

Chapter III

Theory

It is known that zinc (Zn), gallium (Ga) and aluminium (Al) can form a large number of addition compounds by coordination other substances such as oxygen, nitrogen, boron carbon and other systems. Zinc oxide, gallium oxide, aluminium oxide, zinc gallate(zinc gallium oxide), and zinc aluminium oxide(zinc aluminate) are the compound that are important commercial forms. Physical and chemical properties of them have been studied to include preparation procedure and their advantages.

3.1 Zinc (Zn)

Zinc is Chemical element number 30. It is a malleable, ductile, gray metal with atomic weight 65.38 and a relatively active metal. Its compounds are stable. Because of chemical similarities among zinc, cadmium, and mercury, these three metals are classed together in group IIB of the periodic table of elements.

Thirteen isotopes of zinc are known, of which five are stable, having atomic masses of 64, 66, 67, 68, and 70. About half of ordinary zinc occurs as the isotope of atomic mass 64.

Zinc and zinc compounds have long been considered moderately poisonous, but in general they are not.

The most important use of zinc is as a protective coating on other metals. Coating iron or steel with zinc is called galvanizing.

Zinc is a lustrous, blue-white metal, which can be formed into virtually any shape by the common metal-forming techniques such as rolling, drawing, extruding, etc. The hexagonal close-packed crystal structure governs the behavior of zinc during fabrication. Physical properties are given in Table 3.1.

Table 3.1. Physical Properties of Zinc[1,2]

Property	Value
Ionic radius, Zn ²⁺ , nm	0.074
Covalent radius, nm	0.131
Metallic radius, nm	0.138
Ionization potential, eV	
first	9.39
second	17.87
third	40.0
Density solid, g/cm ³	
at 25°C	7.133
at 419.5°C	6.830
Melting point, °C	419.5
Boiling point, °C	907
Heat of fusion at 419.5°C, kJ/mol	7.387
Heat of vaporization at 907°C, kJ/mol	114.8
Thermal conductivity, W/(m•K)	
solid at 18°C	113.0
at 419.5°C	96.0
Heat capacity, J/(mol•K)	
solid	22.39+10 ⁻² T ^a
liquid	31.39
gas	20.80

^aT = 298-692.7 K.

Zinc is a fairly active metal chemically. It can be ignited with some difficulty to give a blue-green flame in air. The Zn^{2+} is colorless, so that the relatively few zinc compounds that are not colorless in large crystals, or white as powders, receive their color through the influence of the other constituents.

3.2 Zinc compounds

Zinc usually occurs as the sulfide but significant quantities of the oxide, carbonate, silicate, and basic compounds.

Zinc forms quite stable compounds and, as such, resemble magnesium. Bonding in zinc compounds tends to be covalent, as in the sulfide and oxide. With strongly electropositive elements, e.g., chlorine, the ammonia $[\text{Zn}(\text{NH}_3)_2]^{2+}$, cyanide $[\text{Zn}(\text{CN})_4]^{2-}$, hydroxyl $[\text{Zn}(\text{OH})_4]^{2-}$.

In compounds such as the oxide, borate, and silicate, the covalent bonds with oxygen are very stable.

Zinc compounds are generally colorless unless the other component, e.g., chromate, is colored. The lack of color of most zinc compounds in visible light is a great advantage in that they do not color paint films, plastics, rubber, cosmetics, etc.

3.2.1 Zinc oxide

3.2.1.1 Physical properties

Some of the physical properties of zinc oxide are listed in Table 3.2. Of great importance is the fact that it completely absorbs ultraviolet light below 266 nm and, thus, is unique among white pigments. Its high refractive indexes make it a good white pigment where its mean diameter for maximum light scattering is 0.25 μm . The crystal

structure of zinc oxides is likely to stabilize defect, e.g., zinc excess or deficiency and inclusion of foreign ions, and therefore has useful semiconductor properties.

Table 3.2 Physical properties of zinc oxide[1,2]

Property	Value
Melting point, °C	ca 1975 (subl)
Color	White in finely divided form
Refractive index, 0.5 m	2.015, 2.068
Specific gravity	5.68
Water solubility, minimum at pH	9.7
Heat capacity (at 25°C), J/(mol•°C)	40.26
Conductivity, W/(m•K)	25.2
Crystal structure	Hexagonal, wurtzite

3.2.1.2 Chemical properties

Zinc oxide, as an amphoteric, reacts with acids to form zinc salts and with strong alkalies to form zincates. Zinc oxide reacts with carbon dioxide in moist air to form oxycarbonate.

3.3 Zinc gallate (ZnGa₂O₄)

ZnGa₂O₄ is a binary oxide consisting of ZnO and Ga₂O₃ that crystallizes in spinel structure[1,2,3,6,7,8]. The unit cell of spinels is represented by formula of AB₂O₄. The Zn²⁺ ions occupy the tetrahedrally coordinated A site and Ga³⁺ ions occupy the octahedrally coordinated B sites [1,2,3,6,7,8]. The structure of zinc gallate is shown in Figure 3.3.

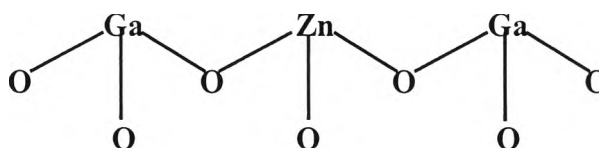


Figure 3.1 Structure of zinc gallate

3.3.1 Preparation procedure of zinc gallate

Zinc gallate powders have been prepared by several methods. The physical and chemical properties of zinc gallate are quite different by the process of preparation.

3.3.1.1 Coprecipitation [6]

Coprecipitation involves the growth of crystals from a solvent of different composition to the crystals. The solvent may be one of the constituents of the desired crystals, e.g., crystallization of salt hydrate crystals using water as the solvent, or the solvent may be entirely separate liquid element or compound in which the crystals of interest are partially soluble, e.g., SiO_2 and various high melting silicate may be precipitated from low melting borate or halide melts. In these cases, the solvent melts are sometimes referred to as fluxes since they effectively reduce the melting point of the crystals by a considerable amount.

The method has recently been used to growth of zinc gallate using zinc nitrate and gallium nitrate as the starting materials.

3.3.1.2 Chemical vapor deposition (CVD) method [10]

Chemical vapor deposition (CVD) is a process to deposit solids, in the form of a film or particles, using gaseous components. Extensive effort has been devoted to preparing ultrafine particles of metal, metal oxide and other inorganic compound. It is usual for the synthesis of particles by CVD method, to carry out the reaction at high temperatures in order to avoid incomplete reaction. Attempts were made to use metal organic compounds as the starting material in CVD, which may lower the reaction temperature. One of the attractive features of the low temperature CVD is the possibility of producing a material possessing a structure, which is unstable at high temperatures.

3.3.1.3 Solvent evaporation epitaxy method [8]

Zinc gallate was prepared by pulverizing single crystals by a flux method using Li_3PO_4 at high temperatures such as 1200°C . The result on the growth of oriented ZnGa_2O_4 thin films.

The solvent evaporation epitaxy technique was developed on growing oriented thin films of the oxide-superconductor Bi-Sr-Ca-Cu-O.

PbF_2 , which was reported to be a good flux used for the growth of spinel ZnGa_2O_4 single crystals, was employed as a solvent.

3.3.1.4 Sol-gel process [7]

The preparing of the zinc gallate thin film by a sol-gel process using inorganic salt as raw materials. The precursors: $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Ga}(\text{NO}_3)_3 \cdot 4.3\text{H}_2\text{O}$ were dissolved in a mixed solution of ethanol and acetyl acetone. SiO_2 glass substrate was dipped in the solution and withdrawn. Then it was heated up to a temperature using and

electric furnace and kept at the temperature. After the sintering, the sample was cooled in the furnace naturally to room temperature. In order to increase the film thickness, the coating and sintering process was repeated several times.

3.3.1.5 Hydrothermal method [4]

Hydrothermal method utilizes water under pressure and at temperatures above its normal boiling point as a means of speeding up the reactions between solids. The water in the system performs two roles. The water -as liquid or vapor- serves as the transmitting medium. In the addition, some or all of the reactant is partially soluble in the water under pressure and this enables reaction to take place in, or with the aid of, liquid and/or vapor phases. Under these conditions, reactions may occur that, in the absence of water, would occur only at high temperatures. The method is therefore particularly suited for the synthesis of phases that are unstable at higher temperatures. It is also a useful technique for growth of single crystals; by arranging for a suitable temperature gradient to be present in the reaction vessel, dissolution of the starting material may occur at the hot end and reprecipitation at the cooler end.

Zinc gallate powders were prepared by hydrothermal method from $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Ga}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$

3.3.1.6 Glycothermal method

Glycothermal method has been developed for the synthesis of metal oxide and binary metal oxide by using glycol solvents such as 1,4-butanediol instead of water in hydrothermal method. The use of glycol instead of water in the synthetic procedure, intermediate phase occurred to be different form and found that stabilities of the intermediate phase by this method was not strong. So, this intermediate phase was easily converted to product under quite mild condition.

In this study, zinc gallate were prepared by glycothermal method from the reaction of zinc acetate and gallium acetylacetonate in various organic solvents; 1,4-butanediol, 1-butanol, 2-propanol and toluene, so called “solvothermal synthesis”. The reaction carried out under autoclave condition yield zinc gallate with high surface area and thermally stable. The physical and chemical properties of this product depended on kind of the organic solvents and the reaction conditions.

3.4 Zinc aluminate (ZnAl_2O_4)

ZnAl_2O_4 is a binary oxide consisting of ZnO and Al_2O_3 that crystallizes in spinel structure[1,2,4,5,9]. The unit cell of spinels is represented by formula of AB_2O_4 . The Zn^{2+} ions occupy the tetrahedrally coordinated A site and Al^{3+} ions occupy the octahedrally coordinated B sites [3,4,9].

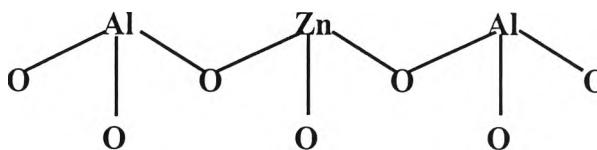


Figure 3.2 Structure of zinc aluminate

3.4.2 Preparation procedure of zinc aluminate

3.4.2.1 Coprecipitation method [9]

Zinc aluminate have been prepared by coprecipitation of nitrates. From an initial pH of 2, the pH was brought to 7.5, through addition of aqueous solution of ammonium carbonate. The precipitates were washed with demineralized water and the obtain gels were then calcined.

3.4.2.2 Sol-gel process [9]

Zinc aluminate were prepared by dissolving aluminum tri-*sec*-butoxide in isopropyl alcohol (the alcohol/alkoxide molar ratio was 60). The mixture was kept under reflux for 1 h. An aqueous solution of zinc nitrate with an aliquot of concentrated nitric acid was added to the alcohol-alkoxide mixture. The water/alkoxide molar ratio was 30. The reflux was continued until gelling. The solvent excess was eliminated by distillation. The obtained gel was aged for 24 h and dried in a vacuum oven at 110°C for 8 h. Calcination was performed. The gelling process was accomplished by adding a mixture of tetra-butyl-tin, zinc nitrate, isopropyl alcohol, water and concentrated nitric acid to the alcohol-alkoxide mixture.

3.4.2.3 Wet mixing method [9]

Zinc aluminate was prepared by a wet mixing method, using zinc oxide and boehmite to obtain a stoichiometric ratio, $\text{Al}_2\text{O}_3/\text{ZnO} = 1$. Water was added until a homogeneous paste was obtained. The mixture was dried at 110°C for 2h and calcined.

3.5 Gallium (Ga)[1,2]

Gallium, atomic number 31, is a scarce element and is found most commonly in association with its immediate neighbors in the periodic table: zinc, germanium, and aluminum.

Gallium, atomic weight 69.717, has two stable isotopes, ^{69}Ga and ^{71}Ga . The radius of the atom is 0.138nm, and the ionic radius of Ga^{3+} is 0.062 nm and that of Ga^+ is 0.133 nm.

3.5.1 Physical properties

Solid gallium has a bluish-gray color; the crystal are orthorhombic. Liquid gallium, which resembles mercury, is silver-white with a bright mirror surface. The hardness of the crystal is 1.5 (Mohs scale). The crystals are highly anisotropic, the electrical conductivity, heat conductivity, and coefficient of expansion varying greatly from one crystal axis to another.

Gallium is different from most metals (but similar to water) in that it expands on solidifying. This property, coupled with its freezing point of 29.8°C makes it necessary to use elastic containers, such as rubber bulbs or flexible plastic bottles for shipment, since alternate freezing and melting of the gallium would cause breakage of a rigid container and loss or contamination of the metal.

Table 3.3 Physical properties of Gallium [1,2]

Property	Value
Melting point, °C	29.77-29.78
Boiling point, °C	Ca 2200
Density at melting point, g/cm ³	
Solid	5.904
liquid	6.095
Heat of fusion, J/g	79.8
Heat capacity, J/(kg•K) at 30°C	381.5
Thermal conductivity, W/(m•K)	
Solid	a 88.4
	b 16.0
	c 40.8

Table 3.3 (continued)

Property	Value
Crystallographic properties	Orthorhombic Cmca space group a = 0.45189 nm b = 0.76602 nm c = 0.45258 nm

3.5.2 Chemical properties

Gallium is chemically similar to aluminum. It is amphoteric but slightly more acid than aluminum. The normal valence of both aluminum and gallium is 3+, and the two metals form corresponding hydroxides, oxides and salts.

Gallium forms alloys readily with many metals. With aluminum, it forms a eutectic that a freezing point of 26.3°C. Gallium forms low-melting alloys (binary and ternary) with tin and indium, and mixes with tin all properties.

3.6 Gallium(III) oxide (Ga₂O₃)[1,2]

Ga₂O₃ is the single gallium oxide that is stable under normal conditions. Like alumina, it exists in several crystalline forms; the conditions of their formation are summarized in Table3.4. The most stable form is the oxide, mp ca 1725°C, which is obtained by calcination at 600°C of the hydroxides or certain salts, e.g., nitrate, acetate, and oxalate. The oxide can be obtained by heating the monohydroxide, GaOOH, at 300-500°C.

Gallium(III) oxide is very stable. It is more reactive than alumina and is strongly amphoteric, forming gallium salts with acids and gallates(III) with bases.

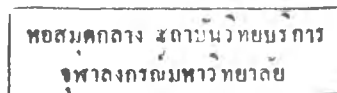


Table 3.4 Properties and preparation of gallium oxide [1,2]

Compound	Means of preparation	Crystal structure	Density, g/cm ³
α -Ga ₂ O ₃	-	trigonal	6.44
β - Ga ₂ O ₃	-	monoclinic	5.88
γ - Ga ₂ O ₃	By rapid dehydration of gel at ca 400°C	cubic	-
δ - Ga ₂ O ₃	By decomposition of Ga(NO ₃) ₃ at 250°C	cubic	5.18
ϵ - Ga ₂ O ₃	By brief heating of δ -Ga ₂ O ₃ at ca 550°C	orthorhombic	-

3.7 Gallate(III)[1,2]

The alkali metal gallates(III) are the only gallates(III) that are soluble in water. The solid gallates (III) of numerous elements have been studied and include gallates(III) of alkaline and other metals. The former group includes: Li₅GaO₄, LiGaO₂, and LiGa₅O₈; MGaO₂, where M = Cs, K, Na or Rb; and Na₂0.54Ga₂O₃ and Na₂0.7Ga₂O₃ (ion conductors, of the type of alumina). The latter group includes: MGaO₂ (M = Cu or Ag); MGa₂O₄ (M = Ba, Sr, Co, Cu, Fe, or Zn); CaO.*n*Ga₂O₃ (n = 0.33-1 or 2); AlGaO₃; and LnGaO₃ and Ln₃Ga₅O₁₂ with the lanthanides. Among these compounds, a number are studied for their useful magnetic or electric properties, especially spinels, perovskites, and above all, garnets.

3.8 Aluminum (Al)[1,2]

Chemical elements number 13, aluminum, Al, is a metal of low density and high reflectance. Its ability to form a protective coating aluminum oxide increases its range of usefulness.

Aluminum is a silvery-white metal, with an atomic weight of 26.98. The specific gravity is about 2.7 (density 0.098 lb/in.)

Table 3.5 Physical properties of Aluminum [1,2]

Properties	Value
Crystal structure	face centered cubic (fcc)
Density at 25°C, kg/m ³	2698
Melting temperature, °C	660.2
Boiling point, °C	2494
Thermal conductivity at 25°C, W/(m•k)	234.3
Latent heat of fusion, J/g (cal/g)	395 (94)
Latent heat of vaporization at bp, kJ/g (kcal/g)	10,777 (2576)

Aluminum ordinarily has a valence of +3 and is amphoteric; that is, it may be either acid-forming or base-forming. Thus, with the common acids, it forms salts such as the chloride, nitrate, and sulfate, whereas with strong bases, aluminates are formed.

3.9 Aluminum compounds[1,2]

The most important compound is the oxide (Al₂O₃). The exist in several crystalline forms, of which the form (corundum) is the most common and most important.

The aluminum oxide trihydrate is the raw material used for making most aluminum compounds. There are two varieties of trihydrate, clearly identifiable by their x-ray diffraction patterns. The trihydrate (Gibbsite), the more common form, occurs in bauxite. The form is produced by precipitation under special conditions. Both are readily soluble in acids and caustic alkalies.

The monohydrate also exists in two forms. The form (Boehmite) occurs in monohydrate bauxite. The form is in the mineral diasporite. The monohydrate is much less readily dissolved than the trihydrate, in either acid or alkaline solutions. Each of these different hydrates has its own distinctive x-ray diffraction pattern.

3.10 Aluminate[1,2]

A negative ion usually given the formula AlO_2^- and derived from aluminum hydroxide. Solutions of aluminates are strongly basic.

3.11 Metal alkoxides[1]

Metal alkoxides are compounds in which a metal is attached to one or more alkyl groups by an oxygen atom (Figure 3.3). Alkoxides are derived from alcohols by the replacement of the hydroxyl hydrogen by metal.

Sodium ethoxide was the first metal alkoxide described by J. Liebig in 1837. The alkoxides of many transition metals were developed after World War II, especially by Bradley and also by Mehrotra. Today some alkoxides, including those of sodium, potassium, magnesium, aluminum, zirconium, and titanium, are commercially important. The name metal alkoxide is preferred, although metal alcoholates is also used.

Alkoxides of nonmetals can be found under the corresponding compounds, e.g., Boron or Silicon compounds. Metal alkyls, in which the alkyl group is bound directly to the metal, are discussed under the corresponding elements, e.g., Aluminum compounds and Organometallics.

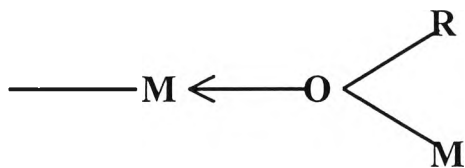


Figure 3.3 The structure of metal alkoxide.

3.11.1 Physical properties

The metal alkoxides exhibit great differences in physical properties, depending on the position of the metal in the periodic table, and secondarily on the alkyl group. Many alkoxides are strongly associated by intermolecular forces which depend on the size and shape of the alkyl groups.

Many metal alkoxides are soluble in the corresponding alcohols, but magnesium alkoxides are practically insoluble. Only the distillable alkoxides, like those of aluminum, titanium, and zirconium alkoxides as examples.

In recent decades, much work has been done on the structure of the metal alkoxides. The simple alkali alkoxides have an ionic lattice and a layer-like structure, but alkaline earth alkoxides show more covalent character. The aluminum alkoxides have been thoroughly studied and there is no doubt as to their covalent nature, the lower alkoxides are cyclic (Figure 3.4), even in solution and in the vapor phase.

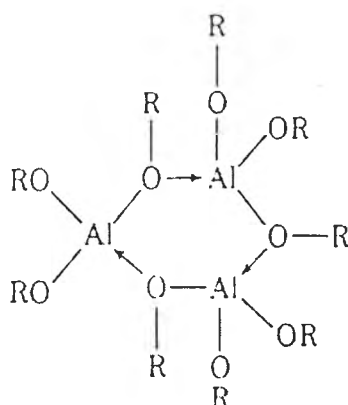


Figure 3.4 Aluminum alkoxide

Structures are highly varied among the transition metals. Metal alkoxides are colored when the corresponding metal ions are colored, otherwise not.

3.11.2 Chemical properties

The most outstanding property of the metal alkoxides is ease of hydrolysis. Uranium hexa-*tert*-butoxide is an exception and does not react with water.

3.12 Spinel[1,2]

3.12.1 The spinel group of minerals

The spinels are a group of oxides that have very similar structures. The spinel group contains over twenty members, but only a few are considered common. Named after their sole gemstone representative, spinel, this is an important group of minerals. It includes one of the most important ores of iron, magnetite; an important ore of chromium, chromite; an important ore of lead, minium; a once important ore of manganese, iron and zinc; franklinite and many other interesting members. The general formula of the Spinel Group is AB_2O_4 . The A represents a divalent metal ion such as

Magnesium, Iron, Nickel, Manganese and/or Zinc. The quad valent lead ion can also occupy this site. The **B** represents trivalent metal ions such as Aluminum, Iron, Chromium and/or Manganese, Titanium may also occupy this site with a +4 charge and lead at +2 can occupy this site. Solid solutioning is common in this group of minerals, meaning that they may contain certain percentages of different ions in any particular specimen.

The structure of spinel is based on the structure of diamond, which has the same high symmetry. The position of the **A** ions is nearly identical to the positions occupied by carbon atoms in the diamond structure. This could explain the relatively high hardness and high density typical of this group. The arrangement of the other ions in the structure conform to the symmetry of the diamond structure. But, they disrupt the cleavage as there is no cleavage directions in any member of this group. The arrangement of the ions also favors the octahedral crystal habit which is the predominant crystal form and is in fact the trademark of the spinels. All members of this group that share the spinel structure show the same type of twinning that is named after spinel.

These minerals are some of the more common minerals of the spinel group:

- Chromite (Iron chromium oxide)
- Franklinite (Zinc iron manganese oxide)
- Gahnite (Zinc aluminum oxide)
- Magnesiochromite (Magnesium chromium oxide)
- Magnetite (iron oxide)
- Minium (Lead oxide)
- Spinel (Magnesium aluminum oxide)

3.12.2 Spinel structure

Several of the commercially important magnetic oxides have the spinel structure. The parent spinel is MgAl_2O_4 . It has an essentially cubic close packed array of oxide ions with Mg^{2+} , Al^{3+} in tetrahedral and octahedral interstices, respectively. There are well over a hundred compounds with the spinel structure reported to date. Most are oxides. Some are sulphides, selenides and tellurides. A few are halides. Many different cations may be introduced into the spinel structure and several different charge combinations are possible, viz. :

2, 3	as in	MgAl_2O_4
2, 4	as in	Mg_2TiO_4
1, 3, 4	as in	LiAlTiO_4
1, 3	as in	$\text{Li}_{0.5}\text{Al}_{2.5}\text{O}_4$
1, 2, 5	as in	LiNiVO_4
1, 6	as in	Na_2WO_4

Similar cation combinations occur with sulphides, e.g. 2, 3: ZnAl_2S_4 and 2, 4: CuSnS_4 . With halide spinels, cations are limited to charges of 1 and 2, in order to give an overall cation:anion ratio of 3:4, e.g. Li_2NF_4 .

Two extreme types of behavior may be distinguished. In normal spinels, the cations are in the sites that would be expected from the formula AB_2O_4 , i.e. with A in tetrahedral sites and B in octahedral sites. Examples of normal spinels are MgAl_2O_4 and MgTi_2O_4 .

Inverse spinels, half of the B ions are in tetrahedral sites, leaving the remaining B ions and the A ions occupy the octahedral sites. Usually, the occupancy of these octahedral sites is disordered. Examples of inverse spinels are MgFe_2O_4 and Mg_2TiO_4 .

A representative selection of normal and inverse spinels is listed in Table3.6.

Table3.6 Crystallographic data for some spinels[1].

Crystal	Structure
MgAl ₂ O ₄	Normal
CoAl ₂ O ₄	Normal
CuCr ₂ S ₄	Normal
CuCr ₂ Se ₄	Normal
CuCr ₂ Te ₄	Normal
MgTi ₂ O ₄	Normal
Co ₂ GeO ₄	Normal
Fe ₂ GeO ₄	Normal
MgFe ₂ O ₄	Inverse
NiFe ₂ O ₄	Inverse
MgIn ₂ O ₄	Inverse
MgIn ₂ S ₄	Inverse
Mg ₂ TiO ₄	Inverse
Zn ₂ SnO ₄	Inverse
Zn ₂ TiO ₄	Inverse