CERAMICS: Properties 1 (Physical, Chemical, Mechanical)

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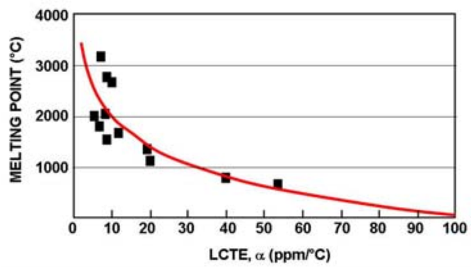
We will approach all of the major categories of ceramic properties in this module – physical, chemical, and mechanical – with key examples for each one. In the following module we will focus on brittle fracture of ceramic materials.

PHYSICAL PROPERTIES

Mass properties, thermal, and electrical properties.

1. **Mass Properties (e.g., density)**
   Ceramics are intermediate (density = ρ = 2.00-6.00 gms/cm^3)
   Different for ALLOTROPES (e.g., glass, cristobalite, tridymite, quartz)
2. **Thermal properties:**
   Melting points high (600-4000C)
   Thermal conductivities are low (insulators)
   Thermal expansion values are low (1-15 ppm/C)

Ceramic	α (LCTE) =	Tm =
CsCl	54 ppm/C	646 C
NaCl	40	800
PbS	20	1120
CaF_2	20	1330
Fe_2O_3	9	1560
SiO_2 (Crist.)	12	1710
TiO_2	7	1840
ZnO	6	1975
Al_2O_3	8	2050
ZrO_2	10	2700
MgO	9	2800
TiC	7	3190



3. **Electrical properties:**
   Electrical conductivity (insulator or semi-conductor)

MASS PROPERTIES include things like density. Ceramics are intermediate in density between polymers (lower) and metals (higher) in the range of 2-6 gms/cm^3. Non-crystalline materials are less dense than crystalline ones. Compositions with several **ALLOTROPES** such as SiO_2 will have minor differences in density.

[CLICK] THERMAL PROPERTIES of ceramics are governed by the type of bonding (covalent to ionic) and number of bonds present . **[CLICK]** Generally for all materials, the expansion from absolute zero to the melting temperature is about 15%, so materials with higher Tm values have lower LCTE values. This is apparent in the table. **[CLICK]** You can see that the relationship is semi-logarithmic as shown in the figure. Also, because most ceramics have crystal structures that are not cubic ones, they tend to be **ANISOTROPIC**. This means they will have different properties in different directions.

[CLICK] Ceramics are electrical insulators under most circumstances. Hydroxyapatite crystals are insulating. Dentin enamel is 89 volume percent hydroxyapatite. Dentin is 50 volume percent hydroxyapatite crystals. Tooth structure therefore is insulating.

PHYSICAL PROPERTIES

Optical properties.

3. **Optical properties:**
   Transparency; Translucency
   Color: depends on visible light interaction with “ions” or “pigments”
   (Color from ions [typically 0.2-0.4%] depends on the oxidation state)

Characteristic Ionic Colors

Ion	Atomic Number	Characteristic Color	
		Oxidized	Reduced
Ti	23	Yellow	None
Cr	24	Yellow-green	Dark green
Mn	25	Light-purple	NONE
Fe	26	Light yellow	Light green
Co	27	Blue-violet	Blue-violet
Ni	28	Violet to brown	Violet to brown
Cu	29	Green blue	Red
U	92	Yellow	Green

Inorganic Pigments

Characteristic Color	Semi-Vitrified Products:	
	Material	Comments
White	TiO_2	Precipitated from solution
	XrO_2	Precipitated from solution
	SnO_2	Inert
	ZnS	Inert
Purple		
Brown		From Co containing glasses
Green	Cr_2O_3	
Yellow	$PbCrO_4$	
	CdS	Low temperature
Orange	$PbCrO_4$-PbO	Basic lead chromate
	$Pb(Cr,Mo)O_4$	
Red	Fe_2O_3	Brown-red
	CdSe	Low temperature
Black	MnO_2	

Precious (Gems) Minerals

Rubies	Al_2O_3 with <<<3-4% Cr^{+3}
Blue Sapphires	Al_2O_3 with <<<3-4% Co^{+2}
Emeralds	Be-Al-Silicate
Opals	Hydrated Silica
Amethysts	Silica with Mg impurity
Topaz	Hydrated F-Al-Silicate
Pearls	Calcium carbonate and impurities

Inorganic Pigments

Characteristic Color	Organic coatings:	
	Material	Comments
White	TiO2	
	$2PbCo_3$-$Pb(OH)_2$	White Lead
Purple	$MnPO_4$	Very weak
Blue	$Fe_4[Fe(CN)_6]_3$	Prussion blue
	Ultramarine	Colored glass
Green	Prussian Blue + $PbCrO_4$	
Yellow	$PbCrO_4$	
	CdS	
	$Fe(OH)_3$	Brown-yellow
Orange	$PbCrO_4$-PbO	
	$Pb(Cr,Mo)O_4$	
	Pb_3O_4	Red lead
Red	CdSe	
Black	Carbon	

Most ceramics are clear (i.e., transparent). Translucency presumes some transparency with some scattering or diffusion of light. Color depends on interaction of light with ions in the main ceramic or pigments that are added to the ceramic as a secondary phase.

[CLICK] Examine the table of characteristic ionic colors for key ions in an oxidized or reduced state. In these cases, the ions function as substitutional defects. **[CLICK]** To see how this could work, look at precious minerals. Rubies are alumina with small amounts (<<<3%) of Cr+3 included in the composition and generally far less than that. Typical concentrations are 0.4% and would be considered at the impurities. Most of the precious gems are based on aluminas or silicas, that have been very slightly modified.

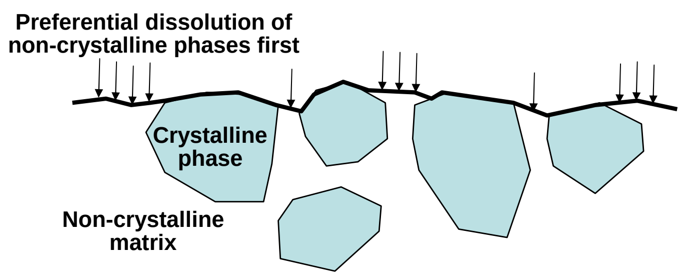
[CLICK] The other way to produce color is to add in colored phases (i.e., inorganic pigments). **[CLICK]** If these same phases are mixed into polymers they are usually called organic pigments or dyes.

CHEMICAL PROPERTIES

Chemical and electrochemical properties.

1. **Chemical / Electrochemical corrosion properties:**
   Very few under normal circumstances.

2. **Solubility:**
   Soluble in certain strong acids (HF) and strong bases
   Usually non-crystalline (glassy) phases dissolve first.
   Capable of selective ion leaching and ion-exchange reactions



Ceramics rarely undergo anything comparable to metal chemical corrosion or electrochemical corrosion.

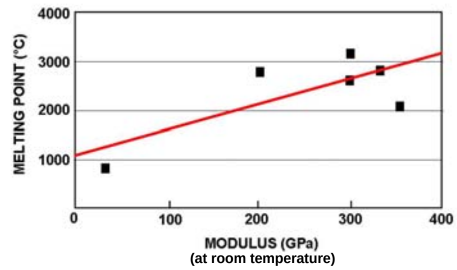
[CLICK] Ceramics generally have good chemical resistance to weak acids and weak bases. However, very strong acids or strong bases tend to produce ion exchange reactions and dissolve the structures. HF is commonly used to intentionally etch ceramic surfaces composed of silicates. It is the F- ion that causes the actual damage. In dentistry, most 2-phase silica-based restorations are treated with 10% HF solutions to etch them. This produces different dissolution that creates micromechanical relief prior to micromechanical bonding.

MECHANICAL PROPERTIES

Properties depend both on temperature and degree of crystallinity.

1. **Mechanical properties versus melting temperature:**
   Generally strength and modulus go up and down together.
   Modulus (E) at 25C linearly related to melting temperature (Tm).
   (Ceramics = 30-350 GPa, Metals = 50-200 GPa, Polymers = <50 GPa)

Ceramic:	E (GPa) =	Tm (C) =
Al_2O_3	310	2050
SiC	345	>2800
TiC	207	3180
BeO	310	2585
MgO	366	2800
NaCl	34	801

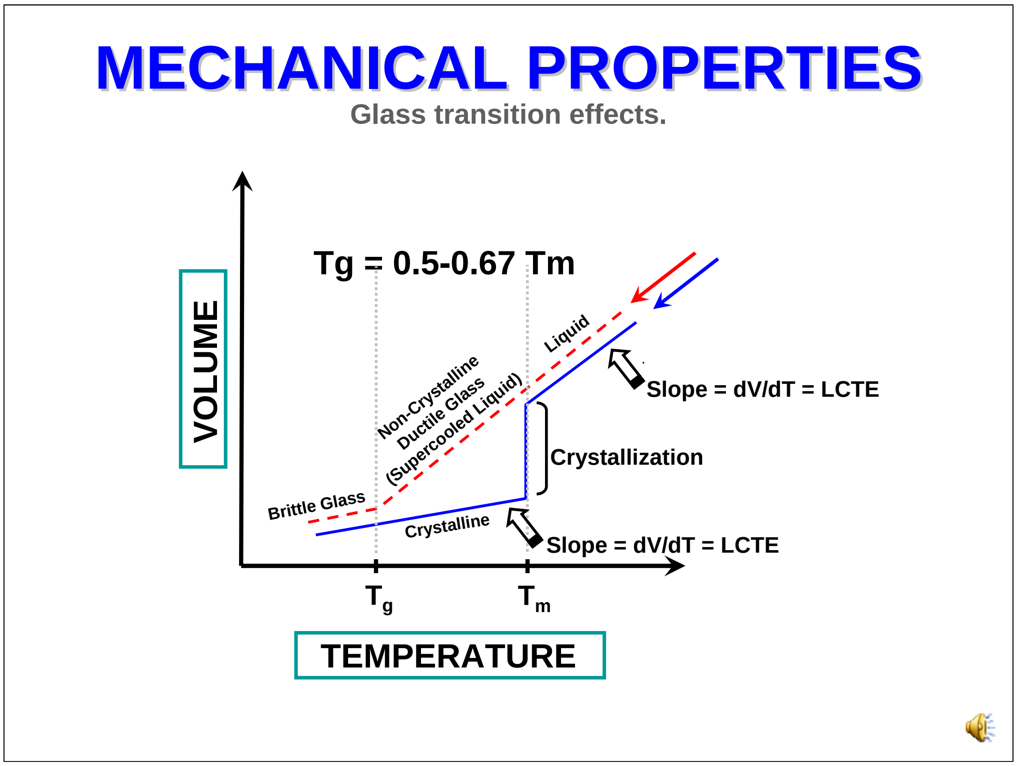


2. **Mechanical properties versus degree of crystallinity:**
   Crystalline phases are stronger.
   At low T's, crystalline and non-crystalline phases are brittle.
   At high T's approaching Tm, non-crystalline phases are ductile.

Ceramics tend to be rigid and brittle (i.e., not capable of much plastic deformation). However, their properties depend both on temperature and on the amount of crystallinity. Lower temperatures and higher crystallinity content tend to increase the modulus and the brittleness. Let's look at each effect separately.

[CLICK] The figure shows an approximately linear relationship between melting temperature and modulus at room temperature (i.e., 25C). Remember that if the actual temperature changes, then the stress-strain properties change. Going up in temperature decreases all values. Going down in temperature increases all values.

[CLICK] Next let's look the mechanical properties versus the actual temperature. Crystalline and non-crystalline phases behave differently at low and high temperatures. At low temperatures, both types of phases are brittle. At high temperatures, crystalline phases are brittle but non-crystalline ones are ductile. To understand this we need to look at why this happens.



To understand this behavior you need to understand the GLASS TRANSITION temperature that is associated with the non-crystalline phase. Let's go through the diagram shown.

[CLICK] The y-axis is volume. The x-axis is temperature. This is a little bit strange because T is usually the y-axis but this is the way this is usually presented.

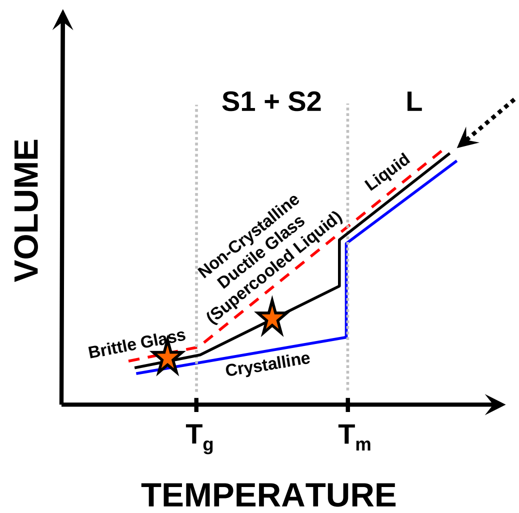
[CLICK] Start in the far upper right-hand corner of the diagram and cool down a solid from the liquid to the solid and then down to absolute zero. Crystalline material tries to freeze at Tm, undergoes a significant contraction on crystallization, and then continues to shrink with cooling. The slope of the line in the L or in the S is the coefficient of thermal expansion or LCTE.

[CLICK] Now let's follow material which does not crystallize at Tm. It freezes at Tm but continues to behave like a liquid with the same LCTE. It is contracting more than that of crystallized material. It can never be more well packed than the crystalline material, so at some point, it reaches a very dense arrangement that is almost like the crystalline solid and then behaves like the crystalline solid. The temperature at which this occurs is called the GLASS TRANSITION or Tg. Below Tg, the material behaves like a brittle glass. Above Tg, the material behaves as a ductile glass (like a liquid).

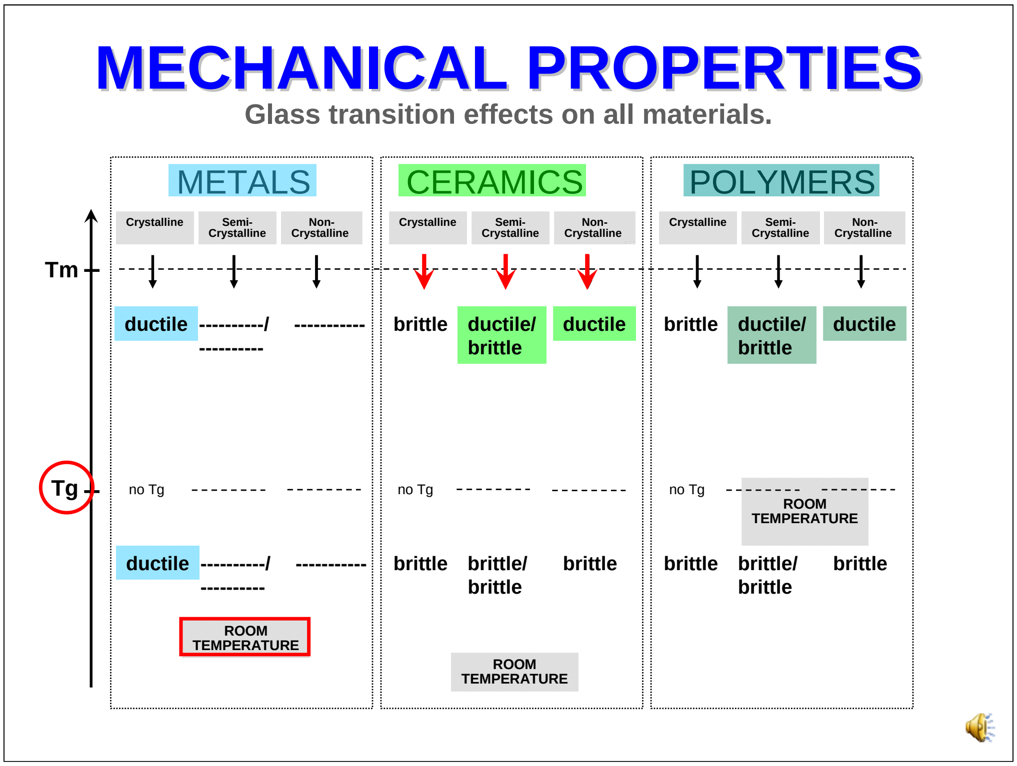
[CLICK] The Tg is approximately half of the absolute temperature for Tm.

MECHANICAL PROPERTIES

Glass transition effects.



Only the non-crystalline material has a Tg. Only the crystalline material has a Tm. Consider a solid that is 50% crystalline and 50% non-crystalline phases. **[CLICK]** Let's look at the potential combinations of brittle-ductile properties. **[CLICK]** Below Tg, both phases are brittle. **[CLICK]** Above Tg, the crystalline phase is brittle but the non-crystalline phase is ductile. Above Tm, both phases melt and the material is entirely ductile.



The glass transition temperature is relevant to any solid that contains non-crystalline material. Metals are difficult to keep from crystallizing but if quenched fast enough, they can exhibit non-crystalline phases. Ceramics are often semi-crystalline. Polymers are generally non-crystalline.

The table shown reports the expected behaviors above and below the Tg for materials as a function of the Tg **[CLICK]** and room temperature. **[CLICK]** Most metals and **[CLICK]** almost all ceramics are usually well below their Tg at room temperature. **[CLICK]** Polymers are often above their Tg at room temperature.

Now look within the category of ceramics. **[CLICK]** 100% crystalline materials are brittle above and below Tg. Semi-crystalline ones have brittle crystalline and non-crystalline phases below Tg. **[CLICK]** But above Tg, the non-crystalline phase becomes ductile. **[CLICK]** Totally non-crystalline material is brittle below Tg and ductile above it.

The same principles apply to polymers but for them room temperature is generally above their Tg.

QUICK REVIEW

Review of physical, chemical, and mechanical properties of ceramics.

- **What happens to LCTE when Tm increases?**
  DECREASES
- **What produces ionic colors in ceramics?**
  SUBSTITUTIONAL DEFECTS OF METAL IONS
- **As Tm increases, what happens to E?**
  INCREASES
- **What phase is Tg associated with in a semi-crystalline material?**
  NON-CRYSTALLINE PHASE
- **What is the rule-of-thumb relating Tg to Tm?**
  Tg = ½ Tm (on the absolute temperature scale)
- **What is the ductile-brittle behavior below Tg for mixed phases?**
  BOTH CRYSTALLINE AND NON-CRYSTALLINE ARE BRITTLE
- **How does the LCTE compare for each mixed phase below Tg?**
  LCTE FOR NON-CRYSTALLINE APPROXIMATELY CRYSTALLINE.

Here is a quick review of the concepts from this module.

[CLICK] (1) What happens to the LCTE when Tm increases?
[CLICK]

[CLICK] (2) What produces ionic colors in ceramics?
[CLICK]

[CLICK] (3) As Tm increases, what happens to E?
[CLICK]

[CLICK] (4) What phase is Tg associated with in a semi-crystalline material?
[CLICK]

[CLICK] (5) What is the rule-of-thumb relating Tg to Tm?
[CLICK]

[CLICK] (6) What is the ductile-brittle behavior below Tg for mixed phases?
[CLICK]

[CLICK] (7) How does the LCTE compare for each mixed phase below Tg?
[CLICK]

THANK YOU

THANK YOU.