	200	140	200
Mg	170	320	140	320
$\text{Ca}_2\text{Mg}_5\text{Zn}_5$ [10, 14]	200	250	200	250
MgZn [13]	250	250	250	250
$\text{Ca}_2\text{Mg}_5\text{Zn}_{13}$ [10–12]	290	320	290	320

3.4.2 Dynamic XRD

The annealing XRD was useful for identifying the crystal phases present, but not many differences between the evolution rates of the bulk or film could be observed. Thus samples were subjected to dynamic XRD over their most active 2θ range of $31 - 60^{\circ}$ to observe changes *in-situ*. This allowed the crystallisation to be actively observed over the range of $35 - 185^{\circ}\text{C}$, showing how phases evolved over time as the temperature was raised in 5°C increments.

The dynamic XRD data shows that many phases seen in the bulk nucleate at different temperatures, are not observed as strongly, or fail to nucleate in the film. The initial Mg and $\text{Mg}_{51}\text{Zn}_{20}$ peak at 32.1° is first clearly seen in the bulk at a temperature of 170°C . In

the film the first clear evidence of this peak is at 90°C, although its resolution is poor from 150-170°C. The Mg, Mg₅₁Zn₂₀, and Ca₂Mg₅Zn₅ peak at 34.3° is seen at 75°C in the bulk, but not till 115°C in the film. The Mg and Mg₅₁Zn₂₀ peak at 47.7° is seen in both the bulk and film at 170°C.

In the bulk a double peak at 38° and 39° begins to emerge at 125°C, phases which never evolve in the film. The bulk Ca₂Mg₅Zn₅ peaks at 42.3° and 43.7° start to emerge at 165°C and 170°C respectively, but are never seen in the film. A faint Mg₅₁Zn₂₀ and Ca₂Mg₅Zn₅ peak at 53.3° is seen in the bulk at 175°C, but never in the film. The final small Mg and Mg₅₁Zn₂₀ 57.2° peak at 170°C is also never seen in the film. These observations are tabulated in Table 7. The bulk dynamic XRD is shown in Figure 11, and the film in Figure 12. Normalised plots allowing for easy identification of differences between the bulk and film are shown in Figures 13, 14, and 15.

Table 7: Main dynamic XRD peaks for both the bulk and the film. Data shows minor shifting for peaks 3 and 8, large start temperature differences for peaks 1 and 2, and failure of peaks 4 – 7, 9, and 10 to nucleation in the film.

Peak	Bulk 2θ	Film 2θ	Change %	Bulk Start °C	Film Start °C	Change %	Phases at%
1	32.1	32.1	0.0%	170	90	-47.1%	Mg, Mg ₅₁ Zn ₂₀
2	34.3	34.3	0.0%	75	115	53.3%	Mg, Mg ₅₁ Zn ₂₀ , Ca ₂ Mg ₅ Zn ₅
3	36.6	36.5	-0.3%	130	130	0.0%	Mg, Mg ₅₁ Zn ₂₀
4	38.0	N/A	N/A	125	N/A	N/A	Mg ₅₁ Zn ₂₀ , Ca ₂ Mg ₅ Zn ₅
5	39.0	N/A	N/A	125	N/A	N/A	Mg ₅₁ Zn ₂₀
6	42.3	N/A	N/A	165	N/A	N/A	Ca ₂ Mg ₅ Zn ₅
7	43.7	N/A	N/A	170	N/A	N/A	Ca ₂ Mg ₅ Zn ₅
8	47.7	47.6	-0.2%	170	170	0.0%	Mg, Mg ₅₁ Zn ₂₀
9	53.3	N/A	N/A	175	N/A	N/A	Mg ₅₁ Zn ₂₀ , Ca ₂ Mg ₅ Zn ₅
10	57.2	N/A	N/A	170	N/A	N/A	Mg, Mg ₅₁ Zn ₂₀

It was also observed that there was a some minor peak shifting between the Mg, Mg₅₁Zn₂₀, and Ca₂Mg₅Zn₅ phases in the dynamic bulk and film XRD. The largest shifts were seen in the Ca₂Mg₅Zn₅ 34.6° peak and Mg₅₁Zn₂₀ 39.1° peak, with shifts of 1.4% and 1.0% respectively. These shifts are tabulated in Table 8.

4 DISCUSSION

The use of a 60K DSC heating rate (β) compared to the more commonly used 20K rate [sources] shifts peaks for the bulk Mg₆₅Zn₃₀Ca₅ alloy about 8 - 15 degrees higher. This higher β s were used because crystallisation events for the films were difficult to

Table 8: Location of the dynamic bulk and film XRD peaks for the Mg, Mg₅₁Zn₂₀, and Ca₂Mg₅Zn₅ compounds.

Mg			Mg ₅₁ Zn ₂₀			Ca ₂ Mg ₅ Zn ₅		
Bulk	Film	Change %	Bulk	Film	Change %	Bulk	Film	Change %
32.1	32.1	0.0%	32.1	32.1	0.0%	34.1	34.1	0.0%
34.3	34.3	0.0%	34.3	34.3	0.0%	34.6	35.1	1.4%
36.6	36.5	-0.3%	36.6	36.5	-0.3%	36.0	35.7	-0.8%
47.7	47.6	-0.2%	38.0	38.2	0.5%	38.0	38.2	0.5%
57.2	57.1	-0.2%	39.1	39.5	1.0%	42.3	42.2	-0.2%
			45.1	45.2	0.2%	43.7	43.3	-0.9%
			47.7	47.6	-0.2%	53.3	53.0	-0.6%
			53.3	53.0	-0.6%			
			57.2	57.1	-0.2%			

differentiation at the lower β s. Films show little shift to high temperature peaks with increases β s, but large shifts with relaxation. Bulk show the opposite behaviour, larger peaks shifts with higher β s and little shift with relaxation.

5 CONCLUSIONS

6 ACKNOWLEDGEMENTS

Yu Wang for his assistance with XRD experimentation and Rietveld refinement.

7 REFERENCES

- [1] J. Q. Wang, N. Chen, P. Liu, Z. Wang, D. V. Louzguine-Luzgin, M. W. Chen, and J. H. Perepezko. The ultrastable kinetic behavior of an Au-based nanoglass. *Acta Materialia*, 79(0):30–36, 2014.
- [2] R. Busch, W. Liu, and W. L. Johnson. Thermodynamics and kinetics of the Mg₆₅Cu₂₅Y₁₀ bulk metallic glass forming liquid. *Journal of Applied Physics*, 83(8):4134–4141, 1998.
- [3] C. A. Angell and S. Borick. Specific heats C_p , C_v , C_{conf} and energy landscapes of glassforming liquids. *Journal of Non-Crystalline Solids*, 307 - 310:393–406, 2002.
- [4] Shuai Wei, Zach Evenson, Isabella Gallino, and Ralf Busch. The impact of fragility on the calorimetric glass transition in bulk metallic glasses. *Intermetallics*, 55:138–144, 2014.

- [5] Samir K. Ashour and Mahmood A. Abdel-hameed. Approximate skew normal distribution. *Journal of Advanced Research*, 1(4):341–350, 2010.
- [6] Yuzo Yamamoto, Yuichi Inoue, Teruaki Onai, Chikashi Doshu, Hiroshi Takahashi, and Hiroki Uehara. Deconvolution analyses of differential scanning calorimetry profiles of β -crystallized polypropylenes with synchronized x-ray measurements. *Macromolecules*, 40(8):2745–2750, 2007.
- [7] Charles H. Spink. *Differential Scanning Calorimetry*, volume Volume 84, pages 115–141. Academic Press, 2008.
- [8] Charles H. Spink. The deconvolution of differential scanning calorimetry unfolding transitions. *Methods*, 76:78–86, 2015.
- [9] Balázs Schäffer, Béla Schäffer, and D. Lőrinczy. Decomposition of dsc curves of dairy products with gaussian functions. *Journal of Thermal Analysis and Calorimetry*, 82(2):531–535, 2005.
- [10] Y. N. Zhang, G. J. Rocher, B. Briccoli, D. Kevorkov, X. B. Liu, Z. Altounian, and M. Medraj. Crystallization characteristics of the Mg-rich metallic glasses in the Ca-Mg-Zn system. *Journal of Alloys and Compounds*, 552:88–97, 2013.
- [11] Yi-Nan Zhang, Dmytro Kevorkov, Xue Dong Liu, Florent Bridier, Patrice Chartrand, and Mamoun Medraj. Homogeneity range and crystal structure of the $\text{Ca}_2\text{Mg}_5\text{Zn}_{13}$ compound. *Journal of Alloys and Compounds*, 523:75–82, 2012.
- [12] Yi-Nan Zhang, Dmytro Kevorkov, Florent Bridier, and Mamoun Medraj. Experimental study of the Ca-Mg-Zn system using diffusion couples and key alloys. *Science and Technology of Advanced Materials*, 12(2):025003, 2011.
- [13] Y. Khan. Dynamic temperature crystallization behaviour of amorphous and liquid $\text{Mg}_{70}\text{Zn}_{30}$ alloy. *Journal of Materials Science*, 24(3):963–973, 1989.
- [14] Jake D. Cao, Thomas Weber, Robin Schäublin, and Jörg F. Löffler. Equilibrium ternary intermetallic phase in the Mg-Zn-Ca system. *Journal of Materials Research*, 31(14):2147–2155, 2016.

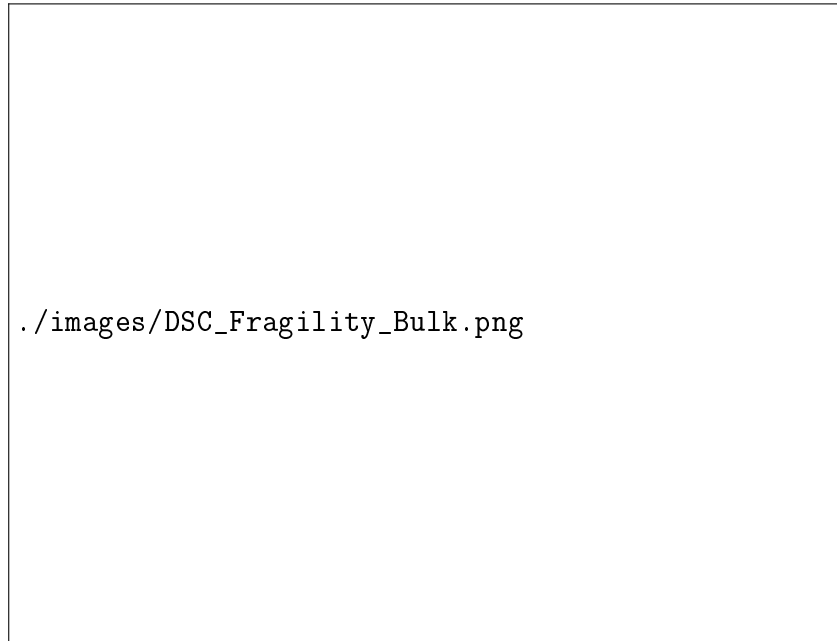



Figure 2: Bulk $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ relaxed at 120 °C for 10 minutes and heated at various heating rates (β s) from 5 to 100K/*min*. The insert stacks the differential scanning calorimetry (DSC) curves and labels the T_g and T_x s of the $\beta = 100\text{K}/\text{min}$ curve.



Figure 3: Unrelaxed film $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ heated at various heating rates (β s) from 15 to 100K/*min*. The insert stacks the DSC curves and labels the T_g and T_x s of the $\beta = 100\text{K}/\text{min}$ curve.



./images/Bulk_Film_Fragility.png

Figure 4: Fitted fragility (m) for the $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ system obtained from the T_g of DSC at various heating rates (β s) for the bulk and film.



Figure 5: DSC deconvolution for the bulk at various heating rates (β s). From left to right, top to bottom, $\beta = 5, 10, 15, 20, 30, 40, 60, 80, 100$ K/min.



Figure 6: DSC deconvolution for the film at various heating rates (β). From left to right, top to bottom, $\beta = 15, 20, 30, 40, 60, 80, 100 \text{ K/min}$.

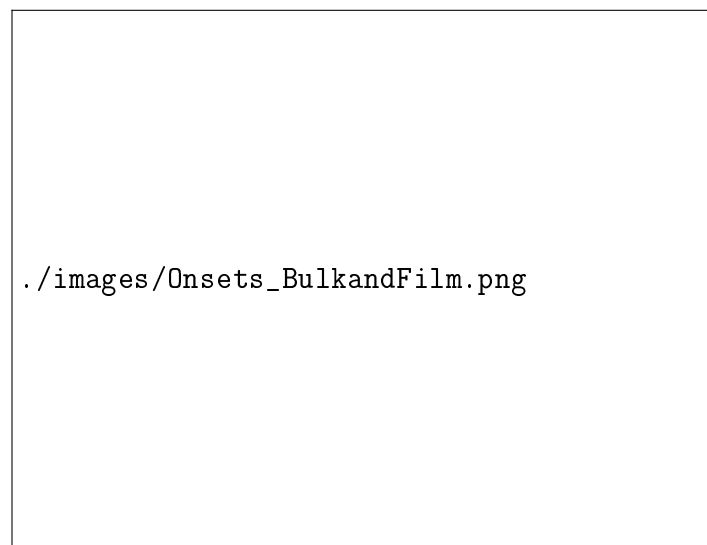


Figure 7: The T_g s and T_x s plotted at each DSC heating rate (β) for both the bulk and film $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$. Bulk is shown in black, and film in red.

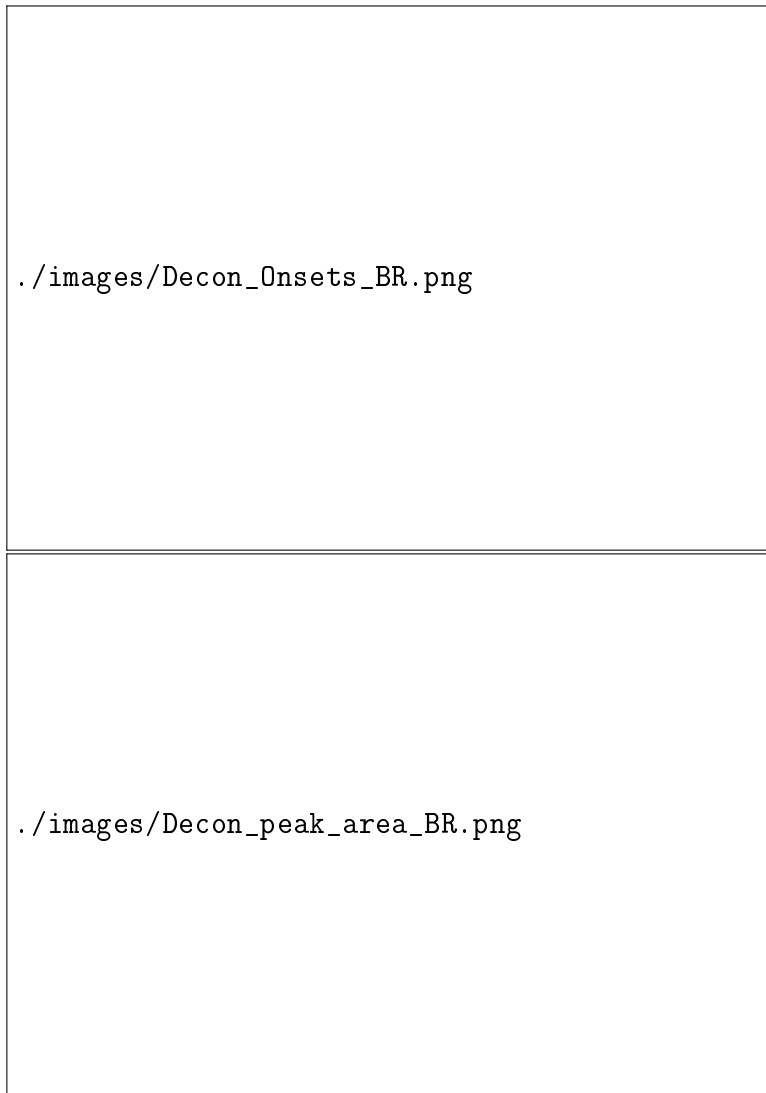


Figure 8: DSC T_x onset temperatures and specific enthalpy (h) of crystallisation formation for the bulk and film at each heating rate (β). Bulk is shown in black, and film in red.

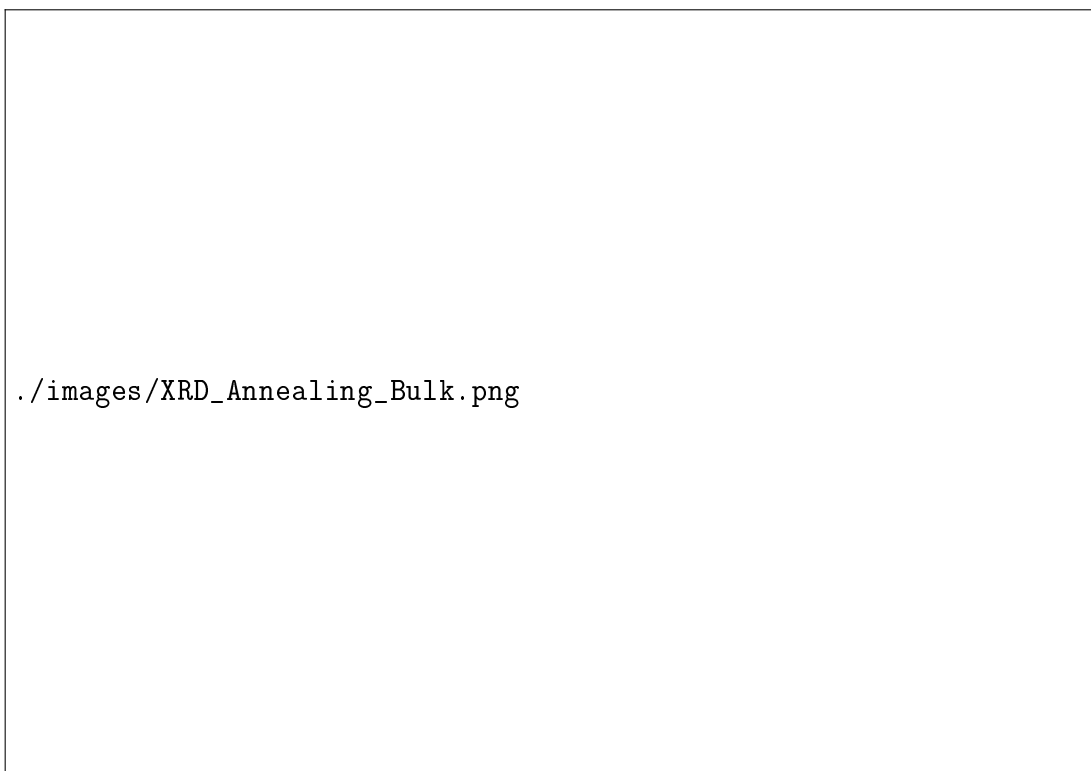


Figure 9: XRD pattern for bulk $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ heated treated to several temperatures for crystallisation peak identified from DSC. Each phase is identified by a tracer at the temperature it was most strongly observed.

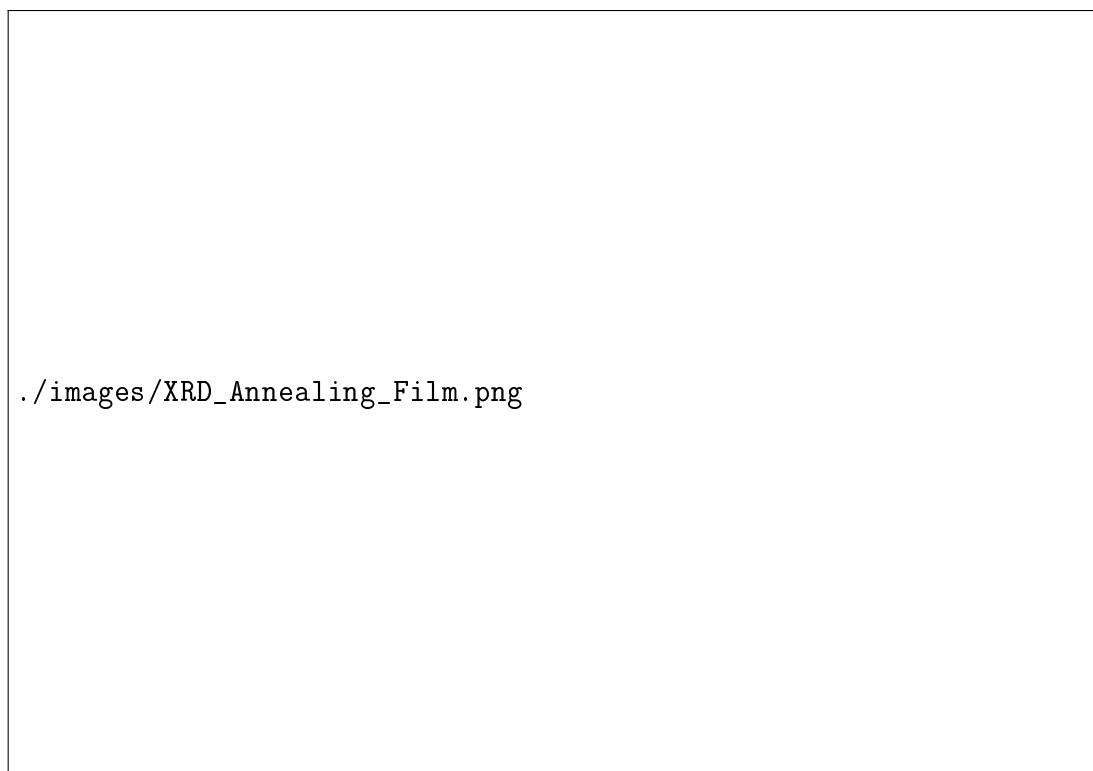



Figure 10: XRD pattern for film $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ heated treated to several temperatures for crystallisation peak identified from DSC. Each phase is identified by a tracer at the temperature it was most strongly observed. Note the Al substrate peaks have been faceted as to not dwarf all other peaks.



`./images/XRD_Dynamic_Bulk.png`

(a)



`./images/Bulk_Heated_XRD_Waterfall3D_Smooth2.png`


(b)

Figure 11: (a) Stacked XRD patterns from the incremental dynamic *in-situ* heating of bulk $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$. Note the peak around 51° is attributed to the AlN heating element. (b) The same XRD patterns as (a) presented in a cascading layout.



./images/XRD_Dynamic_Film.png

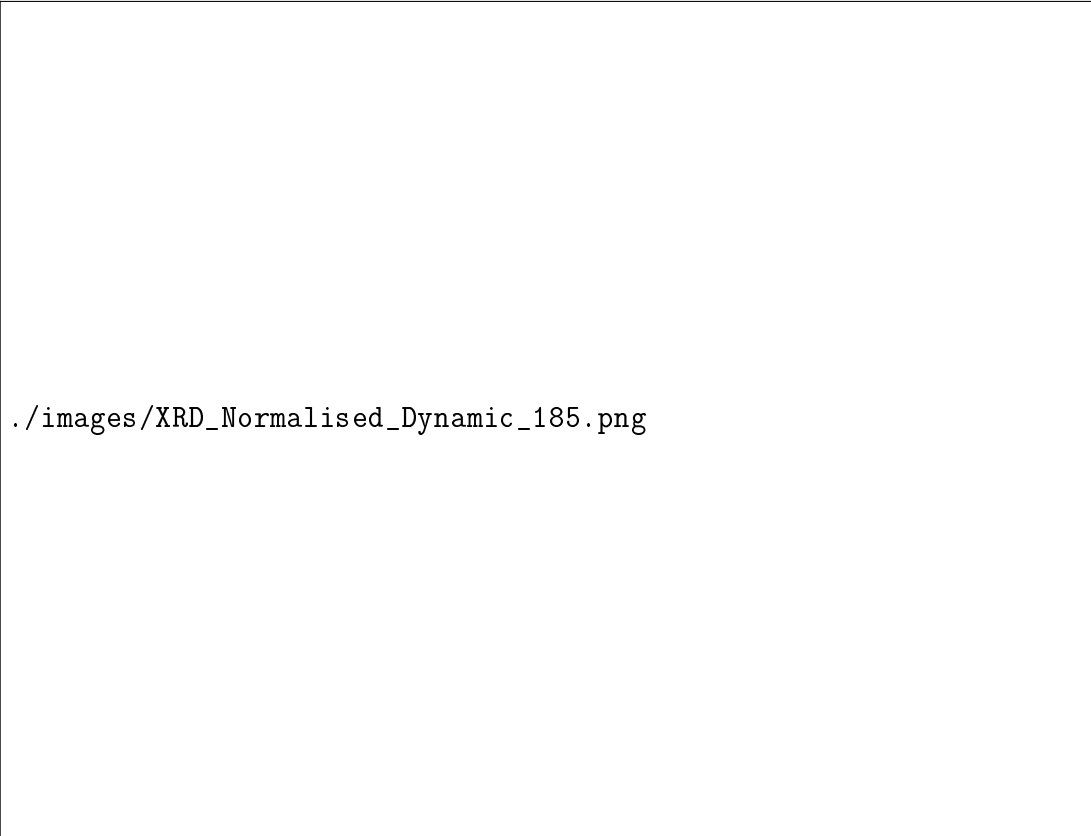
(a)



./images/TF_Facet_HeatXRD_Waterfall3D_Smooth.png

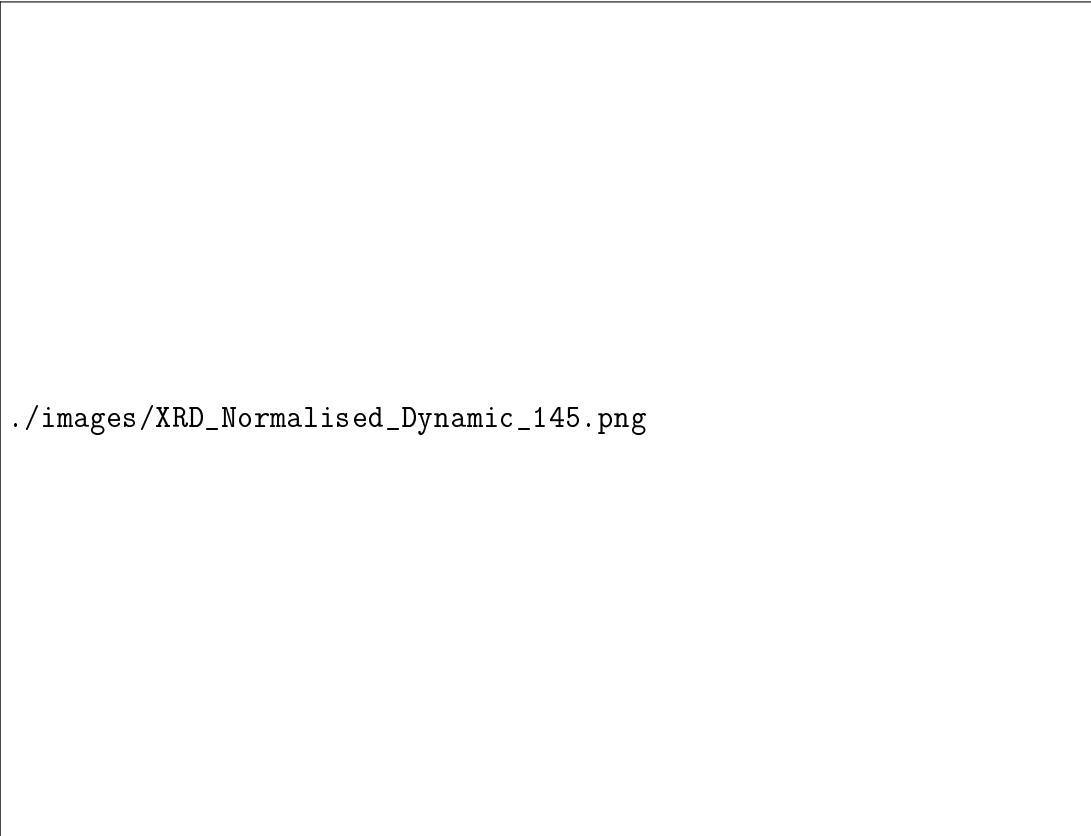
(b)

Figure 12: (a) Stacked XRD patterns from the incremental dynamic *in-situ* heating of film $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$. Note the peak around 51° is attributed to the AlN heating element, and the Al substrate peaks have been faceted as to not dwarf all other peaks. (b) The same XRD patterns as (a) presented in a cascading layout.



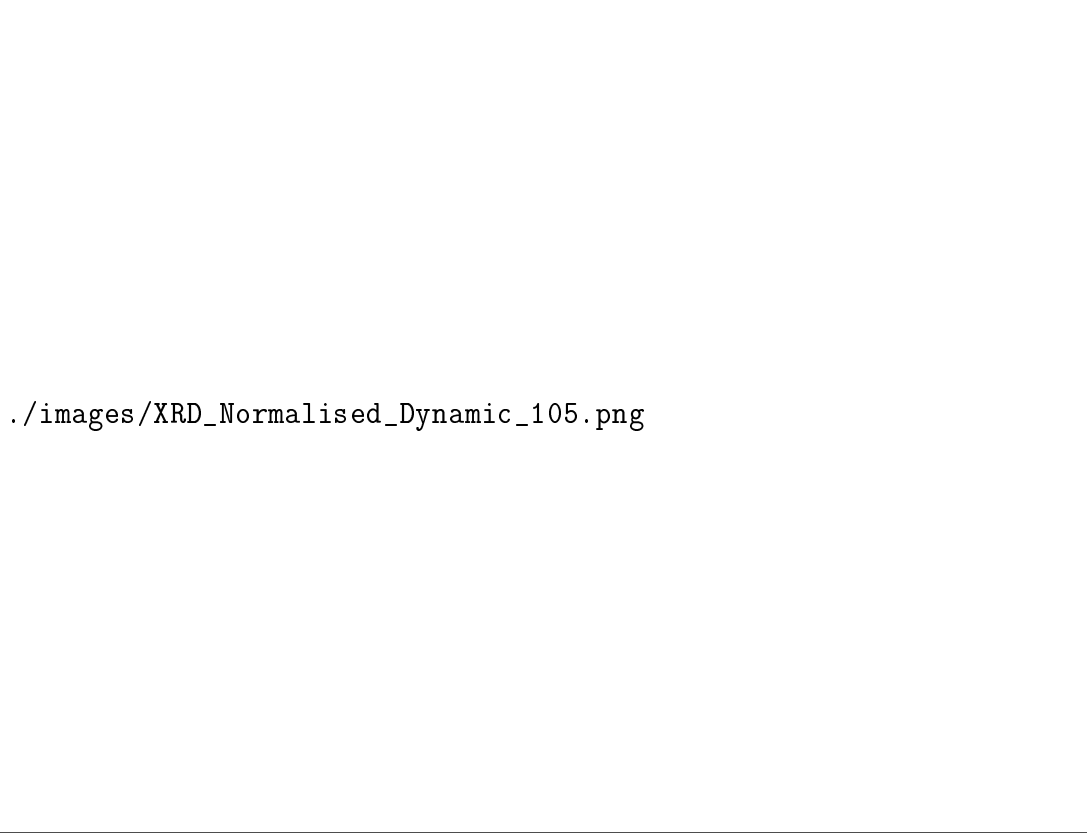
./images/XRD_Normalised_Dynamic_185.png

Figure 13: Normalised dynamic XRD from 150 – 185°C. Large bulk peaks have been faceted as to not dwarf smaller peaks and details.



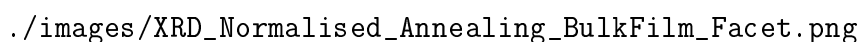
./images/XRD_Normalised_Dynamic_145.png

Figure 14: Normalised dynamic XRD from 110 – 145°C.



./images/XRD_Normalised_Dynamic_105.png

Figure 15: Normalised dynamic XRD from 35 – 105°C.



./images/XRD_Normalised_Annealing_BulkFilm_Facet.png

Figure 16: Supplementary: Normalised annealing XRD pattern for both bulk and film $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ heated treated to several temperatures for crystallisation peak identified from DSC. Bulk is shown in black, and film in red. Note the Al substrate and other high intensity peaks have been faceted as to not dwarf all other peaks.

Table 9: Supplementary: Annealing XRD 2θ peak pattern list. Peaks which appear in both the bulk and film are marked "Both," peaks only appearing on the bulk are marked "Bulk Only," and peaks only appearing on the film are marked "Film Only."

Mg		Mg ₅₁ Zn ₂₀		Ca ₂ Mg ₅ Zn ₅		Ca ₂ Mg ₅ Zn ₁₃		MgZn	
32.2640	Both	15.1461	Bulk Only	10.8738	Both	12.114	Both	12.6360	Both
34.5053	Both	17.5798	Bulk Only	14.0992	Both	13.935	Both	14.7520	Both
36.7065	Both	19.4290	Both	17.9698	Both	20.165	Both	20.639	Both
47.9250	Both	21.6753	Bulk Only	21.7787	Both	21.035	Both	22.263	Both
57.4721	Both	23.2049	Bulk Only	23.5826	Both	23.329	Both	23.580	Both
63.2000	Both	24.5533	Film Only	26.1221	Both	24.641	Both	28.871	Both
67.4268	Both	27.6680	Bulk Only	28.3477	Both	25.281	Both	32.054	Both
68.7541	Both	30.4946	Bulk Only	30.3272	Both	27.947	Both	33.797	Both
70.1210	Both	32.0757	Bulk Only	32.8866	Both	29.258	Both	34.743	Both
72.6686	Both	34.0114	Both	34.2311	Both	30.699	Both	35.892	Both
77.9616	Both	36.3948	Both	34.9708	Bulk Only	31.589	Both	37.121	Both
81.7143	Both	36.9487	Bulk Only	36.3289	Both	33.929	Both	38.101	Both
		37.8181	Both	37.6976	Both	35.308	Both	39.312	Both
		39.1701	Both	38.1445	Both	35.892	Bulk Only	40.416	Both
		42.4369	Both	39.7631	Both	36.806	Both	41.989	Both
		43.2937	Both	41.2057	Both	37.281	Both	42.824	Both
		44.8168	Both	42.4410	Both	38.269	Both	43.917	Both
		47.9318	Both	43.9276	Both	40.041	Both	47.046	Both
		57.4692	Both	45.3071	Both	40.991	Both	48.376	Both
		63.2267	Both	48.1674	Both	42.195	Both	49.498	Both
		64.1349	Film Only	52.0808	Both	43.038	Both	51.285	Both
		65.0419	Bulk Only	53.6599	Both	43.917	Both	53.211	Both
		65.3533	Film Only	56.9387	Both	44.600	Both	55.660	Both
		68.5726	Bulk Only	58.5610	Both	45.306	Both	57.955	Both
		70.0382	Both	60.5081	Both	46.535	Both	60.026	Both
		72.6234	Both	61.8530	Both	47.306	Film Only	62.260	Both
		76.4763	Bulk Only	62.9999	Both	48.104	Bulk Only	63.687	Both
		77.2025	Bulk Only	64.3501	Both	50.079	Both	65.186	Both
		78.3347	Both	65.6320	Both	51.285	Both		
		82.0596	Both	66.8310	Both	56.178	Bulk Only		
				68.7827	Both	58.601	Both		
				70.1095	Both	59.940	Both		
				71.8163	Both	62.028	Both		
				72.8322	Bulk Only	63.590	Both		
				74.9981	Both	64.427	Both		
				78.0830	Both	66.229	Both		
				81.5094	Bulk Only	67.362	Both		
				82.6818	Film Only	68.198	Both		
				83.1204	Both	69.524	Both		
						70.480	Both		
						72.032	Bulk Only		
						73.329	Both		
						73.997	Bulk Only		
						76.736	Both		
						78.690	Both		
						79.631	Both		

./images/XRD_Normalised_Dynamic_BulkFilm_Facet.png

Figure 17: Supplementary: Normalised dynamic XRD pattern for both bulk and film $\text{Mg}_{65}\text{Zn}_{30}\text{Ca}_5$ heated incrementally *in-situ* from 35 – 185°C for crystallisation peak identified from DSC. Bulk is shown in black, and film in red. Note the Al substrate and other high intensity peaks have been faceted as to not dwarf all other peaks.