

## HIGH TEMPERATURE MATERIALS AND SOLID STATE CHEMISTRY

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### Summary

Solid state chemistry is a branch of science which deals with the preparation, chemical, physical and structural properties of elements and compounds in the condensed phase (solid state). Solids on the basis of their internal structure can be classified as *crystalline* or *amorphous*. A crystalline solid is identified by its crystal system, space group and unit-cell parameters. In order to understand the factors which determine the crystal structures and the physical and chemical properties, an introduction to some fundamental solid state chemistry concepts is given. A chemical classification of solids is made. Covalent, ionic and metallic solids are presented, together with examples of those containing in the crystal lattice more than one type of bond. A correlation between the bonding and the physical properties of a solid is discussed and, in particular, the difference between metals and non metals in the light of the band theory. The following four selected classes of inorganic compounds are presented: a) *hybrid organic-inorganic layered perovskite halides*; b) *inorganic materials for lithium-ion batteries*; c) *inorganic and molecule-based superconductors*; d) *multifunctional organic-inorganic hybrid solids*. The last section deals with high temperature materials; the methods of synthesis along with some chosen examples on the basis of their technological application will be described.

## 1. Introduction

In the past century solid state chemistry has enjoyed an increase of interest due to the discovery of new materials, such as intercalation compounds, high- $T_c$  ceramic and organic superconductors, molecule-based magnetic materials and transition metal complexes, all exhibiting unusual electrical, optical and magnetic properties. The field includes also materials for heterogeneous catalysis (zeolites), non linear optical compounds, electrode materials for lithium-ion batteries and fuel-cells, magnetic materials for data recording, etc; chemists have provided the expertise for the chemical synthesis and characterization of new complex materials. As far as concerning the study of the electronic structure and the physical properties of solids, this has largely been the domain of physicists, but in the last few decades the situation has changed, due to the discovery of new synthetic materials, where the contribution of chemists has been found to be fundamental. New solids exhibiting unusual electric and magnetic properties were prepared, structurally characterized and studied. In this regard, it is noteworthy to mention the synthesis of new organic conductors known as “molecular metals” in 1970s, and the discovery of the first organic superconductor of formula  $[TMTSF]_2[PF_6]$  by K. Bechgaard ten years later. [K. Bechgaard, 1980] Pure organic and inorganic solids as well as hybrid organic-inorganic compounds have been characterized with the aim of finding new materials for science and technological applications in the field of heterogeneous catalysis, for energy needs (batteries, fuel-cells, photovoltaic), sensors, electrical transportation, or for health (new drugs), agriculture etc. The purpose of this topic is to give an overview of solid state chemistry and put to the attention of the reader some examples of inorganic and hybrid organic-inorganic solids chosen on the basis of their novel solid-state chemical and physical properties. As far as the high temperature materials are concerned, the attention is restricted mainly on the methods of synthesis of some inorganic solids of interest for technological applications.

## 2. The Importance of Solids

An important motivation for studying today solids is that they form the basis for many technological applications (integrated circuits, lasers, magnetic recording tape, solar energy converter, energy storage, molecular sieves, catalysis, fertilizers etc.). These applications are related to several properties such as: electrical and ionic conduction, chemical reactivity, optical, magnetic and mechanical properties etc. A summary of the most important of these properties and prototype compounds are reported in Table 1.

1.	<i>Mechanical Properties</i>	
	Metals and Alloys,	Titanium metal for aeronautical industry, Light alloys, stainless steel
	Cement	$Ca_3SiO_5$
	Ceramics	Clays, BN, SiC,
	Lubricants	Graphite, $MoS_2$
	Abrasives	Diamond , Quartz ( $SiO_2$ ), Corundum ( $Al_2O_3$ )
2.	<i>Electrical Properties</i>	
	Metallic conductors	Cu, Ag, Fe

	Superconductors	Nb <sub>3</sub> Sn, YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub> , MgB <sub>2</sub>
	Semiconductors	Si, GaAs
	Electrolytes	LiI, Li[PF <sub>6</sub> ] in lithium-ion batteries
	Piezoelectricity	Quartz (SiO <sub>2</sub> )
	Ferroelectricity	BaTiO <sub>3</sub> , KNbO <sub>3</sub> , Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub>
3.	<i>Magnetic Properties</i>	
	Magnetic materials	Fe, Ni
	Tape recording materials	CrO <sub>2</sub> , Fe <sub>3</sub> O <sub>4</sub>
4.	<i>Optical properties</i>	
	Photochromism	Fe(phen) <sub>2</sub> (NCX) <sub>2</sub>
	Electrochromism	Na <sub>x</sub> WO <sub>3</sub>
	Luminescence	CaWO <sub>4</sub> /Mn <sup>2+</sup>
	Phosphors	YVO <sub>4</sub> : Eu <sup>3+</sup>
	Lasers	ruby laser 0.05 %Cr <sup>3+</sup> /Al <sub>2</sub> O <sub>3</sub>
5.	<i>Sensors</i>	
	Oxygen sensor	ZrO <sub>2</sub> /CaO solid solution

Table 1. Physical Properties of Solids

Studying solids means therefore to respond to the needs of modern society and improvement in functionality of existing materials is an important task of the solid state chemistry. This target can be pursued by the introduction of new materials into existing technology or by the introduction of a new way of making well-established materials. Examples are represented by a) the replacement of aluminum with copper wiring in integrated circuits, b) the use of organic materials instead of the inorganic ones in light-emitting devices (LED), c) the synthesis of new zeolites, such as ZSM5, which is used to catalyze processes such as the hydrocarbon cracking. Studying solids means also to understand the relation between their electronic structure, crystal structure, chemical and physical properties, and possibly to design new solids with better performances. However, one of the nice aspects of science in general and, in particular, in solid state chemistry is their unexpected discoveries. It is difficult to say in advance which kind of crystal structure is formed when a set of elements reacts and which kind of properties they will show. Several remarkable discoveries in solid state chemistry were done by serendipity. A quite recent and interesting example is provided by the anhydrous Li<sub>x</sub>CoO<sub>2</sub>, and the corresponding sodium compound, *i.e.* [Na<sub>0.3</sub>CoO<sub>2</sub>] $\cdot$ yH<sub>2</sub>O, y = 1.3, [K. Takada, 2003], both having a layered crystal structure consisting of fully edge sharing [CoO<sub>6</sub>] octahedra. The first one is anhydrous and capable of intercalating Li in between layers. The study of its electrolytic properties by J. B. Goodenough in 1980 has led to extensive commercial exploitation in Li-ion battery technology. [J. B. Goodenough, 1980] The analogous sodium compounds are known for their exceptional high conductivity and thermoelectric properties. Quite unexpected the parent hydrated [Na<sub>0.35</sub>CoO<sub>2</sub>] $\cdot$ yH<sub>2</sub>O, y = 1.3, with a similar layered crystal structure is found superconducting at low temperatures, *i.e.* at  $T = 4.5$  K.

## 2.1. Crystalline Solids

Solids are formed upon cooling of liquids by freezing or solidification. These processes,

depending on the solidification conditions, can generate *crystalline* or *amorphous solids*. Crystalline solids can grow either as single-crystals or as a polycrystalline powder (assembly of randomly oriented microscopic single-crystals). *Crystalline solids* are those in which the atoms or molecules are packed in a regular array, while the *amorphous* ones are solids in which there is a lack of the long-range order of a crystal. In nature we can find crystals, where the external shape reflects the internal order and this is the case of the crystals of NaCl or, crystalline solids where there is no external evidence of such an order, like in a marble. More than 90% of naturally occurring and artificially prepared solids are crystalline. Minerals, sand, clay, limestone, metals, carbon (diamond and graphite), salts (NaCl, KCl etc.), all have crystalline structures. In a crystal the constituent atoms, ions, or molecules are packed together in the *crystal lattice*, the pattern of which is repeated periodically *ad infinitum* as reported in Figure 1.

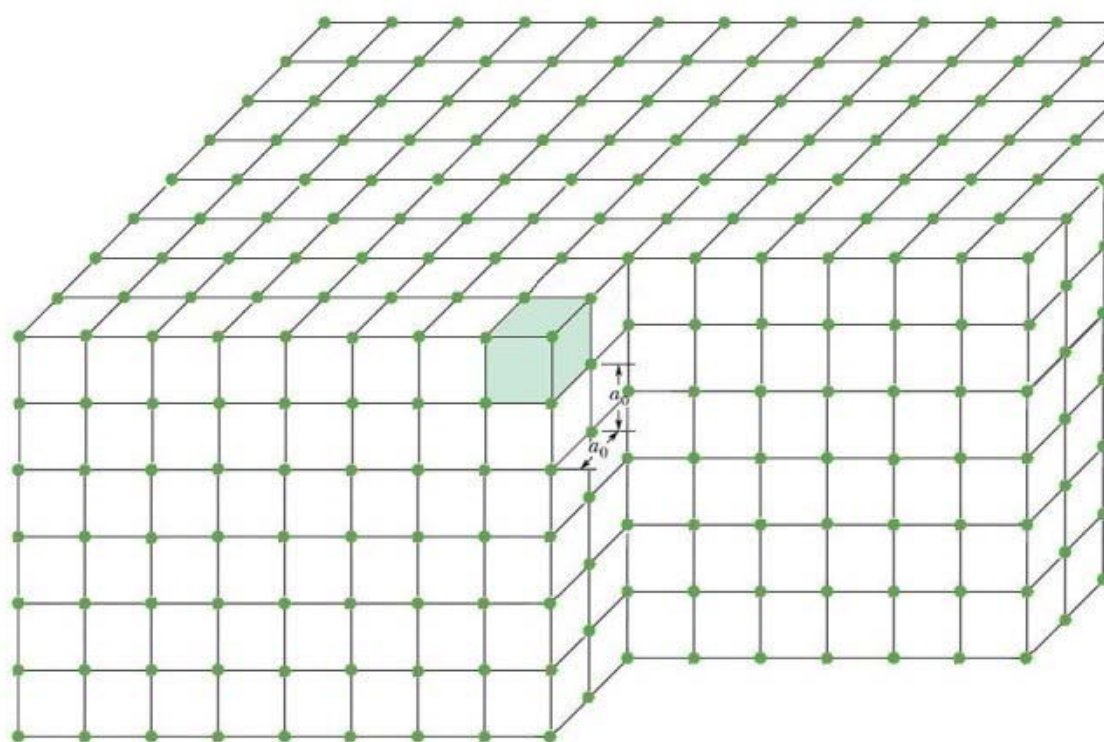
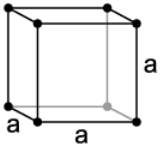
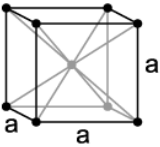
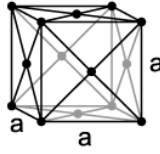
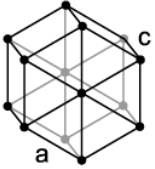
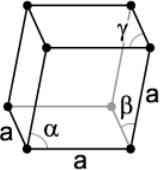
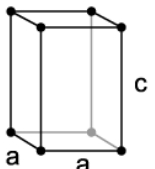
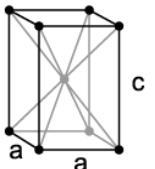
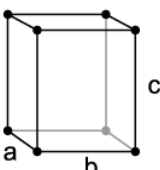
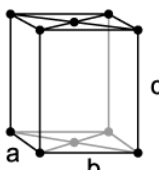
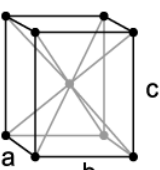
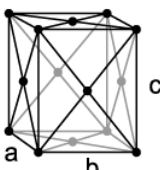
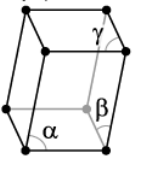
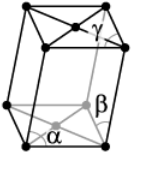


Figure 1. Crystal lattice in 3D: the smallest complete repeating 3D unit is called unit cell

The smallest complete repeating three-dimensional unit, which shows the full symmetry of the crystal structure, is called *unit-cell*, the latter being identified by three vectors  $\mathbf{a}$ ,  $\mathbf{b}$  and  $\mathbf{c}$ . [C. Kittel 1986] The number of possible lattices is however limited by the combined symmetry and translation operations. In three-dimensional space only fourteen possible lattices are allowed. These fourteen different lattice structures are termed *Bravais lattices*, from the French crystallographer Auguste Bravais (1811-1863) who first established them. The Bravais lattices can be divided in four different types: a primitive lattice,  $P$ , characterized by having only a lattice point at each corner of the unit-cell; a body-centered lattice,  $I$ , containing lattice points at each corner and at the centre of the unit cell; a face-centered lattice  $C$ , which possesses lattice points at the corners of the unit cell and at either the centers of just one pair of faces; or else the

lattice F with lattice points at the corners of the unit cell and at the centers of all three pairs of faces. Bravais lattices can be grouped on the basis of the restrictions on cell axes and angles in seven crystal systems: *cubic*, *tetragonal*, *hexagonal*, *trigonal*, *orthorhombic*, *monoclinic*, *triclinic*, see Table 2, which identify the shape of the unit cell.

System	P	C	I	F
Cubic $a=b=c$ $\alpha=\beta=\gamma=90^\circ$				
Hexagonal $a=b \neq c$ $\alpha=\beta=90^\circ$ ; $\gamma=120^\circ$				
Trigonal $a=b \neq c$ $\alpha=\beta=\gamma \neq 90^\circ$				
Tetragonal $a=b \neq c$ $\alpha=\beta=\gamma=90^\circ$				
Orthorhombic $a \neq b \neq c$ $\alpha=\beta=\gamma=90^\circ$				
Monoclinic $a \neq b \neq c$ $\alpha=\gamma=90^\circ \neq \beta$				

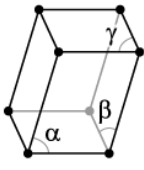
System	P	C	I	F
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$				

Table 2. The Bravais lattices and crystal systems

A crystal structure is therefore described by the unit cell structure: *i.e.* by the size and shape of the cell and the position of the atoms inside the cell. The position of a point in a unit-cell is specified in term of atomic coordinates:  $x$ ,  $y$ , and  $z$ . Each coordinate is a fraction of the axial length  $a$ ,  $b$  and  $c$  in the direction of the coordinate axis, with the origin taken at one corner of the unit cell. Thus the coordinates of the body centre of a cell are  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  and those of the face centers are  $(\frac{1}{2}, \frac{1}{2}, 0)$ ,  $(0, \frac{1}{2}, \frac{1}{2})$  and  $(\frac{1}{2}, 0, \frac{1}{2})$ . Often this is not enough to represent a crystal structure by one unit cell and a picture of more than one cell is required in order to show the arrangement relative to each other, their coordination numbers, interatomic distance *etc.* Two possible ways of describing the structures are the *close packing approach* and the *space-filling polyhedron* approach. In order to complete the information on the subject a few common crystal structures are reported and described. In Figure 2 are depicted the following four crystal structures: (a) NaCl structure, (b) CsCl structure, (c) diamond and (d) zinc blende structure.

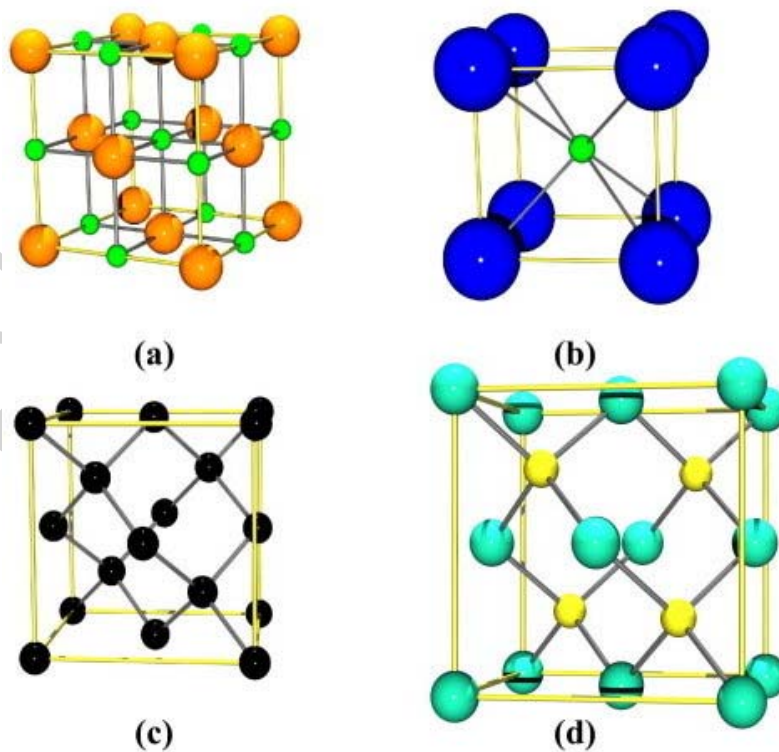
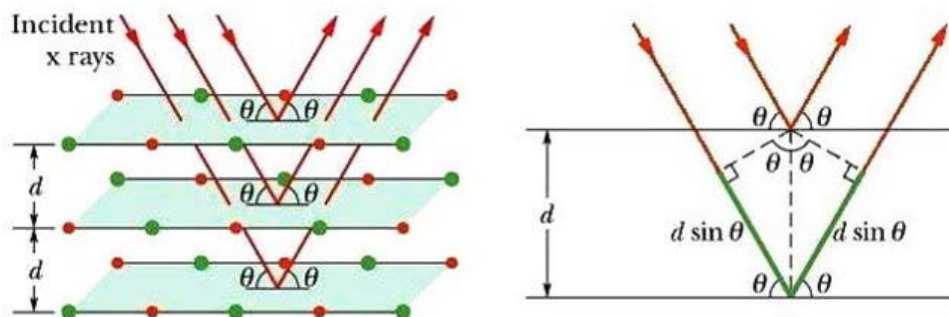


Figure 2. Crystal structures of prototype compounds: (a) NaCl, (b) CsCl, (c) diamond and (d) zinc blende

In NaCl structure sodium and chloride ions alternates in three directions at right angles. The unit cell is cubic with the unit-cell parameter,  $a$ , corresponding to 5.63 Å. The lattice can be thought as an interpenetration of two cubic face centered arrays: one made of  $\text{Na}^+$  cations and the other by  $\text{Cl}^-$  anions. The coordination number (number of nearest neighbor) around each  $\text{Na}^+$  ion is six. According to this, the content of the unit cell can be deduced from the Figure 2(a) as following: at each corner  $\text{Na}^+$  contribute by 1/8, which multiplied by eight corners per cube contribute as 1. The  $\text{Na}^+$  ions on each face contribute for 1/2 and, because the number of faces in a cube is six, the sum is 3, and in total the content is 4  $\text{Na}^+$  units/unit cell. As far as concerning the  $\text{Cl}^-$  anions, they are located at the edges of the cube and contribute 1/4 which multiplied by 12 edges per cube contribute as 3, and 1  $\text{Cl}^-$  anion located in the centre of the cube, in total the content is 4  $\text{Cl}^-$  units/unit cell. In conclusion four NaCl units are present in the cell. CsCl crystal structure is shown in Figure 2(b) and it consists of one  $\text{Cs}^+$  ion at the body centered position and eight  $\text{Cl}^-$  ions at the corners of the cube. Each  $\text{Cl}^-$  is coordinated to eight  $\text{Cs}^+$  and therefore there is one CsCl unit per primitive cell. The diamond structure is a cubic structure with a tetrahedral bond arrangement (see Figure 2(c)) where each carbon atom has four nearest neighbors. The zinc blende structure, reported in Figure 2(d), is cubic and is related to the diamond structure. The determination of the unit-cell (dimension and symmetry) of a given substance, and the position of the atoms within it represent one of the most important tasks in solid state chemistry. The knowledge of the crystal structure is of paramount importance in the study of the electronic structure of a solid, as well as the correlation of it to the physical and chemical properties of the solid itself. The determination of the crystal structure is carried out mainly by X-ray and neutron diffraction techniques on both single-crystal and on microcrystalline powder. The techniques are based on the phenomenon of the diffraction of waves, when interacting with diffracting centers, which are spaced at distances of the same order of magnitude as the wavelength of the particular radiation employed. This is analogous to the interference pattern observed when visible light is shone on a grating (the spacing between lines on a grating is 0.5 to 1  $\mu\text{m}$ , comparable with the wavelength of the visible light, *i.e.* 0.4  $\mu\text{m}$  to 0.8  $\mu\text{m}$ ). X-ray diffraction is based on the interaction of an incoming X-ray photon with the electron density in the crystal, and therefore with the atoms. Since hydrogen atoms have low electron density, they are not revealed and often are missed in the crystal structures determined by X-ray diffraction. To locate hydrogen in such cases, diffraction experiments are carried out by using a beam of neutrons of a single known velocity on deuterated solids (*i.e.* compounds in which the hydrogen atoms are replaced by the Deuterium isotope). In all instances the radiation used must have wavelengths in the range 0.1 to 10 Å (Å =  $10^{-10}$  m), because the resolution to which a radiation can yield useful information has to be comparable to the average distance between adjacent atoms in the crystal, which is  $\sim 10^{-10}$  m. The geometrical condition which must be satisfied for diffraction to occur in a crystal is known as the Bragg law:  $n\lambda = 2d \sin \theta$ , where  $d$  represents the spacing between the parallel planes of atoms,  $\lambda$  is the wavelength of the monochromatic (single-wavelength) X-ray incident radiation,  $\theta$  the angle at which it is “reflected” and  $n$  an integer. In other word, constructive interference of X-rays from successive planes of atoms occurs when the path difference is an integral number  $n$  of wavelength,  $n \cdot \lambda$ ; on the contrary they will tend to cancel (See Figure 3).



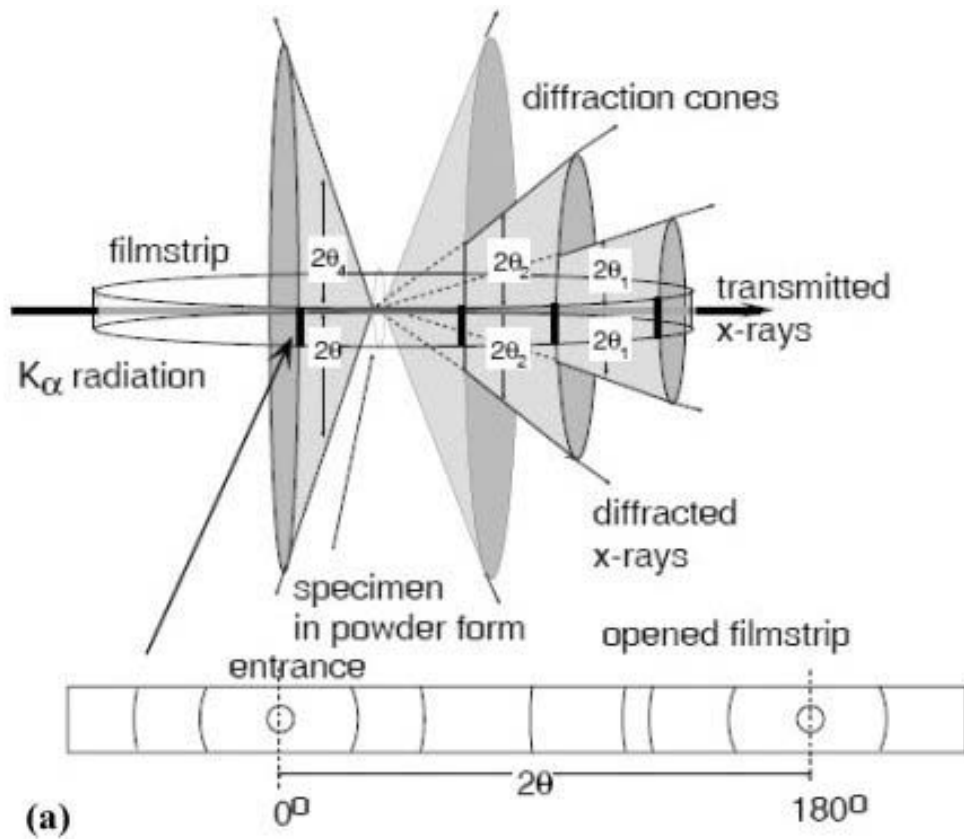
$$\text{Bragg law: } n\lambda = 2d_{hkl} \sin(\theta_{hkl})$$

Figure 3. Derivation of Bragg law:  $2d \sin \theta = n\lambda$ . See text

Bragg reflections can occur only if  $\lambda \leq 2d$ . This is why we cannot use visible light in the determination of crystal structures. The Bragg law is a consequence of the periodicity of the lattice and it does not refer to the composition of the basis of atoms associated with every lattice point, which determines the relative intensity of various orders of diffraction (denoted by  $n$ ) from a given set of parallel planes. Now, if a single crystal is rotated in a monochromatic X-ray beam, a pattern of spots of reinforced X-rays can be collected on a photographic film or electron photon counter (detectors). Both the position and the intensities of the spots are the data from which the crystal structure can be deduced. If a powdered crystalline solid is examined then the diffraction pattern will consist of a series of concentric rings, due to the random orientation of the crystals in the powder (See Figure 4a).

In the latter case the information could be limited. However each single crystallographic phase of a chemical substance is characterized by its own characteristic diffraction pattern and therefore it is possible from this pattern to identify a known substance. X-ray powder diffraction pattern of known elements, compounds or minerals are catalogued in JCPDS data file [see Figure 4b] and it can be used to identify crystalline compound or elements, either in pure phase or as a mixture. The Rietveld method [H.M. Rietveld, 1969] is presently used by solid state chemists and physicists in solving crystal structures of simple inorganic solids by using both X-ray and neutron diffraction techniques. It is also possible to solve the full crystal structure “*ab initio*” from X-ray powder diffraction data, provided that the space group and unit-cell parameters of the substance and some chemical information are known. The field is the main domain of crystallography and solid state physics, but nowadays many inorganic and solid state chemists are familiar with these techniques. Another important property of a crystal is the anisotropy. In a single crystal, the physical and mechanical properties often differ with orientation. It can be seen from looking at our models of crystalline structure that atoms should be able to slip over one another or distort in relation to one another easier in some directions than others.





LiMn<sub>2</sub>O<sub>4</sub>

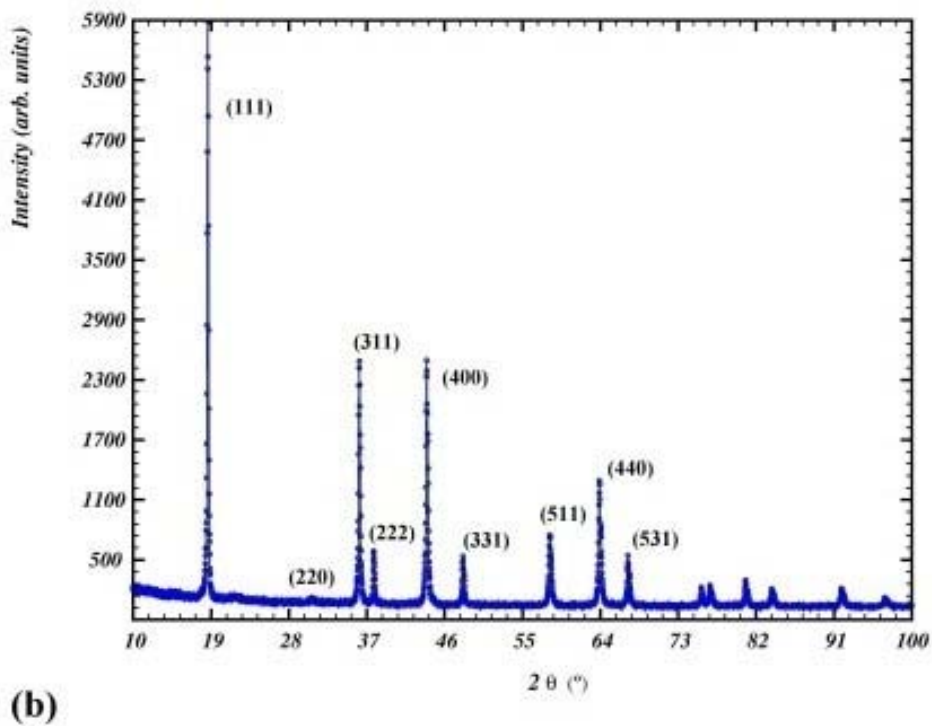


Figure 4. (a) Scattering of X-rays into cones by a powder sample (Debye-Scherrer method; after MIT Solid State Lectures) (b) X-ray powder diffraction pattern of a microcrystalline sample of LiMn<sub>2</sub>O<sub>4</sub>

When the physical properties of a material vary with different crystallographic orientations, the material is said to be **anisotropic**; alternately, when the properties of a material are the same in all directions, the solid is said to be **isotropic**. Isotropic crystalline substances are limited to those of cubic symmetry, although amorphous solids such as glasses are also isotropic. Finally in the “real” solid the crystal structure is not perfect and defects, impurities and surface dislocations may have a strong influence on its electronic properties (see below). The disorder can be further increased and then we are dealing with glasses. A crystalline solid, like quartz ( $\text{SiO}_2$ ), if heated above the melting point and cooled again, does not crystallize, but assume a glass state. Cooling down from the liquid state we come to the melting temperature  $T_m$ , which corresponds to the melting point temperature of the thermodynamically stable crystalline state. But the crystallization is prevented by the high viscosity of the melt, giving rise to a *non crystalline* or *amorphous* solid, known as glass, in which the atoms are disordered in similar way to the liquid. Amorphous solids do not show a sharp phase change from solid to liquid at a definite melting point, but rather soften gradually when they are heated. There are two types of glass: 1) those, in which the coordination number, often characteristic of a crystal, is maintained, and this is the case of vitreous silicon dioxide, ( $\text{SiO}_2$ ), in which every Si atom is bonded to four oxygen atoms and each oxygen bridged to two adjacent silicon atoms (see Figure 5); 2) those, in which the number of nearest neighbors of each atom is not necessary integral and an example is given by metallic glasses.

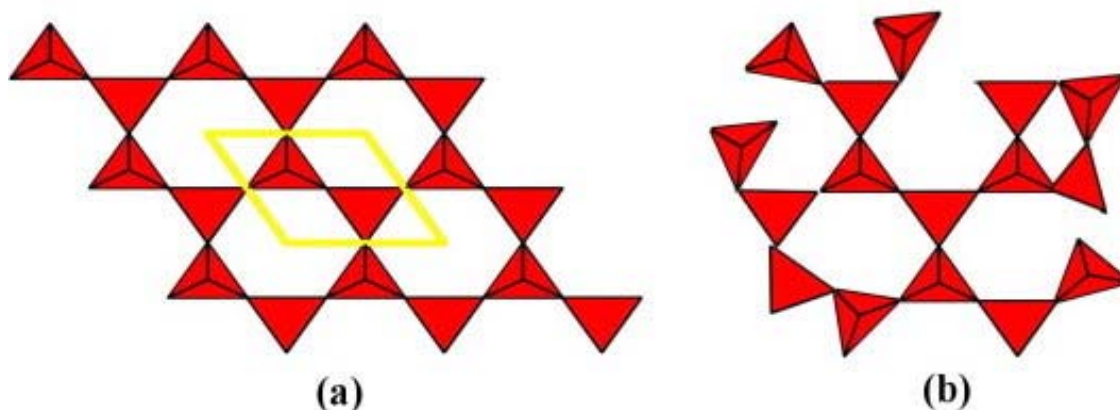


Figure 5. Schematic representation of (a) of tridimite ( $\text{SiO}_2$ ) crystal structure and (b) of a random network of a quartz glass

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## Bibliography

### Books

- Borg R.J., Dienes G.J. (1992). *The Physical Chemistry of Solids*, 584 pp. Academic Press, San Diego USA: [An interesting textbook of solid state physical chemistry]
- Greenwood N.N., Earnshaw A. (1984). *Chemistry of Elements*, 1542 pp. Pergamon Press, New York, USA: [A fundamental textbook of Inorganic Chemistry]
- Hummel R.E. (1993). *Electronic Properties of Materials*, 404 pp. Springer-Verlag Berlin: [An advanced text book on the electrical, optical and magnetic properties of materials devoted to materials and electrical engineers]
- Jones W. Editor (1997). *Organic Molecular Solids: Properties and Applications*, 426pp, CRC Press inc.: [a book on organic materials with a wide variety of physical properties, such as non linear optics, electrical conductivity and superconductivity, magnetism etc.]
- Kittel C. (1986). *Introduction to Solid State Physics*, 646 pp. J. Wiley and Sons, New York, USA: [A fundamental textbook of all aspects of solid state physics]
- Schubert U., Hüsing N. (2000). *Synthesis of Inorganic Materials*, 396 pp., Wiley-VCH, Weinheim: [Comprehensive overview of current methods of synthesis of inorganic materials]
- Swaddle T.W. (1997). *Inorganic Chemistry: an Industrial and Environmental Perspective*, 482 pp. Academic Press, San Diego, USA: [An interesting introductory book for undergraduates of inorganic chemistry in terms of their relevance to the world of industry and environmental protection]
- Wakihara. M., Yamamoto O. (1998). *Lithium Ion Batteries: Fundamentals and Performances*, 247 pp. J. Wiley and Sons, New York, USA: [A fundamental book on lithium ion batteries, written by several outstanding contributors to the field].
- West A. R. (1988). *Basic Solid State Chemistry*, 415 pp. J. Wiley and Sons, New York, USA: [An introductory textbook of all aspects of solid state chemistry]
- Young R.A. (1993). *The Rietveld method*, 298 pp. Oxford University Press, Oxford, UK: [Monograph on the Rietveld Method, which allows the extraction of crystal structural information from X-Ray and neutron powder diffraction data]

### Reviews

- Aricò A.S., Bruce P., Scrosati B., Tarascon J-M., van Schalkwijk W. (2005). Nanostructured materials for advanced energy conversion and storage devices, *Nature Nanomaterials* **4**, 366-377: [This reviews describes the properties of new nanophasic materials used in lithium batteries and fuel cells]
- Bellitto C., Day P. (1996). Layered Perovskite Halides, *Comprehensive Supramolecular Chemistry* **7**, 293-313, J.R. Atwood *et al.* Eds, Pergamon Press, New York: [This review deals with the synthesis, structures and physical properties of a subgroup of hybrid organic-inorganic perovskite structures, *i.e.* layered perovskite metal halides]
- Cava R.J. (2005). Contemporary superconducting materials, *Chem. Commun.* 5373-5377. [This review deals with most recent discoveries on inorganic superconductors]
- Coronado E., Day P. (2004). Magnetic Molecular Conductors. *Chem. Rev.* **104**, 5419–5448. [This review presents examples of magnetic molecular compounds]
- Mitzi D.B. (1999). Synthesis, structure and properties of organic-inorganic perovskites and related materials. *Progress in Inorganic Chemistry* **48**, 1–121. [This review deals with hybrid organic-inorganic perovskite structures]
- Winter M., Brodd R.J. (2004). What are batteries, fuel cells and supercapacitors, *Chem. Rev.* **104**, 4245-4269. [A recent review on batteries, fuel cells and supercapacitors]

### Journals

Akimitsu J., Nagamatsu J., Nakagawa, Muranaka T. (2001). Superconductivity at 39K in Magnesium diboride, *Nature* **410**, 63-64.[A paper reporting on the discovery of superconductivity in MgB<sub>2</sub>]

Berdnoz J.G., Müller K.A. (1986). Possible high T<sub>c</sub> superconductivity in the Ba-La-Cu-O system," *Z. Phys.* **B64**, 189-193.[The first report on superconductivity in high T<sub>c</sub> superconductors]

Haddon R.C. et al. (1991). Conducting films of C<sub>60</sub> and C<sub>70</sub> by alkali metal doping, *Nature* **350**, 320.[Synthesis of alkali metal doped fullerenes]

Hebard A.F. et al. (1991). Superconductivity at 18K in potassium-doped C<sub>60</sub>, *Nature* **350**, 600.[Discovery of superconductivity in alkali metal doped fullerenes]

Jérome D., Mazoud A., Ribault M., Beechgard K. (1980). Superconductivity in a synthetic organic conductor (TMTSF)<sub>2</sub>PF<sub>6</sub>, *J. Phys. Lett.* **41**, L95-L98: [Discovery of superconductivity in organic metals]

Kratschmer W., Lamb L.D., Fistoropoulos K., Huffman D.R. (1990). Solid C<sub>60</sub>: a new form of carbon, *Nature* **347**, 354.[Synthesis of C<sub>60</sub>]

Mitzushima, K., Jones P.C., Wiseman P.J., Goodenough J.B. (1980). Li<sub>x</sub>CoO<sub>2</sub> (0 < x < 1): A new cathode material for batteries of high energy density, *Mater. Res. Bull.* **15**, 783-789.[First report on the intercalation/deintercalation of Li in LiCoO<sub>2</sub>]

Padhi A.K., Nanjundaswamy K.S., Goodenough J.B. (1997). Phospho-olivines as positive electrode materials for lithium batteries, *J. Electrochem. Soc.* **144**, 1188-1194.[First report on the synthesis of LiFePO<sub>4</sub>]

Rietveld H.M. (1969), A Profile Refinement Method for Nuclear and Magnetic Structures, *J. Appl. Crystallogr.* **2**, 65-71.[Monograph on Rietveld method: a powerful method for extracting crystal structure information from X-ray and neutron powder diffraction data]

Takada K., Sakurai H., Takayama-Muromachi E., Izumi F., Dilanian R.A., Sasaki T. (2003). Superconductivity in two-dimensional CoO<sub>2</sub> layers, *Nature* **422**, 53-55. [Report on superconductivity of [Na<sub>0.35</sub>CoO<sub>2</sub>] × yH<sub>2</sub>O, y = 1.3]

### Biographical Sketches

**Dr. Carlo Bellitto** was born in Italy, Penne (Pescara), on 1946, August 21<sup>st</sup>. He obtained the degree of Doctor in Chemistry from the University of Perugia in 1970. In 1973 he was appointed "Ricercatore" at the Consiglio Nazionale delle Ricerche, (CNR) Roma. In 1987 he took up the position of "Primo Ricercatore". He spent a post-doctoral period, *i.e.* from 1975 to 1977, at the Inorganic Chemistry Laboratory of Oxford University (U.K.) working in the group of Prof. P. Day. From 1995 he is a "Direttore di Ricerca" at Istituto di Struttura della Materia of CNR. He is author and co-author of more than 100 papers, published on the most renowned journals of inorganic and solid state chemistry. Current Research Interests: *Molecule-based magnets; molecular metals and superconductors; transition metal oxides as cathode materials for lithium-ion batteries; multifunctional hybrid organic-inorganic compounds.* He is Member of the Italian Chemical Society (Rome) and of the Royal Society of Chemistry (London), UK.

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SAMPLE CHAPTERS