IR-11 Solids (Draft March 2004)

CONTENTS

IR-11.1   INTRODUCTION

IR-11.1.1   **General**

This chapter deals with some aspects of the nomenclature of solids. However, in cases where detailed structural information is to be conveyed, fully systematic names can be difficult to construct. An attempt to deal with this problem is described in Ref. 1.

IR-11.1.2   **Stoichiometric and non-stoichiometric phases**

In binary and multi-component systems, intermediate crystalline phases (stable or metastable) may occur. Thermodynamically, the composition of any such phase is variable. In some cases, such as sodium chloride, the possible variation in composition is very small. Such phases are called stoichiometric. However, in other phases appreciable variations in composition can occur, for example in wustite (nominally FeO).

These are called non-stoichiometric phases. In general, it is possible to define an ideal composition relative to which the variations occur. This composition, called the stoichiometric composition, is usually that in which the ratio of the numbers of different atoms corresponds to the ratio of the numbers of normal crystallographic sites of different types in the ideal (ordered) crystal.

This concept can be used even when the stoichiometric composition is not included in the homogeneity range of the phase. The term 'non-stoichiometric' does not mean phases with complex formulae, but those with *variable composition* (for which the term *solid solution* is also used).

IR-11.2   NAMES OF SOLID PHASES

IR-11.2.1   **General**

Names for stoichiometric phases, such as NaCl, are derived simply as in Chapter IR-5, whereas formulae are derived as presented in Chapter IR-4. Although NaCl in the solid state consists of an infinite network of units, $(NaCl)_\infty$, the compound is named sodium chloride and represented symbolically as NaCl.

However, for non-stoichiometric phases and solid solutions, formulae are preferable to names, since strictly systematic names tend to be inconveniently cumbersome. They should be used only when unavoidable (*e.g.* for indexing) and should be constructed in the following style.

Examples:

    1.   iron(II) sulfide (iron deficient)

    2.   molybdenum dicarbide (carbon excess)

IR-11.2.2   **Mineral names**

Mineralogical names should be used only to designate actual minerals and not to define chemical composition. Thus, the name calcite refers to a particular mineral (contrasted with

other minerals of similar composition) and is not a term for the chemical compound the composition of which is properly expressed by the name calcium carbonate.

A mineral name may, however, be used to indicate the structure type. Where possible, a name that refers to a general group should replace a more specific name. For example, large numbers of minerals have been named that are all spinels, but which have widely differing atomic constituents. In this case, the generic name *spinel* type should be used rather than the more specific names chromite, magnetite, *etc*. The mineral name, printed in italics, should be accompanied by a representative chemical formula. This is particularly important for *zeolite* types.[2]

Examples:

    1. $NiFe_2O_4$ (*spinel* type)

    2. $BaTiO_3$ (*perovskite* type)

IR-11.3   CHEMICAL COMPOSITION

IR-11.3.1   **Approximate formulae**

The formula used in any given case depends upon how much information is to be conveyed. A general notation, which can be used even when the mechanism of the variation in composition is unknown, is to put the sign ~ (read as *circa*, or 'approximately') before the formula.

Examples:

    1.   ~ FeS

    2.   ~ CuZn

If it is desirable to give more information, one of the notations described below may be used.

IR-11.3.2   **Phases with variable composition**

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For a phase where the variation in composition is caused solely or partially by isovalent substitution, the symbols of the atoms or groups that replace each other may be separated by a comma and placed together between parentheses. If possible, the formula is written so that the limits of the homogeneity range, when one or the other of the two atoms or groups is lacking, are represented. The order of citation should be alphabetical although exceptions are allowed when it is desired to emphasize structural information.

Examples:

    1.   (Cu,Ni) denotes the complete range of compositions from pure Cu to pure Ni.

    2.   K(Br,Cl) comprises the range from pure KBr to pure KCl.

Phases for which substitution also results in vacant positions are denoted in the same way.

Examples:

    3. $(Li_2,Mg)Cl_2$ denotes the solid solution intermediate in composition between $LiCl$ and $MgCl_2$

    4. $(Al_2,Mg_3)Al_6O_{12}$ represents the solid solution intermediate in composition between $MgAl_2O_4$ ($= Mg_3Al_6O_{12}$) and Al_2O_3 (*spinel* type) ($= Al_2Al_6O_{12}$).

In general, however, a notation in which there are variables which define composition should be used. The ranges of the variables can also be indicated. Thus, a phase involving substitution of atom A for B is written $A_{m+x}B_{n-x}C_p$ ($0 \leq x \leq n$). The commas and parentheses called for above are not then required.

Examples:

    5. Cu_xNi_{1-x} ($0 \leq x \leq 1$) is equivalent to (Cu,Ni) but conveys more information.

    6. KBr_xCl_{1-x} ($0 \leq x \leq 1$) is equivalent to K(Br,Cl).

    7. $Li_{2-2x}Mg_xCl_2$ ($0 \leq x \leq 1$) is equivalent to $(Li_2,Mg)Cl_2$ but shows explicitly that one vacant cation position appears for every 2 Li^+ replaced by Mg^{2+}.

    8. $Co_{1-x}O$ indicates that there are vacant cation sites; for $x = 0$ the formula corresponds to the stoichiometric composition CoO.

9. $Ca_xZr_{1-x}O_{2-x}$ indicates that Zr has been partly replaced by Ca, resulting in vacant anion sites; for $x = 0$ the formula corresponds to the stoichiometric composition ZrO_2.

If the variable x is limited this may be shown by using δ or ε instead of x. A specific composition or composition range can be indicated by stating the actual value of the variable x (or δ, or ε). This value can be written in parentheses after the general formula. However, the value of the variable may also be introduced in the formula itself. This notation can be used both for substitutional and for interstitial solid solutions.[2]

Examples:
10. $Fe_{3x}Li_{4-x}Ti_{2(1-x)}O_6$ ($x = 0.35$), or $Fe_{1.05}Li_{3.65}Ti_{1.30}O_6$
11. $LaNi_5H_x$ ($0 < x < 6.7$)
12. $Al_4Th_8H_{15.4}$
13. $Ni_{1-\delta}O$

IR-11.4   POINT DEFECT (KRÖGER-VINK) NOTATION

IR-11.4.1   **General**

As well as the chemical composition, information about point defects, site symmetry, and site occupancy can be given by using additional symbols. These symbols may also be used to write quasi-chemical equilibria between point defects.[3]

IR-11.4.2   **Indication of site occupancy**

In a formula, the main symbols indicate the species present at a certain site, defined with respect to empty space. This will generally be the symbol of an element. If a site is vacant this is denoted by the italicized symbol V. (In certain contexts other symbols, such as a square box, $\square$, are used for vacancies, but the use of italicized V is preferred, the element vanadium being written with the upright symbol V).

The site and its occupancy in a structure of ideal composition are represented by right lower indexes. The first index indicates the type of site, and the second index (if used), separated from the first by a comma, indicates the number of atoms on this site. Thus, an atom A on a site normally occupied by A in the ideal structure is expressed by A_A; an atom A on a site normally occupied by B is expressed A_B; and $M_{M,1-x}N_{M,x}M_{N,x}N_{N,1-x}$ stands for a disordered alloy, where the ideal composition is M_MN_N with all M atoms on one type of crystallographic site and all N atoms on a second type of crystallographic site.

An alternative description is $(M_{1-x}N_x)_M(M_xN_{1-x})_N$. A species occupying an interstitial site (*i.e.* a site which is unoccupied in the ideal structure) is indicated by the subscript 'i'.

Examples:

1. $Mg_{Mg,2-x}Sn_{Mg,x}Mg_{Sn,x}Sn_{Sn,1-x}$ shows that in Mg_2Sn some of the Mg atoms are present on Sn sites and *vice versa*.

2. $(Bi_{2-x}Te_x)_{Bi}(Bi_xTe_{3-x})_{Te}$ shows that in Bi_2Te_3 some of the Bi atoms are present on Te sites and *vice versa*.

3. $Na_{Na,1-x}V_{Na,x}Cl_{Cl,1-x}V_{Cl,x}$ shows that x Na and x Cl sites in NaCl are vacant, giving Schottky defects.

4. $Ca_{Ca,1}F_{F,2-x}V_{F,x}F_{i,x}$ shows that in CaF_2, x F sites are vacant, while x F ions are situated on interstitial sites, creating Frenkel defects.

5. $(Ca_{0.15}Zr_{0.85})_{Zr}(O_{1.85}V_{0.15})_O$, or $Ca_{Zr,0.15}Zr_{Zr,0.85}O_{O,1.85}V_{O,0.15}$ shows that in CaO-stabilized ZrO_2, 0.85 of the Zr sites are occupied by Zr, 0.15 of the Zr sites are occupied by Ca, and that, of the two oxygen sites, 1.85 sites are occupied by oxygen ions, leaving 0.15 sites vacant.

6. $V_{V,1}C_{C,0.8}V_{C,0.2}$ shows that 0.2 C-sites are vacant in a vanadium carbide.

The defect symbols can be used in writing quasi-chemical reactions.

Examples:

7. $Na_{Na} \rightarrow V_{Na} + Na(g)$ indicates the evaporation of a Na atom, leaving behind a sodium vacancy in the lattice.

8. $1/2Cl_2(g) + V_{Cl} \rightarrow Cl_{Cl}$ indicates the incorporation of a chlorine atom, from a chlorine molecule, on a vacant chlorine site in the lattice.

IR-11.4.3 **Indication of crystallographic sites**

Crystallographic sites can be distinguished by subscripts, *e.g.* tet, oct and dod, denoting tetrahedrally, octahedrally and dodecahedrally coordinated sites, respectively. The use of subscripts such as a, b, . . ., which are not self-explanatory, is not approved. In some cases, such as oxides and sulfides, the number of subscripts can be reduced by defining specific symbols to indicate site symmetries, *e.g.* ( ) for tetrahedral sites, [ ] for octahedral

sites, { } for dodecahedal sites. To avoid confusion, such enclosing marks should be restricted to cases where they are not being used to express multiplication. The meaning of the symbols should be clearly stated in the text.

Examples:

1. $Mg_{tet}Al_{oct,2}O_4$ or $(Mg)[Al_2]O_4$ denotes a normal spinel.
2. $Fe_{tet}Fe_{oct}Ni_{oct}O_4$ or $(Fe)[FeNi]O_4$ denotes $NiFe_2O_4$ (*inverse spinel* type)

IR-11.4.4   **Indication of charges**

Charges are indicated by a right upper index. When formal charges are given, the usual convention holds: one unit of positive charge is indicated by a superscript $+$, n units of positive charge by a superscript $n+$, one unit of negative charge by superscript $-$, n units of negative charge by a superscript $n-$. Thus A^{n+} denotes n units of formal positive charge on an atom of symbol A. In defect chemistry, charges are defined preferably with respect to the ideal unperturbed crystal. In this case, they are called *effective charges.* One unit of positive effective charge is shown by a superscript dot, $^{\bullet}$, (not to be confused with the radical dot described in Section IR-4.6.2) and one unit of negative effective charge by a prime '; n units of effective charge are indicated by superscript $^{n\bullet}$ or $^{n\prime}$. The use of double dots $^{\bullet\bullet}$ or double primes " in the case of two effective charges is also allowed. Thus $A^{2\bullet}$ and $A^{\bullet\bullet}$ indicate that an atom of symbol A has two units of effective positive charge. Sites that have no effective charge relative to the unperturbed lattice may be indicated explicitly by a superscript cross, *i.e.* $^{\text{'x'}}$.

Examples:

1. $Li_{Li,1-2x}Mg^{\bullet}_{Li,x}V^{\prime}_{Li,x}Cl_{Cl}$ and $Li^{x}_{Li,1-2x}Mg^{\bullet}_{Li,x}V^{\prime}_{Li,x}Cl^{x}_{Cl}$ are   equivalent expressions for a substitutional solid solution of $MgCl_2$ in $LiCl$.

2. $Y_{Y,1-2x}Zr^{\bullet}_{Y,2x}O^{\prime\prime}_{i,x}O_3$ and $Y^{x}_{Y,1-2x}Zr^{\prime}_{Y,2x}O^{\prime\prime}_{i,x}O^{x}_3$ are equivalent expressions for an interstitial solid solution of ZrO_2 in Y_2O_3.

3. $Ag_{Ag,1-x}V^{\prime}_{Ag,x}Ag^{\bullet}_{i,x}Cl_{Cl}$ indicates that a fraction x of the Ag^+ ions is removed from the Ag sites to interstitial sites, leaving the silver site vacant.

Formal charges may be preferred in cases where the unperturbed crystal contains an element in more than one oxidation state.

Examples:

4. $\quad La^{2+}_{La,1\text{-}3x} La^{3+}_{La,2+2x} V_{La,x} S^{2-}_4 \; (0 < x < 1/3)$

5. $\quad Cu^{+}_{Cu,2\text{-}x} Fe^{3+}_{Cu,x} Tl^{+}_{Tl} Se^{2-}_{Se,1+2x} Se^{-}_{Se,1\text{-}2x} \; (0 < x < 1/2)$ shows that Fe^{3+}

   partly replaces Cu^+ in $Cu^+_2 Tl^+ Se^{2-} Se^-$

Free electrons are denoted by e', free holes by $h^\bullet$. As crystals are macroscopically neutral bodies, the sums of the formal charges and of the effective charges must be zero.

Table IR-11.1 Examples[a] of defect notation in $M^{2+}(X^-)_2$ containing a foreign ion Q

interstitial M^{2+} ion	$M_i^{\bullet\bullet}$	M atom vacancy	V_M^x
interstitial X^- ion	X_i'	X atom vacancy	V_X^x
M^{2+} ion vacancy	V_M''	normal M^{2+} ion	M_M^x
X^- ion vacancy	$V_x^\bullet$	normal X^- ion	X_X^x
interstitial M atom	M_i^x	Q^{3+} ion at M^{2+} site	$Q_M^\bullet$
interstitial X atom	X_i^x	Q^{2+} ion at M^{2+} site	Q_M^x
interstitial M^+ ion	$M_i^\bullet$	Q^+ ion at M^{2+} site	Q_M'
M^+ ion vacancy	V_M'	free electron	e'
		free hole	$h^\bullet$

[a] Consider an ionic compound $M^{2+}(X^-)_2$. The formal charge on M is 2+, the formal charge on X is 1−. If an atom X is removed, one negative unit of charge remains on the vacant X site. The vacancy is neutral with respect to the ideal MX_2 lattice and is therefore indicated by V_x or V_X^x. If the electron is also removed from this site, the resultant vacancy is effectively positive, *i.e.* $V_x^\bullet$. Similarly, removal of an M atom leaves V_M, removal of an M^+ ion leaves V_M', removal of an M^{2+} ion leaves V_M''. If an impurity with a formal charge of three positive units Q^{3+} is substituted on the M^{2+} site, its effective charge is one positive unit. Therefore it is indicated by $Q_M^\bullet$.

IR-11.4.5 **Defect clusters and use of quasi-chemical equations**

Pairs or more complicated clusters of defects can be present in a solid. Such a defect cluster is indicated between parentheses. The effective charge of the cluster is indicated as an upper right index.

Examples

1. $(Ca_K^{\bullet} V_K')^x$ denotes a neutral defect pair in a solid solution, for example of $CaCl_2$ in KCl.

2. $(V_{Pb}'' V_{Cl}^{\bullet})'$ or $(V_{Pb} V_{Cl})'$ indicates a charged vacancy pair in $PbCl_2$.

Quasi-chemical reactions may be written for the formation of these defect clusters.

Examples:

3. $Cr_{Mg}^{\bullet} + V_{Mg}'' \rightarrow (Cr_{Mg} V_{Mg})'$ describes the association reaction of a Cr^{3+} impurity in MgO with magnesium vacancies.

4. $2Cr_{Mg}^{\bullet} + V_{Mg}'' \rightarrow (Cr_{Mg} V_{Mg} Cr_{Mg})^x$ gives another possible association reaction in the system of Example 3.

5. $Gd_{Ca}^{\bullet} + F_i' \rightarrow (Gd_{Ca} F_i)^x$ describes the formation of a dipole between a Gd^{3+} impurity and a fluorine interstitial in CaF_2.

IR-11.5   PHASE NOMENCLATURE

IR-11.5.1   **Introduction**

The use of the Pearson notation[4] (see also Section IR-3.5.3) is recommended for the designation of the structures of metals and solid solutions in binary and more complex systems. The use of Greek letters, which do not convey the necessary information, and of the *Strukturbericht* designations, which are not self-explanatory, is not approved.

IR-11.5.2   **Recommended notation**

The Pearson symbol consists of three parts: first, a lower-case italic letter (*a, m, o, t, h, c*) designating the crystal system; second, an italic capital letter (*P,S,F,I,R*) designating the lattice setting and, finally, a number designating the number of atoms in the conventional unit cell. Table IR-3.1 summarizes the system.

Examples:

1. Cu, symbol (*cF*4), indicates copper of cubic symmetry, with face-centred lattice, containing 4 atoms per unit cell.

2. NaCl, symbol (*cF*8), indicates a cubic face-centred lattice with 8 atoms per unit cell.

3.   CuS(*hP*12), indicates a hexagonal primitive lattice with 12 atoms per unit cell.

If required, the Pearson symbol can be followed by the space group and a prototype formula.

Example:

4.   Ag$_{1.5}$CaMg$_{0.5}$(*hP*12, *P*6$_3$/*mmc*) (*MgZn$_2$* type).

IR-11.6.   NON-STOICHIOMETRIC PHASES

IR-11.6.1   **Introduction**

There are a number of special problems of nomenclature for non-stoichiometric phases which have arisen with the improvements in the precision with which their structures can been determined. Thus, there are references to homologous series, non-commensurate and semi-commensurate structures, Vernier structures, crystallographic shear phases, Wadsley defects, chemical twinned phases, infinitely adaptive phases, and modulated structures. Many of the phases that fall into these classes have no observable composition ranges although they have complex structures and formulae; an example is $Mo_{17}O_{47}$. These phases, despite their complex formulae, are essentially stoichiometric and possession of a complex formula must not be taken as an indication of a non-stoichiometric compound (*cf.* Section IR-11.1.2).

IR-11.6.2   **Modulated structures**

Modulated structures possess two or more periodicities in the same direction of space. If the ratio of these periodicities is a rational number, the structures are called *commensurate*; if the ratio is irrational, the structures are called *non-commensurate* or *incommensurate*. Commensurately modulated structures exist in many stoichiometric and non-stoichiometric compounds; they may be regarded as superstructures and be described by the usual rules. Non-commensurately modulated structures occur in several stoichiometric compounds (and some elements), usually in a limited temperature range, *e.g.* U, SiO_2, TaS_2, $NbSe_3$, $NaNO_2$, Na_2CO_3, and Rb_2ZnBr_4.

Many modulated structures can be regarded as being composed of two or more substructures. The substructure with the shortest periodicity often represents a simple *basic structure,* while the other periodicities cause modulations of the basic structure. The

basic structure often remains unchanged within a certain composition range, while the other substructures take up the change in stoichiometry. If this change takes place continuously, a non-stoichiometric phase with a non-commensurate structure results. If the change occurs discontinuously, a series of (essentially stoichiometric) *homologous compounds* with commensurate structures (superstructures of the basic structure) may result or, in the intermediate case, a series of compounds with *semi-commensurate* or *Vernier* structures.

Examples

1. Mn_nSi_{2n-m}

The structure is of the *TiSi₂* type which has two atom substructures, the Mn array being identical to that of the Ti array in $TiSi_2$ and the Si_2 array being identical to that of the Si_2 array in $TiSi_2$. Removal of Si leads to a composition Mn_nSi_{2n-m} in which the Mn array is completely unchanged. The Si atoms are arranged in rows and, as the Si content falls, the Si atoms in the rows spread out. In this case there will be a Vernier relationship between the Si atom rows and the static Mn positions which will change as the composition varies, giving rise to non-commensurate structures.

2. $YF_{2+x}O$

The structure is of the *fluorite* type with extra sheets of atoms inserted into the parent YX_2 structure. When these are ordered, a homologous series of phases results. When they are disordered, there is a non-commensurate, non-stoichiometric phase, while partial ordering will give a Vernier or semi-commensurate effect. Other layer structures can be treated in the same way.

Misfit structures consist of two or more different, often mutually non-commensurate, units which are held together by electrostatic or other forces; no basic structure can be defined. The composition of compounds with misfit structures is determined by the ratio of the periodicities of their structural units and by electroneutrality.

Examples:

3. $Sr_{1-p}Cr_2S_{4-p}$ with $p = 0.29$, where chains of compositions Sr_3CrS_3 and $Sr_{3-x}S$ lie in tunnels of a framework of composition $Cr_{21}S_{36}$; the three units are mutually non-commensurate.

4. $LaCrS_3$, which is built from non-commensurate sheets of $(LaS)^+$ and $(CrS_2)^-$.

IR-11.6.3   **Crystallographic shear structures**

Crystallographic shear planes (*CS* planes) are planar faults in a crystal that separate two parts of the crystal which are displaced with respect to each other. The vector describing the displacement is called the crystallographic shear vector (*CS* vector). Each *CS* plane causes the composition of the crystal to change by a small increment because the sequence of crystal planes that produces the crystal matrix is changed at the *CS* plane. (From this it follows that the *CS* vector must be at an angle to the *CS* plane. If it were parallel to the plane, the succession of crystal planes would not be altered and no composition change would result. A planar boundary where the displacement vector is parallel to the plane is more properly called an *antiphase boundary*).

Because each *CS* plane changes the composition of the crystal slightly, the overall composition of a crystal containing a population of *CS* planes will depend upon the number of *CS* planes present and their orientation. If the *CS* planes are disordered, the crystals will be non-stoichiometric, the stoichiometric variation being due to the *CS* plane 'defect'. If the *CS* planes are ordered into a parallel array, a stoichiometric phase with a complex formula results. In this case, a change in the separation of the *CS* planes in the ordered array will produce a new phase with a new composition. The series of phases produced by changes in the spacing between *CS* planes forms an *homologous* series. The general formula of a particular series will depend upon the type of *CS* plane in the array and the separation between the *CS* planes. A change in the *CS* plane may change the formula of the homologous series.

Examples:

1. Ti_nO_{2n-1}

The parent structure is TiO_2 (*rutile* type). The *CS* planes are the (121) planes. Ordered arrays of *CS* planes can exist, producing an homologous series of oxides with formulae Ti_4O_7, Ti_5O_9, Ti_6O_{11}, Ti_7O_{13}. Ti_8O_{15}, Ti_9O_{17}. The series formula is Ti_nO_{2n-1}, with *n* between 4 and 9.
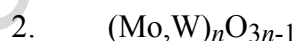
2. $(Mo,W)_nO_{3n-1}$

The parent structure is WO_3. The *CS* planes are the (102) planes. Ordered arrays of *CS* planes can form, producing oxides with formulae Mo_8O_{23}, Mo_9O_{26}, $(Mo,W)_{10}O_{29}$, $(Mo,W)_{11}O_{32}$, $(Mo,W)_{12}O_{35}$, $(Mo,W)_{13}O_{38}$, and $(Mo,W)_{14}O_{41}$. The series formula is $(Mo,W)_nO_{3n-1}$, with *n* between 8 and 14.

3. W_nO_{3n-2}

The parent structure is WO_3. The *CS* planes are the (103) planes. Ordered arrays of *CS* planes can form, producing oxides with formulae W_nO_{3n-2}, with *n* between approximately 16 and 25.

IR-11.6.4 Unit cell twinning or chemical twinning

This is a structure-building component in which two constituent parts of the structure are twin-related across the interface. The twin plane changes the composition of the host crystal by a definite amount (which may be zero). Ordered, closely spaced arrays of twin planes will lead to homologous series of phases. Disordered twin planes will lead to non-stoichiometric phases in which the twin planes serve as the defects. There is a close parallel between chemical twinning and crystallographic shear.

Example:

1. $(Bi,Pb)_nS_{n-4}$

    The parent structure is PbS which has the *cF*8 (*NaCl* type) structure. The twin planes are (311) with respect to the PbS unit cell. Two members of the homologous series are known, $Bi_8Pb_{24}S_{36}$ and $Bi_8Pb_{12}S_{24}$, but other members are found in the quaternary Ag-Bi-Pb-S system. The difference between compounds lies in the separation of the twin planes; each structure is built from slabs of PbS of varying thickness, alternate slabs being twinned across (311) with respect to the parent structure.

IR-11.6.5 Infinitely adaptive structures

In some systems it would appear that any composition can yield a fully ordered crystal structure over certain temperature and composition ranges. As the composition changes, so the structure changes to meet this need. The term *infinitely adaptive structures* has been applied to this group of substances.[5]

Examples:

1. Compounds in the Cr_2O_3-TiO_2 system between the composition ranges $(Cr,Ti)O_{2.93}$ and $(Cr,Ti)O_{2.90}$.

2. Compounds in the Nb_2O_5-WO_3 system with block-type structure between the composition limits Nb_2O_5 and $8WO_3.9Nb_2O_5$ ($Nb_{18}W_8O_{69}$).

IR-11.6.6 Intercalation compounds

There are several materials in which a guest species is inserted into a host matrix. The process is called intercalation, and the product is called an *intercalation compound*. Common examples of intercalated materials are found in the clay silicates, layered dichalcogenides, and electrode materials for lithium batteries; graphite intercalation is considered in detail in Ref. 6. Intercalated materials can be designated by conventional chemical formulae such as Li_xTaS_2 ($0<x<1$) or by host-guest designations, such as TaS_2:xLi ($0<x<1$). If the stoichiometry is definite, ordinary compound designations may be used, *e.g.* $TaS_2(N_2H_4)_{4/3}$, $TiSe_2(C_5H_5N)_{1/2}$, and KC_8. (In this particular instance, fractional indexes may be used).

Many intercalation compounds are layered structures and intercalation is a two-dimensional reaction. The term *insertion* is sometimes used for three-dimensional examples, as in the tungsten bronzes, *e.g.* Na_xWO_3, and the spinels, *e.g.* $Li_xMn_2O_4$.

IR-11.7 POLYMORPHISM

IR-11.7.1 **Introduction**

A number of chemical compounds and elements change their crystal structure with external conditions such as temperature and pressure. These various structures are termed polymorphic forms of the compounds, and in the past have been designated using a number of labelling systems, including Greek letters and Roman numerals; the use of such non-systematic labels is discouraged. A rational system based upon crystal structure should be used wherever possible (*cf.* Sections IR-3.5.3 and IR-4.2.5).

Polytypes and polytypoids can be regarded as a special form of polymorphism and are treated in more detail in Ref. 7.

IR-11.7.2 **Use of crystal systems**

Polymorphs are indicated by adding an italicized symbol denoting the crystal system after the name of formula. The symbols used are given in Table IR-3.1. For example, zinc sulfide (*c*) or ZnS(*c*) corresponds to the zinc blende structure or sphalerite, and ZnS(*h*) to the wurtzite structure. Slightly distorted lattices may be indicated by using the *circa* sign ~. Thus, a slightly distorted cubic lattice would be expressed as (~*c*). In order to give more information, simple well-known structures should be designated by giving the type compound in parentheses whenever possible. For example, AuCd above 343 K should be designated AuCd (*CsCl* type) rather than AuCd(*c*).

Properties which strongly depend on lattice and point symmetries may require the addition of the space group to the crystal system abbreviation. For more details see Ref. 8.

IR-11.8   FINAL REMARKS

This Chapter deals with the basic nomenclature of solid state chemistry. In some areas, such as amorphous systems and glasses, the nomenclature needs further development. The reader is also referred to the work of the International Union of Crystallography.

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