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# XPS valence band spectra and theoretical calculations for investigations on thiogermanate and thiosilicate glasses

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**Abstract**

This paper reports on investigations of thiogermanate and thiosilicate crystals and glasses by means of XPS valence band spectra and theoretical calculations (FLAPW method). The calculations were achieved on three crystallized phases $GeS_2$, $Na_2GeS_3$ and $SiS_2$ and valence band spectra (visualization of the occupied electronic density of states) were precisely interpreted through modulated density of states and charge density maps. This information was used to go further in the structural investigations of some thiogermanate and thiosilicate glasses. In sodium thiogermanates, an increase in Ge–Ge bonds was revealed as the modifier content ($Na_2S$) increases. In thiosilicates, the evolution of the valence spectra according to the nature of the alkaline atoms (Li, Na) has been interpreted as changes in the local connectivity of units (edge or corner sharing tetrahedra).

This study exhibits the potentialities of valence band spectra to provide information on glassy systems.


*Keywords:* XPS; Valence bands; Band structure calculations; Glass; Thiogermanate; Thiosilicate

## 1. Introduction

Chalcogenide glasses have been the subject of intense study due to their optical properties (IR transparency, photosensitivity, giant photo-expansion, etc.) and their high conductivity when silver, copper or alkaline ions are incorporated in the glassy network. These properties have induced numerous application-oriented developments [1–4] like infrared waveguides for (integrated) optical devices, chemical sensors (ion selective electrodes for example), solid state micro-batteries for energy storage based upon the use of a glassy electrolyte, etc.

Different approaches have been used to get a better insight of both their structural characteristics and their diffusion properties. Conductivity and NMR spin lattice relaxation measurements have been used to investigate the cation-hopping dynamics [5–12]. Neutron diffraction studies, NMR, Raman, IR, etc. analyses have also been carried out in order to probe the local and intermediate range structure in these glasses [13–24].

X-ray photoelectron spectroscopy (XPS) is also an interesting tool to yield information not only on the local structure but also on the electronic structure of materials. In previous papers [25–28], XPS core peak analysis has been successfully used to study different families of chalcogenide glasses (thioborate, thiosilicate, thiogermanate and thioarseniate glasses). However, XPS valence band spectra, which correspond to the visualization of the occupied density of states, are rarely used. Recording and interpretation of these data require careful and patient experimentation but they present very interesting potentialities. Indeed, they are scrutinizing the less bound electrons of the materials, those that are directly involved in the bonds between atoms

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and consequently that contain the highest potential information. Their detailed analysis needs band structure calculations and especially theoretical density of states. The aim of this work was to go further in the structural investigation of sodium thiogermanate and lithium and sodium thiosilicate glasses by means of valence band spectra analysis.

Firstly, a detailed analysis of the XPS valence band spectra confronted with band structure calculations was achieved for the three crystalline phases $GeS_2$, $Na_2GeS_3$ and $SiS_2$. Secondly, valence spectra of the glasses were analysed on the basis of these XPS results.

## 2. Experimental and computational details

### 2.1. Sample preparation

Glasses with adequate compositions were synthesized in evacuated silica tubes from previously prepared $GeS_2$, $SiS_2$ and $M_2S$ (M = Na, Li) following a procedure already described [5,13,14]. X-ray diffraction measurements did not reveal the presence of crystalline impurities in the samples.

### 2.2. XPS

The XPS analyses were performed with a Surface Science Instruments spectrometer (Model 301) using focused (diameter of the irradiated area = 300 or 600 μm) monochromatised Al Kα radiation (1486.6 eV). The residual pressure inside the analysis chamber was ca. $5 \times 10^{-8}$ Pa. The spectrometer was calibrated by using the photoemission lines of Au (Au $4f_{7/2} = 83.9$ eV, with reference to the Fermi level) and Cu (Cu $2p_{3/2} = 932.5$ eV); for the Au $4f_{7/2}$ line the full width at half maximum (FWHM) was 0.86 eV under the recording conditions. The peaks were recorded with a constant pass energy of 50 eV.

To avoid any contamination, the fresh surfaces of the samples were analysed just after being fractured in an ultra high vacuum ($5 \times 10^{-8}$ Pa) or after a fine grinding in the glove box. Neutralisation of the surface charge was performed using a low energy flood gun.

The reproducibility of the measurements was checked on different fractures or grinding on several samples and by further XPS analysis. The binding energy scale was calibrated using the C(1s) line (284.6 eV) from the carbon contamination (an atomic percentage of about 8% has always been

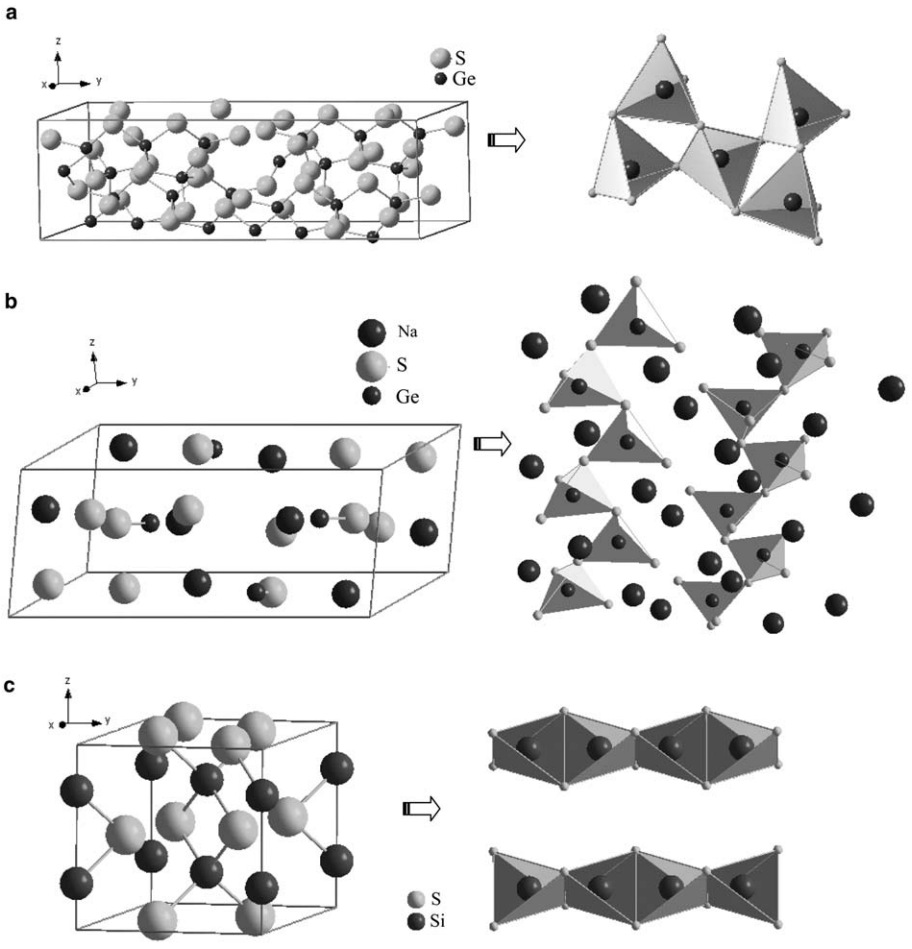


Fig. 1. Unit cells and visualization of infinite chains of tetrahedra sharing edges or corners for $GeS_2$ (a), $Na_2GeS_3$ (b) and $SiS_2$ (c) (lattice parameters, space group and atomic positions from [32], [33] and [34], respectively).