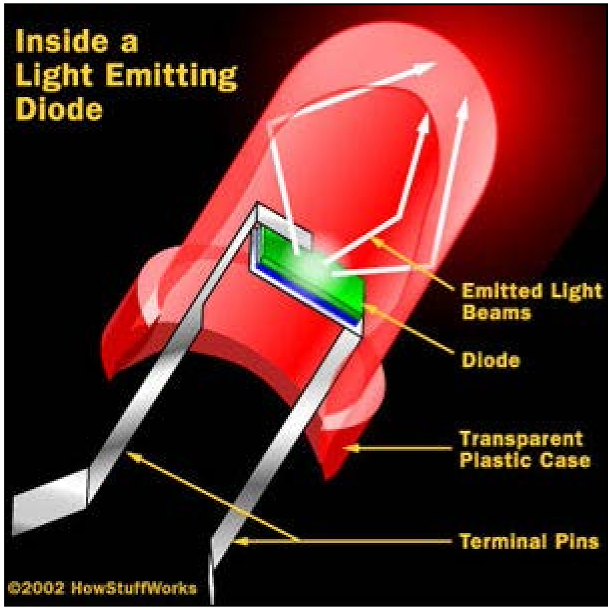
Thermal Properties of Materials
[재료의 열적 성질]

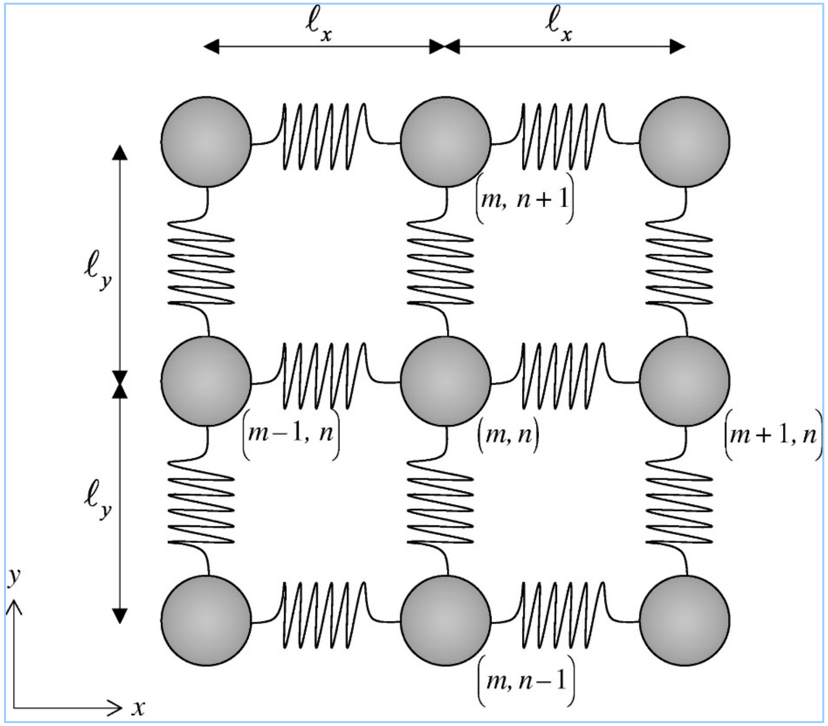
1. 가장 높은 열전도도를 갖는 물질은 무엇인가?
2. 0 혹은 음의 열팽창 계수를 가지는 물질은 존재하는가?
3. Chandra x-ray 망원경 기판거울로 사용된 물질은 무엇인가?
4. 극 고온과 저온으로부터 우주선을 보호하기 위한 차폐재료는?

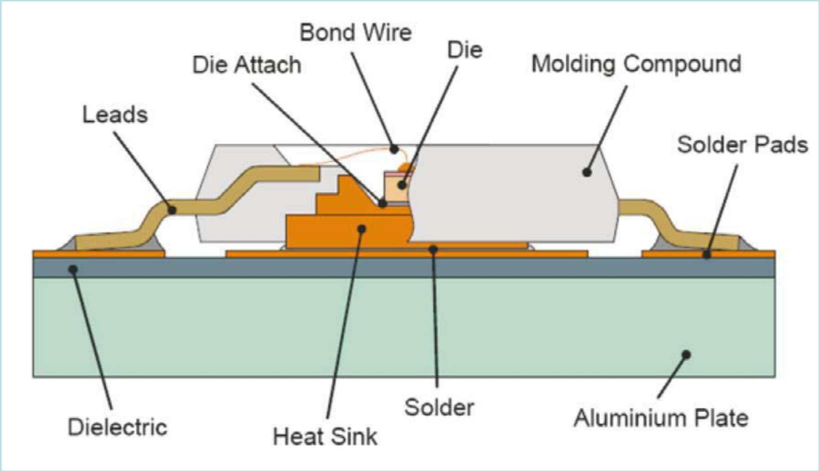
핵심용어: 열용량, 비열, 열팽창계수, 열전도도, 열충격, Phonon, Lorentz상수

Phonon: A packet of elastic waves. It is characterized by its energy, wavelength, or frequency, which transfers energy through a material. [재료에 에너지를 전달하는 탄성파]

참고자료: LED, Phonon 등







고온: Nonradioative transition 분율 증가

21.1. Heat Capacity and Specific Heat

❖ The heat capacity(열용량) is the energy required to raise the temperature of one mole of a material by one degree. [cal/mol•K]

❖ The specific heat(비열) is defined as the energy needed to increase the temperature of one gram of a material by 1℃. [cal/g•K]

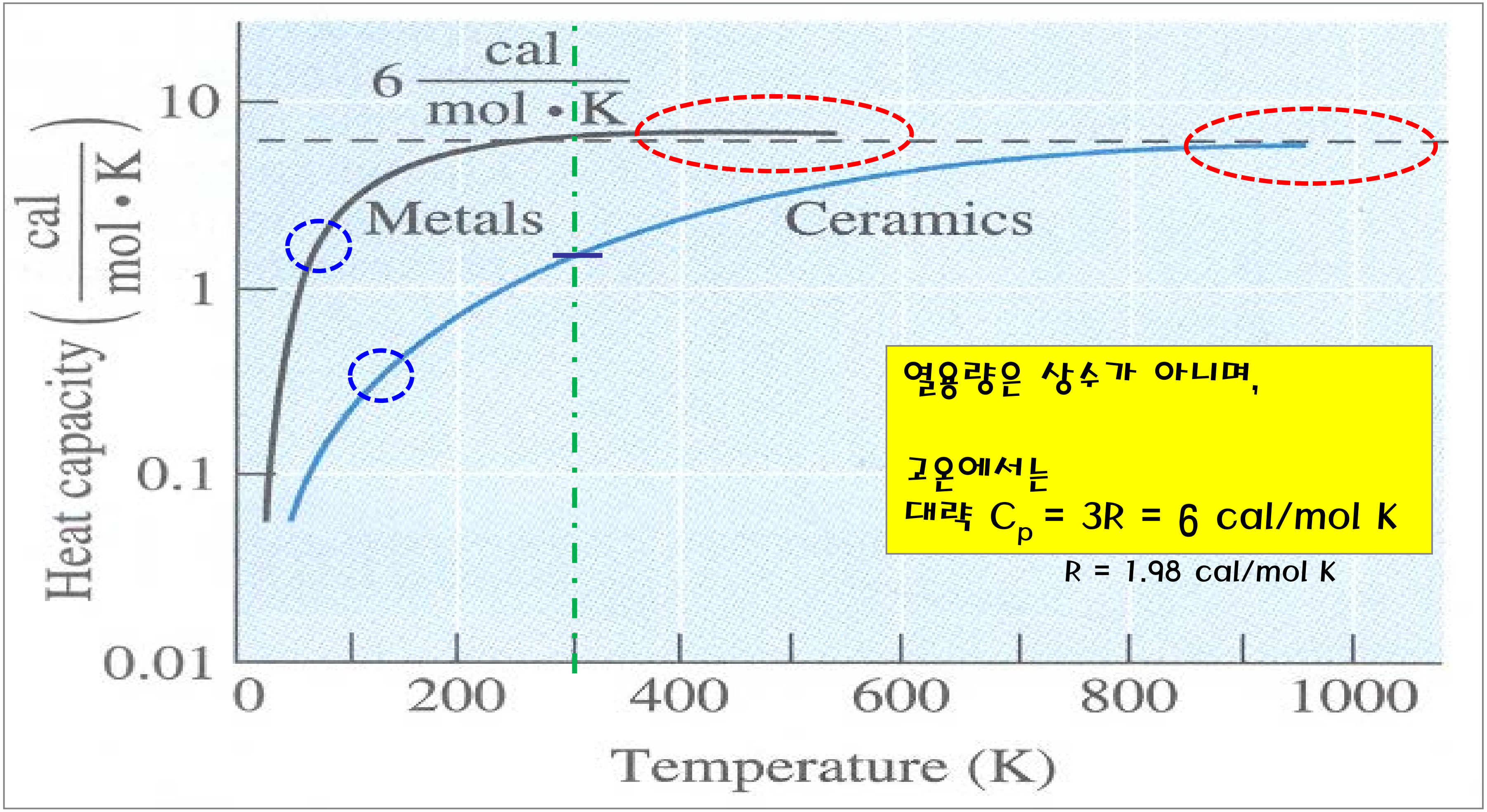
❖ Neither the **heat capacity** nor the **specific heat** depends significantly on the structure of the material; thus, changes in dislocation density, grain size, or vacancies have little effect.

❖ **The most important factor affecting specific heat is the lattice vibration or phonons.**

** 열용량과 비열을 구분 설명하시오

21.1. Heat Capacity and Specific Heat

[Fig. 21-1]



Heat capacity as a function of temperature for metals and ceramics.

21.1. Heat Capacity and Specific Heat

[Table 21-1]

Material	Specific Heat $\left(\frac{cal}{g \cdot K}\right)$	Material	Specific Heat $\left(\frac{cal}{g \cdot K}\right)$
Metals:		Ceramics:	
Al	0.215	Al_2O_3	0.200
Cu	0.092	Diamond	0.124
B	0.245	SiC	0.250
Fe	0.106	Si_3N_4	0.170
Pb	0.038	SiO_2 (silica)	0.265
Mg	0.243	Polymers:	
Ni	0.106	High-density polyethylene	0.440
Si	0.168	Low-density polyethylene	0.550
Ti	0.125	6,6-nylon	0.400
W	0.032	Polystyrene	0.280
Zn	0.093	Other:	
		Water	1.000
		Nitrogen	0.249

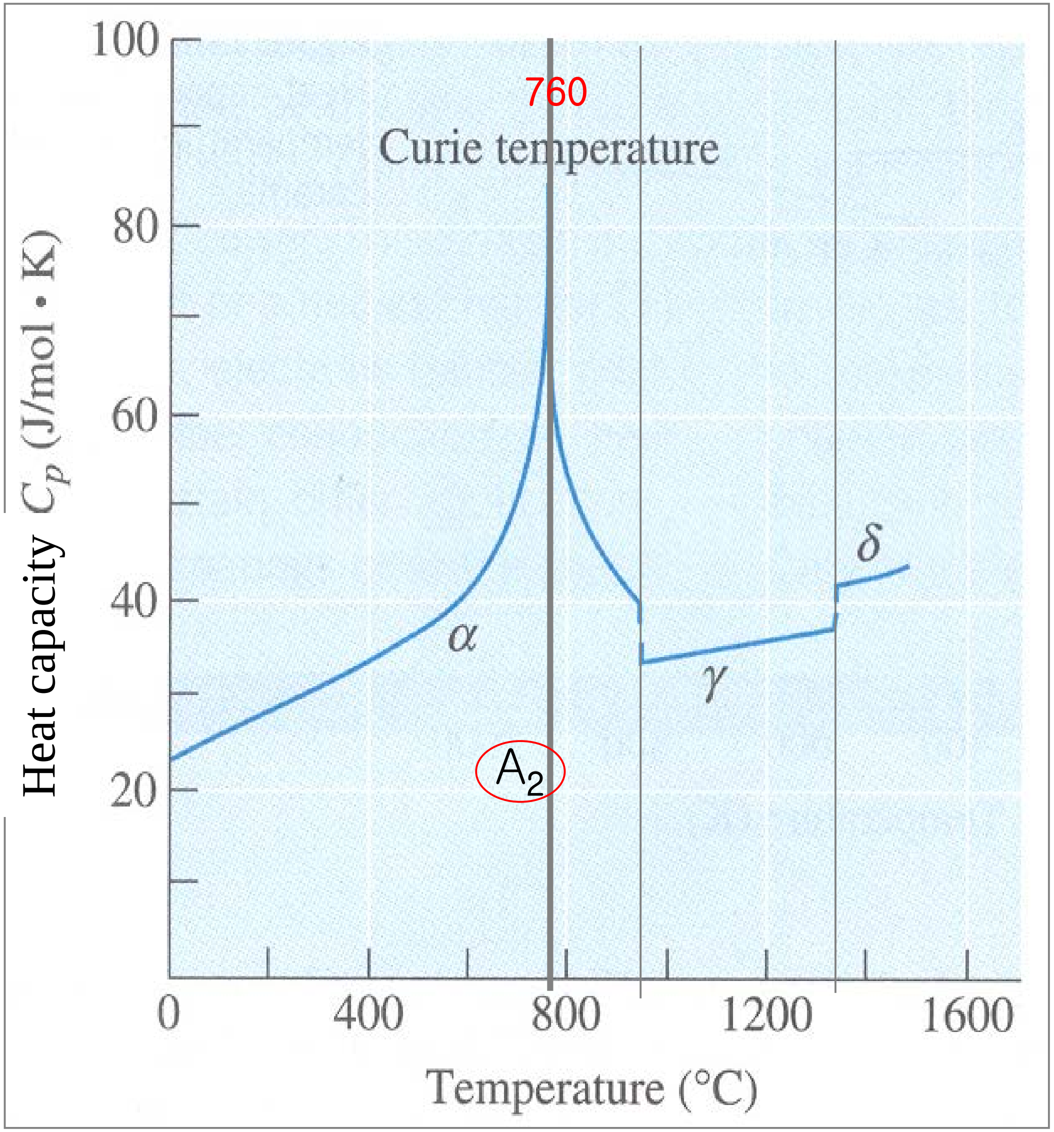
Note: $1 \frac{cal}{g \cdot K} = 4184 \frac{J}{kg \cdot K}$

* 물의 비열은 1로써, 금속에 비해 매우 크다!!

The **specific heat** of selected materials **at 27℃**

21.1. Heat Capacity and Specific Heat

[Fig. 21-2]



1 cal = 4.18 Joule 이고,
6 cal/mol K = 25 Joule/mol K

✓ 1 cal : 물 1 g의 온도를 1K올리는데 필요한 열량

The effect of temperature on the heat capacity of iron.

Both the change in **crystal structure** and the change from **ferromagnetic to paramagnetic** behavior are indicated.

결자구조의 변화 혹은 자기적 성질이 변화하는 온도에서 열용량은 크게 변화한다.

21.2. Thermal Expansion

◆ Linear coefficient of thermal expansion(CTE) α:

$$\alpha = \frac{l_f - l_0}{l_0(T_f - T_0)} = \frac{\Delta l}{l_0 \Delta T} = \frac{\varepsilon}{\Delta T}$$

Where T_o and T_f are the initial and final temperatures and

l_o and l_f are the initial and final dimensions of the material and ε is the strain. (선 열팽창 계수).

CTE의 중요성에 대해 설명하시오.

Thin film on Si wafer at high temp. process

21.2. Thermal Expansion

The coefficient of thermal expansion of a material is related to the strength of the atomic bonds.

1. The expansion characteristics of some materials, particularly single crystals or materials having a preferred orientation, are anisotropic.

2. Allotropic materials have abrupt changes in their dimensions when the phase transformation occurs. These abrupt changes contribute to the cracking of refractories on heating or cooling and quench cracks in steels. [$\alpha \rightarrow \gamma$]

3. The linear coefficient of expansion continually changes with temperature. Normally, α either is listed in handbooks as a complicated temperature-dependent function or is given as a constant for only a particular temperature range.

4. Interaction of the material with electric or magnetic fields produced by magnetic domains may prevent normal expansion until temperatures above the curie temperature are reached. This is the case for **Invar, a Fe-36% Ni alloy, which undergoes practically no dimensional changes at temperatures below the Curie temperature(200℃).** This makes Invar attractive as a material for bimetallics.

21.2. Thermal Expansion

• Tailored multi-phase materials can have a **zero or negative** thermal-expansion coefficient. (열팽창계수가 Zero인 물질의 설계원리)

❖ **Zerodur™ is a glass-ceramic material that can be controlled to have zero or slightly negative thermal expansion developed by Schott Glass Technologies.**

• It consists of a 70~80wt% crystalline phase that has a high-quartz structure.

• The remainder is a glassy phase. **The negative thermal expansion coefficient of the glassy phase** and the positive thermal expansion of the crystalline phase cancel for each other out, leading to a zero-thermal-expansion material. **Zerodur™ has been used as the mirror substrate on the Hubble telescope and Chandra x-ray telescope**.

21.2. Thermal Expansion : [Polymer > Metal > Ceramics]

[Table 21-2]

Metal: 10~25, Polymer: 50~100, Ceramics: 3~7 ppm

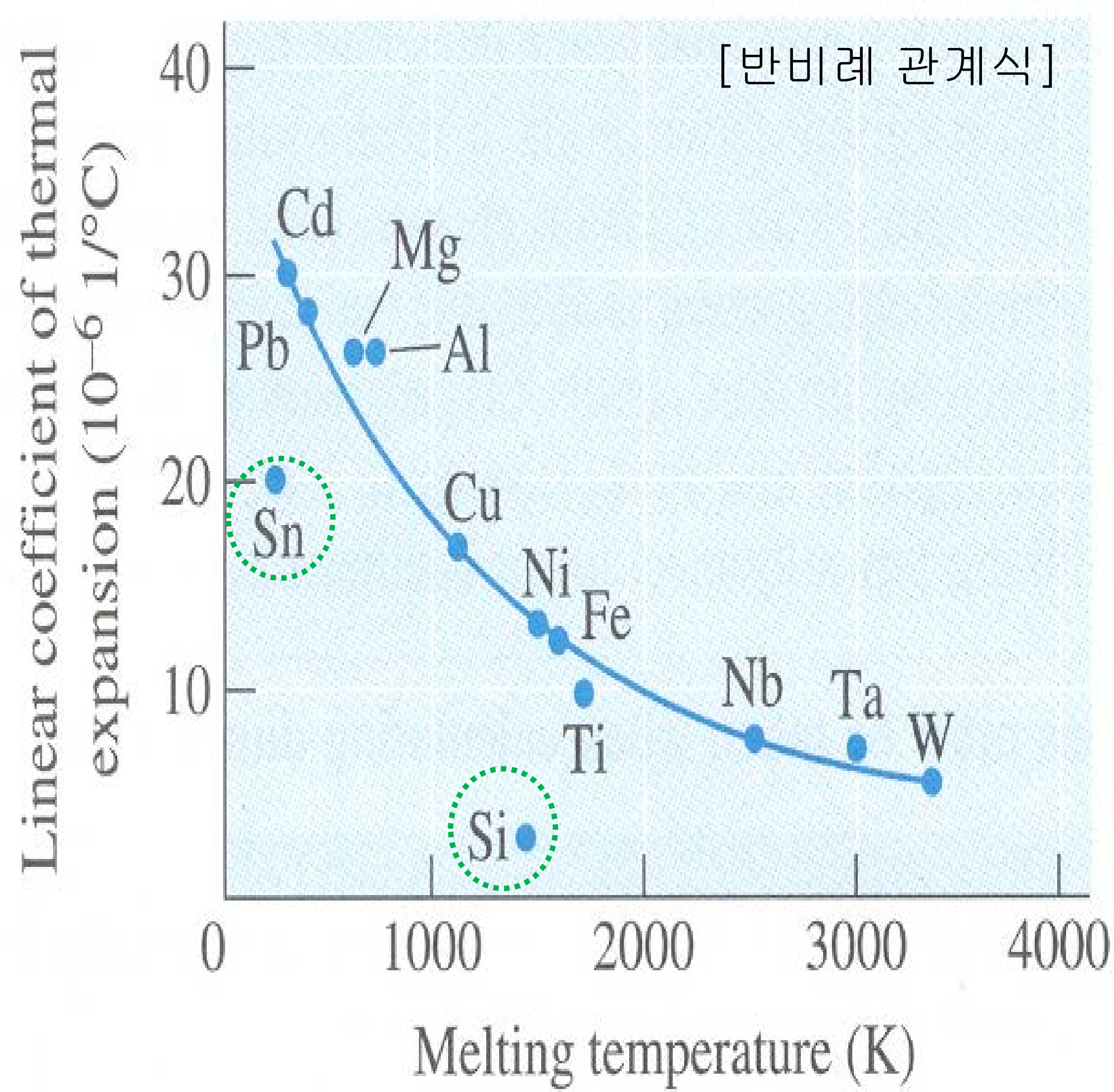
** LCTE for Si = 3 ppm

Material	Linear Coefficient of Thermal Expansion ($\times 10^{-6}$ 1/0°C)
Al	25.0
Cu	16.6
Fe	12.0
Ni	13.0
Pb	29.0
Si	3.0
W	4.5
1020 steel	12.0
3003 aluminum alloy	23.2
Gray iron	12.0
Invar (Fe-36% Ni)	1.54
Stainless steel	17.3
Yellow brass	18.9
Epoxy	55.0
6,6-nylon	80.0
6,6-nylon—33% glass fiber	20.0
Polyethylene	100.0
Polyethylene—30% glass fiber	48.0
Polystyrene	70.0
Al_2O_3	6.7
Fused silica	0.55
Partially stabilized ZrO_2	10.6
SiC	4.3
Si_3N_4	3.3
Soda-lime glass	9.0

The linear coefficient of thermal expansion at room temperature for selected materials

21.2. Thermal Expansion

[Fig. 21-3]



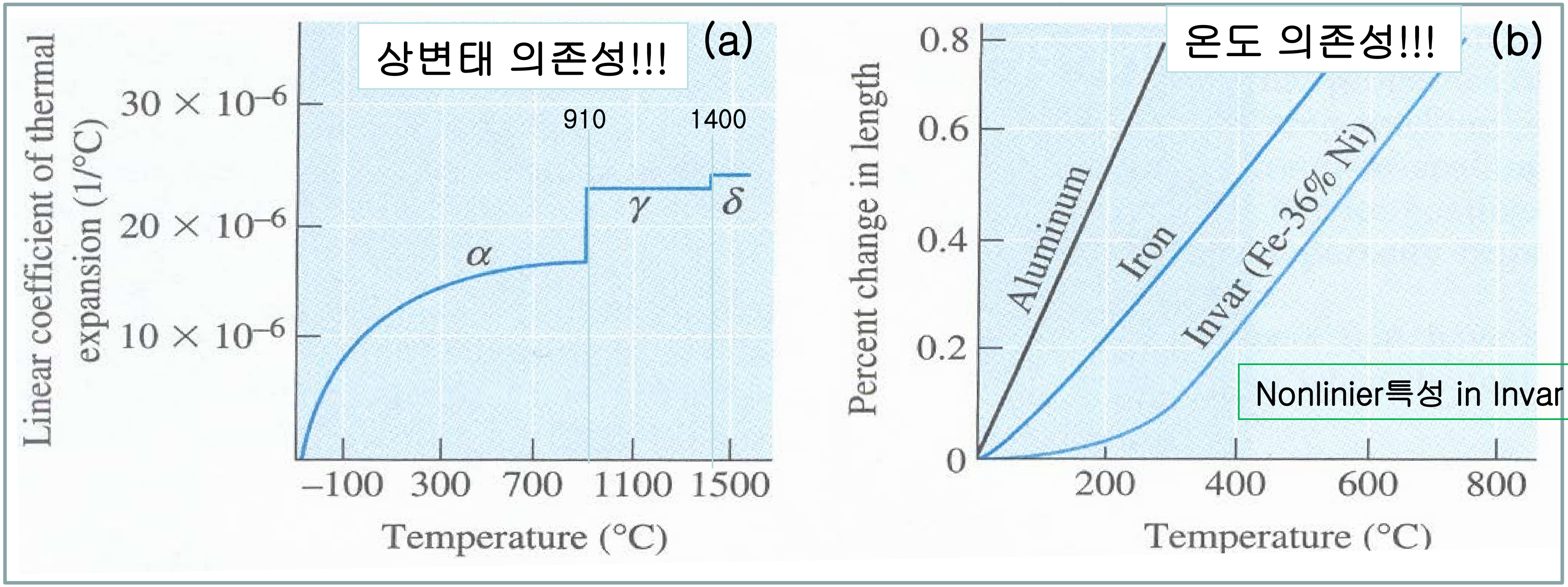
The relationship between the linear coefficient of thermal expansion and the melting temperature in metals at 25℃.

Higher melting point metals tend to expand to a lesser degree.

** Sn과 Si의 경우: 강한 공유결합
➔ 열팽창계수가 더욱 낮아짐.

21.2. Thermal Expansion

[Fig. 21-4]



(a) The linear coefficient of thermal expansion of iron changes abruptly at temperature where an allotropic transformation occurs.

(b) The expansion of Invar is very low due to the magnetic properties of the material at low temperatures.

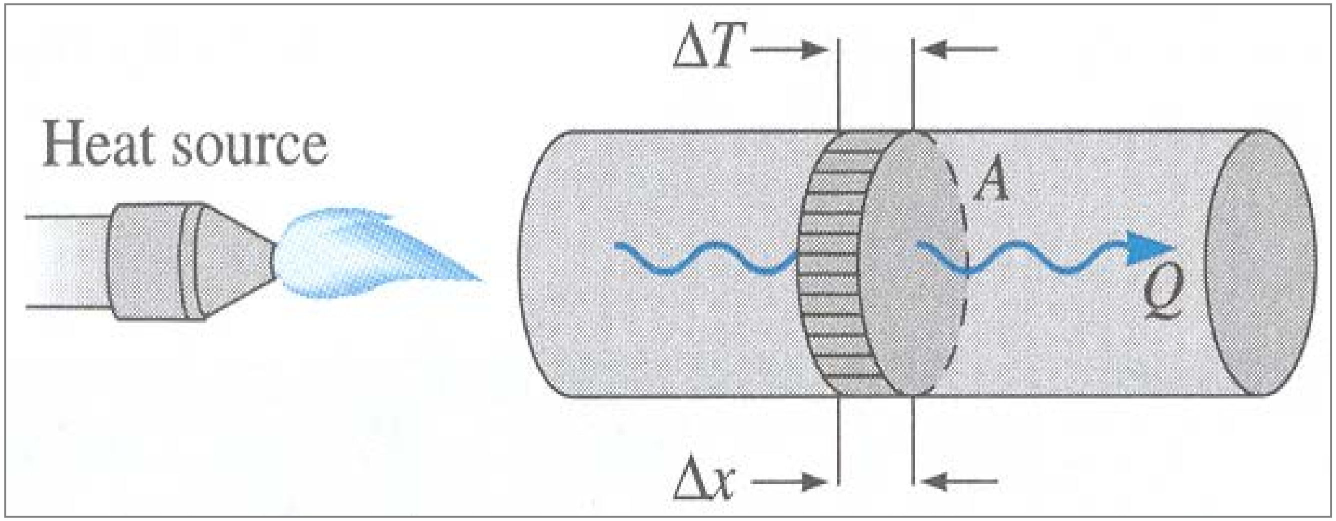
단, VCTE = 3 LCTE(α) 의 값을 가지며, 열응력(σ) = $\alpha E \Delta T$ *(22-5)*

21.3. Thermal Conductivity

[Fig. 21-5]

The thermal conductivity(k)의 정의 : a measure of the rate at which heat is transferred through a material.

[단위 면적당, 열의 흐름은 온도 기울기에 비례함 ➔ 기울기가 열전도도[k].



$$\frac{Q}{A} = k\frac{\Delta T}{\Delta x}$$

$$k = \rho\,\alpha\,C_p$$

f(k)=[밀도, 열확산도, 비열]

When one end of bar is heated, a heat flux Q/A flows toward the cold end at a rate determined by the temperature gradient produced in the bar.

** 열에너지는 두 가지의 중요한 기구에 의해서 전달됨 : 자유전자와 격자진동(phonon)

21.3. Thermal Conductivity [k]

[Table 21-3]

Metal: 20~450, Polymer: < 0.5, Ceramics: 10~300, Carbon: >335 (W/(m·K

Material	Thermal Conductivity $(W \cdot m^{-1} \cdot K^{-1})$	Material	Thermal Conductivity $(W \cdot m^{-1} \cdot K^{-1})$
Pure Metals:		Ceramics:	
Ag	430		
Al	238	Al_2O_3	16–40
Cu	400	Carbon (diamond)	2000
Fe	79	Carbon (graphite)	335
Mg	100	Fireclay	0.26
Ni	90		
Pb	35	Silicon carbide	up to 270
Si	150	AlN	up to 270
		Si_3N_4	up to 150
Ti	22	Soda-lime glass	0.96–1.7
W	171	Vitreous silica	1.4
Zn	117	Vycor™ glass	12.5
Zr	23	ZrO_2	4.2
Alloys:		Polymers:	
1020 steel	100	6,6-nylon	0.25
3003 aluminum alloy	280	Polyethylene	0.33
304 stainless steel	30	Polyimide	0.21
Cementite	50	Polystyrene	0.13
		Polystyrene foam	0.029
Cu-30% Ni	50	Teflon	0.25
Ferrite	75		
Gray iron	79.5		
Yellow brass	221		

Note: 1 cal/cm · s · K = 418.4 W · m⁻¹ · K⁻¹

** 금속, polymer, 세라믹 열전도도 비교!!!

$k = \rho\, \alpha\, C_p$

단위: watts per meter kelvin (W/(m·K)).

Typical values of room temperature thermal conductivity of selected materials.

21.3. Thermal Conductivity

Plasmon?

❖ Thermal energy is transferred by two important mechanisms: transfer of free electrons and lattice vibrations (phonons).

❖ **Valence electrons gain energy, move toward the colder areas of the material, and transfer their energy to other atoms.**

• The amount of energy transferred depends on **the number of excited electrons [plasmons: 고체내에서] and their mobility**; these in turn, depend on the type of material, lattice imperfections, and temperature.

❖ **In addition, thermally induced vibrations of the atoms [Phonon] transfer energy through the material.**

◆ Thermal Conductivity를 지배하는 핵심 인자: **[자유전자와 Phonon]**, their mobility

21.3. Thermal Conductivity-Metal

The thermal conductivity of **metals** is due primarily to the **electronic contribution**. [Carrier의 숫자와 mobility의 trade off 관계!!]

- When the temperature of the material increases, **two off-setting factors** affect thermal conductivity. [온도가 높아지면, 2개의 factor가 열전도를 지배 함]

- Higher temperature are expected to increase the energy of the electrons, **creating more "carriers"** and **increasing the contribution from lattice vibration**; these effects increase the thermal conductivity. [열전도도 증가 요소]

- However, **the greater lattice vibration scatters the electrons**, **reducing their mobility,** and therefore tends to decrease the thermal conductivity.

- The combined effect of these factors leads to very different behavior for different metals. → [온도 증가 : 금속의 열전도도는 Phonon의 [+]쪽 기여와 electron의 [-]쪽 기여의 총합으로 결정]

Thermal conductivity in metals also depends on crystal structure defects, microstructure, and processing.

** Lorentz 상수(L): 금속에서 열전도도와 전기전도도는 비례하는데 이때 상수값 ($k / \sigma T = L$)

21.3. Thermal Conductivity-Ceramics [Glass]

- **The energy gap[Eg] in ceramics is too large for many electrons to be excited into the conduction band except at very high temperatures.** Consequently, the transfer of heat in ceramics occurs **primarily by lattice vibrations (phonons).** ➔ Since the electronic contribution is absent, the thermal conductivity of most ceramics is much lower than that of metals. (세라믹스의 열전도도가 금속에 비해 낮은 이유)

- *However, the main reason (why the experimentally observed conductivity of ceramics is low) is the* **level of porosity**.

- Materials with a close-packed structure and high modulus of elasticity produce high-energy phonons that encourage high thermal conductivities. **[열전도도 = 확산계수x밀도x비열]➔** $k = \rho\, \alpha\, C_p$

- **Glasses have low thermal conductivity**. The amorphous **loosely packed structure** minimizes the points at which silicate chains contact one another, making it more difficult for the phonons to be transferred. **[Phonon의 전달은 contact mode에 크게 의존함]**

[**Contact modes**: point contact, line contact, surface contact 등이 있음, LED의 방열판?]

*** Ceramic와 glass는 왜 이론 값보다 실험 값의 열전도도가 낮을까? [loosely packed structure ➔ low contact]**

21.3. Thermal Conductivity-반도체, 폴리머

◆ ***Semiconductors*:** 열전도도는 에너지 밴드갭[Eg]의 크기와 온도에 의존

• Heat is conducted in semiconductors by both phonons and electrons.

• At low temperatures, phonons are the principal carriers of energy, but at higher temperatures, electrons are excited through the small energy gap into the conduction band and thermal conductivity increases significantly. **[반도체: 저온과 고온에서 열전달 기구가 달라짐]**

◆ ***Polymers*:** 열전도도는 낮고, 폴리머 고분자의 진동과 이동에 의해 결정

• The thermal conductivity of polymers is very low-even in comparison with silicate glasses.

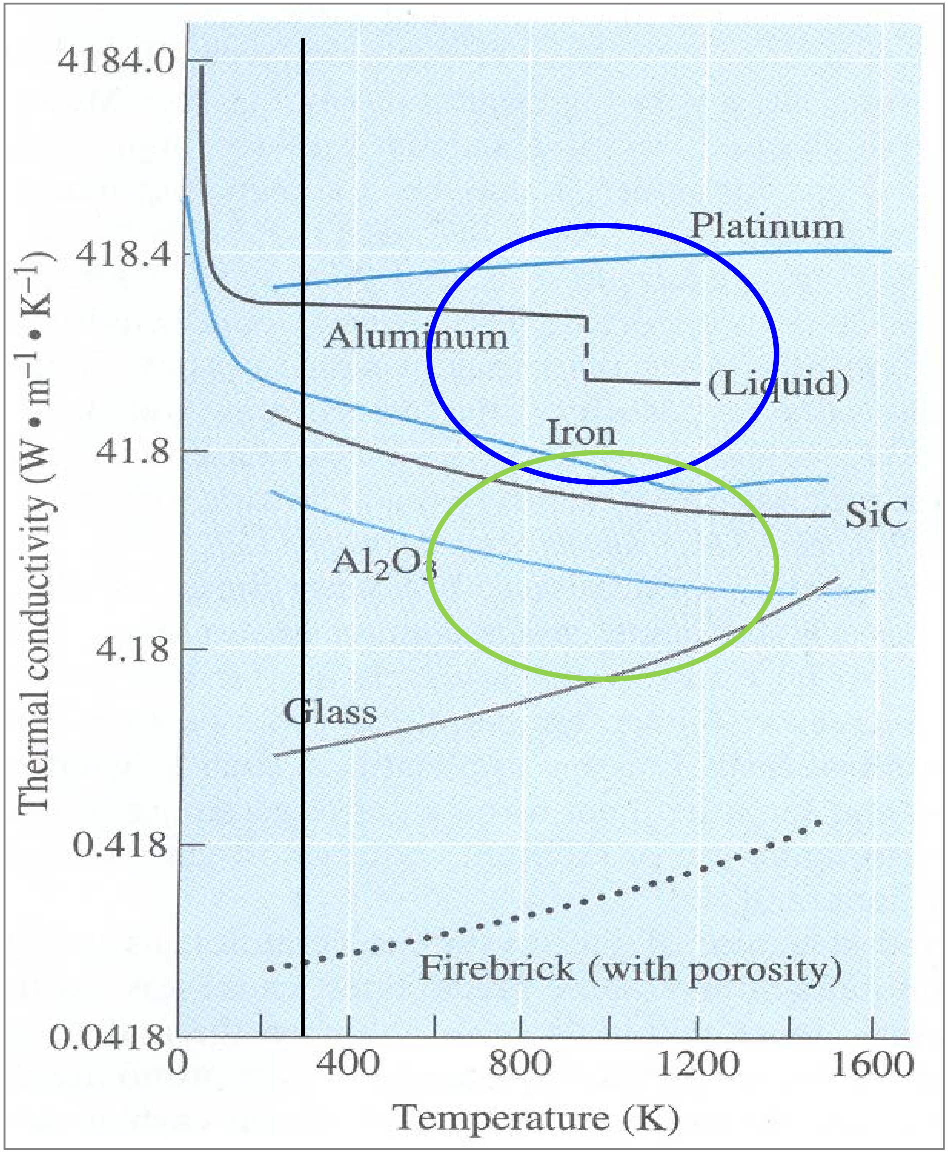
• 폴리머에서 열전달은 폴리머 고리분자의 진동과 이동에 의함.

• 커피컵의 설계: 뛰어난 열절연성을 가지도록 함.

✓ **중요 질문: [금속, 세라믹, glass, 반도체, 폴리머]의 열전도 특성을 각각 요약 설명하시오.**

21.3. Thermal Conductivity

[Fig. 21-6]



온도 증가에 따른 열전도도 변화 이유?
[온도 증가시:
금속, 세라믹, 유리, 폴리머의 열전도도 변화]

1) Glass: 규칙도 증가 ➔ Phonon의 산란 감소
➔ 열전도도 증가

1) 금속(Al): 격자진동 활발 ➔ 전자 이동도 감소
➔ 열전도도 감소[열전도도 감소]
➔ 반면, Phonon의 기여는 증가[열전도도 증가]

1) SiC의 높은 열전도도: close-packed 구조 때문
➔ 세라믹: 전자의 기여는 거의 없음.

The effect of temperature on the thermal conductivity of selected materials.

Note the log scale on the y-axis.

** 왼쪽 그림의 의미를 해석!!!

21.4. Thermal Shock [열충격]

The failure of a **brittle material** caused by stresses induced by **sudden changes in temperature** is known as ***thermal shock(열충격)***. (정의: 열응력에 의한 재료의 취성파괴!!)

[취성 파괴를 일으키는 응력의 source?? ← 열응력 ← 열변형 ← 급작스런 온도변화]

Thermal shock parameter: **$R = \sigma_f \cdot K (1-\nu) / E \cdot \alpha$**

Thermal shock behavior is affected by several factors [5개]:

[열충격에 강한 재료는 아래 인자들이 커야 하는지? 작아야 하는지?]

1. ***Coefficient of thermal expansion[CTE: α]***: A low coefficient minimizes dimensional changes and increases[??] the ability to withstand thermal shock. **[낮은 TEC ➔ 열충격 방지에 유리함]**

2. ***Thermal conductivity[K]***: The magnitude of the temperature gradient is determined partly by the thermal conductivity of the material. A high thermal conductivity helps to transfer heat and reduce temperature differences quickly in the material. **[높은 열전도 ➔ 열충격 방지에 유리함]**

21.4. Thermal Shock

$R = \sigma_f \cdot K(1-\nu) / E \cdot \alpha$

3. ***Modulus of elasticity[E]***: A low modulus of elasticity permits large amounts of strain before the stress reaches the critical level required to cause fracture.

[낮은 E ➔ 소성변형 때문에 열충격 방지에 유리함]

4. ***Fracture stress[σ_f]***: A high stress required for fracture permits larger strains. The fracture stress for a particular material is high if flaws are small and few in number. **[높은 파괴응력 ➔ 재료내부에 존재하는 flaw의 개수와 크기가 작을 열충격 방지에 유리함]**

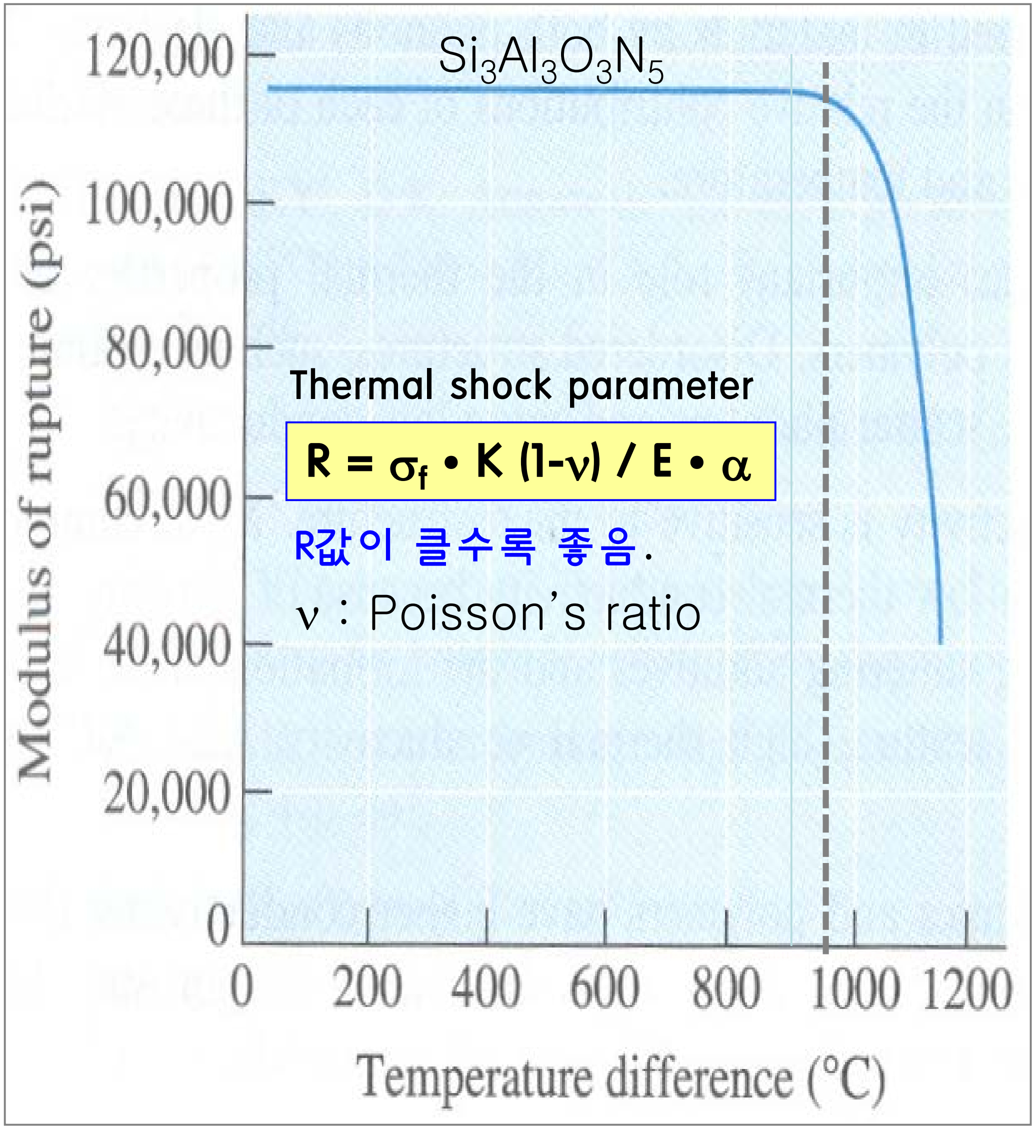
5. ***Phase transformations***: Additional dimensional changes can be caused by phase transformations. Transformation of silica from quartz to cristobalite, for example, introduces residual stresses and increase problems with thermal shock. Similarly, we cannot use pure $PbTiO_3$ ceramics since the stresses induced during the cubic to tetragonal transformation will cause the ceramic to fracture.

[상변태 ➔ 상변태로 인한 추가의 응력발생 ➔ 열충격 방지에 불리함]

21.4. Thermal Shock

$R = \sigma_f \cdot K(1-\nu) / E \cdot \alpha$

[Fig. 21-7]



Thermal shock parameter

$R = \sigma_f \cdot K(1-\nu) / E \cdot \alpha$

R값이 클수록 좋음.

ν : Poisson's ratio

열충격 저항력 측정: 기계적 특성에 영향을 미치지 않으면서 급냉하는 동안 재료가 견딜 수 있는 최대 온도차.

➔열축격 계수의 정의: 재료가 파단없이 급냉할 수 있는 최대 온도 변화.

➔높은 열충격 계수(R)값의 의미: 열충격에 대한 저항이 좋은 것을 의미함.

The effect of quenching temperature difference on the modulus of rupture of sialon.

The thermal shock resistance of the ceramic is good up to about 950℃ [➔열충격에 강한 소재]

[숙 제]

$k = \rho\ \alpha\ C_p$

1. 다음의 용어를 정의하시오:
   열용량, 비열, 열팽창계수, 열전도도, 열충격, Phonon, Lorentz상수
2. 전기전도도와 열전도도의 기구(mechanism)에 대해서 구분 설명하시오.
   [금속재료, 반도체 재료, 세라믹 재료, 폴리머 재료 /
   ← 기본 공식, 주요 열전도 기여 인자(electron, phonon, Eg)을 사용해서]

$k / \sigma T = L$ 의 의미? :

금속에서, *thermal conductivity* (k)와 *electrical conductivity*(σ)의 관계식.

** 본 단원의 모든 예제문제를 이해한 후, 풀이과정을 기술해서 제출하시오