

CERAMICS

Terminology and Classification

S.C. BAYNE,¹
J.Y. Thompson²

¹University of Michigan
School of Dentistry,
Ann Arbor, MI 48109-1078
sbayne@umich.edu

²Nova Southeastern
College of Dental Medicine,
Ft. Lauderdale, FL 33328-2018
jeffthom@nova.edu



Ceramics are not intuitive for most students in dentistry because their focus on biology and organic chemistry. However, they follow all the rules that we have laid out. To begin, we need to negotiate a mine field of complicated terminology -- but it is do-able -- and should make key discussions meaningful later.

INTRODUCTION

Definitions and prevalence.

“Ceramic” is derived from the Greek word “keramos” meaning the art and science of making and using solid articles formed by the action of heat on earthy materials.

CERAMIC = any material composed of predominantly metal and non-metal elements (= working definition). [There are a very few exceptions like C or GaAr.]



COMPONENTS of earth's crust:

O = 50%	Fe = 5%	K = 2.5%
Si = 26%	Ca = 3%	Mg = 2%
Al = 8%	Na = 2.5%	H = 1%



The word “ceramic” comes from the Greek term “keramos” that means making solid articles out of baked earthy materials. But what is ceramic and what is not? **[CLICK]** Assuming that you know the composition of a solid, you can tell if it is ceramic by the presence of both metallic and non-metallic elements. This is a very practical definition. Non-metallic elements are usually oxygen or carbon. **[CLICK]** Is SiO_2 a ceramic? YES. It contains metallic (Si) and non-metallic (O) elements. **[CLICK]** Is $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ a ceramic? YES. It contains a variety of metallic and non-metallic elements.

In our normal world, the surface that you see is predominantly an organic one. You see trees, and grass, and water. However, the solid external skin of the planet is primarily ceramic. **[CLICK]** Almost 85% of the earth's crust is composed of three major elements Si, Al, and O combined into ceramic materials of SiO_2 or Al_2O_3 or any of the analogs of these compositions. So in fact, ceramics are more prevalent than you might have expected.

TERMINOLOGY

Several names are possible for any ceramic material.

1. **Elemental Name: describe metallic and non-metallic elements**
 - a. M = Metallic part
 - b. X = Non-metallic part
2. **Elemental formula ratio:**
 - a. Stoichiometric compounds = simple M/X integer ratios
 - b. Non-Stoichiometric cpds = complex M/X integer ratios
Represented as mixtures of stoichiometric cpds
 $\text{Ca}_{0.4}\text{Si}_3\text{O}_{6.4} = 2\text{CaO} \cdot 15\text{SiO}_2$
3. **Chemical Name: (based on the oxidation or reduction state)**
 - a. Utilize IUPAC terminology for stoichiometric compounds.
 - b. Names do not indicate arrangement, bonding, chemical impurities, or defects present in the material.)
4. **Historical Name:**
 - a. Based on feel of "earthy" materials.
 - b. Based on people's names, things, or places related to the discovery of the material.



What is often very confusing to folks new to ceramic science is that there is wide range of terms that mean the same thing.

So let's consider the four major systems of terminology:

- (1) elemental composition: this deals simply with identification of the metallic and non-metallic portions of a ceramic.
- (2) elemental formula ratio: this tries to describe any ceramic in terms of a mixture of stoichiometric compounds.
- (3) IUPAC chemical name: this reports the chemically correct name based on the oxidation states of the materials involved.
- (4) historical name: this is one or more common names that might have been identified historically with the material.

Now let's see what this means for an important ceramic material for dentistry like SiO_2 . The elemental name is "silicon oxide." The name based on elemental ratios is "silicon dioxide." The IUPAC name is also "silicon dioxide." The common or historical name is "silica." They all refer to the same composition.

As we will see shortly, silica can exist in different crystalline forms. Each one has a special name as well.

NAMES vs. FORMULAS

Examples of key terms (gray marked rows) you need to know.

<i>Stoichiometric Formula</i>	<i>Elemental Name</i>	<i>Chemical Name</i>	<i>Historical Name</i>
ZnO	Zinc Oxide	Zinc Oxide	Chinese White
MgO	Magnesium Oxide	Magnesium Oxide	Periclase
CaO	Calcium Oxide	Calcium Oxide	Lime; Calcia
SiO ₂	Silicon Oxide	Silicon Dioxide	Silica
Fe ₂ O ₃	Iron Oxide	Ferric Oxide	Hematite
Fe ₃ O ₄	Iron Oxide	Ferrous Oxide	Magnetite
Al ₂ O ₃	Aluminum Oxide	Aluminum Oxide	Corundum, Alumina
Cr ₂ O ₃	Chromium Oxide	Chromium Sesquioxide	Green Cinnabar
ZnS	Zinc Sulfide	Zinc Sulfide	Zinc Blende, Wurtzite
Cu ₂ S	Copper Sulfide	Cuprous Sulfide	Chalcoite
ZnCO ₃	Zinc Carbonate	Zinc Carbonate	Smithsonite
MgCO ₃	Magnesium Carbonate	Magnesium Carbonate	Magnesite
CaCO ₃	Calcium Carbonate	Calcium Carbonate	Calcite
K ₂ CO ₃	Potassium Carbonate	Potassium Carbonate	Potash
BaSO ₄	Barium Sulfate	Barium Sulfate	Barite
CaSO ₄	Calcium Sulfate	Calcium Sulfate	Anhydrite
CaSO ₄ ·2H ₂ O	Calcium Sulfate	Calcium Sulfate Dihydrate	Gypsum
CaMoO ₄	Calcium Molybdate	Calcium Molybdate	Powellite
KAlSi ₃ O ₈	Aluminosilicate	K-Al-Silicate	Feldspar
(Na, K)(Al, Si)Si ₂ O ₄	Aluminosilicate	Nepheline
Ca ₁₀ (PO ₄) ₆ (OH) ₂	Calcium Phosphate	Cal. Phosph. Hydroxide	Hydroxyapatite
Ca ₃ (PO ₄) ₂	Calcium Phosphate	Tricalcium Phosphate	Whitlockite
Ca ₅ (PO ₄) ₃ F ₂	Fluoroapatite	Cal Phos Fluoride	Apatite



Here are about 2 dozen ceramic materials arranged in terms of the 4 types of names, but with their stoichiometric formulas presented first. Familiarize yourself with terms on the list. Memorize those terms that are highlighted with gray backgrounds. These will be referred to often when we deal with dental materials. You should remember silica, hematite, alumina, cinnabar, gypsum, and hydroxyapatite.

Consider the terms associated with Al₂O₃. It also can be called aluminum oxide, corundum, or alumina.

CLASSIFICATION METHODS

Different systems in use.

Traditional (but artificial) classifications of ceramics:

- | | |
|---------------------------|----------------------------------|
| a. Vitreous | = based on non-crystallinity |
| b. Ionic | = based on aqueous behavior |
| c. Stoichiometric | = based on elemental ratios |
| d. Phosphates, Carbonates | = based on chemical class |
| e. Semi-conductor | = based on electrical properties |
| f. Refractory | = based on thermal properties |
| g. Magnetic | = based on magnetic properties |

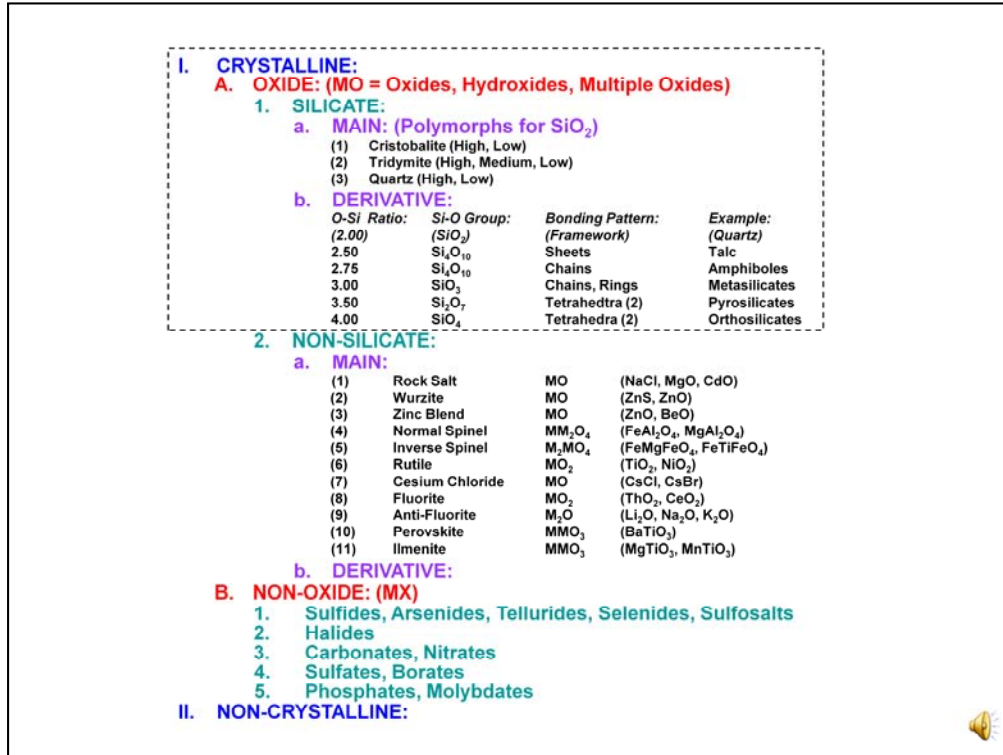
Classification by A-B-C-D for Materials Structure (next slide):

- a. Crystalline vs. Non-Crystalline
- b. Oxide vs. Non-Oxide
- c. Silicate vs. Non-Silicate Types
- d. Main Structures vs. Derivative Structures



There are many classification systems that are associated with ceramics but all are of convenience and not very rigorous in dealing with the full range of materials that are truly ceramics. Some are listed here – such as vitreous character, ionic behavior, stoichiometry, or magnetic properties.

For our purposes, it is much more convenient to array all ceramics in terms of Arrangement-Bonding, Composition-Defects – by classifying their crystallinity, oxide character, silicate character, and structure. This is an artificial classification method but parallel to our view of the structure of materials. A complete presentation follows on the next slide.



Look at the framework for ceramics that is provided in the chart using a sequential hierarchy for ARRANGEMENT (crystalline versus non-crystalline), BONDING (oxide versus non-oxide), COMPOSITION (silicate versus non-silicate), and DEFECTS (main structure versus derivative structure).

The most important oxide used in dentistry is SiO₂ (silica). Pure silica that is allowed to crystallize is classified as crystalline, oxide, silicate, and main structure. If the O-Si ratio is different than 2.0, then it would be called a derivative structure. Consider a chemical mixture of 80% silica with 20% alumina that is crystalline. The classification will be crystalline, oxide, silicate, and derivative type.

If you study the diagram above you will notice that under silicates there are three crystalline forms -- cristobalite, tridymite, and quartz -- that are stable at different temperatures. All are important for dental materials. We will explore these more in detail in a later module.

CERAMICS CRYSTALLIZATION

Thermodynamic, kinetic, and mechanistic views.

1. **THERMODYNAMIC CONSIDERATIONS:** Symmetry
 - a. Trying to maximize the packing efficiency of the ions
 - b. Trying to maximize the coordination number

2. **KINETIC CONSIDERATIONS:**
 - a. Sufficient thermal energy to diffuse into positions
 - b. Sufficient time for diffusion to occur

3. **MECHANISMS of Crystallization:**
 - a. Nucleation and growth of crystals



As we have emphasized earlier for metals, all materials try to crystallize during solidification to reduce their overall energy. Crystallization requires symmetry options, available thermal energy for molecular motion, and sufficient time for diffusion. Ceramics crystallize much more slowly than metals. Simple compositions have a much better chance of crystallizing. The mechanism of crystallization is exactly the same – nucleation and growth. If you look at a crystalline microstructure then you will see the same architectures of crystals (grains) as you did for metals.

SPECIAL DEFINITIONS

Do not get confused by the variety of terms to describe ceramics.

1. Definitions relating to crystallization:

- a. Crystalline
- b. Semi-crystalline
- c. Non-Crystalline = Amorphous, Vitreous, Glassy

2. Definitions relating to composition:

- a. REFRACTORY = high MP, strong ceramic, usually crystalline
- b. ENAMEL = ceramic coating (over a substrate)
- c. PORCELAIN = vitreous ceramic based on $K_2O-Al_2O_3-SiO_2$

QUARTZ = anhydrous silicate

FELDSPAR = anhydrous alumino silicate

CLAY = hydrated alumino silicate



Just like there are many different terms for the same composition, there are many different terms used to describe non-crystalline materials, especially ceramic ones. Amorphous, vitreous, and glassy all mean that the material is non-crystalline. Learn these terms and become comfortable with using them all. They will come up again and again.

There are other terms that are also often confusing. Let's address them at the start. Refractory materials are ceramics with very high melting temperatures, that are generally very strong, and usually crystalline. They are commonly used in fabrication techniques for ceramic restorations.

Any material that forms a ceramic coating can be called an enamel. Obviously, dental enamel is an example of this situation.

Porcelain is widely used commercially for a huge number of applications. A special version of porcelain is used for esthetic materials in dentistry. It is a mixture of potassium oxide, alumina, and mostly silica. While you can create the composition by mixing pure oxides, it is generally easier to get to the same overall composition by mixing naturally occurring materials that contain the oxides – quartz, feldspar, and clay. Quartz is entirely silica. Feldspar contains silica and alumina as alumino silicate but no water. Clay is a hydrated form of alumino silicate.

The purity of these three raw materials vary widely around the world. Therefore, the type of porcelain you get depends strongly on the source of these raw materials.

QUICK REVIEW

Review of definitions, terminology, and classification systems.

- **What are the 3 major elements in the earth's crust?**
OXYGEN, SILICON, ALUMINUM
- **What are 4 systems of ceramic terminology?**
Elemental Name, Formula, Chemical Name, Historical Name
- **Classify alumina using an A-B-C-D structural approach?**
Crystalline, Oxide, Non-Silicate, Main Structure
- **What are 3 synonyms for the term non-crystalline?**
AMORPHOUS, VITREOUS, GLASSY
- **What are the 3 main oxides that comprise porcelain?**
 K_2O , Al_2O_3 , and SiO_2
- **What ceramic raw materials are often mixed to make porcelain?**
QUARTZ, FELDSPAR, CLAY



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

[CLICK] (1) What are the 3 major elements in the earth's crust?

[CLICK]

[CLICK] (2) What are 4 systems of ceramic terminology?

[CLICK]

[CLICK] (3) Classify alumina using an A-B-C-D structural approach?

[CLICK]

[CLICK] (4) What are 3 synonyms for the term non-crystalline?

[CLICK]

[CLICK] (5) What are the 3 main oxides that comprise porcelain?

[CLICK]

[CLICK] (6) What ceramic raw materials are often mixed to make porcelain?

[CLICK]



THANK YOU



THANK YOU.