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The Rare-Earth Doping of Binary and Ternary Chalcogenides

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Experimental evidence on the rare-earth doping of the II:VI compounds and a knowledge of the rare-earth chalcogenide structures is used to suggest a set of principles with which to predict the ultimate doping limit for the binary and ternary chalcogenides. The validity of these rules is tested by experiment.

1. Introduction

The rare-earth doping of bulk II:VI crystals particularly cadmium sulphide, zinc sulphide and zinc selenide has received considerable attention over the past few years. In most instances the doping of the single crystal has been done during the growth phase [1-3]. A few samples have, however, been doped after growth by diffusion of the metal or rare earth chalcogenide [4]. In all cases the concentration of rare earth actually incorporated into the crystals was very low, of the order of 0.02 mole %. It has often been suggested that the low rare earth content in the vapour grown crystal was a consequence of the highly refractory nature of the rare earth chalcogenides and that better transport and incorporation of the rare earth ion might be achieved if it were in solid solution with the host starting material. Such a solid solution can in principle be prepared by melting together the rare earth chalcogenides and the relevant II:VI compound. Once again, however, the same low dopant concentrations are obtained. The use of melt growth techniques [5] gives single crystals with a more consistent doping level but once again the solubility limit is low.

A summary of the reported doping levels for rare-earth doped zinc sulphide are given in table I. In this table the inclusion of a reference without a value for the doping level merely indicates that the presence of the rare earth was confirmed but that no estimate of the concentration was given. It should be noted that the two reports of crystals doped with neodymium to a 1 % level are anomalies in the table, and may be due to some rare earth sulphide precipitate in the crystal. The conclusion that may be drawn from the above table is that rare earths have only been incorporated at low level in zinc sulphide. This conclusion may be generalised to all the II:VI compounds and further it may also be concluded from the literature that the cadmium chalcogenides are more readily doped than the zinc ones.

TABLE I The doping of zinc sulphide with rare earth elements

Element	Concentration (mole %)	Reference
Pr	—	[4]
Nd	—	[4]
	0.1	[1]
	0.02	[3]
	0.1	[3]
Sm	—	[2]
	—	[4]
Eu	—	[4]
Tb	<0.02	[1]
	0.02	[3]
	<0.03	[5]
Dy	<0.02	[1]
	—	[4]
Er	—	[4]
Tm	<0.02	[1]
	0.02	[3]
	—	[4]

It is worthwhile at this point, therefore, to ask the question as to whether the doping levels are due to (a) a failure to find the correct preparative technique (b) inherent difficulty of incorporating trivalent rare earth ions because of their size or the necessity of charge compensation or (c) a direct consequence of the chemical and physical properties of the host materials. It is the purpose of this report to show that of these three possibilities the most probable reason for the low doping levels lies in the third possibility, (c). To justify this assertion the doping of a number of binary compounds has been attempted experimentally including the CdS:R_2S_3 (R refers to a rare earth) and In_2S_3:R_2S_3 systems and from these experiments and knowledge of the relevant crystal structures a set of general principles are proposed for the rare earth doping of the chalcogenides.

Using these principles, other possible ternary chalcogenide host lattices are then suggested in which doping with, at least, certain of the rare earth ions should be readily achieved and the suitability of two of these ternaries has been tested by experiment.

2. The Binary Chalcogenide Structures

Before exploring the limitations on the doping mechanisms in the binary chalcogenides it is worth comparing the structures of the various potential host lattices with those of the rare earth chalcogenides. Throughout this paper the classification *chalcogenide* is used as a collective term for the sulphides, selenides and tellurides but does not include the oxides, since the factors which influence the isomorphic replacement of ions in the oxides are known to be markedly different to those for the other chalcogenide structures. In the ionic oxides it is generally accepted that the possibility of isomorphic replacement of one ion for another depends mainly on ionic size, the dopant ions having to occupy a hole of a certain size within a lattice of approximately close packed oxygen ions. In that case the particular properties of the individual ion are of minor importance. In the chalcogenides, on the other hand, due to the covalent nature of the bonds, the incorporation of the dopant is likely to be dominated by the need to form a fixed number of bonds and thus the term ionic size has only limited meaning in these dominantly covalent materials. The change in covalency between the two situations is not necessarily always large, for example 90% ionicity in ZnO to 70% in ZnS, but it is these small changes which determine the requirements for doping.

An example of a typically covalent structure is the diamond structure and this is associated with all the non-metallic elements of group IV. Each atom in this regular face-centred cubic structure is in an identical site of regular tetrahedral co-ordination. If two atoms A and B are substituted alternatively for the atoms in the diamond structure the structure becomes that of cubic zinc blende, which can be regarded as a close packed face-centred cubic structure of anions with the cations in the tetrahedral interstices, or *vice versa*. A reduction in the symmetry of the zinc blende from cubic to hexagonal with the retention of the tetrahedral co-ordination yields the wurtzite structure. This has more polarised bonds than zinc blende as it reduces the distance between unlike charges to a minimum.

The ionic equivalent of the diamond structure is the cubic sodium chloride structure where all the ions have a similar octahedral co-ordination. More generally in the ionic crystal structures the cations are distributed throughout a close packed array of larger anions, the packing arrangement providing the appropriate ion co-ordination.

The following four sections set out the structures of those binary chalcogenides which have been considered as potential host lattices for the rare earth ions and the structures of the rare earth chalcogenides themselves.

2.1. The IIA Chalcogenides (Be, Mg, Ca, Sr, Ba)

The structure of these chalcogenides are given in table II. Only those of beryllium show strongly covalent bonding characteristics throughout the series. The remaining elements tend to form more ionic or polarised bonds, the tendency being strongest in the calcium, strontium and barium compounds. The change in bond characteristics between beryllium, magnesium and calcium in the telluride series is clearly reflected in the structural change from zinc blende to wurtzite to sodium chloride. The co-ordination number of the group is six with the exception of the beryllium compounds and magnesium telluride where it is four.

2.2. The IIB Chalcogenides (Zn, Cd, Hg)

The elements in this series tend to form covalent

TABLE II The structure of the chalcogenides of the elements of group IIA, formula MX

	S	Se	Te
Be	ZB [4]	ZB [4]	ZB [4]
Mg			W [4]
Ca			
Sr		NaCl [6]	
Ba			

W = wurtzite
ZB = zinc blende
[*x*] = co-ordination number of the cation

bonds, the covalency once again decreasing with increasing atomic weight of the cations. The structures of the various chalcogenides are given in table III. They all have either zinc blende or wurtzite structures with the exception of mercury which is exceptional in that it can also form a complex covalent helical structure with sulphur [6].

TABLE III The chalcogenides of the elements of group IIB, formula MX

	S	Se	Te
Zn	W/ZB [4]	ZB/W [4]	ZB [4]
Cd	W/ZB [4]	W/ZB [4]	ZB [4]
Hg	ZB [4]	ZB [4]	ZB [4]

W = wurtzite
ZB = zinc blende
[x] = co-ordination number of the cation

2.3. The IIIA Chalcogenides (Al, Ga, In)

Only three of the possible IIIA elements have been considered because of the limited information on the chalcogenides of boron and thallium. In general once again the elements of this group have an increasing tendency with atomic weight to form polarised bonds. Despite the compound formula M_2X_3 the zinc blende and wurtzite structures predominate (table IV). This is accomplished by the random filling of two thirds of the cation positions (that is one third of the total number of tetrahedral positions) in the zinc blende and wurtzite structures: the inequality in the numbers of unlike atoms being compensated by defects in the structures.Thus as the covalent nature of the atoms decreases from tellurium to sulphur and aluminium to indium the structure changes from that of zinc blende to wurtzite. The preference of indium to form a polar bond is clearly demonstrated when it is coupled with the less strongly covalent anions sulphur and selenium (see table IV). The structure here changes to that of the defect spinel γ–Al_2O_3. The co-ordination numbers of all the cations within the group are four except for indium where a value of six is found.

2.4. The Rare Earth Chalcogenides Including Sc, Y and La

Table V lists the structures of the various known rare earth chalcogenides. The structure in every case resembles that of an ionic or strongly polarised compound. This is in line with the expected behaviour of the lanthanides in that they prefer to form such bonds, the polarisation being slightly less for the higher atomic number elements. This is reflected in a reduction of co-ordination number from eight to six in certain of the compounds. The chalcogenides of the general formula RX have the cubic sodium chloride structure. The sulphides of the form R_2S_3 in the first half of the lanthanide series have the Th_3P_4 structure (cubic with a tetramolecular unit cell) while those from dysprosium to thulium inclusive have a monoclinic structure and the final two of the series have the γ–Al_2O_3 structure. The selenides R_2Se_3 and the tellurides R_2Te_3 have structures that change from the Th_3P_4 structure to the orthorhombic structure of Sc_2S_3 at holmium and terbium respectively. Just below the transition point a complex double chain U_2S_3 structure is formed together with a non-stochiometric form of the Th_3P_4 structure. The only known form for the R_3X_4 chalcogenides is the Th_3P_4 structure. The co-ordination number of all the rare earths in these structures is six or eight except for the U_2S_3 structure where it becomes seven.

TABLE IV The structure of the chalcogenides of the elements of group IIIA, formula M_2X_3

	S	Se	Te
Al	(a) W-random [4] (b) corundum [6]	W-defect [4]	—
Ga	α-β-W-random [4] γ-ZB-random [4]	ZB-defect [4]	ZB-defect [4]
In	γ-defect spinel [6], [4] β-corundum [6]	defect spinel [6], [4]	ZB-defect [4]

W = wurtzite
ZB = zinc blende
[x] = co-ordination number of the cation

3. Experimental

3.1. The II:VI Compounds

Considerable effort has been expended by previous workers [1–5] on the preparation of rare-earth-doped II-VI compounds, particularly by growth techniques, but in every case the ultimate doping level has been low, of the order of 100 ppm. Further, in cases where the doping has been successful there is strong evidence that there is no unique site into which the rare earth prefers to substitute. There is however some evidence [7] which seems to indicate that, if anything, octahedral sites are preferred. For example in the presence of a silver impurity, complexes are readily formed in which the rare earth ion is

TABLE V The structure of the chalcogenides of the rare elements

R.E. Calcide formula	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Sulphide														
1:1	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]
2:3	γ [8]	γ [8]	γ [8)	γ [8]	γ [8]	no cpd	γ [8]	δ [6]	δ [6]	δ [6]	δ [6]	δ [6]	R [6]	R [6]
3:4	γ [8]	γ [8]	γ [8]	γ [8]	γ [8]	γ [8]	no cpd		no cpd					
Selenide														
1:1	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	
2:3	γ [8]	γ [8]	γ [8]	γ [8]	γ [8]	no cpd	γ [8], ν [7]	γ [8], ν [7]	γ [8], ν [7]	ω [6]	ω [6]	ω [6]	ω [6]	ω [6]
3:4	γ [8]	γ [8]	γ [8]	γ [8]	γ [8]		no cpd		no cpd					
Telluride														
1:1	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]	C [6]		C [6]	
2:3	γ [8]	γ [8]	γ [8]	γ [8], ν [7]	γ [8], ν [7]	no cpd	ν [7]	ω [6]	ω [6]	ω [6]	ω [6]	ω [6]	ω [6]	ω [6]
3:4	γ [8]	γ [8]	γ [8]	γ [8]	γ [8]									

C = cubic, NaCl type

γ = cubic, Th_3P_4 type, tetramolecular unit cell, Td (143*d*)

δ = monoclinic

R = rhombohedral, corundum a-Al_2O_3 type, CN's-metal 6, nonmetal 4

ν = orthorhombic, U_2S_3 type, a complex double chain structure

ω = orthorhombic, the only sulphide with this structure is Sc_2S_3

[*x*] = co-ordination number of the cation

surrounded by both a tetrahedron of silver atoms and an octahedron of sulphur or selenium atoms. In that particular situation the rare earth ion experiences a more polarised bonding arrangement than in the substitutional site.

The diffusion of the rare earth ion into single crystals gives virtually the same concentrations as in the cases where the rare earths were grown in. The only thing that can be said in favour of diffusion is that the technique is simple to apply and the results are somewhat more reproducible. The temperatures required for the efficient diffusion of the rare earth are normally taken to be between 800 and 1000° C. For example, in CdS the diffusion coefficient for ytterbium is 1.3×10^{-9} cm^2/sec at 960° C [4], so that over a few hours the rare earth will have diffused some 100 μm into the crystal but the concentration at this depth is only 1% of the surface value. Lowering the temperature to 800° C increases the diffusion time from a few hours to a few days for the same penetration depth.

Bearing in mind the information of previous workers three confirmatory doping experiments were carried out on CdS. The first experiment involved melting CdS in the presence of the rare earth sulphide (R_2S_3), the second consisted of reacting together the R_2S_3 and cadmium sulphide powders, while the third involved heating cadmium sulphide in the presence of the rare earth metal vapour. By the first method little or no rare earth was incorporated into the cadmium sulphide and this was indicated by the lack of both rare earth luminescence and esr lines. The added rare earth was rejected either in the form of Cd R_2S_4 or R_2S_3 depending on whether or not the rare earth sulphide reacted with cadmium sulphide to form the new compound, Cd R_2S_4. The presence of the precipitate was indicated by additional lines on an X-ray powder photograph. The second method proved more successful in as much as the rare earth was actually incorporated into the cadmium sulphide albeit at a very low concentration usually not detected by esr. The reaction between the cadmium sulphide and the rare earth metal vapour proved the most successful of the three, giving strong rare earth emissions under both X-ray and ultra-violet excitation and a good esr signal. Prolonged heating at high temperature always resulted in a lowering of the rare earth luminescent intensity and esr signal strength suggesting that the rare earth was migrating to non-active centres or precipitating out as R_2S_3 or Cd R_2S_4. The highest doping levels attained were, however, still less than 0.1 mole% as found by previous workers.

3.2. The III:VI Compounds

Prior to this study very little information was available in the literature on the incorporation of rare earths into these compounds. As in the case of the II:VI materials there is a tendency for a new compound to be formed when the rare earths are reacted with indium sulphide and gallium sulphide [8] the two examples chosen for this study. However, the nature of the new compound does not prohibit the incorporation of the rare earth ion into indium sulphide at least, for single crystals of indium sulphide could be readily prepared containing a few mole % of all rare earth atoms from dysprosium to ytterbium inclusive. The lower atomic number rare earths cannot be incorporated above 100 ppm. Studies by esr of the environment around the rare earth ion [9] indicated that the rare earth tended to replace those indium atoms in the octahedral sites and not those in tetrahedral sites. In gallium sulphide, on the other hand, where all the gallium atoms occupy tetrahedral sites no significant doping of the compound was possible, once again the limit was less than 0.1 mole %.

4. Discussion

4.1. The Binary Chalcogenides

A review of the experimental evidence in conjunction with the structural information set out in section 2 strongly suggests that the following principles might well be applied in further considerations of the doping of the chalcogenide lattices:

(i) In combination with a specific chalcogen each cation has a characteristic co-ordination number. In covalent or predominantly covalent compounds this number is four while in the polarised structures it may be six, or eight. The co-ordination number of most cations will be specifically four or the choice of six or eight. The two exceptions to this are indium and magnesium where the number may be either four or six.

(ii) The structure of the strongly covalent chalcogenides is particularly sensitive to changes in the degree of polarisation of the bond. This suggests that in these cases the substitution of dopant without structural reorganisation, the situation necessary for efficient doping of a host lattice, is only readily achieved when the substitution leaves the polarisation of the bond unchanged.

(iii) Provided there is a real correspondence between bond character and co-ordination number, then to leave the polarisation of the bonds unchanged implies that the cation being substituted has the same co-ordination number in its parent chalcogenide as that of the cation it is replacing.

(iv) In the particular case of the trivalent rare earth ions, they will select that site or compound in which the site occupied by the rare earth ion is the same as that in R_2S_3. This, for example, explains why the rare earth ions from La to Tb inclusive cannot be incorporated into In_2S_3 since they seek sites of eight-fold co-ordination which are not available in In_2S_3.

These then are the conditions for structural acceptance of the dopant rather than what might be called impurity acceptance, the difference in the two situations being the amount of dopant involved. It is therefore necessary to define two types of doping: (a) *normal doping*, in which the dopant occupies well-defined sites at controllable concentrations up to a few per cent and (b) *impurity doping*, in which the dopant location and concentration cannot be controlled but depend on defects in the host lattice. These sites, while involving a large modification to the surroundings of the site, do not alter the overall structure. In the normal doping mode structural acceptance is necessary. The actual level of the boundary between the two types of doping incorporation is not known but experimental evidence suggests that a limit of less than 0.1 mole % may apply for impurity doping. For example the literature suggests that there are two dominant sites in the II:VI compounds, one where the rare earth ion substitutes for the metallic ion and the second where the rare earth ion occupies an interstitial site surrounded by a tetrahedron of such as silver atoms and a dominant octahedron of sulphur or selenium atoms. In both cases the maximum doping level appears to be about 0.01 mole %, which is a level at which the lattice structure as a whole has not been modified.

Therefore, those chalcogenides with a co-ordination number of four may be rejected immediately as possible host lattices for the rare earths at anything above the impurity doping level, that is a few hundred parts per million. The elimination of these lattices leaves: (i) the chalcogenides of Ca, Sr, Ba, and MgS and MgSe; (ii) the chalcogenides of Y and Sc_2S_3 and Sc_2Se_3 and (iii) In_2S_3 and In_2Se_3 as possible binary host lattices. Of these three groups only the third is at present of practical interest as the first two are refractory compounds and as such cannot be readily prepared as single crystals. In both In_2S_3 and In_2Se_3 the dopant rare earth ion must require a co-ordination number of six for efficient doping and table V shows that only the rare earth sulphides from Dy_2S_3 to Lu_2S_3 inclusive have this co-ordination number. The principles outlined above, therefore, satisfactorily explain the observed doping limitations of both In_2S_3 and In_2Se_3 as well as the limited doping levels for the II:VI compounds in respect of the rare earth ions.

4.2 The Ternary Chalcogenides

The observations on the binary chalcogenides indicate that only two of those considered are potential hosts for the rare earth ions. Because of this limitation it may be necessary to consider some of the ternary chalcogenides as potential hosts. In this section therefore we give consideration to the selection of suitable ternary compounds based on the principles outlined in section 3. The main requirements for the host lattice are that there should be cation sites with six- or eight-fold co-ordination; those with six-fold co-ordination being suitable for doping with rare earths from Dy to Lu inclusive while those with eight-fold co-ordinated sites should be suitable for doping with the remainder of the lanthanides. Because of the large number of ternary compounds only two have been experimentally considered (i) $ZnIn_2S_4$ and (ii) $CdIn_2S_4$, both derived from In_2S_3. The experimental determination of the doping limitations in these lattices shows that while Er, Ho, and Yb may be readily incorporated into both lattices Pr, Nd and Sm may not, which is in agreement with the general principles set out in section 3. It is interesting to note that in $ZnIn_2S_4$ the In ion occupies both tetrahedrally and octahedrally co-ordinated sites but the rare earth when doped into the lattice only substitutes for those indium ions in the octahedral sites.

A final point of interest is the fact that the principles outlined in section 3 can be used to shed light onto the fact that CdS and R_2S_3 compounds only react to form Cd R_2S_4 in those cases where the rare earth can retain its octahedral co-ordination. That is to say those rare earth ions which wish to occupy an eight-fold co-ordinated site will not form the spinel Cd R_2S_4.

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