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**STUDY OF SMALL DISTORSIONS IN  $\text{Bi}_{12}\text{MO}_{20}$  OXIDES BY SIMPLE EXAFS TRANSMISSION TECHNIQS**

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**RESUME** : Dans certaines phases de type sillénites  $\text{Bi}_{12}[\text{A}^x\text{B}^y]_{20}\text{O}_{20}$ , les distances interatomiques entre l'oxygène et les cations A et B localisés dans les sites tétraédriques de la structure ont été déterminées par EXAFS et ce, malgré les difficultés d'enregistrement dues à la concentration relativement faible des espèces A et B en présence de bismuth fortement absorbant.

**ABSTRACT** : In some  $\text{Bi}_{12}[\text{A}^x\text{B}^y]_{20}\text{O}_{20}$  sillenite type phases the interatomic distances between oxygen and A or B cations located in tetrahedral sites of the lattice can be determined by EXAFS despite difficult recording conditions due to relatively low concentrations of A and B species in presence of strong absorbing bismuth.

Single crystals of  $\text{Bi}_{12}\text{SiO}_{20}$  and  $\text{Bi}_{12}\text{GeO}_{20}$  pure or doped present very interesting electro-optical properties.

The  $\text{Bi}_{12}\text{MO}_{20}$  sillenite phases crystallize in a body centered cubic lattice (space group I23, Z = 2) (1). The M cation located at the corners and the center of the cube is surrounded by perfect oxygen tetrahedra. When M is substituted by A and B cations, isostructural phases  $\text{Bi}_{12}[\text{A}^x\text{B}^y]_{20}\text{O}_{20}$  are obtained (2). In this case, the crystallographical investigation leads only to average (A-B)-O distances.

EXAFS seemed an appropriate tool for determining more precisely the concerned bond lengths.

**EXPERIMENTAL PROCEDURE AND DATA ANALYSIS**

The X-ray absorption spectra of powdered  $\text{Bi}_{12}[\text{Ge}]_{20}\text{O}_{20}$ ,  $\text{Bi}_{12}[\text{As}^{4/5}\text{V}^{1/5}]_{20}\text{O}_{20}$ ,  $\text{Bi}_{12}[\text{Zn}^{1/3}\text{As}^{2/3}\text{V}^{1/3}]_{20}\text{O}_{20}$  and  $\text{Bi}_{12}[\text{Ga}^{1/2}\text{Mn}^{1/2}\text{V}]_{20}\text{O}_{20}$  have been recorded at room temperature, using transmission technics at DCI(LURE).

Due to the strong absorption of bismuth at the corresponding photon energies (9500 to 12500 eV) and the low concentration of A or B cations (less than 1 for 12 bismuth atoms) the thickness of the samples has to be carefully adjusted.

Let us call  $\mu_1$  and  $\mu_2$  the respective absorption coefficients below and above the K absorption edge for the various cations present (Ge,As,Zn,Ga) and x the thickness of the sample. The optimum thickness conditions is  $\mu_2 x \approx 2$  at the absorption edge of interest. But this requirement can yet be fulfilled as the value of the contrast  $(\mu_2 - \mu_1) x$  should be generally too low to be detected. However, whereas the determination of the number of neighbours requires generally the best possible conditions for data recording, the first shell radius can be considered as a lower limit here due to the critical measuring conditions. Hence, we have adjusted the thickness of the samples so that  $\mu_2 x \approx 4$ , which, in each case leads to a sufficient contrast (i.e.  $(\mu_2 - \mu_1) x > 0.1$ ).

The  $\chi(E)$  data for Ge,As,Ga,Zn at the K-edge are given in Fig.1. The window used for the F.I. of the  $k^3 \chi(k)$  data extended for all samples from 30 eV to 450, 300, 270 and 220 eV for Ge,As,Ga and Zn respectively.

The back transformed contribution of the first oxygen coordination shell has been calculated using theoretical amplitude and phase shift.

Since the distance between germanium and oxygen are known in  $\text{Bi}_{12}[\text{Ge}]_0\text{O}_{20}$ , from the classical crystallographic data, we have used this compound to check the validity of our data treatment method. The value of Ge-O distance is found to be 1.77 Å, value which very well agrees with X-ray diffraction.

For the zinc compound which give the worst experimental data, we have selected ZnO (wurtzite) as a reference compound. We have found the the Zn-O distance was unchanged using a window either from 30 to 600 eV or extending from 30 to 220 eV.

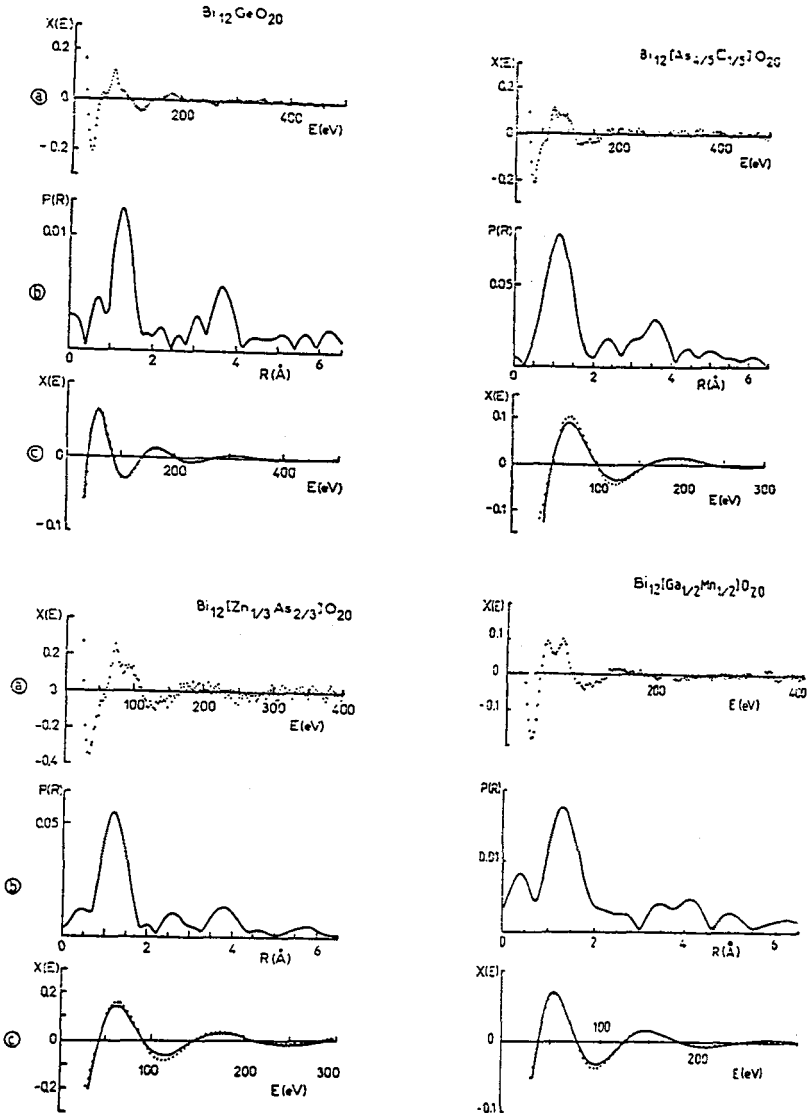


Fig.1 - a) EXAFS spectrum of the studied compounds above the Ge,As,Zn,Ga K-edge.

b) Radial distribution function (without phase shift correction).

c) Back-Fourier transformed contribution of the first neighbour shell : exp.(points), calc.(full line).

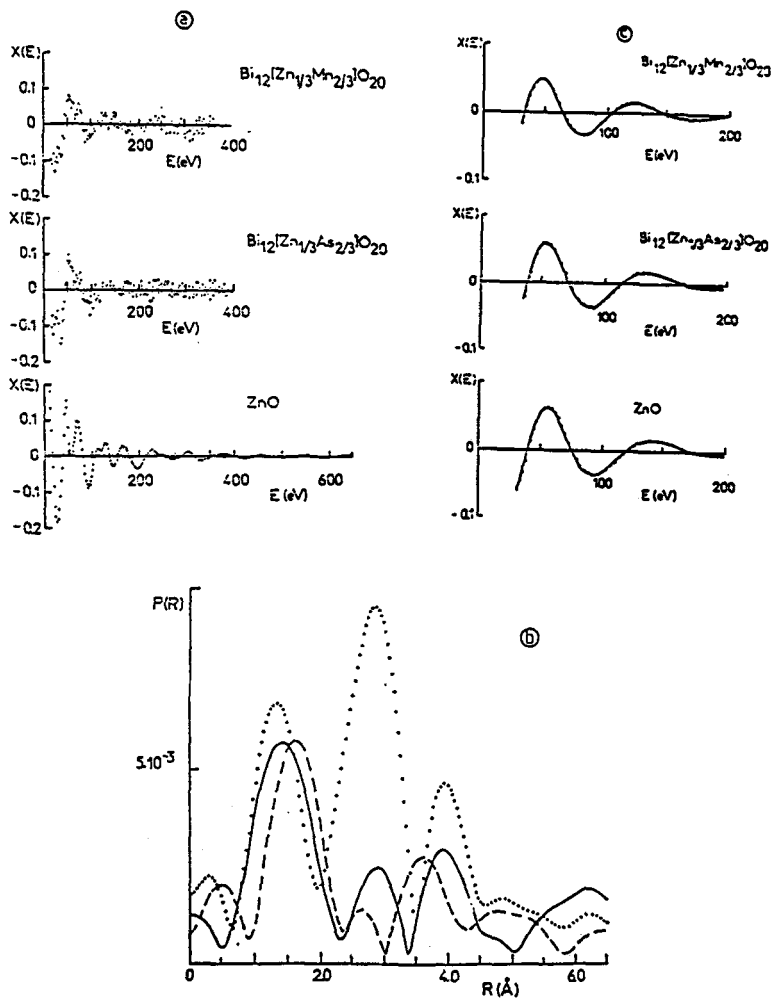


Fig.2 - a) EXAFS spectra of  $\text{Bi}_{12}[\text{Zn}_{1/3}^{\text{II}}\text{Mn}_{2/3}^{\text{IV}}]\text{O}_{20}$ ,  $\text{Bi}_{12}[\text{Zn}_{1/3}^{\text{II}}\text{As}_{2/3}^{\text{V}}]\text{O}_{20}$  and  $\text{ZnO}$  above  $\text{Zn}_{\text{K}}$ -edge.  
 b) Radial distribution functions (without phase shift corrections) :  $\text{Bi}_{12}[\text{Zn}_{1/3}^{\text{II}}\text{Mn}_{2/3}^{\text{IV}}]\text{O}_{20}$  (full line),  $\text{Bi}_{12}[\text{Zn}_{1/3}^{\text{II}}\text{As}_{2/3}^{\text{V}}]\text{O}_{20}$  (dashed line),  $\text{ZnO}$  (points).  
 c) Back-Fourier transformed contributions of the first neighbour shell : exp. (points), calc. (full line).

## RESULTS

The results obtained are summarized in Table I.

In spite of the presence in the materials of a high number of strongly absorbing bismuth atoms, EXAFS has allowed to determine some interatomic distances between oxygen and A and (or) B cations located in the tetrahedral sites of the sillenite type structure.

The most valuable result has been obtained for the  $\text{Bi}_{12}[\text{Zn}_{1/3}^{\text{II}}\text{As}_{2/3}^{\text{V}}]\text{O}_{20}$  oxide for which the Zn-O and As-O distances are respectively 1.83 Å and 1.71 Å. The difference between those values clearly shows that the tetrahedra cannot be identical in the lattice when they are occupied by different cations.

TABLE - Comparison of EXAFS results with crystallographic data.

Phases	EXAFS results				Previous crystallographic data		
	Absorbing cation	(weight)	$E_0$ (eV)	(A-B)-O Distance (Å)	$\sigma$ (Å)	a (Å)	M-O Distance (Å)
$\text{Bi}_{12}[\text{Ge}]_2\text{O}_{20}$	Ge	2.50	{11,101}	1.77	0.08	10.1454	1.758
$\text{Bi}_{12}[\text{As}_{4/5}^{\text{+V}}\square_{1/5}]_2\text{O}_{20}$	As	2.08	{11,862}	1.66	0.08	10.197	unknown
$\text{Bi}_{12}[\text{Zn}_{1/3}^{\text{+II}}\text{As}_{2/3}^{\text{+V}}]_2\text{O}_{20}$	As	1.72	{11,859}	1.71	0.07	10.176	unknown
	Zn	0.75	{9,664}	1.83	0.09		
$\text{Bi}_{12}[\text{Zn}_{1/3}^{\text{+II}}\text{Mn}_{2/3}^{\text{+V}}]_2\text{O}_{20}$	Zn	0.75	{9,665}	1.90	0.06	10.183	unknown
$\text{Bi}_{12}[\text{Zn}_{1/3}^{\text{+II}}\text{Bi}_{2/3}^{\text{+V}}]_2\text{O}_{20}$	Zn	0.73	{9,665}	1.90	0.06	10.193	1.887
$\text{Bi}_{12}[\text{Ga}_{1/2}^{\text{+III}}\text{Mn}_{1/2}^{\text{+V}}]_2\text{O}_{20}$	Ga	1.21	{10,365}	1.87	0.08	10.165	unknown

## REFERENCES

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