


한국자기학회 동계학술대회  
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# Rare-Earth-Free Permanent Magnets : MnBi Bulks and Thin Films

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# 발표 순서

01 연구배경 및 필요성

02 MnBi Bulk

03 MnBi Thin film

04 Further works



**01**

## 연구배경 및 필요성

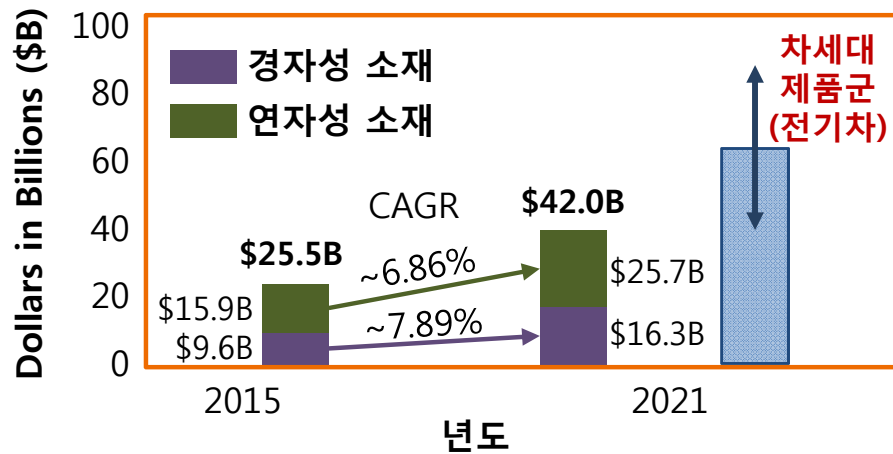
# 자성 재료 시장성

- '14년 28조원 규모 및 CAGR\* >7%의 자성소재 시장 포기할 것인가?
- 현재의 기술장벽/가격장벽 극복 및 독점적 기술/시장 지속을 위한 전략은 있는가?

## 시장성 및 파급효과

### ○ 시장 분석 및 기술/시장 전망

- 소재강국을 위한 선두기술로의 시장 규모 및 성장성



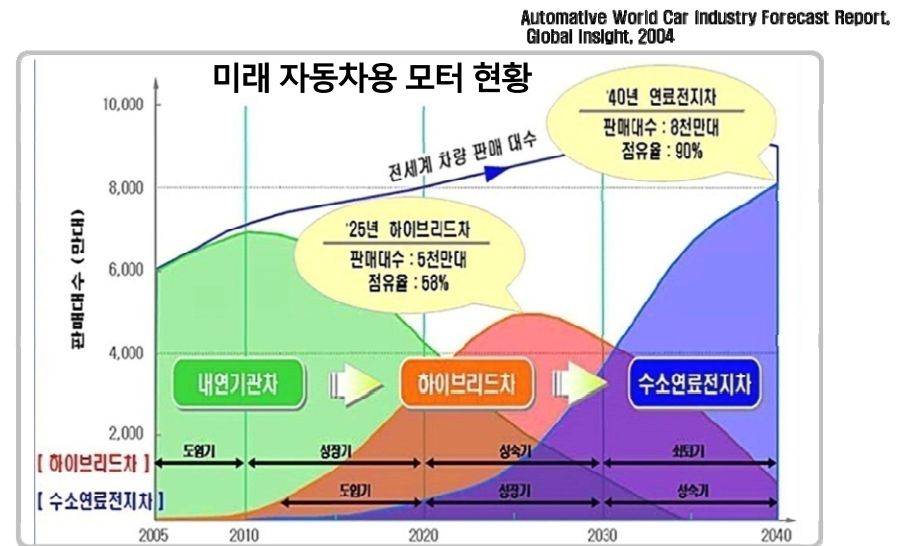
- 전기차/로봇/신재생에너지 등 차세대 제품군 조기 범용화에 의한 폭발적 시장 잠재력

→ 국가 신수종 산업 분야에 대한 독점적 경쟁력 확보

## 기술성과 경제성

### ○ 기술/시장 환경 및 개발 방향 설정

- 소재 기술이 부품-제품 시장에 대한 제 1 요소 (모터/자동차 등 부품/제품 기술 완성도 ~100%)

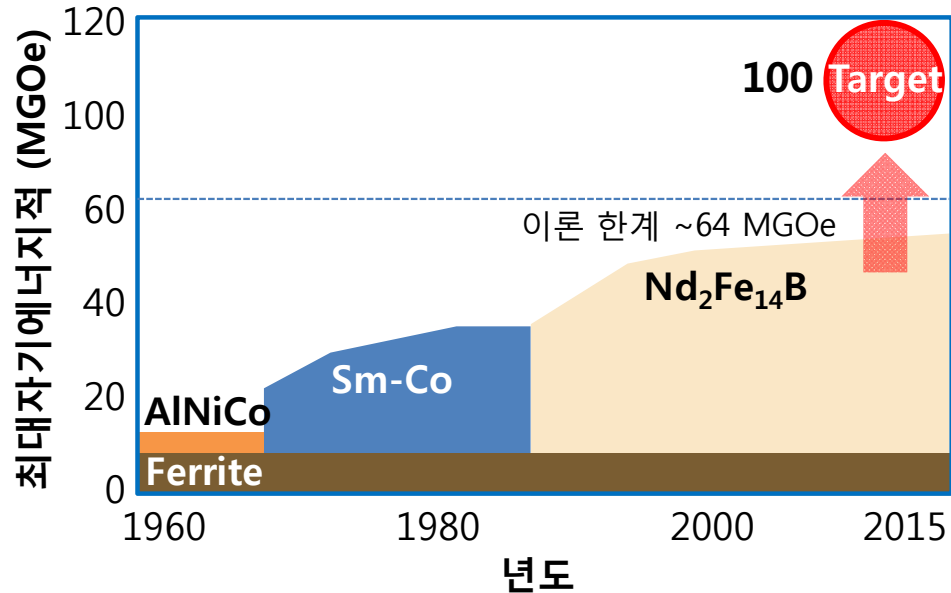


미래 자동차 적용 모터 : 100~120개

\*CAGR: Compound Annual Growth Rate, 연평균성장률

# 신영구자석의 필요성

## 4대 상용 경자성소재 개발 및 현 수준

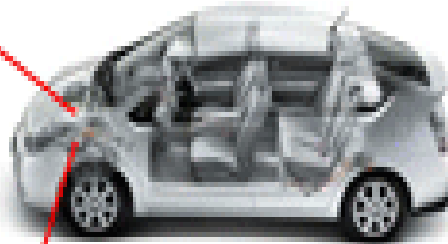
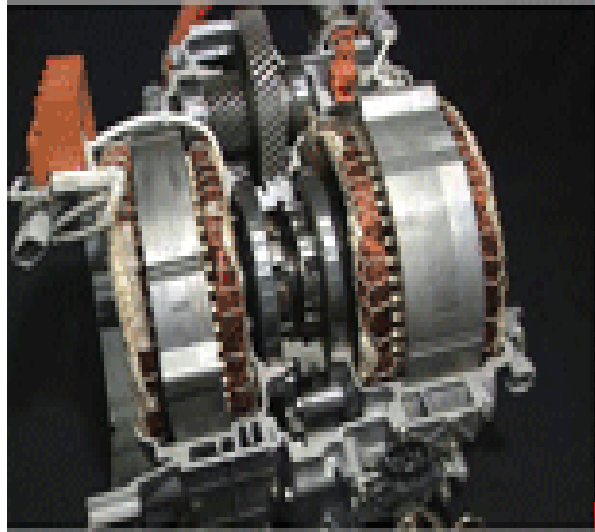


## Needs 및 현 기술 한계

- 차세대 전기자동차 및 풍력을 위한 모터 부품의 **고효율화/소형화** 구현 가능한 창의소재 요구
- 기존 소재로는 구현 불가: **이론한계 80% 도달/복합·나노 구조화 전략 실패**
- 現 자성 발현 이론 또는 공간군 설정 기반 연구의 한계: 소재 설계 정밀도 및 속도 문제

→ 상용소재 물성 한계 극복: **신 영구자석 필요**

# 희토류 영구자석의 이슈



하이브리드 및 전기 자동차

Magnet

Operation temperature: 200°C

고온에서 쉽게 자기특성 저하

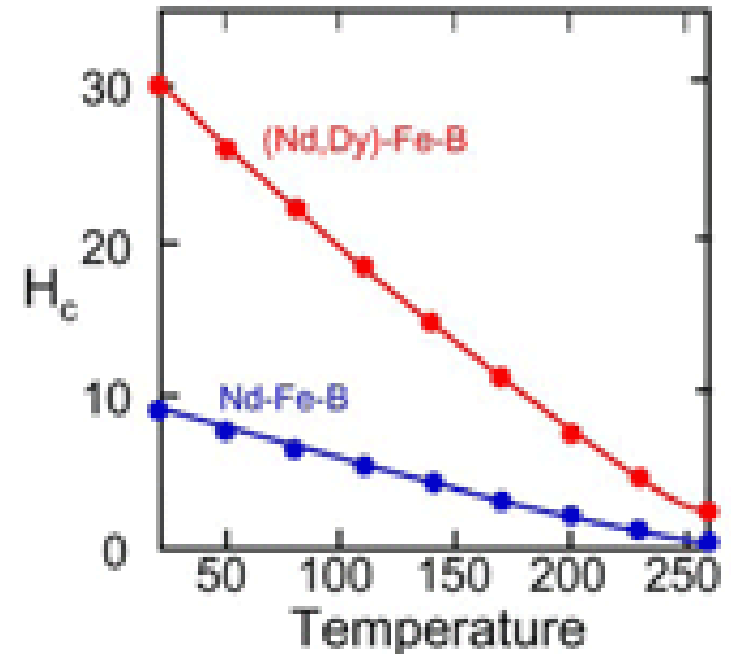
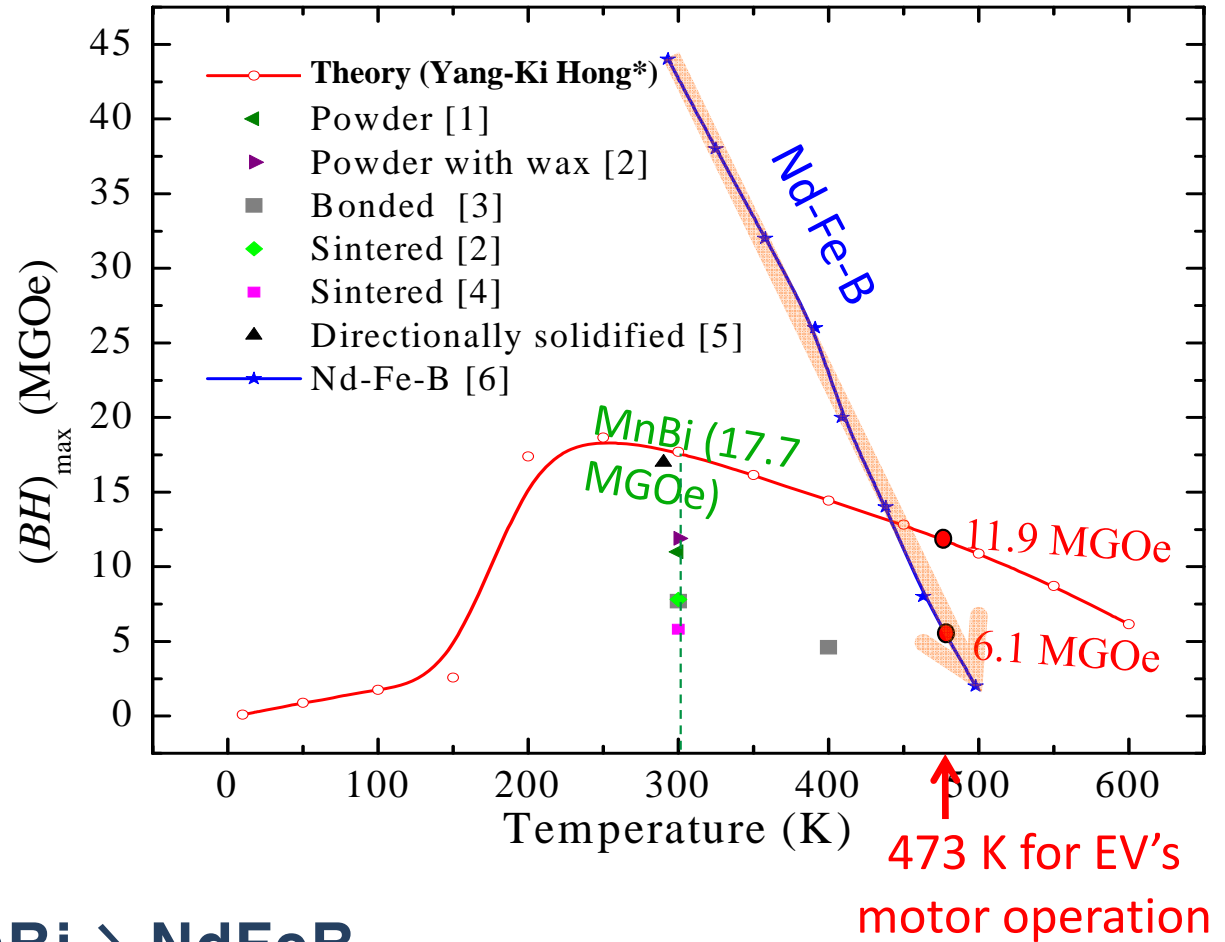
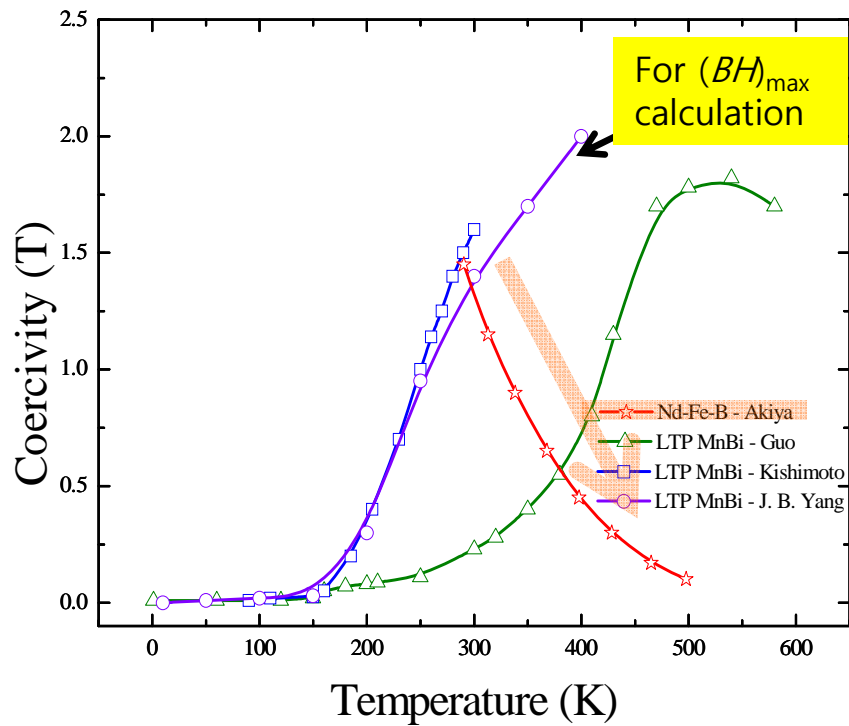


Figure. Permanent magnets in a HV motor and temperature degradation of  $H_c$  for Nd-Fe-B sintered magnets. Source: NIMS, Japan 2009

# NdFeB 자석의 현 문제점



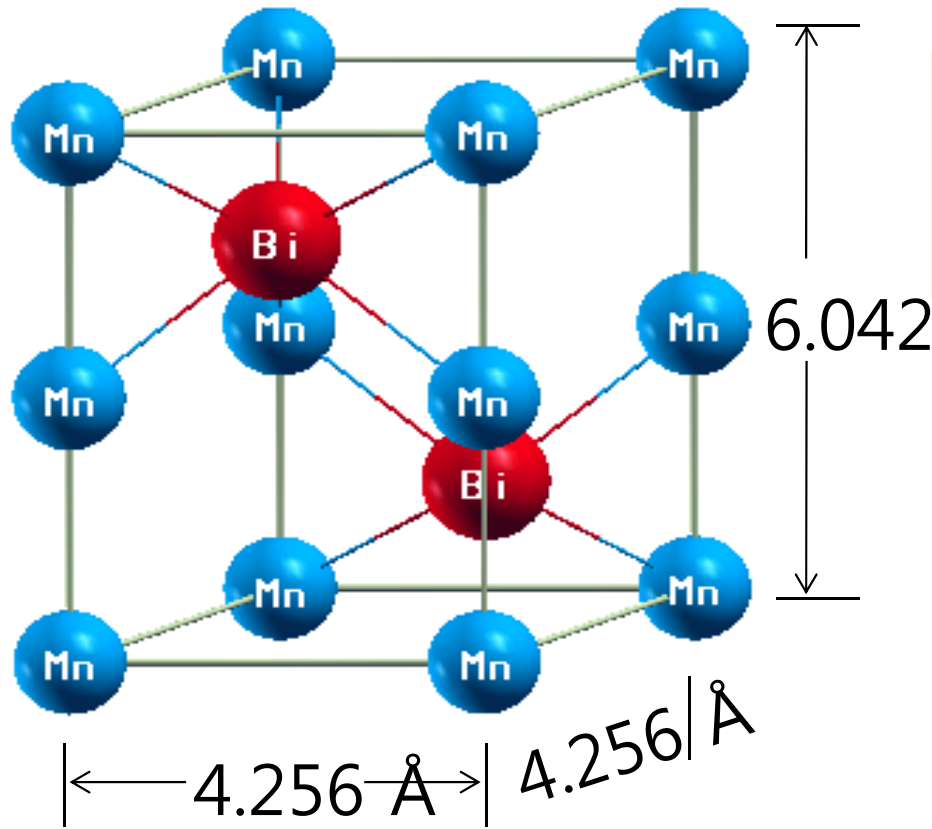
MnBi > NdFeB



높은 보자력 및 최대 에너지적 (HEV 구동온도(200°C))

\* Yang-Ki Hong et al., *Metals* 4, 455 (2014)

# MnBi의 특징



LTP Structure of MnBi

## LTP MnBi의 이론적 자기특성

- 최대자기에너지적 ( $BH_{\max}$ ) : 17MGOe
- 포화자화 ( $M_s$ ) > 8.2 KG
- 보자력 ( $H_c$ ) : 17 kOe

- 높은 자기결정이방성
- HEV 구동온도(200°C)보자력

MnBi > NdFeB

Nd계 대체 가능 경자성체

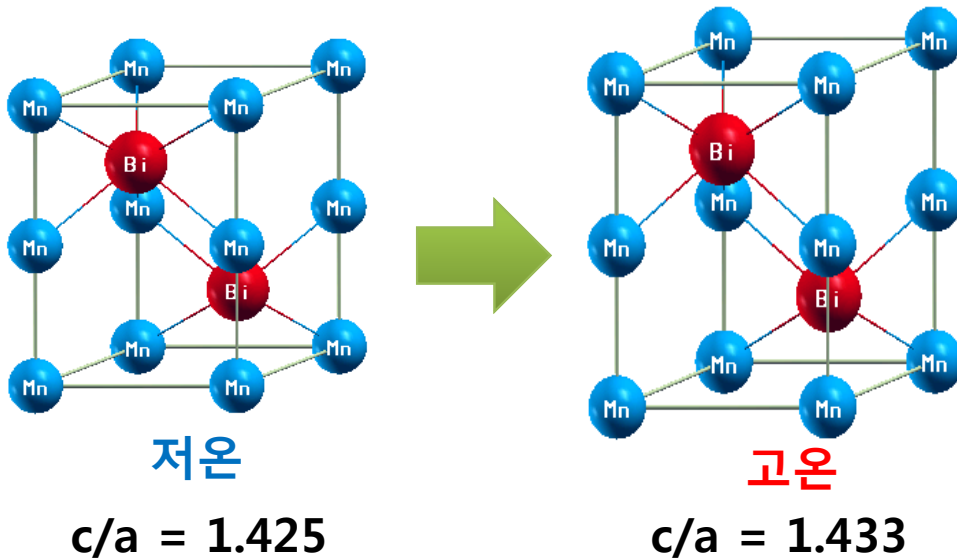


# MnBi의 특징

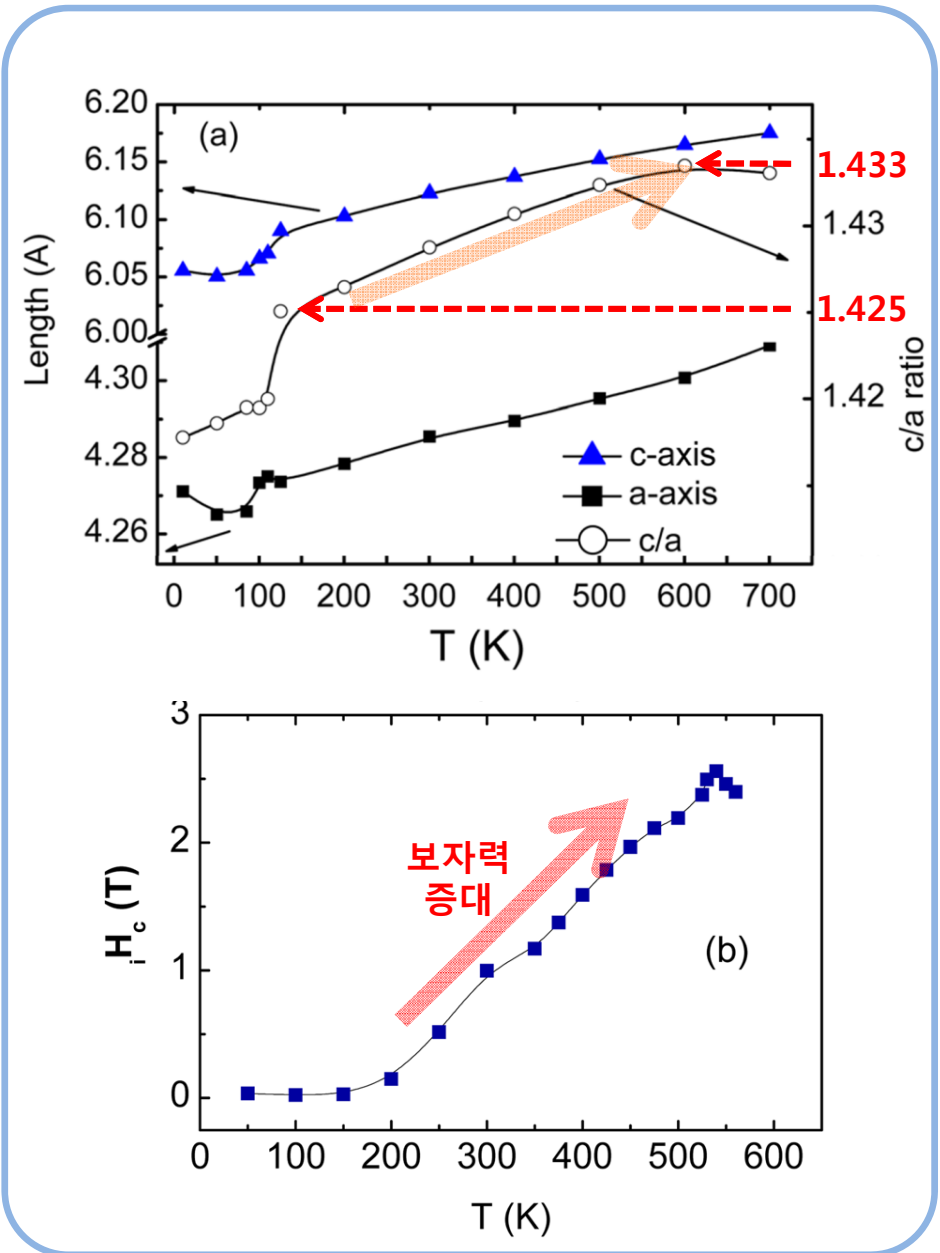
- Magnetocrystalline Anisotropy

$$E_{uniaxial} = K_u \sin^2 \theta$$

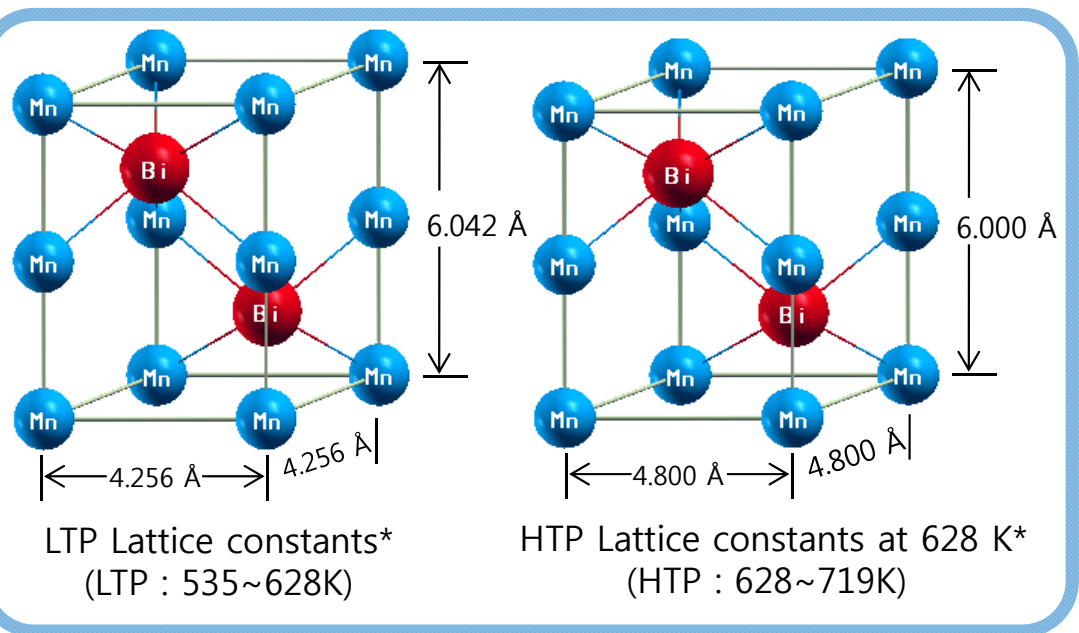
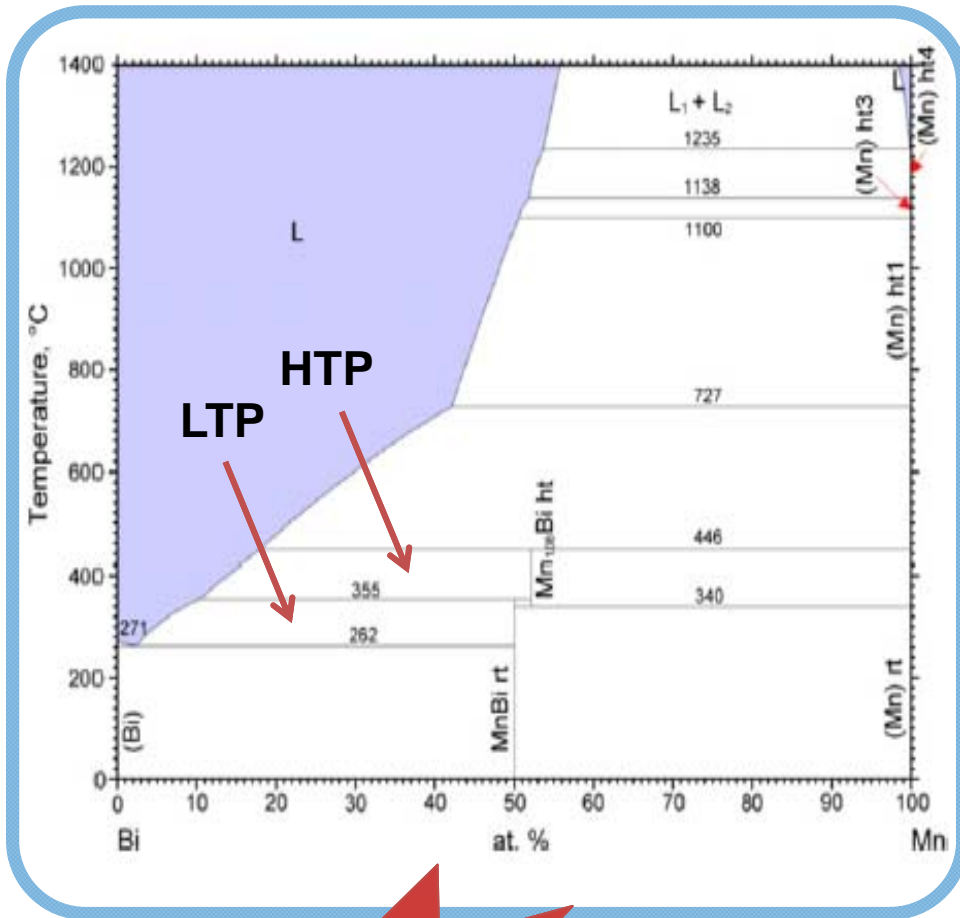
- 온도에 따른 Uniaxial anisotropy



온도가 증가할 수록 Uniaxial anisotropy 증가에 따른 보자력 증대



# Hexagonal MnBi (LTP and HTP)



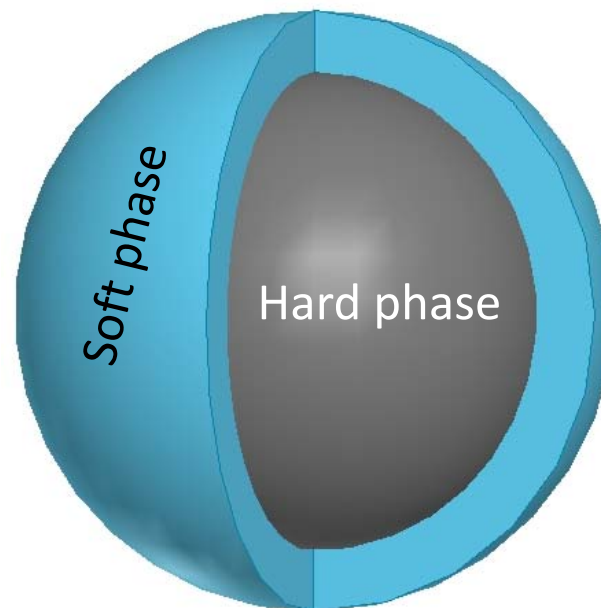
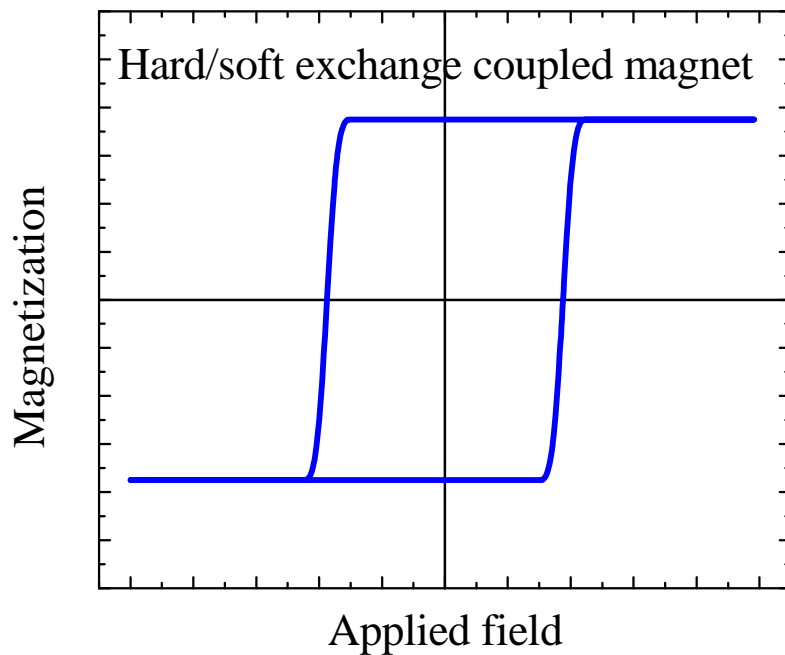
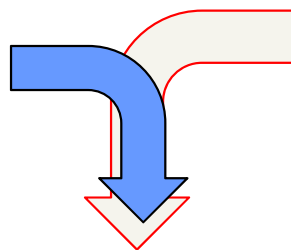
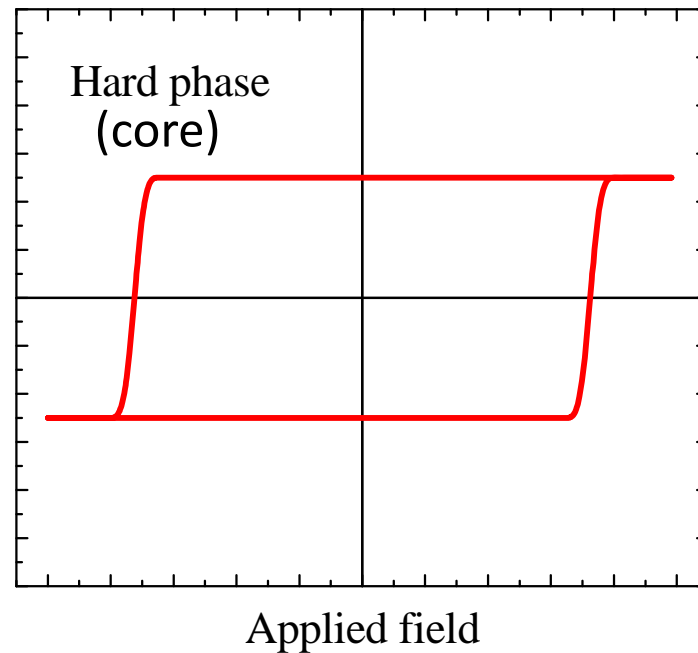
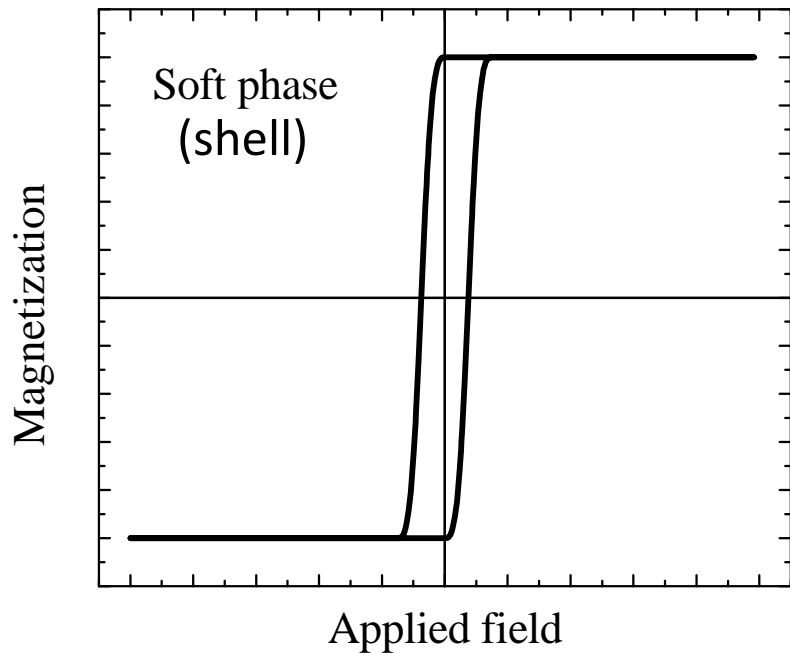
## ● LTP-MnBi 형성 문제점

- 넓은 범위(온도 및 조성)의 포정반응
- 매우 느린 확산 속도(Mn and Bi)



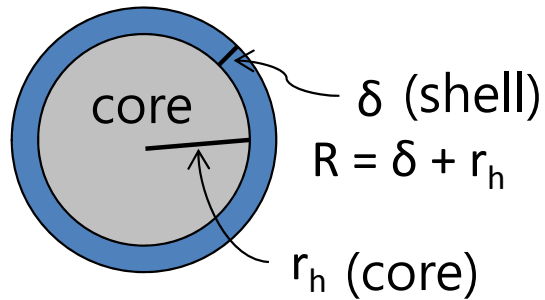
고 순도의 MnBi-LTP 제조

# Exchange-coupled core/shell 모델



Modified Skomski's Model

# Model for Core-Shell Magnet (Two phase)



Shell Thickness ( $\delta$ )

$$\delta = \frac{1}{2} D_h (f_h^{-1/3} - 1) \text{ ---- Eq. (1)}$$

Modified Skomski's Equations for  $(BH)_{max}$

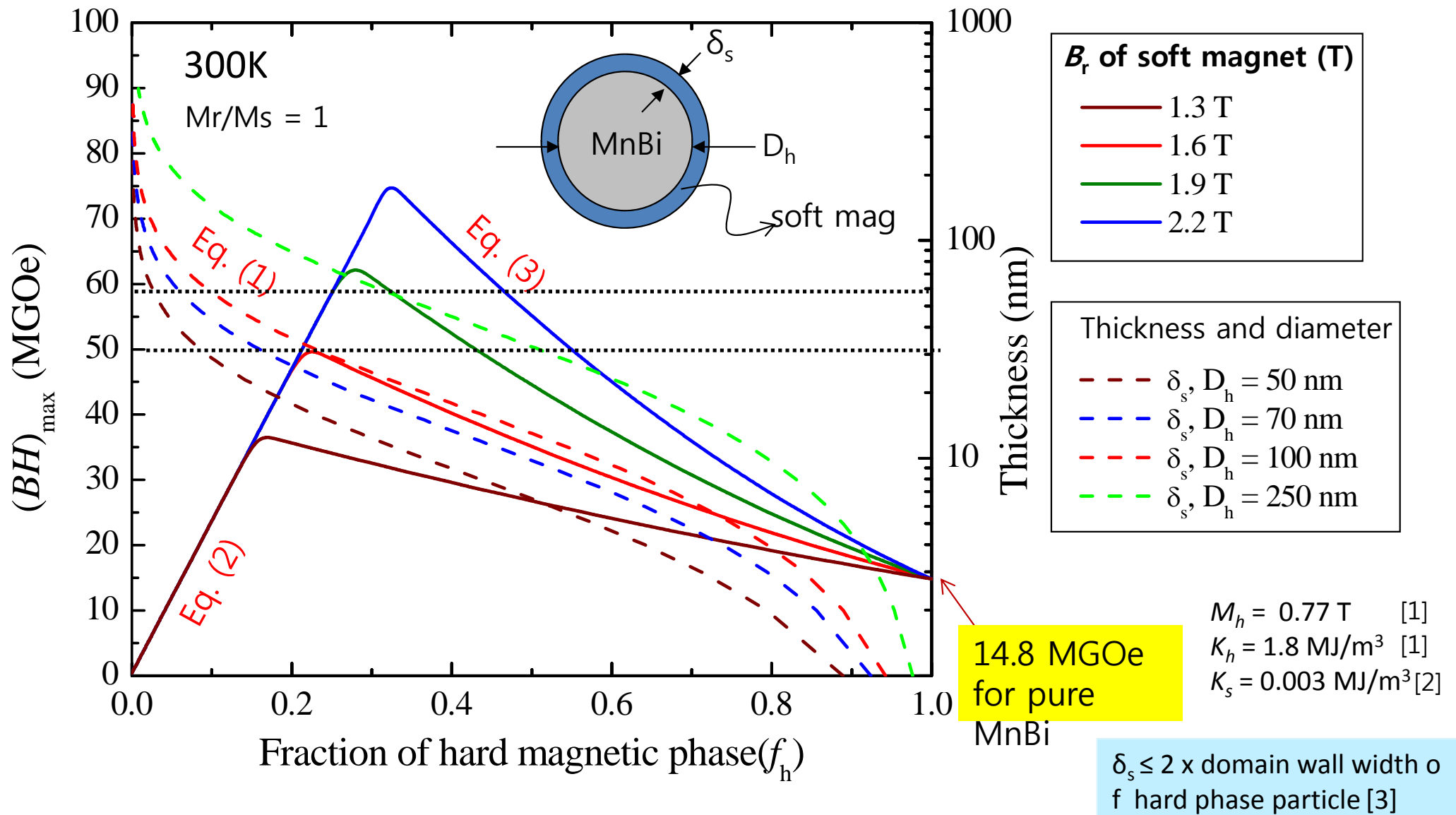
For  $H_N < \frac{M_r}{2}$

$$(BH)_{max} = \frac{4\pi [K_s + f_h (K_h - K_s)]}{10^5} (MGOe) \text{ ---- Eq. (2)}$$

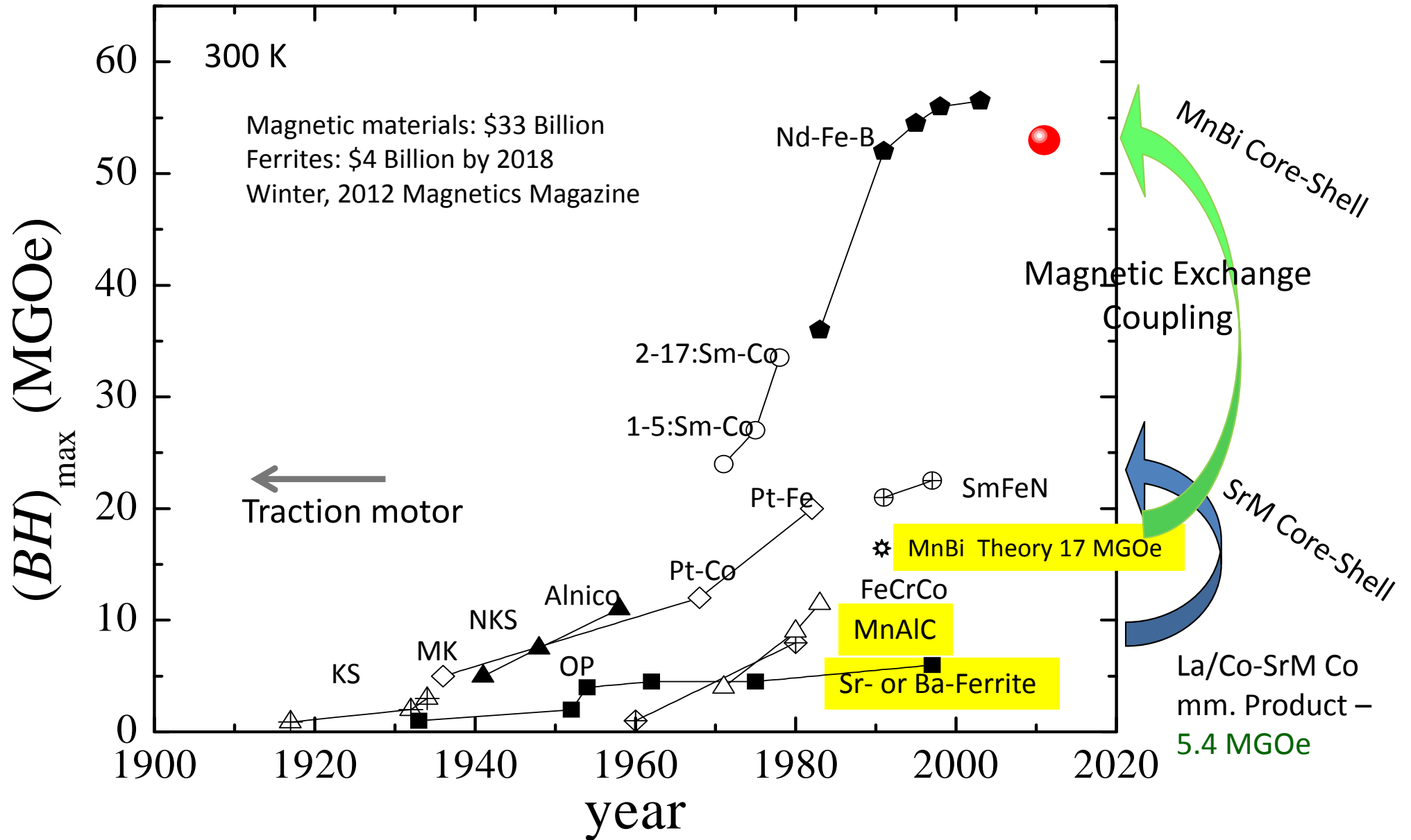
For  $H_N > \frac{M_r}{2}$

$$(BH)_{max} = \frac{[B_{r\_soft} - f_h (B_{r\_soft} - B_{r\_hard})]^2}{4} \times 10^2 (MGOe) \text{ ---- Eq. (3)}$$

# Theoretical $(BH)_{\max}$ -300K of MnBi core - soft Shell nanomagnet



# MnBi core-shell : NdFeB 대체 가능 경자성



# 고특성 MnBi 합성 연구 동향

## ● MnBi Bulk: Anisotropic fully dense MnBi magnet

- High-volume fraction of LTP-MnBi: Melt-spinning & magnetic separation
  - Mn segregation from MnBi liquid through peritectic reaction at  $\sim 450^{\circ}\text{C}$
  - Decomposition of LTP-MnBi at  $\sim 260^{\circ}\text{C}$
  - Formation of MnO
- Right combination of powder synthesis method and consolidation technique



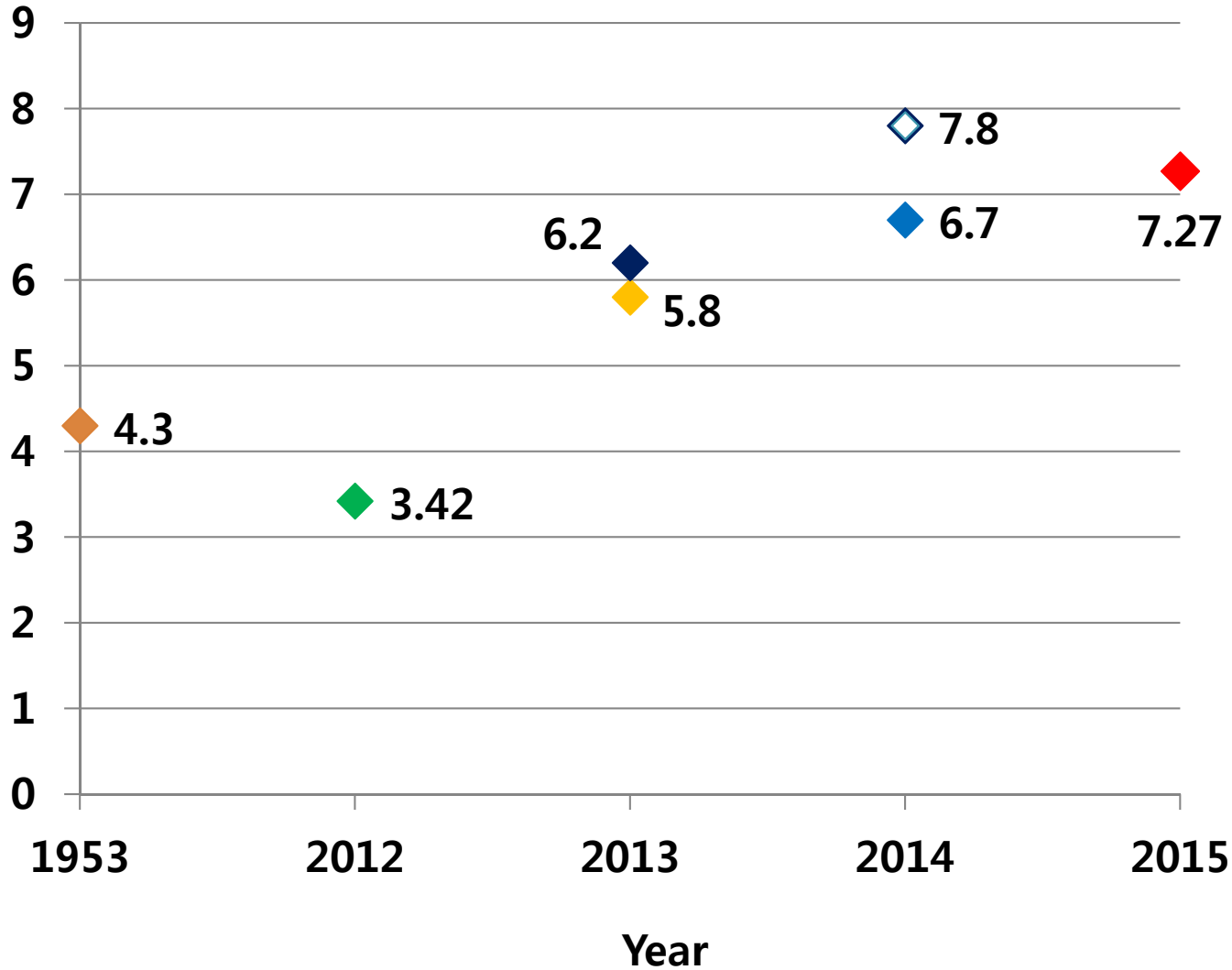
## ● MnBi Films: High-volume fraction of LTP-MnBi

- Optimization of Bi/Mn ratio
- Preheating substrate
- Deposition and annealing in the same chamber



# 그룹-연도별 $(BH)_{\max}$ - MnBi Bulk

$(BH)_{\max}$

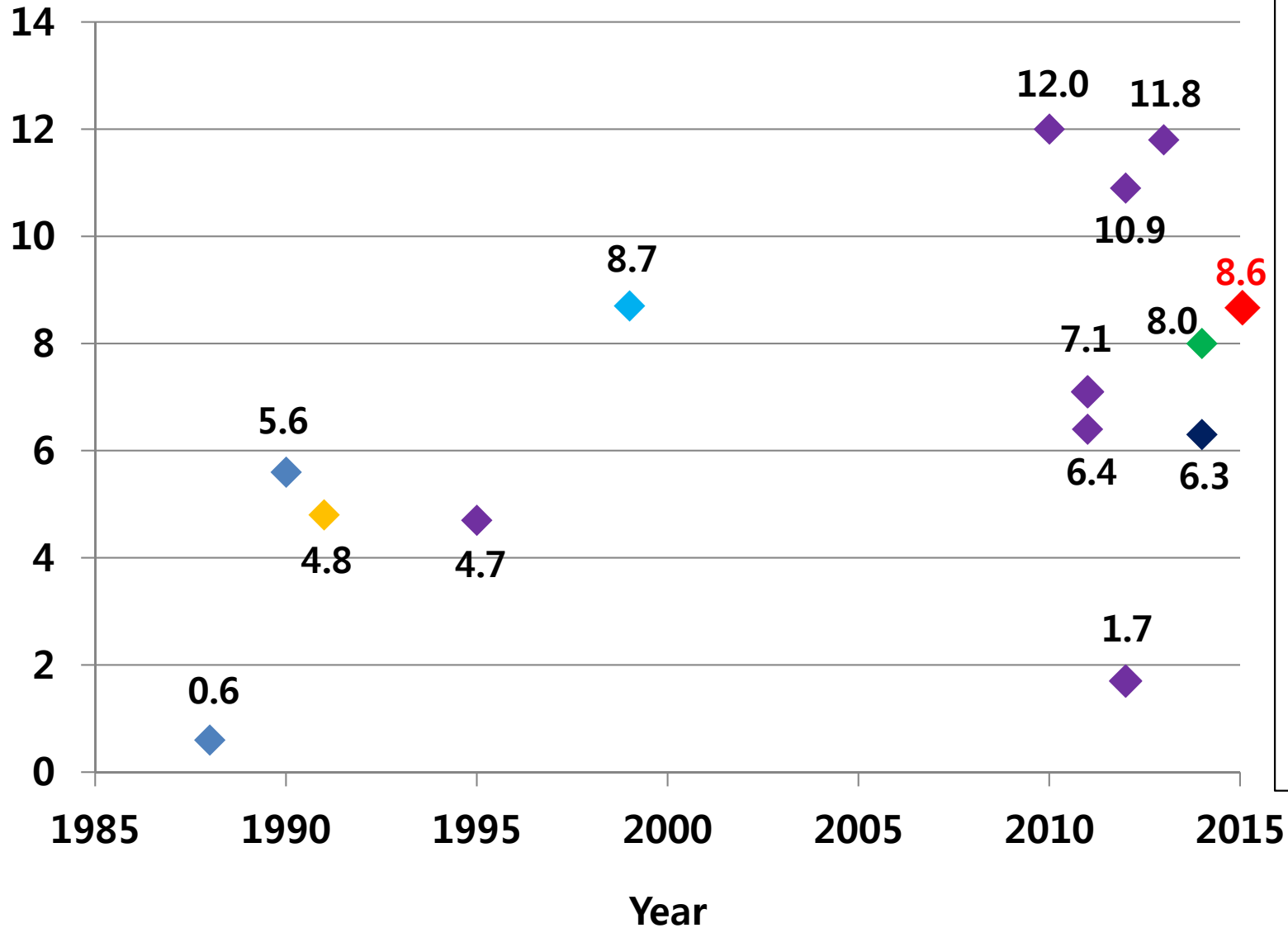


- ◆ W.Y. Lee  
(Yonsei University)
- ◆ Edmond Adams  
(U.S. Naval Ordnance Laboratory)
- ◆ M. Yue  
(Beijing University of Technology)
- ◆ N.V Rama Rao  
(University of Delaware)
- ◆ J Ping Liu  
(University of Texas)
- ◇ J Cui  
(University of Maryland)
- ◆ J.R. Kim  
(Hanyang University, ERICA)



# 그룹-연도별 $(BH)_{\max}$ - MnBi Film

$(BH)_{\max}$



- ◆ W.Y. Lee  
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(Chinese Academy of Science)
- ◆ G. Q. Di  
(Nagoya University)
- ◆ D. J. Sellmyer  
(University of Nebraska)
- ◆ T Zhu  
(Central University for Nationalities)
- ◆ Qianqian Xu  
(Nagoya University)
- ◆ W. Liu  
(Chinese Academy of Science)
- ◆ T. Suzuki  
(University of Alabama)



## 02 MnBi Bulk

# MnBi Bulk 합성

Arc-melting

Rapid solidification  
(melt-spinning)

Cold pressing

Annealing

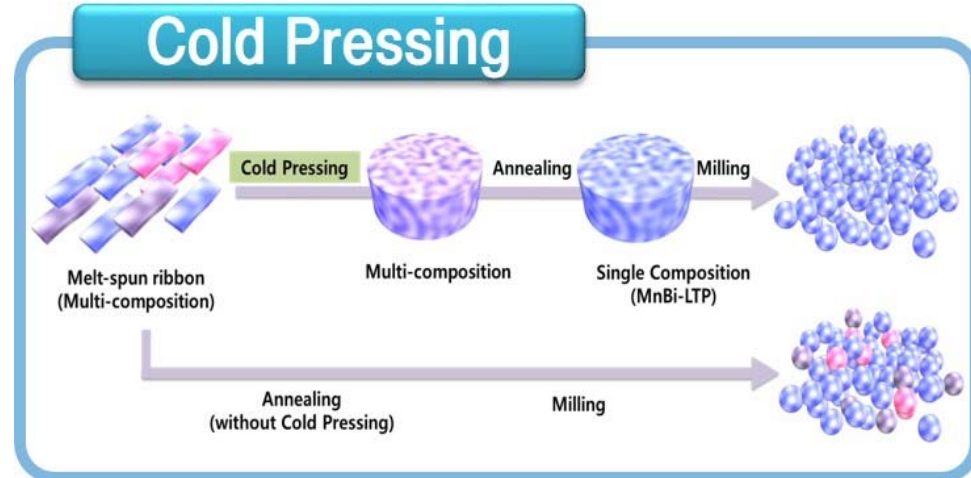
Magnetic separation

Ball-milling  
Jet-milling

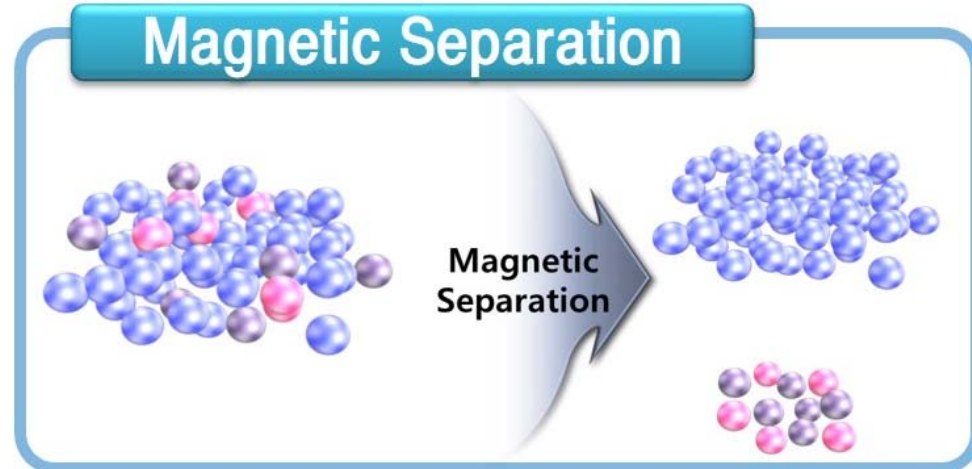
Magnetic pressing

Hot compaction

## Cold Pressing



## Magnetic Separation



- Compaction : 리본 내 확산 → 리본 간 확산
- Multi-composition ribbons → 균일한 초기 조성 유지
- MnBi-LTP가 제대로 생성되지 않은 powder를 분리

고 비율 Low temperature phase 제조

# Melt-spinning(Rapid solidification) 효과

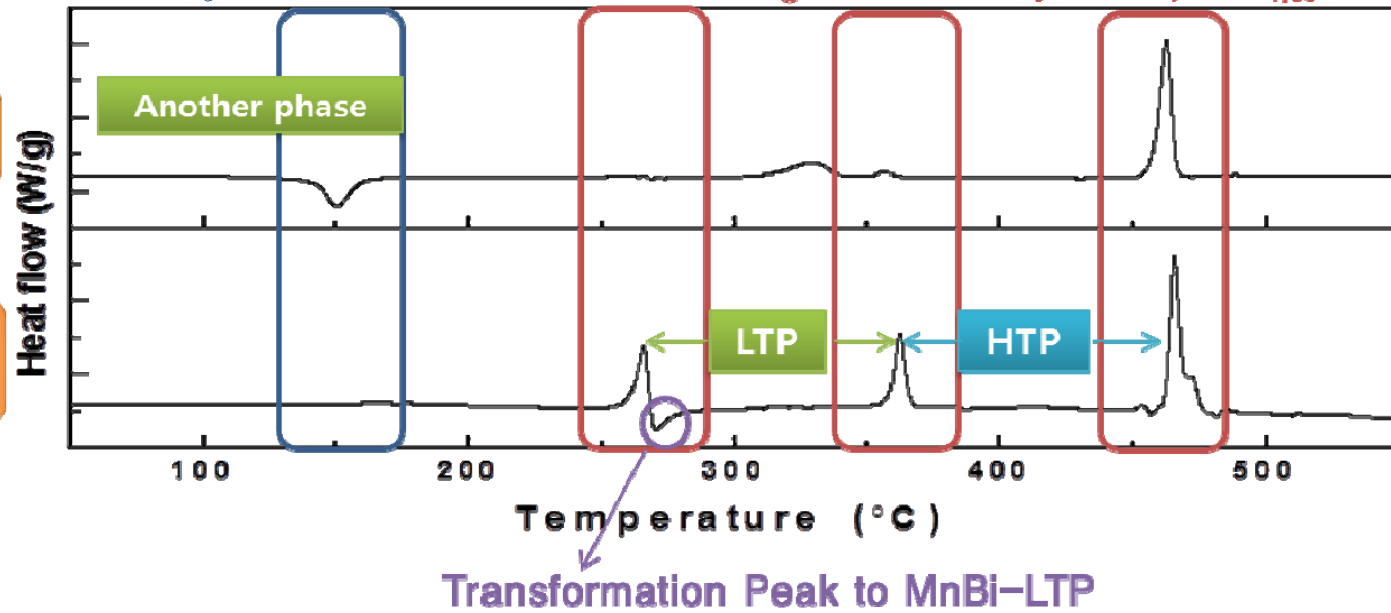
## Differential Scanning Calorimetry (DSC)

Crystallization Peak

Melting Peaks of Bi, MnBi, Mn<sub>1.08</sub>Bi

Non-quenching

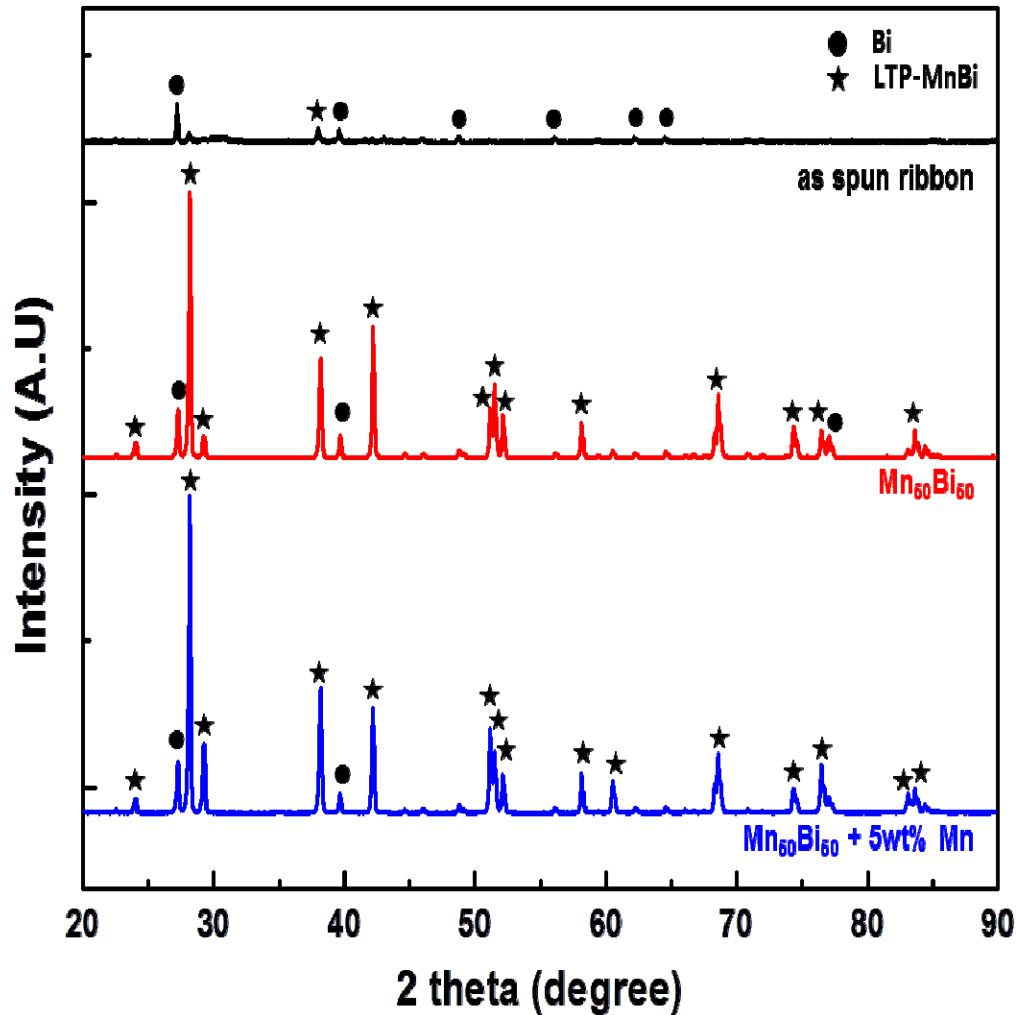
Melt-spun ribbon  
(wheel speed : 55m/s)



● LTP-MnBi 합성에 효과적

# 열처리 온도 및 조성에 따른 결정성

## X-ray Diffraction (XRD)

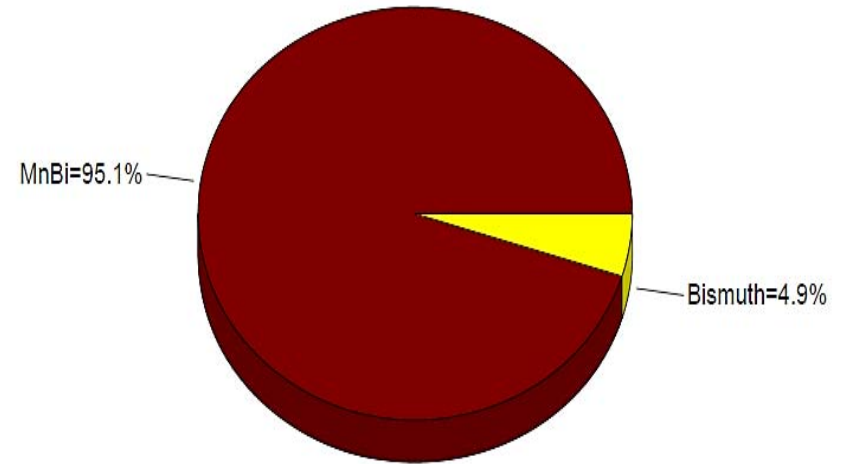


● 300°C 열처리 후 LTP-MnBi 결정성 증가

● 조성 :  $Mn_{50}Bi_{50}$  (+5wt% Mn)에서 가장 우수한 결정성

# 조성 특성 (+5wt% Mn)

- $Mn_{50}Bi_{50}$  (+5wt% Mn)
- Annealed at 300°C for 40h
- LTP-MnBi : 95.1% , Bi : 4.9%

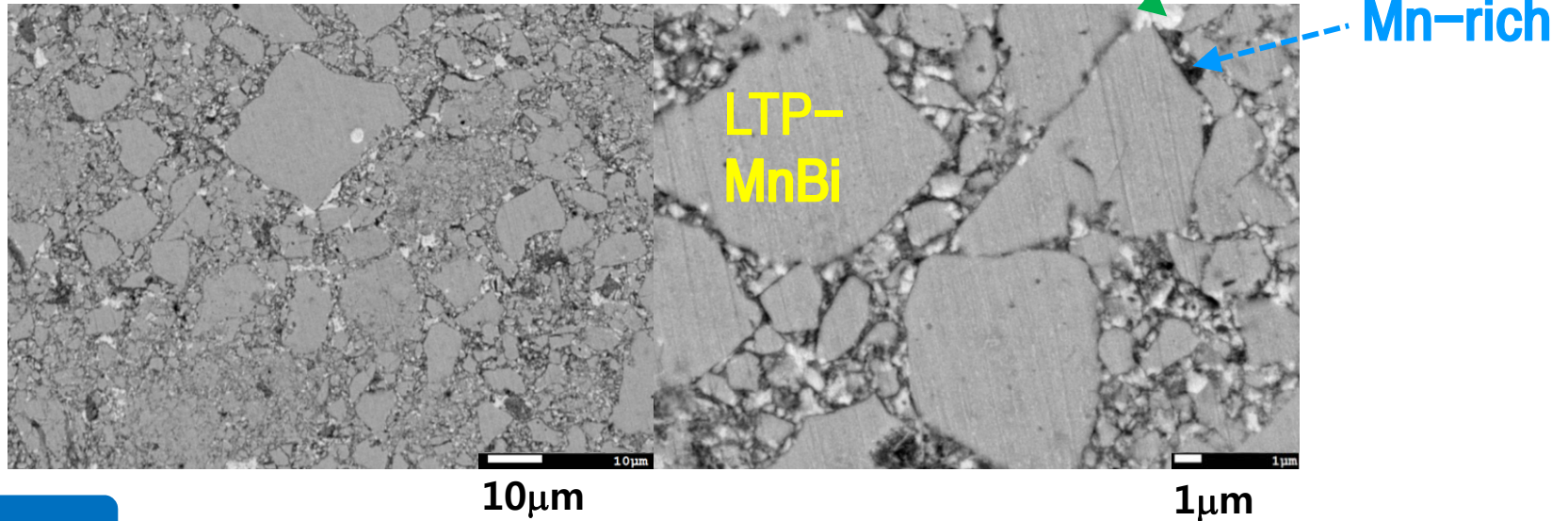


		J B Yang	Rama Rao	J Cui	Wooyoung Lee
연도		2002	2013	2014	2014
소속		Missouri Univ.	Delaware Univ.	Northwest National Lab.	Yonsei Univ.
제조공정		Sintering Melt-Spinning	Arc-melting Melt-Spinning	Arc-melting Melt-Spinning	Arc-melting Melt-Spinning
특징		$Mn_{55}Bi_{45}$ Magnetic separation	$Mn_{50}Bi_{50}$ 573K 24h LEBM : 0.5 ~ 3 $\mu$ m	$Mn_{50}Bi_{50}$ 563K 24h ~5 $\mu$ m	$Mn_{50}Bi_{50}$ (+Mn5%) 573K 40h Magnetic separation
Wt (%)	MnBi	≒ 90%	79%	91.1 %	95.1 %
	Mn	-	3%	5.2 %	-
	Bi	-	18%	3.7 %	4.9 %

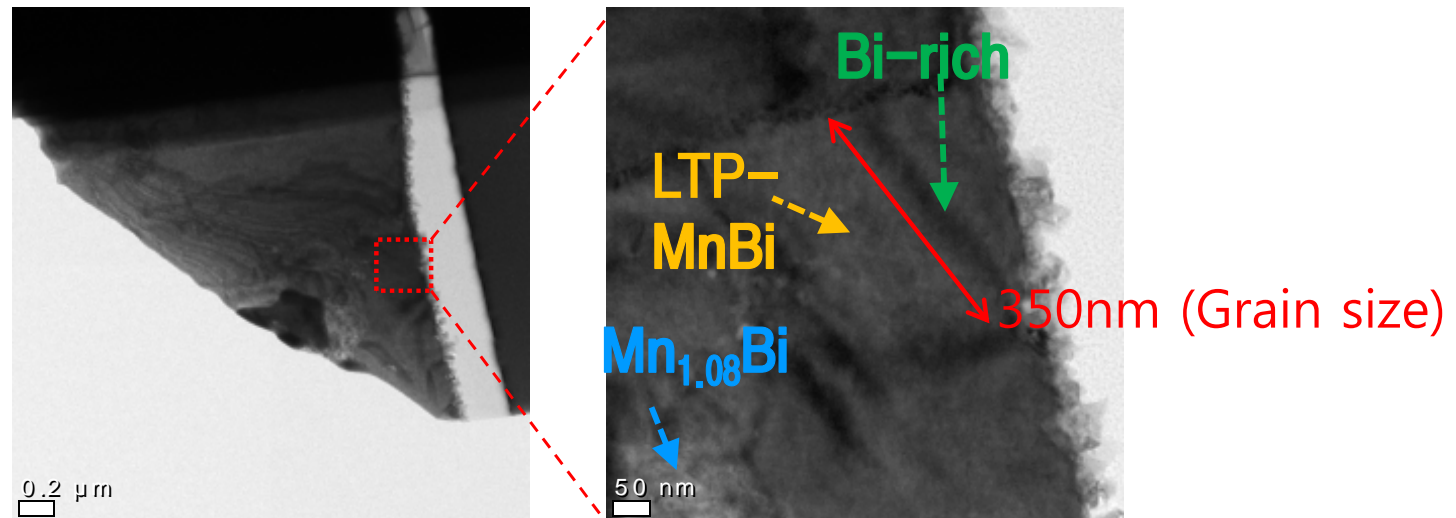
# 미세구조 분석 (Hot compacted magnet)

## SEM(BSE) image

$Mn_{50}Bi_{50}$  (+ 5wt% Mn) , milling time(1h)



## TEM image

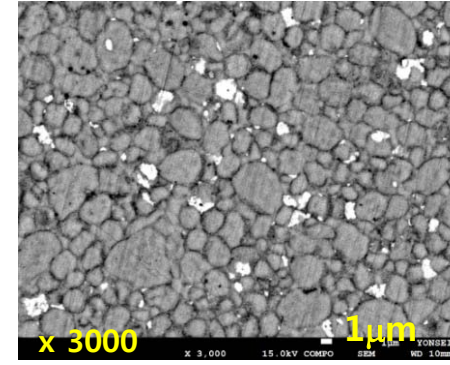
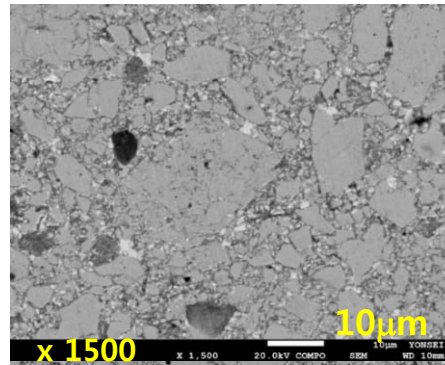
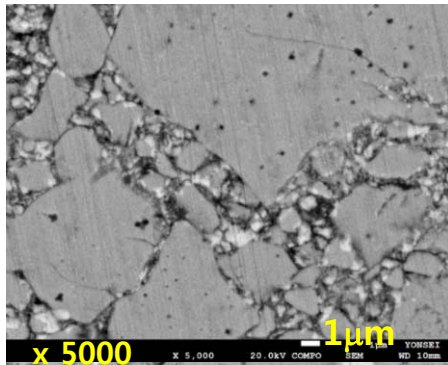


# Particle Distribution

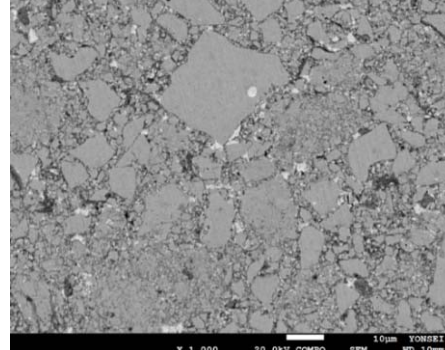
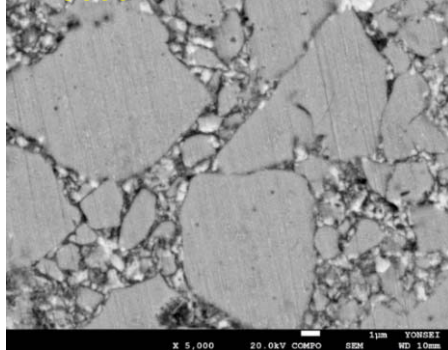
## Ball-mill

## Jet-mill

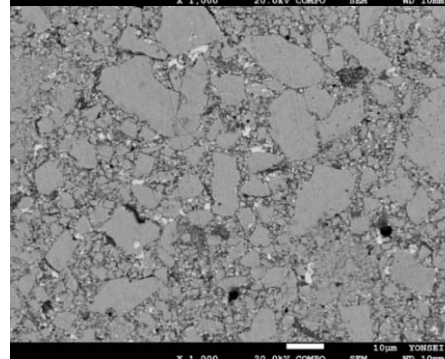
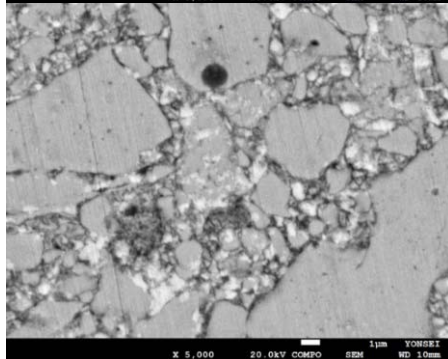
1.0 hr



2.0 hr



2.5 hr

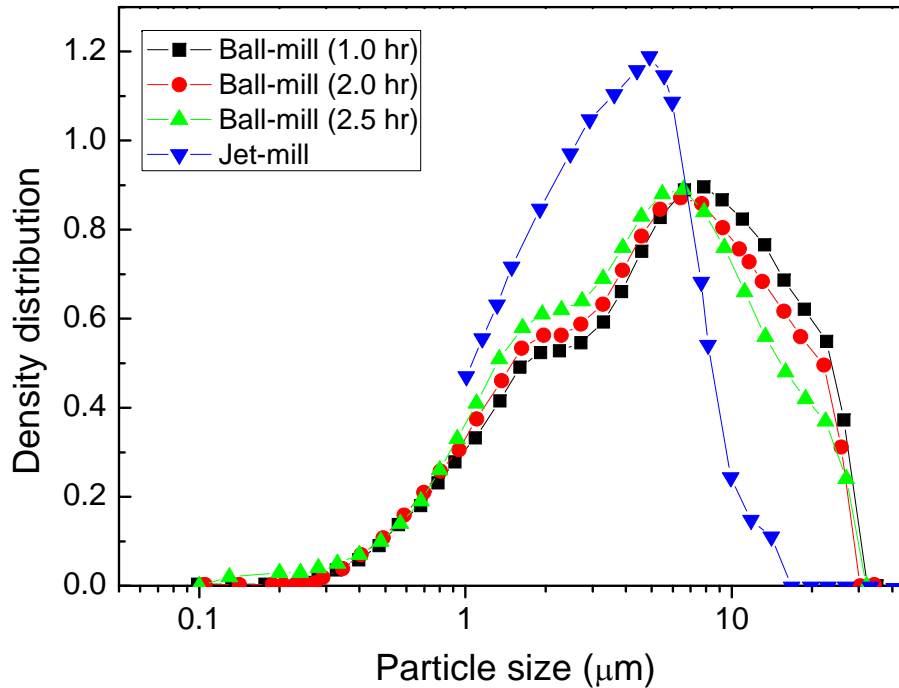


Ball-mill & Jet-mill

- Different distribution in shape and size of particles



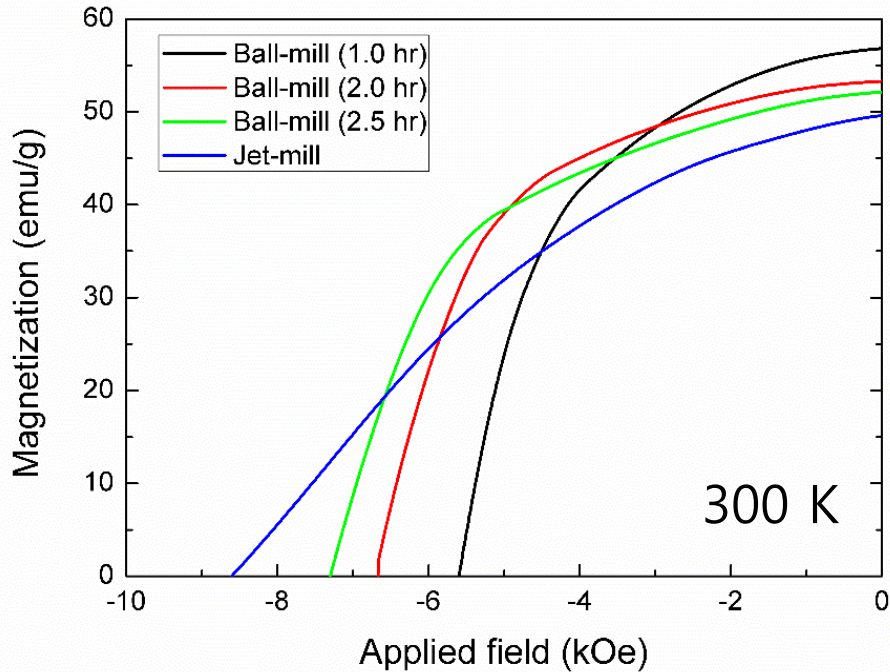
# Particle Size Analysis



	Surface Mean Diameter [μm]	Volume Mean Diameter [μm]	Average Particle Size at maximum Density Distribution
Ball-mill (1.0 hr)	2.99	7.95	7.40
Ball-mill (2.0 hr)	2.77	7.43	6.63
Ball-mill (2.5 hr)	2.27	6.62	6.11
Jet-mill	3.10	3.89	4.90

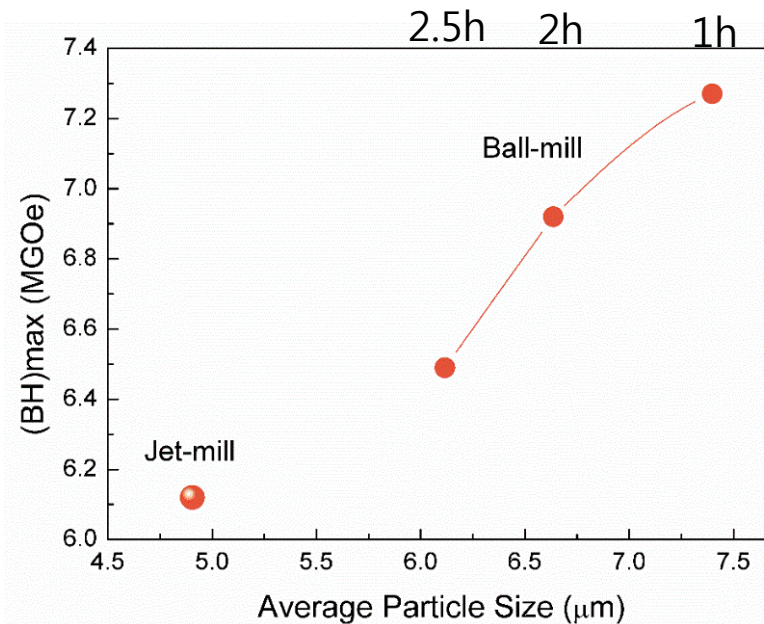
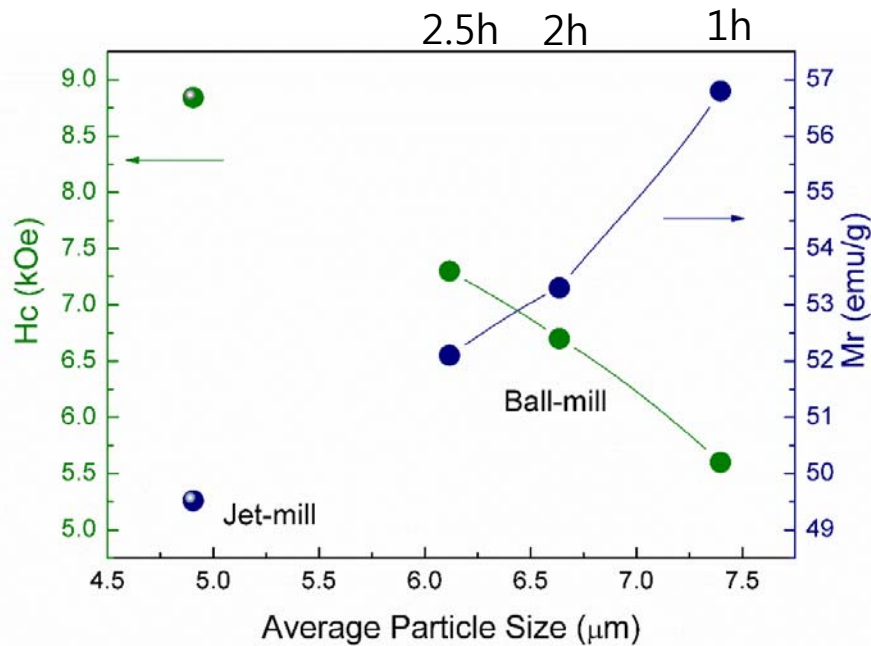
- Ball-milling 시간이 증가함에 따라
  - 입자크기 분포 불균일
  - 평균입자크기 감소
  - 10 μm 이상 감소 & 6 μm 이하 증가
- Jet-milling 평균입자크기 가장 작고 균일한 분포

# 자기 특성 분석



	$H_c$ [kOe]	$M_r$ [emu/g]	$(BH)_{max}$ [MGOe]	Density (g/cm <sup>3</sup> )
1.0 hr	5.6	56.8	7.3	8.10
2.0 hr	6.7	53.3	6.9	8.37
2.5 hr	7.3	52.1	6.5	8.41
Jet-mill	8.6	49.6	6.3	

- Ball-milling 시간이 증가함에 따라  
-  $H_c$  증가 &  $M_r$  감소
- Jet-milling (inlet pressure : 50 psi, N<sub>2</sub>)  
-  $H_c$  더욱 증가 &  $M_r$  더욱 감소



# 자기 특성 분석

## ● Hc 증가:

### Nucleation filed model

H. Kronmüller et al., J. Phys.: Condens. Matter 26, 064210 (2014)

Y. C. Chen et al., Scr. Mater. 107, 131 (2015)

$$H_c = \frac{2K_1}{M_s} \alpha - N_{eff} M_s$$

$K_1$ : Magnetocrystalline anisotropy constant

$M_s$ : Saturation magnetization

$\alpha$ : Misalignment of neighboring grains & width of the region of reduced magnetocrystalline anisotropy

(due to deteriorating effects of the microstructure)

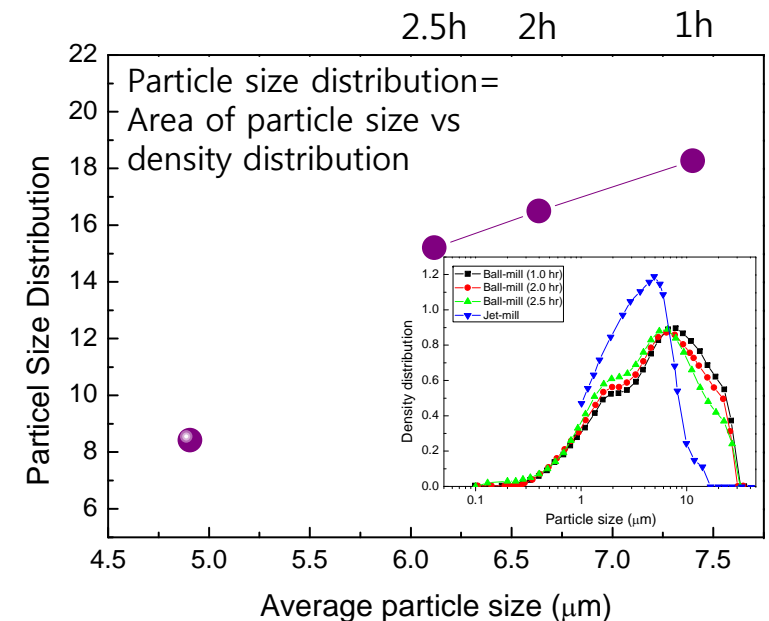
$N_{eff}$ : Effective demagnetization factor ( $N_{\perp} - N_{\parallel}$ )  $\propto$  crystal size

Ball-milling time  $\uparrow$ :  $\alpha_{1h} < \alpha_{2h} < \alpha_{2.5h}$

$N_{eff}^{1h} > N_{eff}^{2h} > N_{eff}^{2.5h}$

$$H_c = \frac{2K_1}{M_s} \alpha - N_{eff} M_s$$

## ● Mr 감소: LTP-MnBi 손실



# MnBi Bulk 요약

- $(\text{Mn}_{50}\text{Bi}_{50} + 5\text{wt}\% \text{Mn})$  조성에서 95.1 % LTP-MnBi 합성
- Cold pressing 과 Magnetic separation 방법으로 고비율 LTP-MnBi powder 제조
- Ball-milling 시간이 증가함에 따라 입자크기 감소, Mr감소, Hc증가
  - Mr 감소 : LTP 손실때문
  - Hc 증가: 미세구조 저하효과 증가 (misaligned grain and deteriorated grain surface) 와 demagnetization factor 감소 때문
- Jet-milling은 입자의 크기와 모양이 균일 분포하게 하나 Hc증가, Mr감소
- Ball-milling 1시간으로 만들어진 powder를 이용한 hot-compact MnBi bulk자석에서 최고  $(\text{BH})_{\text{max}} = 7.3 \text{ MGOe}$  얻음



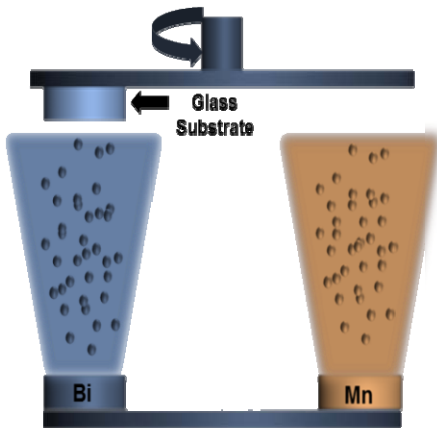
**03**

## MnBi Thin Films

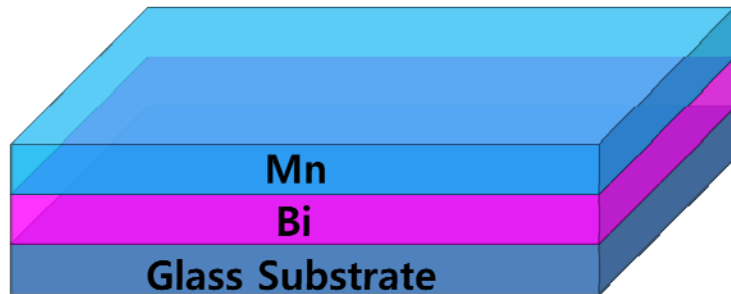
# MnBi Thin Film 합성

## Deposition

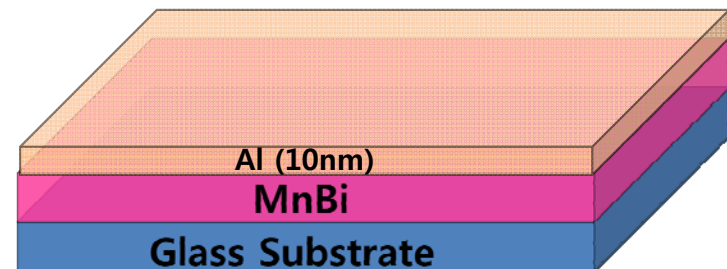
Bi/Mn  
Multilayer on Glass substrate



UHV Magnetron Sputtering System



Bi/Mn multilayer



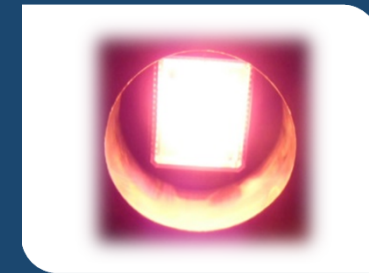
MnBi film

## Annealing

- Ex-situ Annealing



- In-situ Annealing



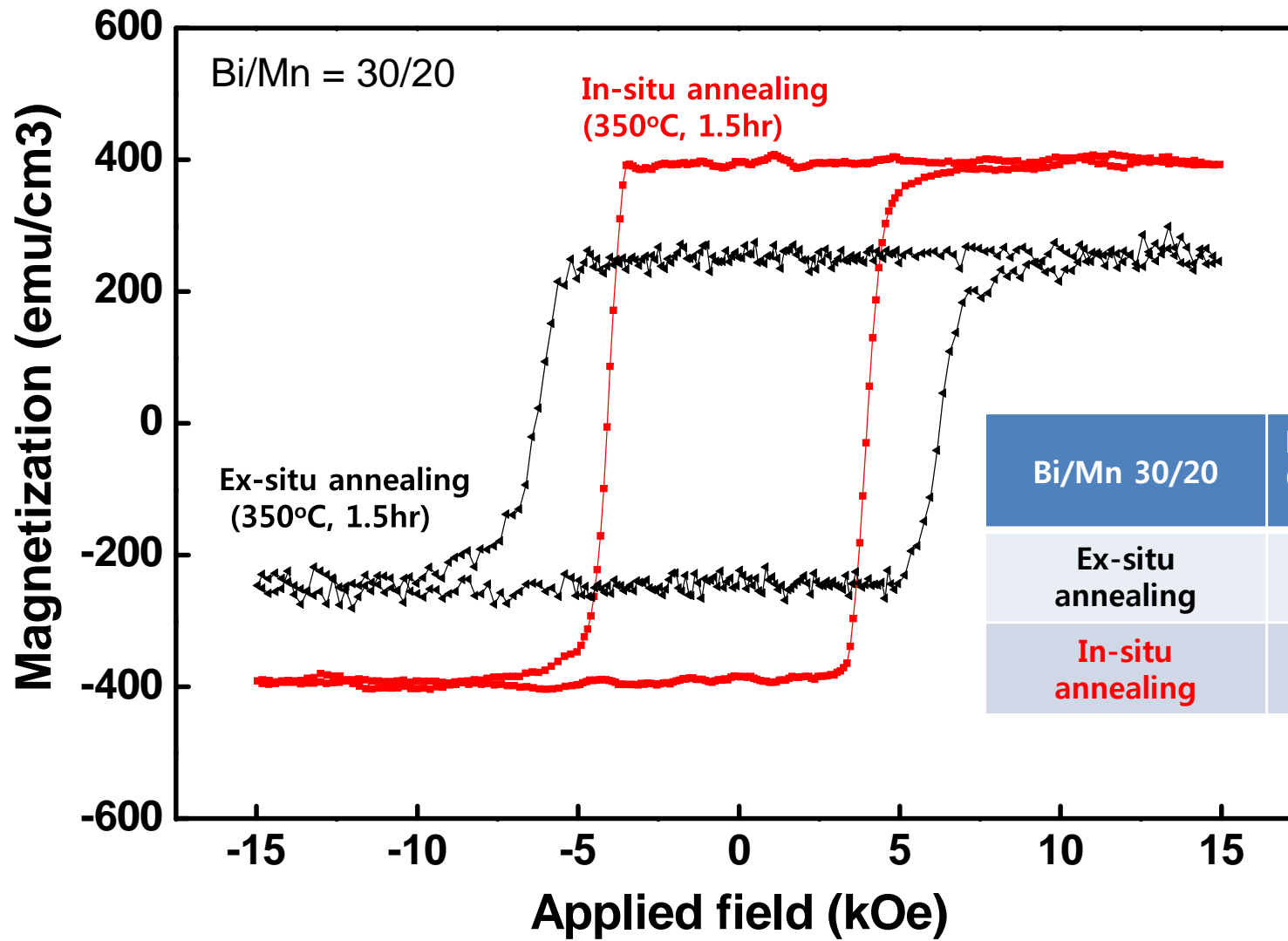
Heating system in UHV chamber

# MnBi Thin Film 합성

- 조성 제어 : Bi, Mn 증착 두께 제어
- MnBi 총 두께 = 50 nm 고정
- Capping layer Al = 10 nm 고정

샘플 종류	증착 순서	Bi/Mn 두께(nm) 비율	
Bilayer	Bi/Mn	28/22, 30/20, 32/18, 34/16, 36/14	
Trilayer	Bi/Mn/Bi	30/20, 32/18, 34/16, 36/14, 38/12	
Multilayer	Bi/Mn (2L)	34/16	Bi/Mn =34/16
	Bi/Mn/Bi (3L)	17/16/17	
	....	....	
	Bi/Mn/Bi/Mn/Bi/Mn/Bi/Mn/Bi/Mn (10L)	6.8/3.2/6.8/3.2/6.8/3.2/6.8/3.2/6.8/3.2	

# Annealing 조건에 따른 자석 특성

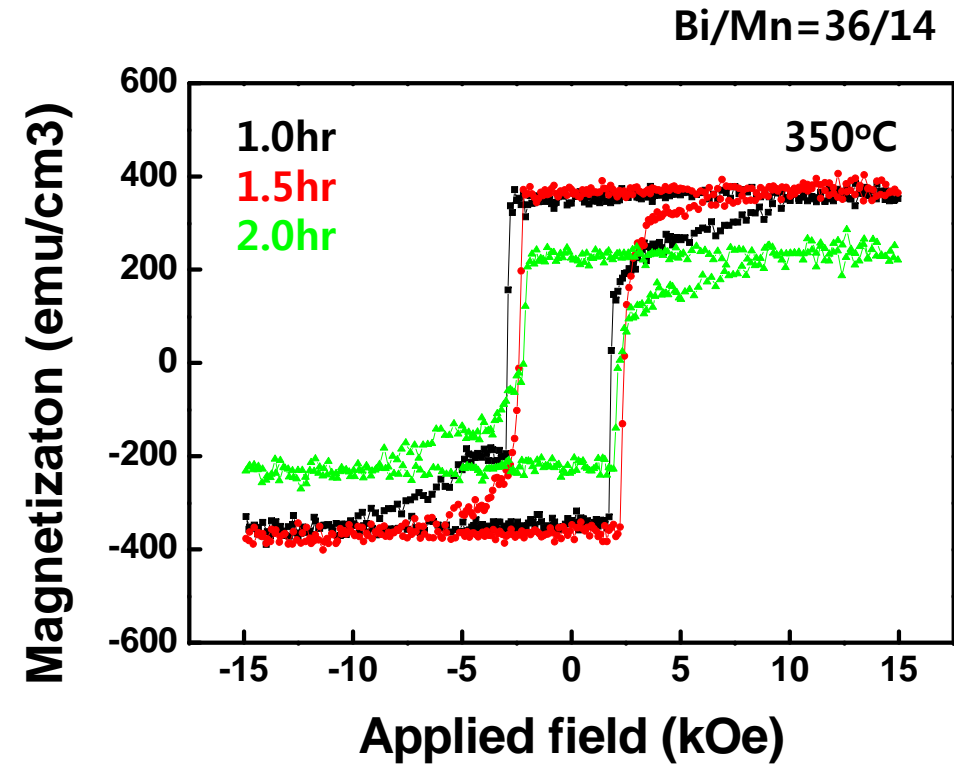
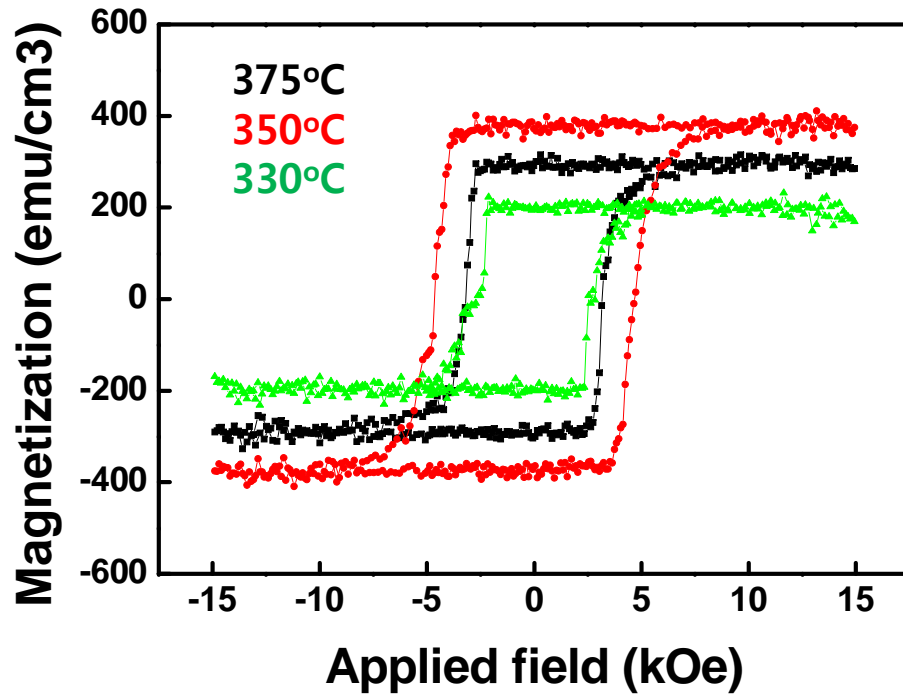


Bi/Mn 30/20	Hc (kOe)	Mr (emu/cm <sup>3</sup> )	BHmax (MGOe)
Ex-situ annealing	3.6	298	3.7
In-situ annealing	4.1	390	6.2

특성 향상

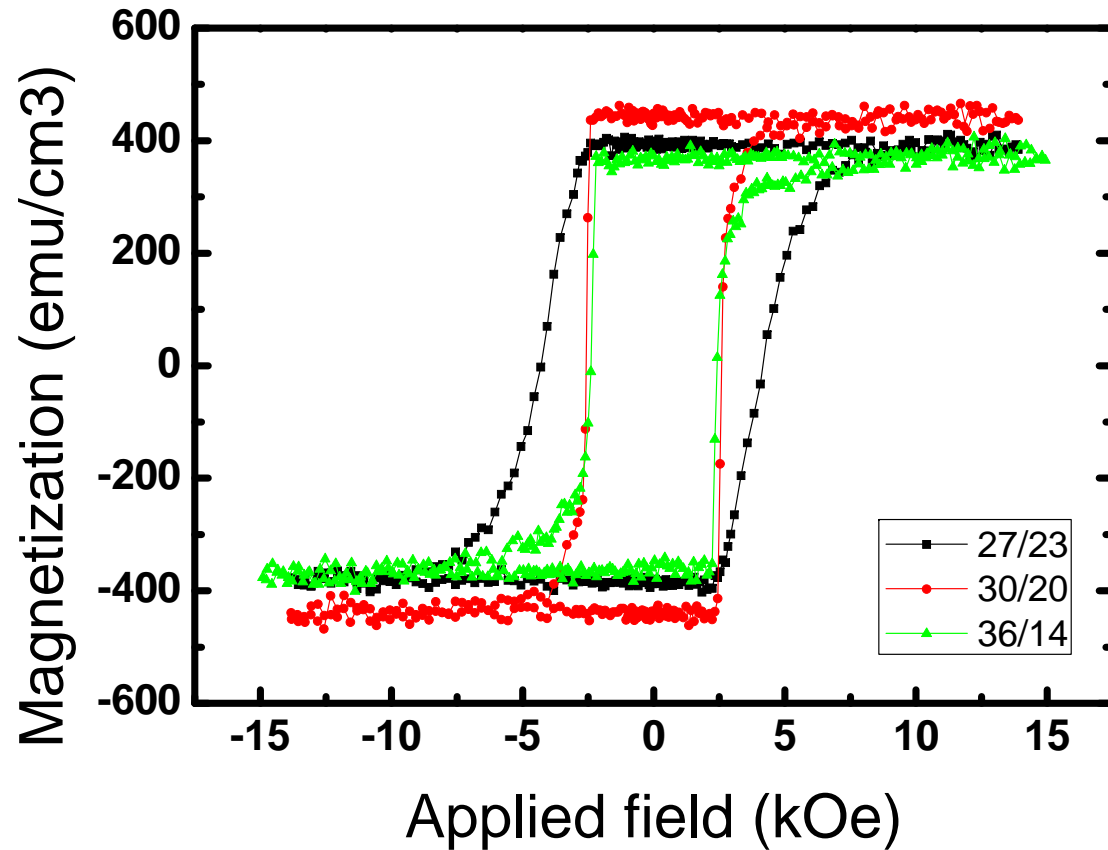


# Annealing 온도 및 시간 조건



● Annealing 조건: 350°C, 1.5hr

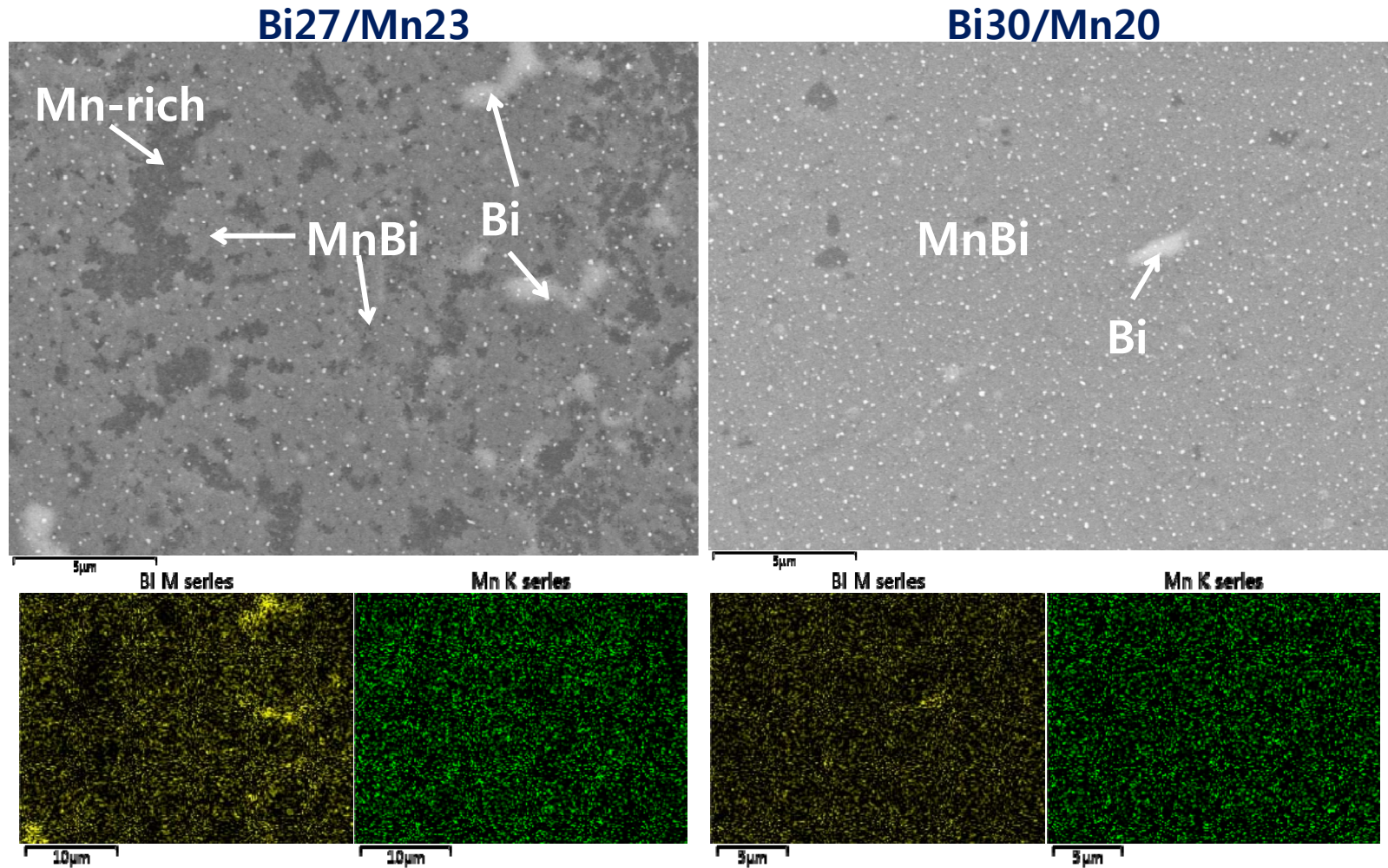
# Bilayer: Bi/Mn ratio



Bi/Mn Ratio	H <sub>c</sub> (kOe)	M <sub>r</sub> (emu/cm <sup>3</sup> )	BH <sub>max</sub> (MGOe)
27/23	4.3	392	5.3
30/20	2.5	445	6.6
36/14	2.4	372	5.4

# 미세구조 분석

## SEM(BSE) image



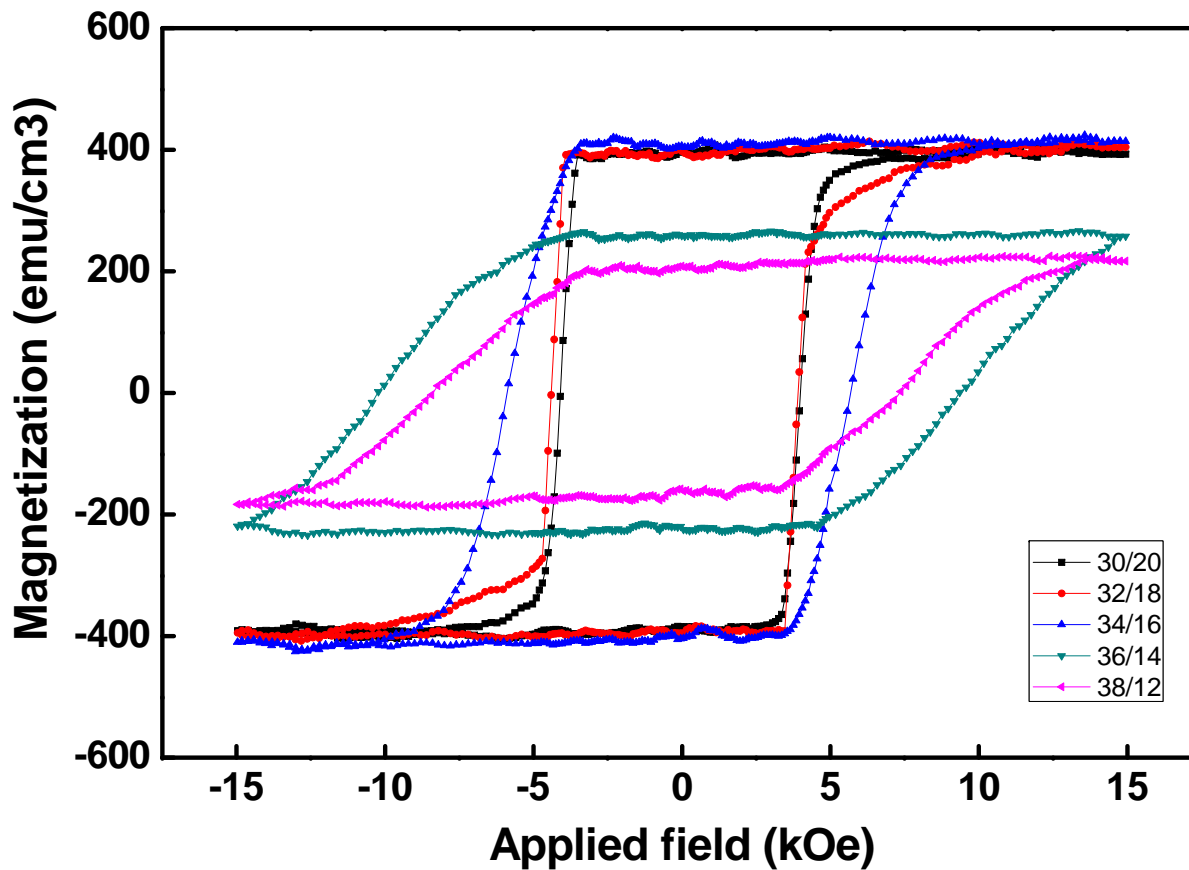
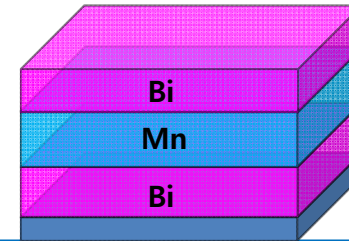
- Bi 증가할수록 MnBi phase 증가 & Mn-rich 감소 (Mr 증가 & Hc 감소)

# Trilayer: Bi/Mn Ratio

## Points

Bi/Mn/Bi trilayer : Bi/Mn 을 제어

Bi 증가  
Mn 감소

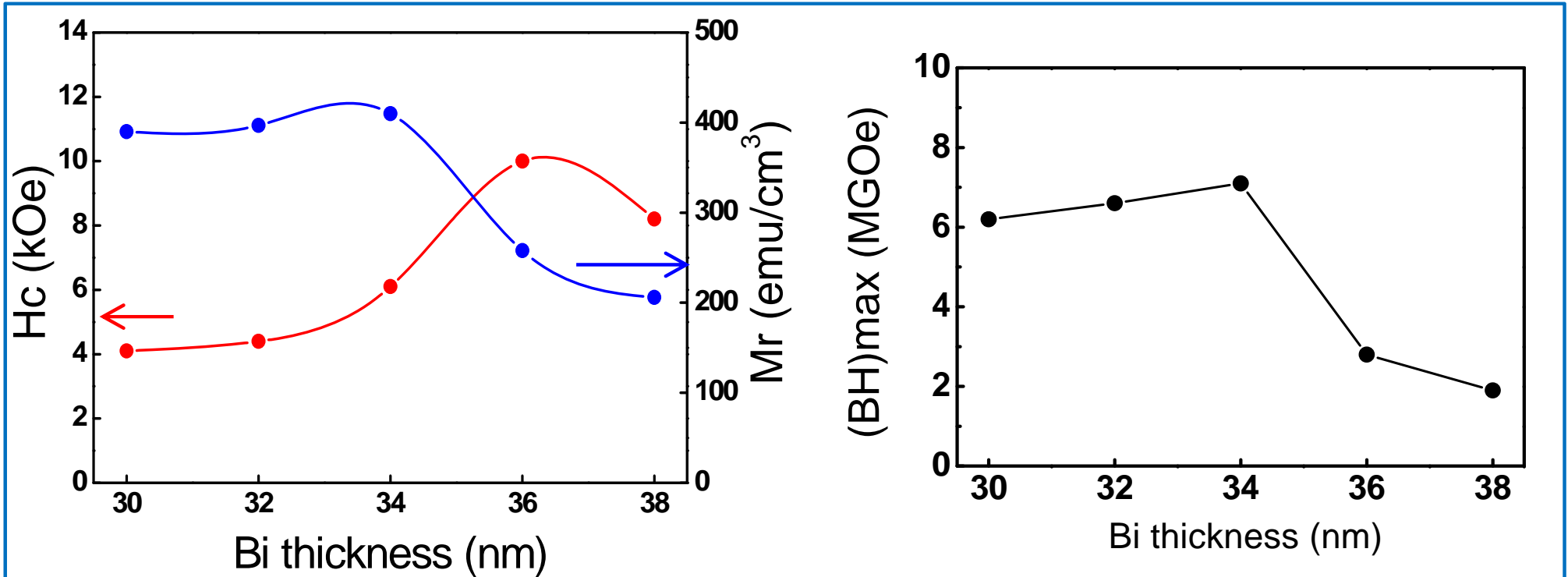


Bi/Mn Ratio	Hc (kOe)	Mr (emu/cm <sup>3</sup> )	BHmax (MGOe)
<b>30/20</b> (20/20/10)	4.1	393	6.2
<b>32/18</b> (20/18/12)	4.4	392	6.6
<b>34/16</b> (18/16/16)	6.1	410	7.1
<b>36/14</b> (22/14/14)	10	258	2.8
<b>38/12</b> (26/12/12)	8.2	206	1.9

● Mn이 위아래층으로 쉽게 확산해 들어가기 위한 trilayer 에서 자석 특성 확인

# Trilayer: Bi/Mn Ratio

## Magnetic Properties

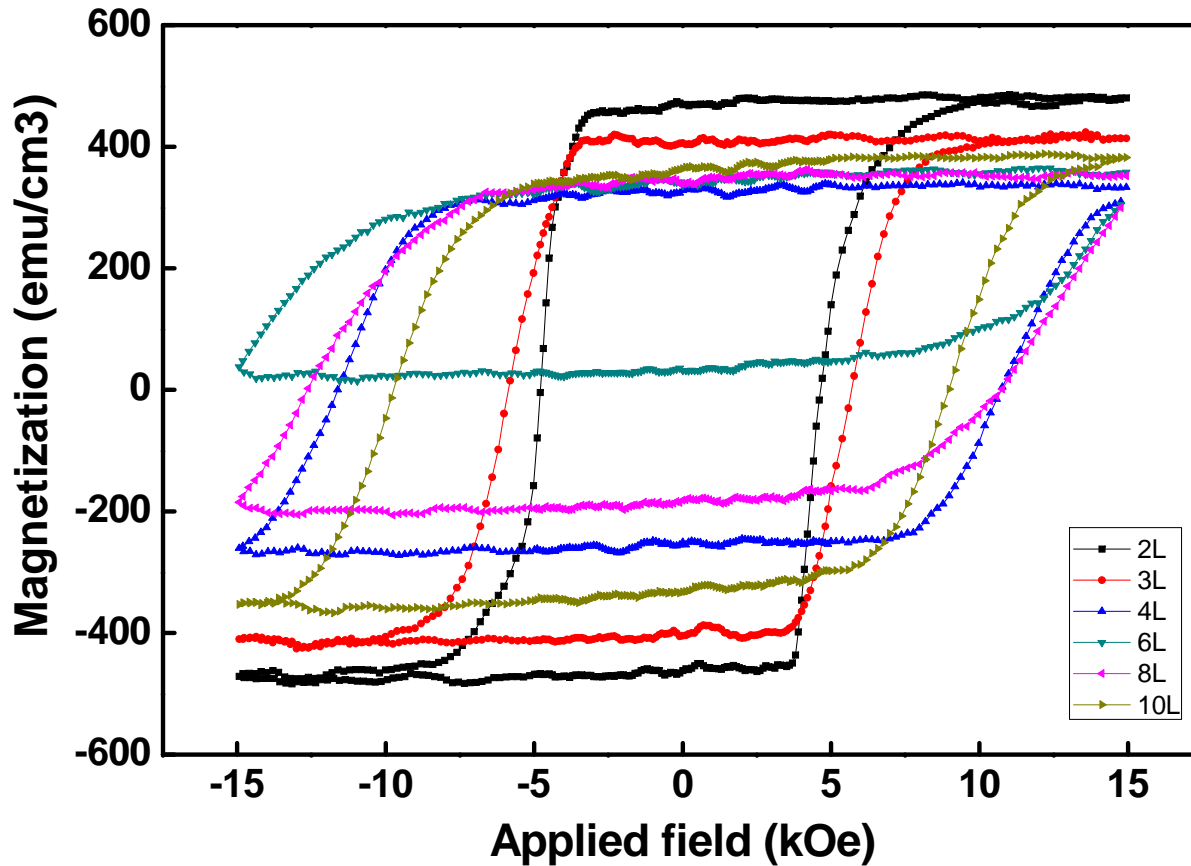
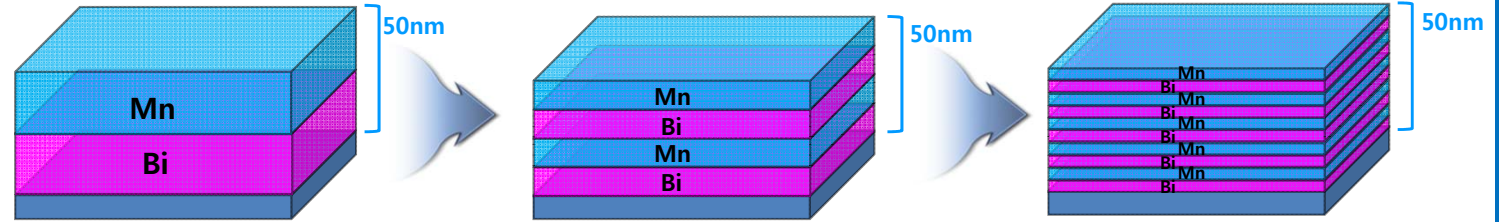


Optimized at **Bi34/Mn16** Ratio ( $BH_{\text{max}} = 7.1$  MGOe)

# Multilayers

## Points

반복  
층수  
제어

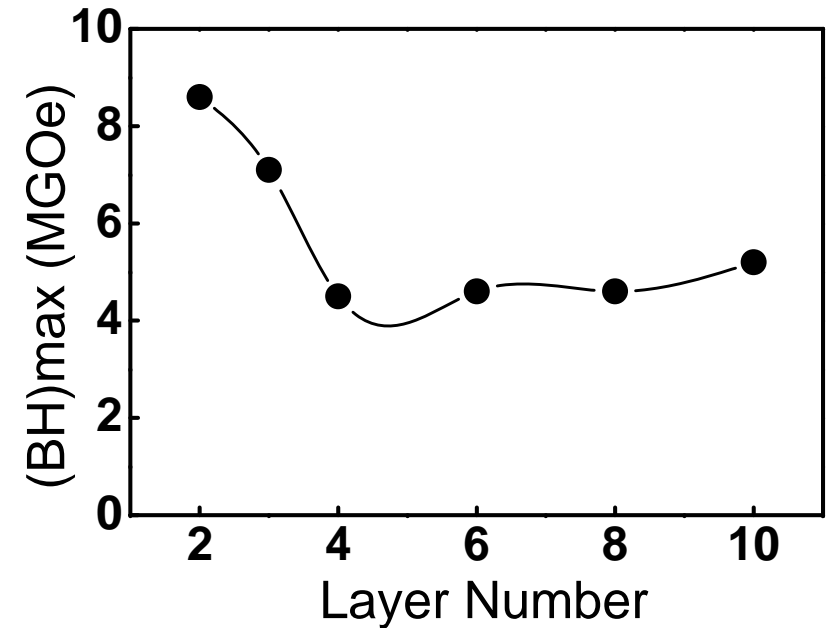
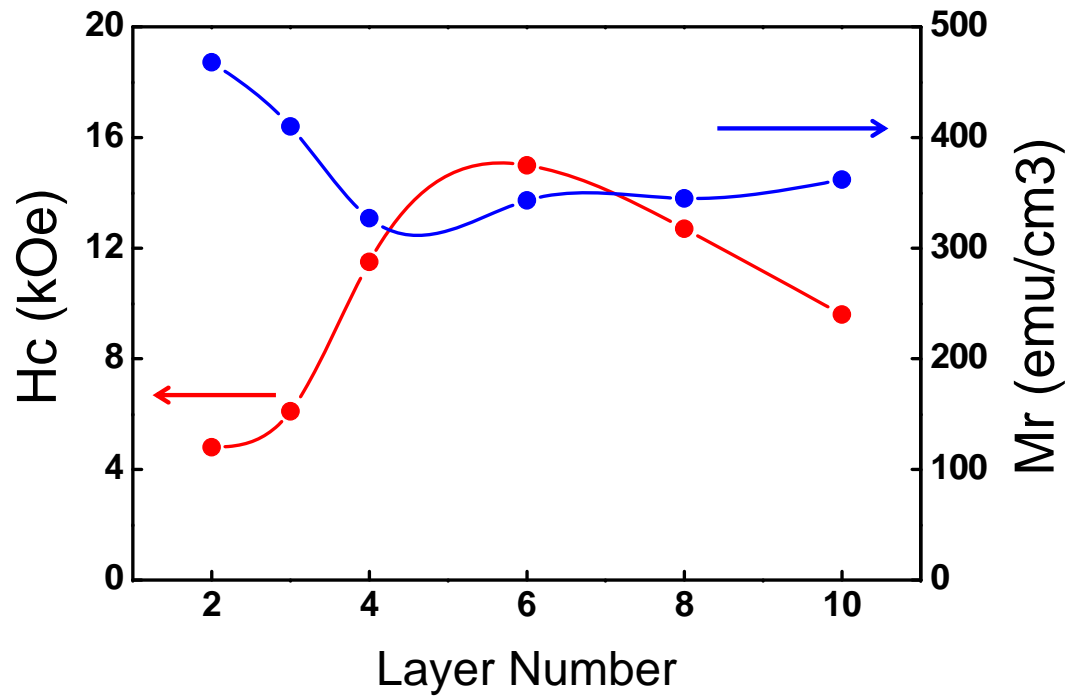


Bi/Mn = 34/16

Number of Layers	H <sub>c</sub> (kOe)	M <sub>r</sub> (emu/cm <sup>3</sup> )	BH <sub>max</sub> (MGOe)
2	4.8	468	8.6
3	6.1	410	7.1
4	11.5	327	4.5
6	15.3	343	4.6
8	12.7	345	4.6
10	9.6	362	5.2

# Multilayers

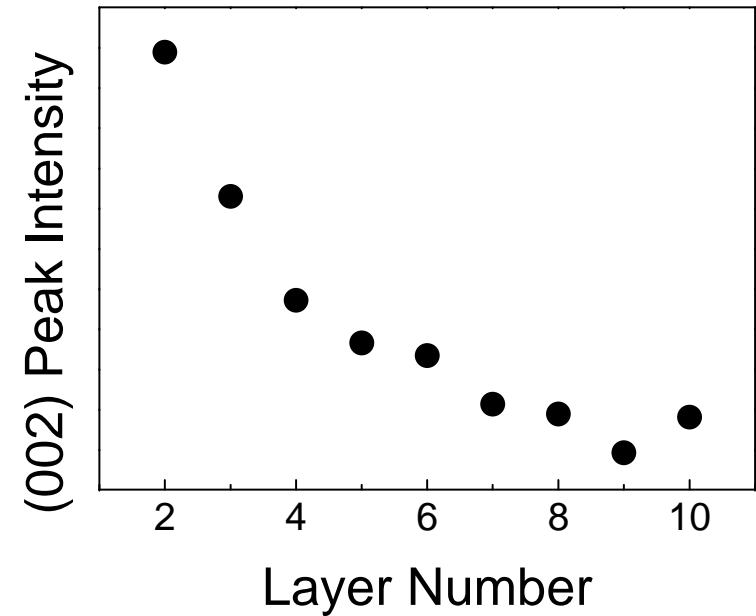
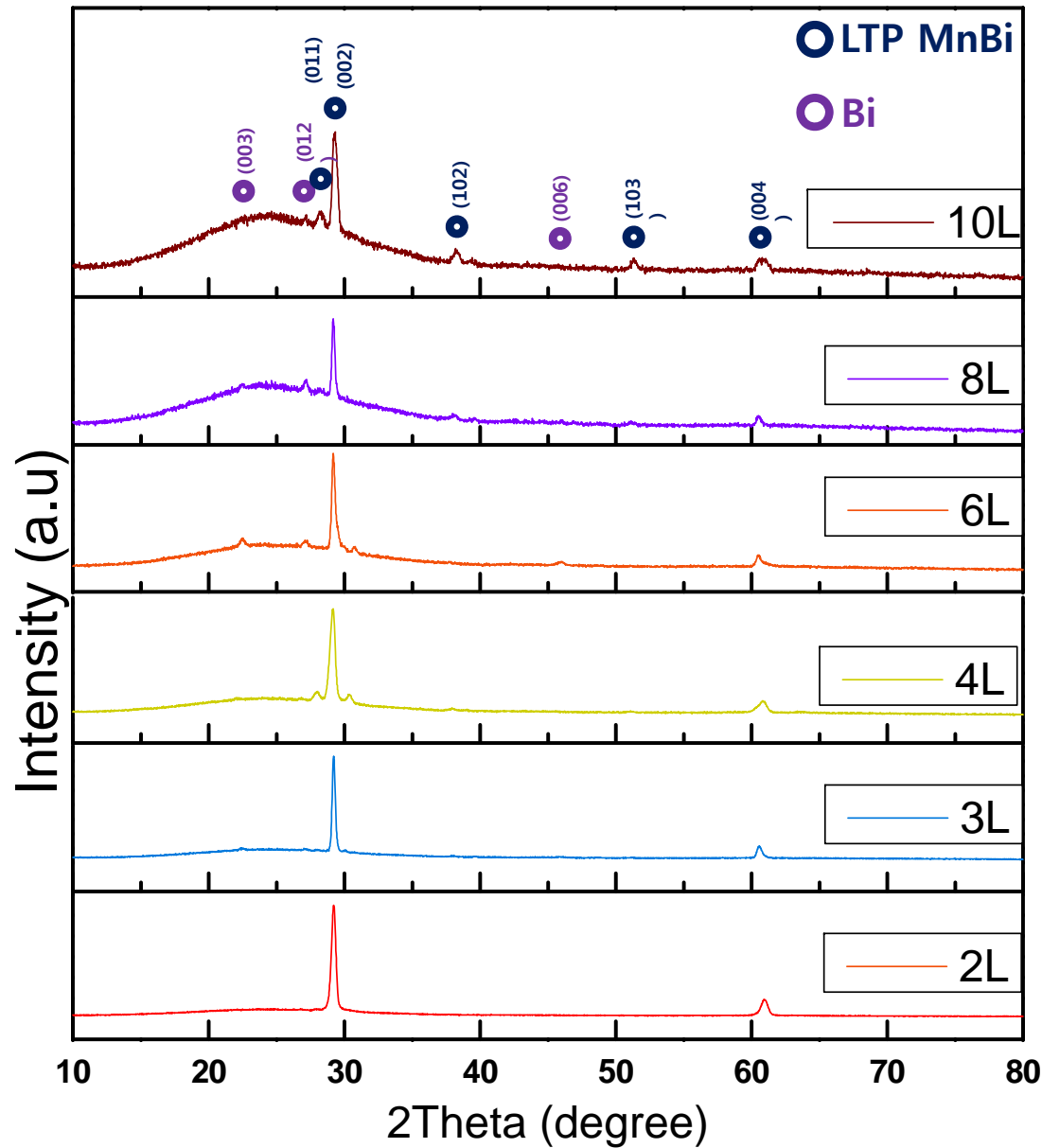
## Magnetic Properties



Optimized at **Bilayer** Structure (BHmax = 8.6 MGOe)

# Multilayers

## Structural Properties (XRD)

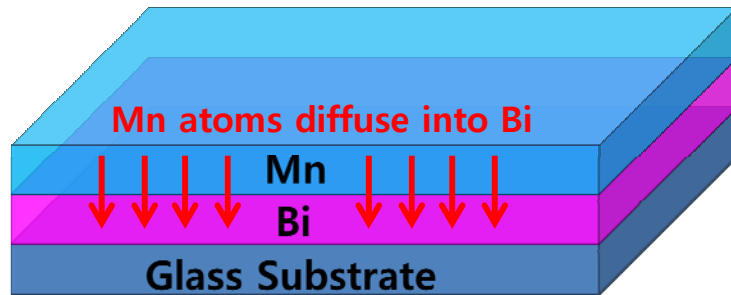


- c-축 성장률 감소
- LTP-MnBi 성장률 감소
- 6L 이상 Bi 성장 증가  
(층수에 따른 Mr 감소율과 비슷)

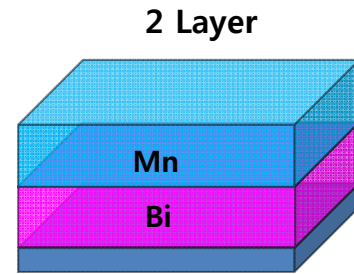


# Multilayers 자석특성 분석

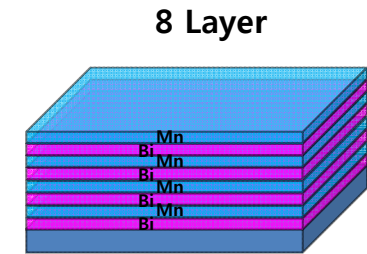
## Layer number dependence



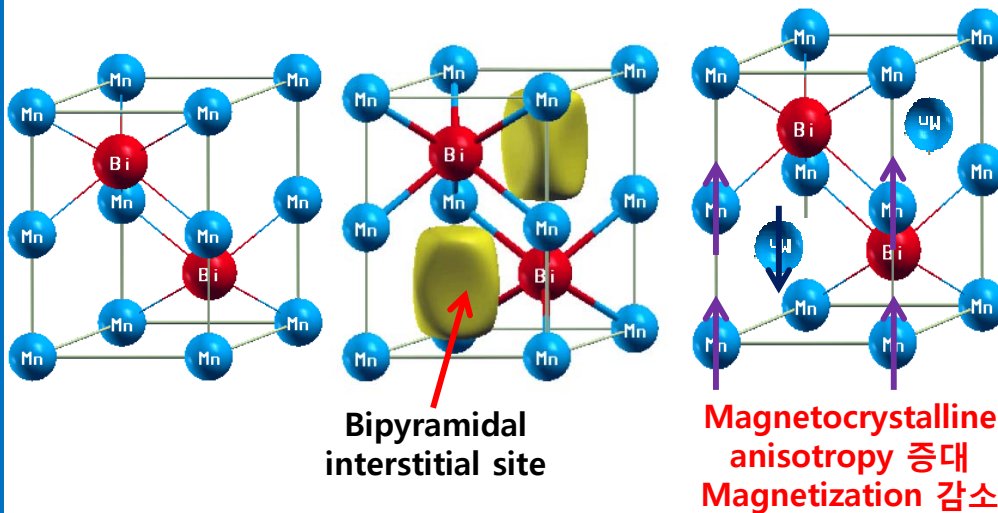
열처리 시 Bi의 Grain boundary 따라 확산하여 MnBi 성장



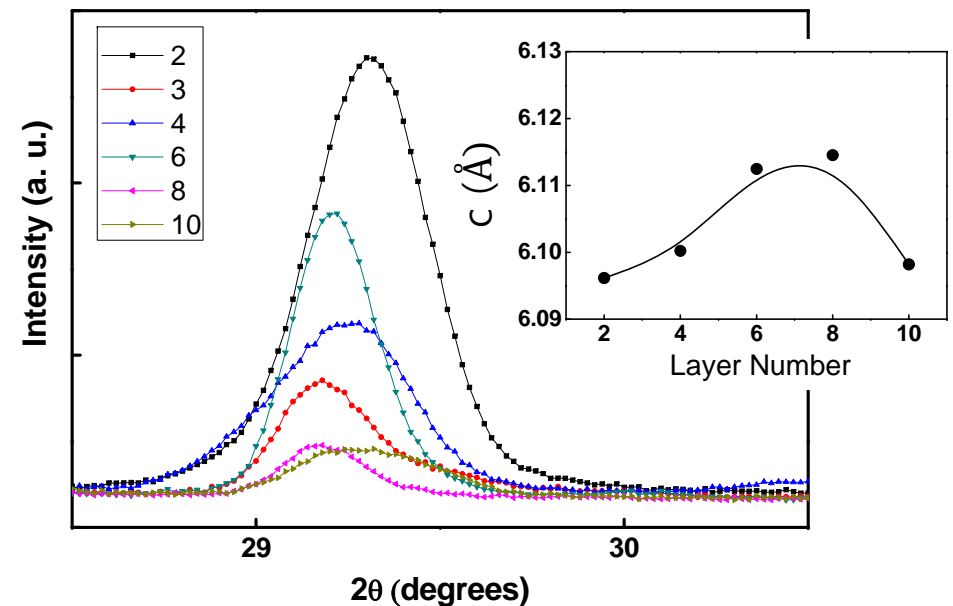
열처리를 통한 적정량의 Mn 확산, MnBi 형성



각 층의 얇은 두께로 인해 Mn 충분한 확산 → Mn의 interstitial site 침입



- Mn 침입을 통한 c-axis 증대, 보자력 증대
- 침입 Mn의 antiferromagnetic coupling을 통한 Mr 감소



# MnBi Thin Film 요약

- In-situ annealing으로 산화억제를 함으로써 MnBi 박막 자석특성 향상
- Bi(34nm)/Mn(16nm) 두께 제어를 통한 MnBi 박막 조성비율 최적화
- Bi/Mn 층수 제어를 통한 MnBi 박막 자석 특성 최적화

Bi(34nm)/Mn(16nm) 조성에서 Multilayer 보다는 Bilayer 일때  
최고특성  $(BH)_{\max} = 8.6 \text{ MGOe}$

# Acknowledgements

**POSCO**

포스코 국내위탁 연구 사업

**교환결합 기반 초고성능 복합 영구자석 개발**

(2013. 12. 16 ~ 2015. 01. 15)



## 04 Further works



여성과학자 지원사업

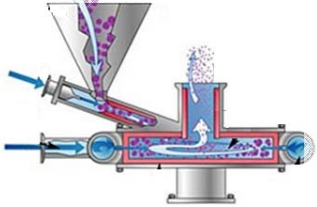
**MnBi 기반 비희토류 복합 영구자석 개발**

(2015. 11. 01 ~ 2018. 10.31)

# 향후 계획(MnBi Bulk)

## 기존 공정을 대체할 신공정 개발

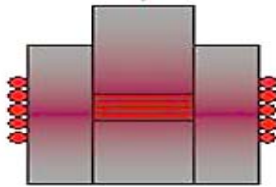
### Jet milling 및 분급기



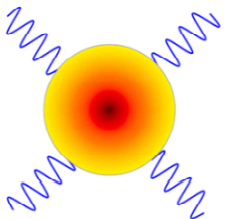
- Ball에 의한 오염 억제 및 순도 증가
- 입자크기 균일화 및 결정립 성장 억제 효과

### DC pulse / Induction 소결

- Heating 방식 변경을 통한 승온 속도 증가
- 결정립 성장 억제
- 공정시간 단축



### Microwave sintering



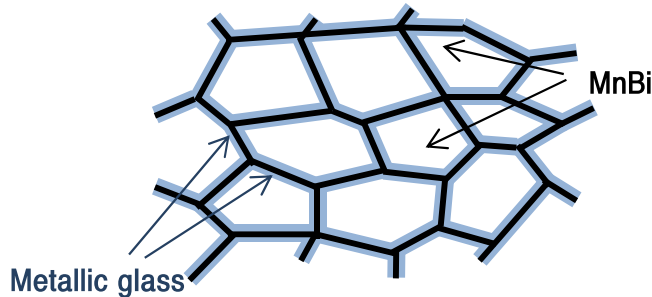
- 신 소결공정
- Susceptor를 이용한 균일 소결 효과
- 결정립 성장 억제
- 기계적 특성 향상
- 공정시간 단축

### 결정립 미세화 및 성장 억제

보자력 및 소결밀도 향상

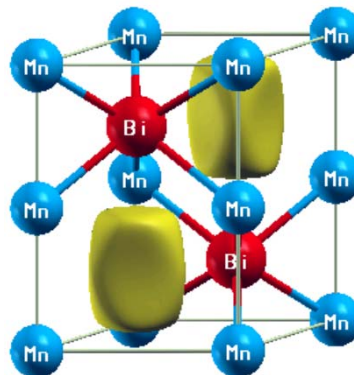
## 소결조제 / 상안정화 원소 첨가

### 소결조제 첨가



- 융점은 높지만 연화점이 낮은 metallic glass를 powder mixing법으로 첨가
- FeSnPCBSi, CrFeMoCBy, CoFeSiBCr ... 등
- 밀도 증가 및 MnBi와의 Exchange coupling 효과로 자기특성 증대 효과

### 상안정화 원소 첨가

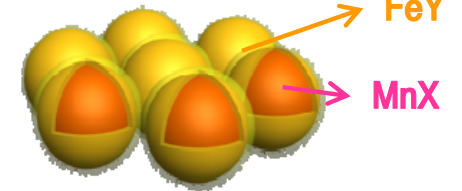


- Pr, Cu, Co 등의 원소를 첨가(침입형, 치환형)
- MnBi-LTP 상안정화를 통한보자력 증대 효과

신물질 첨가를 통한 자기특성 향상

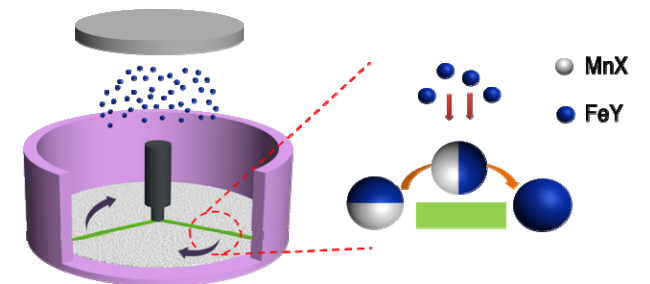
## 교환결합기반 경/연자성 Core/shell

### 경/연자성 Core/shell 이종구조 powder 제조



- 교환결합기반 경/연자성(MnX/FeY) 코어셸 이종구조 powder 제조
- 경자성(MnX)의 높은보자력을 유지함과 동시에 연자성(FeY)의 높은 포화자화값을 통해 전체적인 자기특성 향상 효과 기대

### 교환시스템을 도입한 스퍼터링 공정



New type of powder coating system using sputtering

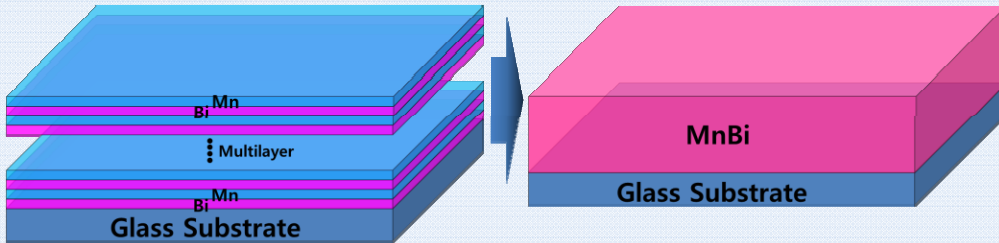
- 스퍼터링 장비에 wire 타입의 blender를 장착
- 경자성에 연자성을 골고루 입혀 교환결합 기반 고특성 Core/shell 이종구조 복합자석 제조

교환결합을 통한 자기특성 향상

# 향후 계획 (MnBi Films)

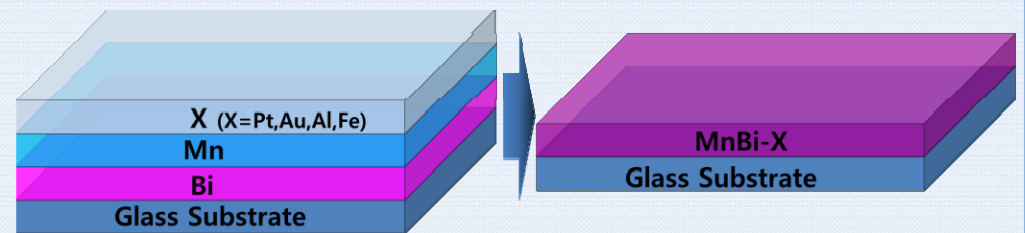
## MnBi 박막 자석

### MnBi Thick film



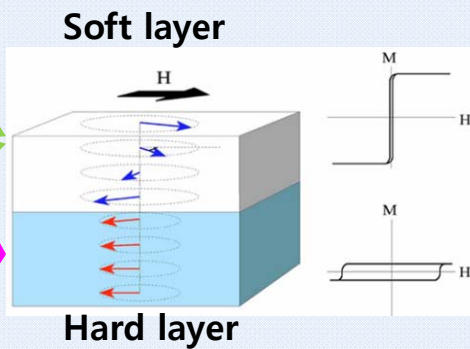
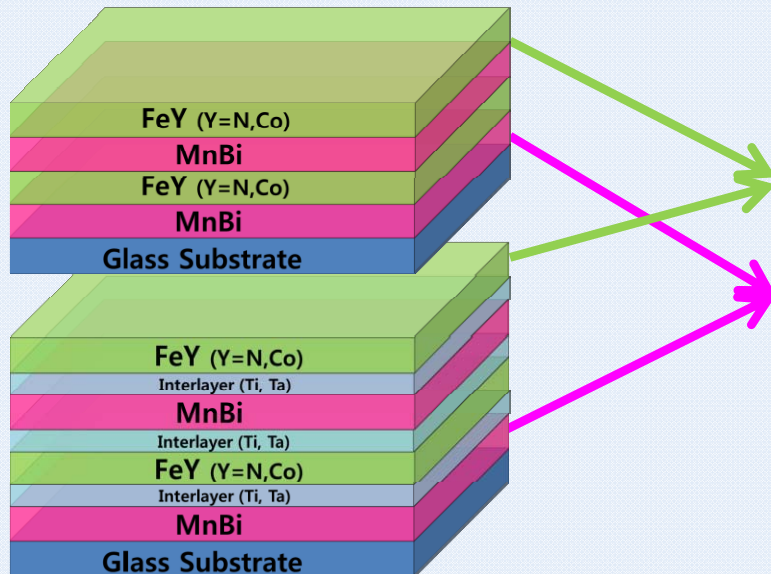
- 다층 증착 및 열처리를 통한 고품질 MnBi Thick film 합성

### Doped MnBi

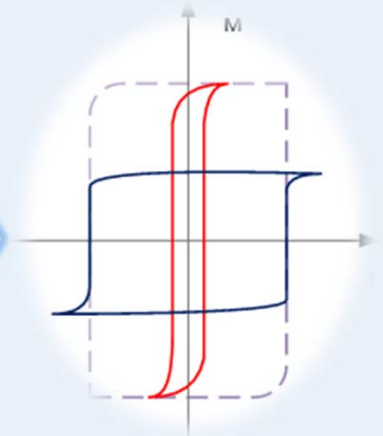


- 도핑 (Pt, Au, Al, Fe)을 통한 보자력 및 자기특성 증대

## Exchange Coupling



Exchange Coupling



- 확산방지층이 삽입된 경/연자성 layer 간의 교환결합을 통한 자기 특성 증대

# Dream on Energy Magnet

