

Preface

There is a vast number of compounds with AB_2X_4 stoichiometry, where A and B refer to cations and X corresponds to the anion, depending on the cation and anion valences to fit the octet rule. They include: (i) $A^{II}B_2^{III}X_4^{VI}$ compounds, like $MgAl_2O_4$, $ZnGa_2S_4$, $CdIn_2Se_4$, and $HgTl_2Te_4$; (ii) $A_2IB^{VI}X_4^{VI}$ compounds, like Li_2SO_4 , Na_2SeO_4 , K_2TeO_4 , Tl_2CrO_4 , Li_2WO_4 , Cs_2MoS_4 , and K_2WS_4 ; (iii) $A_2^{II}B^{IV}X_4^{VI}$ compounds, like Mg_2SiO_4 , Fe_2GeS_4 , Ba_2SnS_4 , and Pb_2SiSe_4 ; and (iv) $A_2IB^{II}X_4^{VII}$ compounds, like Na_2BeF_4 , K_2CoCl_4 , Cs_2CuCl_4 , K_2PdBr_4 , and Rb_2MnI_4 .

All these families of AB_2X_4 compounds have one thing in common; i.e., they have an unbalanced number of cations (3) and anions (4) per formula unit. Therefore, from the point of view of structural phase transitions, these compounds are prone to suffer order-disorder processes under different conditions of pressure and temperature where cations may get mixed with vacancies at cation sites to fulfil the requirements of high-symmetry structures.

In particular, $A^{II}B_2^{III}X_4^{VI}$ chalcogenides is a vast family of compounds that crystallize at ambient conditions in a great variety of structures. However, they can be classified into three main groups: (i) compounds crystallizing in the spinel or related structures; (ii) compounds crystallizing in tetrahedrally coordinated structures, derived from the diamond and zinc-blende structures with ordered vacancies in the unit cell, and known as adamantine-type ordered-vacancy compounds (OVCs); and (iii) other compounds crystallizing in structures not related to those of spinel or to those of OVCs, e.g. layered materials. Usually, oxides belong to the first group, selenides and tellurides to the second group, and sulphides are in the borderline between the two first groups and belong either to the first, to the second or to the third group.

The big number of $A^{II}B_2^{III}X_4^{VI}$ chalcogenides includes compounds with very different properties and with a wide interest ranging from Geophysics, like spinel-related compounds, to many technological applications. The study of the properties of $A^{II}B_2^{III}X_4^{VI}$ chalcogenide compounds under high pressures and of their pressure-induced phase transitions can help to understand the properties of these compounds and the relationship between their properties and their structures which can have profound implications in many fields.

In this book we are going to review the main results obtained in the study of $A^{II}B_2^{III}X_4^{VI}$ chalcogenide compounds at high pressures to date, paying special attention to the pressure-induced phase transitions. We will see that $A^{II}B_2^{III}X_4^{VI}$ chalcogenide compounds are complex materials that crystallize in different structures or with different degree of disorder depending on the crystal growth conditions. Therefore, the growth conditions determine the properties of the materials and their pressure dependence. We will see how high pressure studies show that the different structures of these compounds at ambient conditions in the three main groups stated above, despite not being considered similar or related in the past, bear a strong relationship between them. Furthermore, we will see that high pressure studies in the last years, despite being insufficient yet, will allow in the next future to establish a systematics of the temperature- and pressure-induced phase transitions in the complex family of $A^{II}B_2^{III}X_4^{VI}$ compounds. We hope the present work will promote future works for a better understanding of the structure and properties of these interesting, and still not well studied, materials.

The present book is organised as follows: after the first chapter, written by V. Ursaki and I. Tiginyanu and devoted to the description of the structure and properties of $A^{II}B_2^{III}X_4^{VI}$ chalcogenide compounds at ambient conditions and which serves as introduction and motivation for the studies at high pressures, the book is divided into three parts. In the first part, written by D. Errandonea, D. Santamaría Pérez, J. Ruiz-Fuertes, P. Rodríguez-Hernández and A. Muñoz, different high-pressure studies on indium thiospinel Aln_2S_4 family and spinel-structured oxides are review with the focus on X-ray diffraction and Raman studies in oxospinel and angle-dispersive X-ray diffraction, Raman and optical absorption measurements in thiospinel. The effects of pressure in the spinel structure are described discussing facts like bulk and polyhedral compressibility, cation size and cation substitution. The effects of pressure on the phase stabilities and transformation pathways of spinel-type semiconductors, as well as on their vibrational and electronic properties are also discussed. Finally, we will present a general overview which hopefully will contribute to achieve a better understanding of the behaviour of thiospinels and selenospinel under compression. The experimental data are accompanied by an overview of the theoretical work done from first principles on the structural, elastic, electronic and vibrational properties of spinels under pressure as well as pressure-induced post-spinel phases.

The second part is written by F. J. Manjón, R. I. Vilaplana, O. Gomis Hilario, A. Muñoz and M. Fuentes-Cabrera it being devoted to the experimental and theoretical studies of ordered-vacancy compounds at high pressures. An overview of the effects of pressure on the crystalline structure and physical properties of sulphur-based and selenium-based ordered-vacancy compounds of the $A^{II}B_2^{III}X_4^{VI}$ family is presented. Recent X-ray diffraction and Raman spectroscopy studies are presented with a main focus on the discussion of pressure-induced phase transitions and their inherent cation and cation-vacancy disordering processes.

The experimental data are supported by ab initio calculations within the Density Functional Theory and the Density Functional Perturbation Theory of electronic, dynamical, and elastic properties of defect chalcopyrite, defect stannite and pseudo-cubic chalcopyrite structures of AB_2X_4 ($X = S$ and Se) compound under hydrostatic pressures.

The third part, written by V. V. Ursaki and I. M. Tiginyanu, deals with the few studies devoted to other $A^{II}B_2^{III}X_4^{VI}$ chalcogenides with structures different from those of spinels and ordered-vacancy compounds on the instance of layered $A^{II}InGaS_4$ crystals with Cd , Zn , and Mg as A^{II} cations as well as on the instance of the $Zn-Al-S$ system which provides an initial wurtzite structure in addition to the spinel structure. It is also shown that quaternary solid solutions $ZnAl_{2(1-x)}Ga_{2x}S_4$ obtained by adding gallium atoms to the system demonstrate a systematics of phase transitions different from that inherent to $A^{II}B_2^{III}X_4^{VI}$ compounds with chalcopyrite, stannite and spinel structure.

Finally, an epilogue with some final remarks is presented.

Valencia, Spain
Chisinau, Moldova

Francisco Javier Manjon
Ion Tiginyanu
Veaceslav Ursaki



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