An X-ray absorption study of doped sphalerites

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Abstract: Metal K-edge X-ray absorption spectra of Mn, Mn(Fe), Cu/In, Cu/ln/(Fe) and Cd doped zinc sulfides are reported. The Zn K-edge XANES shows that there is little change on the low-lying vacant electronic states of the Zn. Furthermore, the Zn EXAFS indicates that the coordination site of the Zn is almost unchanged by any of the dopants. Mn, Cu, In and Cd K-edge EXAFS show that the local S tetrahedra around the dopant are compressed for Cu and expanded for Mn, In and Cd. Moreover the second coordination sphere indicates that clustering occurs in the Cu/In- and Cd-doped materials. M-S bond distances of the dopants in sphalerite are: Cd-S, 2.48 Å; In-S, 2.43-2.45 Å; Cu-S, 2.30-2.33 Å; and Mn-S, 2.41-2.43 Å.

Key-words: sphalerite, ZnS, dopant, XAS, EXAFS.

Introduction

Sphalerite, cubic ($Fm3m$) ZnS, is a very important II-VI semiconductor because the size of its band gap can be tuned by the addition of various dopants such that it can convert different forms of energy into visible light. Its band structure is of particular interest and the understanding of this electronic structure has been advanced by band-structure and MO calculations. The structure of sphalerite is flexible enough to accept partial substitution of the Zn by other cations, and it is this property that enables the band gap to be altered with great precision. It has found a wide usage in applied solid-state science, and thus has been studied by a wide variety of band-structure methods (see Vaughan & Craig, 1978; Tossell & Vaughan, 1992). In addition the extent of the substitutions and their effect on the structure has been studied by mineralogists, economic geologists and mineral-processing technologists as sphalerite is one the commonest components of base-metal sulfide ores and is the world’s main source of Zn, Cd and In.

The X-ray absorption spectrum can be divided into two regions: the extended X-ray absorption fine structure (EXAFS) region (from about 30 eV to 1000 eV past the edge) and the X-ray absorption near-edge structure (XANES) region (from ca. 10 eV below the edge to 50 eV above it). It is the XANES region that provides detailed information on the radial distribution about an excited atom (Köningsberger & Prins, 1988), through simulation programs such as EXCURVE. The XANES region holds information of two sorts. The region from about 10 to 50 eV past the edge may be successfully modelled using procedures that take account of the multiple scattering of the

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