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## Synthesis, crystal structure and vibrational spectra of $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$

A. Jrifi<sup>1</sup>, A. El Jazouli<sup>1,a)</sup>, J. P. Chaminade<sup>2</sup> and M. Couzi<sup>3</sup>

<sup>1</sup> Laboratoire de Chimie des Matériaux Solides, Faculté des Sciences Men M'Sik, Université Hassan II-Mohammedia, Avenue Idriss El Harti, Casablanca, Morocco.

<sup>2</sup> CNRS, Université Bordeaux, Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB), 87 avenue Albert Schweitzer, 33608 Pessac, France.

<sup>3</sup> Institut des Sciences Moléculaires, Université Bordeaux 1, CNRS UMR 5255, Batiment A12, 351 cours de la libération, 33405 Talence cedex, France.

### Abstract

$\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$  arsenate was prepared and structurally characterized by powder X ray diffraction and by Raman and infrared spectroscopies. Its structure, which belongs to the Nasicon-type family, was refined by the Rietveld method in the R-3 space group, from X-ray powder diffraction data. The hexagonal unit-cell parameters were determined to be  $a_h=8.965(2)$  Å,  $c_h=23.955(6)$  Å,  $V=1667.43(6)$  Å<sup>3</sup>, and  $Z=6$ . The structure is formed by an ionic three-dimensional network of  $\text{AsO}_4$  tetrahedra and  $\text{ZrO}_6$  octahedra linked by corners with  $\text{Sr}^{2+}$  ions occupying half of the M1 sites in an ordered manner. Raman and infrared spectra were recorded and assignments of the stretching and bending vibrations of the  $\text{AsO}_4^{3-}$  tetrahedra were made. The number of the peaks observed is in good agreement with that predicted by the factor group analysis of the R-3 space group.

**Key words:** nasicon, arsenate, crystal structure, powder diffraction, Raman, infrared

<sup>a)</sup> Author to whom correspondence should be addressed:

Email: eljazouli\_abdelaziz@yahoo.fr, Phone: +212 63296431; Fax: +212 22704675.

## I. INTRODUCTION

Nasicon-type materials have been extensively studied as solid electrolytes, ionic conductors, electrode materials, low thermal expansion ceramics, sensors, etc (Hagman and Kierkegaard, 1968; Hong, 1976; Goodenough *et al.*, 1976; Cherkaoui *et al.*, 1986; Delmas *et al.*, 1988; Rodrigo *et al.*, 1989 ; Bussereau *et al.*, 1992 ; Brian *et al.*, 2001; Aatiq *et al.*, 2001). Their structure, first described for  $\text{NaZr}_2(\text{PO}_4)_3$  (Hagman and Kierkegaard, 1968), consists of a three-dimensional (3D) network formed by  $\text{PO}_4$  and  $\text{ZrO}_6$  polyhedra linked by corners. The site occupied by sodium ions is an elongated trigonal antiprism formed by triangular faces of two  $\text{ZrO}_6$  octahedra along the c axis of the hexagonal cell. This site is usually called M(1). The framework also creates a large eight coordinated site referred to as M(2) site. The two sites may be completely empty as in  $\text{NbTi}(\text{PO}_4)_3$  (Masse *et al.*, 1972), partially occupied as in  $\text{NaZr}_2(\text{PO}_4)_3$  (Hagman and Kierkegaard, 1968) and  $\text{Na}_3\text{CaTi}(\text{PO}_4)_3$  (Krimi *et al.*, 2000), or fully occupied as in  $\text{Na}_5\text{Ti}(\text{PO}_4)_3$  (Krimi *et al.*, 1993). In contrast to the extensive studies of the Nasicon-type phosphates and silicates, only few investigations have been reported for the arsenates analogues. To our knowledge only X-ray powder diffraction patterns have been reported for  $\text{MTi}_2(\text{AsO}_4)_3$  (M=Li, Na, Ag, K),  $\text{M}_{0.5}\text{Ti}_2(\text{AsO}_4)_3$  (M=Mg, Ca, Sr) (Yaakoubi *et al.*, 1991) and  $\text{MeZr}_2(\text{As}_{1-x}\text{P}_x\text{O}_4)_3$  (Me=Na, K) (Mazza *et al.*, 1998). The structures of  $\text{KZr}_2(\text{AsO}_4)_3$  (El Brahimi and Durand, 1990) and  $\text{Na}_3\text{Sc}_2(\text{AsO}_4)_3$  (Harrison and Philips, 2001) have been determined from single-crystal X-ray diffraction data. Structural, electrochemical and vibrational studies of  $\text{A}_3\text{M}_2(\text{AsO}_4)_3$  (A=Li, Na; M=Al, Fe, In) have been reported (Masquelier *et al.*, 1995; Lii and Ye, 1997; Masquelier *et al.*, 1998; Khorari *et al.*, 1997; Winand *et al.*, 1990). The structure of  $\text{NaZr}_2(\text{AsO}_4)_3$  (Chakir *et al.*, 2003) was refined by the Rietveld method in the R-3c space group, from X-ray

powder diffraction data. The structure is formed by a three-dimensional network of  $\text{AsO}_4$  tetrahedra and  $\text{ZrO}_6$  octahedra linked by corners. Na atoms occupy totally the M1 sites. Raman and infrared spectra were recorded and assignments of the stretching and bending vibrations of the  $\text{AsO}_4^{3-}$  tetrahedra were made. Substitution of  $\text{Na}^+$  by divalent ions in  $\text{NaZr}_2(\text{AsO}_4)_3$  led to the synthesis of new arsenates  $\text{M}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$  ( $\text{M} = \text{Ca}, \text{Cd}, \text{Sr}, \dots$ ). The present paper reports the synthesis, crystal structure and vibrational spectra of  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ .

## II EXPERIMENTAL

Crystalline powder of  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$  was prepared from solutions of  $\text{SrCO}_3$  (or  $\text{SrCl}_2 \cdot \text{H}_2\text{O}$ ) (I),  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (II) and  $(\text{NH}_4)\text{H}_2\text{AsO}_4$  (III). Stoichiometric proportions of these reagents (amounts necessary to obtain 2 g of  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ ) were dissolved in 20 ml of dilute nitric acid solution (6M) for the carbonate and in 20 ml of distilled water for the other reagents. After addition of a solution of (III) to a solution of (I+II) at room temperature and heating at  $60^\circ\text{C}$  until complete evaporation, the white solid obtained was successively sintered at 100, 300, 500 and  $700^\circ\text{C}$ , for 24 hours with intermediate grinding, to obtain microcrystalline powder of  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ .

Powder X-ray diffraction data were collected on a Philips PW 3040 ( $\theta$ - $\theta$ ) diffractometer (40kV, 40mA). The structure of  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$  was refined with the Rietveld method using the Fullprof program (Rodriguez Carvajal, 1990). The experimental conditions are given in Table I. Raman spectra were recorded using a LabRam microspectrometer from Jobin Yvon coupled with an Argon ion laser. We used the 515.5 nm emission line for excitation with an incident power of 1 mW at the

sample. Infrared spectra were recorded on a Bruker IFS 113 v FTIR spectrometer as KBr pellets.

### III. RESULTS AND DISCUSSION

#### A. Structural determination

Figure 1 shows the powder X ray diffraction spectra of  $\text{NaZr}_2(\text{AsO}_4)_3$  (R-3c space group) (Chakir *et al.*, 2003) and  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ . The later shows extra peaks at low angles ( $10^\circ < 2\theta < 13^\circ$ ) that could not be indexed in the R-3c space group. The Miller indices of (003) and (101) are premitted in R-3 and R32 space groups. As the isostructural phosphate  $\text{Sr}_{0.5}\text{Zr}_2(\text{PO}_4)_3$  (Fischer *et al.*, 2004) crystallizes in the R-3 space group, the structure of  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$  was refined in this space group. The initial atomic coordinates used for the refinement were those of  $\text{Sr}_{0.5}\text{Zr}_2(\text{PO}_4)_3$  (Fischer *et al.*, 2004). The refinement, using 44 parameters, resulted in the conventional reliability factors  $R_p = 0.082$ ,  $R_{wp} = 0.106$ ,  $R_F = 0.036$  and  $R_B = 0.067$ . The formula calculated from the occupancy values of Sr and Zr is “ $\text{Sr}_{0.495}\text{Zr}_{1.985}(\text{AsO}_4)_3$ ”. The parameters of the equivalent hexagonal cell are:  $a_h = 8.965(2) \text{ \AA}$ ,  $c_h = 23.955(6) \text{ \AA}$ . The atomic positions and the most important interatomic distances and angles are given in Tables II and III, respectively. Figure 2 shows good agreement between the observed and calculated patterns.

The structure of  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$  (Figures 3 and 4) is similar to that of  $\text{Sr}_{0.5}\text{Zr}_2(\text{PO}_4)_3$  (Fischer *et al.*, 2004). It consists of a three-dimensional (3D) network of  $\text{AsO}_4$  tetrahedra and  $\text{ZrO}_6$  octahedra linked by corners. The divalent ion  $\text{Sr}^{2+}$  fully occupies the 3b site of the R-3 space group (the M1 site (6b) in the R-3c space group splits in two M1 sites in R-3 (i.e., (3a) and (3b)). The observed Sr–O distance (2.604  $\text{ \AA}$ )

is slightly larger than that calculated (2.54 Å) from the ionic radii of Sr<sup>2+</sup> and O<sup>2-</sup> (Shannon, 1976), indicating an ionic character of the Sr-O bond. The ordered occupation of the M1 site induces two types of ZrO<sub>6</sub> octahedra: Zr(1)O<sub>6</sub> octahedron which shares one face with the empty M1 site and Zr(2)O<sub>6</sub> octahedron which shares one face with the M1 site occupied by Sr. The observed Zr–O distances [Zr(1)-O(1): 3x2.072 Å; Zr(1)-O(3): 3x2.036 Å; Zr(2)-O(2): 3x2.030 Å; Zr(2)-O(4): 3x2.111 Å] are close to those calculated (2.08 Å) from the ionic radii of Zr<sup>4+</sup> and O<sup>2-</sup> (Shannon, 1976). The zirconium is off centered in the octahedron. Within the Zr(2)O<sub>6</sub> octahedron, the Zr(2) – O(4) distance (2.111 Å) is greater than the Zr(2) – O(2) distance (2.030 Å) due to the O-O repulsions in the empty M1 site, along c axis. Within the Zr(1)O<sub>6</sub> octahedron, the Zr(1)-O(3) distance (2.036 Å) is a little smaller than the Zr(1)-O(1) (2.072 Å) distance because of the attraction between the O(1) oxygen atoms and the Sr<sup>2+</sup> ions. The AsO<sub>4</sub> tetrahedron is a little distorted with As-O distances and O-As-O angles that vary between 1.648 Å and 1.691 Å, and between 103.1° and 111.8°, respectively. Bond valence sums ( $\sigma_i = \sum \exp[(R_{ij}-d_{ij})/b]$  with b=0.37 Å, d<sub>ij</sub>: distance between i and j atoms, R<sub>ij</sub> is relative to O<sup>2-</sup>: 1.928 Å for Zr<sup>4+</sup>, 2.118 Å for Sr<sup>2+</sup> and 1.767 Å for As<sup>5+</sup>), (Brown and Altermatt, 1985; Brese and O’Keeffe, 1991), are in good agreement with the formal oxidation state expected for Zr<sup>4+</sup> and As<sup>5+</sup> (Table II). The low value in the case of Sr<sup>2+</sup> may be due to the relatively high isotropic temperature factor of this ion.

The cell parameters of the arsenate Sr<sub>0.5</sub>Zr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> (a<sub>h</sub> = 8.965(2) Å, c<sub>h</sub> = 23.955(6) Å) are greater than those of the phosphate Sr<sub>0.5</sub>Zr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (a<sub>h</sub> = 8.6937(7) Å; c<sub>h</sub> = 23.299(1) Å) (Fischer *et al.*, 2004). This variation can be explained in the context of the Nasicon-type structure, which is built of (O<sub>3</sub>ZrO<sub>3</sub>M1O<sub>3</sub>ZrO<sub>3</sub>)<sub>∞</sub> infinite rows

connected by  $XO_4$  tetrahedra ( $X = As, P$ ) in three dimensions. As the ionic radii of  $As^{5+}$  ( $r_{As^{5+}} = 0.335 \text{ \AA}$ ) is larger than that of  $P^{5+}$  ( $r_{P^{5+}} = 0.17 \text{ \AA}$ ), the lengths of the O-O tetrahedron edges increase when  $X=As$ , and consequently the cell parameters of arsenate  $Sr_{0.5}Zr_2(AsO_4)_3$  are larger than those found for phosphate  $Sr_{0.5}Zr_2(PO_4)_3$ .

## B. Vibrational spectroscopy

Vibrational analysis for the isolated  $AsO_4^{3-}$  anion with point group  $Td$  leads to four modes:  $A_1(\nu_1)$ ,  $E(\nu_2)$ ,  $2F_2(\nu_3 \text{ and } \nu_4)$ . All of them are Raman active, whereas only  $\nu_3$  and  $\nu_4$  are infrared active. The  $\nu_1$  mode is the totally symmetric stretching vibrational mode of the  $AsO_4^{3-}$  anion,  $\nu_2$  is the doubly degenerate bending mode,  $\nu_3$  is the triply degenerate stretching mode and  $\nu_4$  is the triply degenerate bending mode. In the free  $AsO_4^{3-}$  anion, they are found at 837, 349, 878, and 463  $cm^{-1}$ , respectively (Nakamoto, 1986). In  $Sr_{0.5}Zr_2(AsO_4)_3$  (R-3 space group with  $Z=6$  formula units per primitive unit cell) the arsenic and oxygen atoms occupy general positions ( $C_1$  symmetry). Therefore, from classical factor-group analysis, we expect eight Raman-active modes,  $2\nu_1(A_g+E_g) + 6\nu_3(3A_g+3E_g)$ , and eight IR-active modes,  $2\nu_1(A_u+E_u) + 6\nu_3(3A_u+3E_u)$ , for the stretching vibrations and for the bending vibrations, we expect ten Raman-active modes,  $4\nu_2(2A_g+2E_g) + 6\nu_4(3A_g+3E_g)$ , and ten IR-active modes,  $4\nu_2(2A_{1u}+2E_u) + 6\nu_4(3A_u+3E_u)$ . The external modes consist of the translational vibrations of the  $Sr^{2+}$ ,  $Zr^{4+}$  and  $AsO_4^{3-}$  ions and the rotational vibrations of the  $AsO_4^{3-}$  ions.

Infrared and Raman spectra of  $Sr_{0.5}Zr_2(AsO_4)_3$  ( Figure 5) are similar to those obtained previously for  $NaZr_2(AsO_4)_3$  (Chakir *et al*, 2003). The high frequency parts (800-1200  $cm^{-1}$ ) of these spectra correspond to the stretching vibrations of the  $AsO_4^{3-}$  tetrahedra. The Raman bands observed in the 800-1100  $cm^{-1}$  region could be

decomposed into five peaks located at 824, 854, 862, 942 and 970  $\text{cm}^{-1}$ , whereas five infrared bands are observed at 832, 874, 900, 947, and 1011  $\text{cm}^{-1}$ . The distinction between the  $\nu_1$  and  $\nu_3$  modes is no longer possible since the  $\text{AsO}_4^{3-}$  anion site does not contain any symmetry element. These results are compatible with the factor group analysis which predicts eight Raman-active modes and eight IR-active modes; also, we notice that no overlap occurs between the IR and Raman active modes, as expected for the centrosymmetric space group R-3. The four Raman peaks observed between 300 and 600  $\text{cm}^{-1}$  (i.e., 365, 412, 463 and 480  $\text{cm}^{-1}$ ) are assigned to the different components of the  $\nu_2$  and  $\nu_4$  bending vibrations, whereas the predicted ones are ten. The peaks situated below 300  $\text{cm}^{-1}$  are attributed to the external modes; four Raman peaks are observed between 150 and 300  $\text{cm}^{-1}$  (i.e., 160, 181, 211 and 252.5  $\text{cm}^{-1}$ ).

#### **IV. CONCLUSIONS**

The arsenate  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$  has been synthesized and characterized by mean of X-ray diffraction, Raman and infrared spectroscopies. Its structure, which belongs to the Nasicon-type, has been refined in the R-3 space group. The structure is formed by a 3D network of  $\text{ZrO}_6$  octahedra and  $\text{AsO}_4$  tetrahedra linked by corners. The strontium ions occupy half of antiprismatic sites (i.e., the M1 sites) located between two  $\text{ZrO}_6$  octahedra. Assignments of internal modes of the  $\text{AsO}_4$  tetrahedra have been made. The number of peaks observed in Raman and infrared spectra is in good agreement with that predicted by the factor group analysis of the R-3 space group.

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## Figure Captions

Figure 1. Powder X-ray diffraction of  $\text{NaZr}_2(\text{AsO}_4)_3$  and  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ .

Figure 2. Observed (...), calculated (---) and difference X-ray profiles for  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ .

Figure 3. Structure of  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ .

Figure 4. Fragment of the structure of  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$  showing a row along c axis.

Figure 5. Raman and infrared spectra of  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ .

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## Table's legend

Table 1. Conditions and results of the Rietveld refinement of  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ .

Table 2. Atomic coordinates, isotropic temperature factors and bond valences for  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$

Table 3. Bond distances (Å) and angles (°) for  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ .

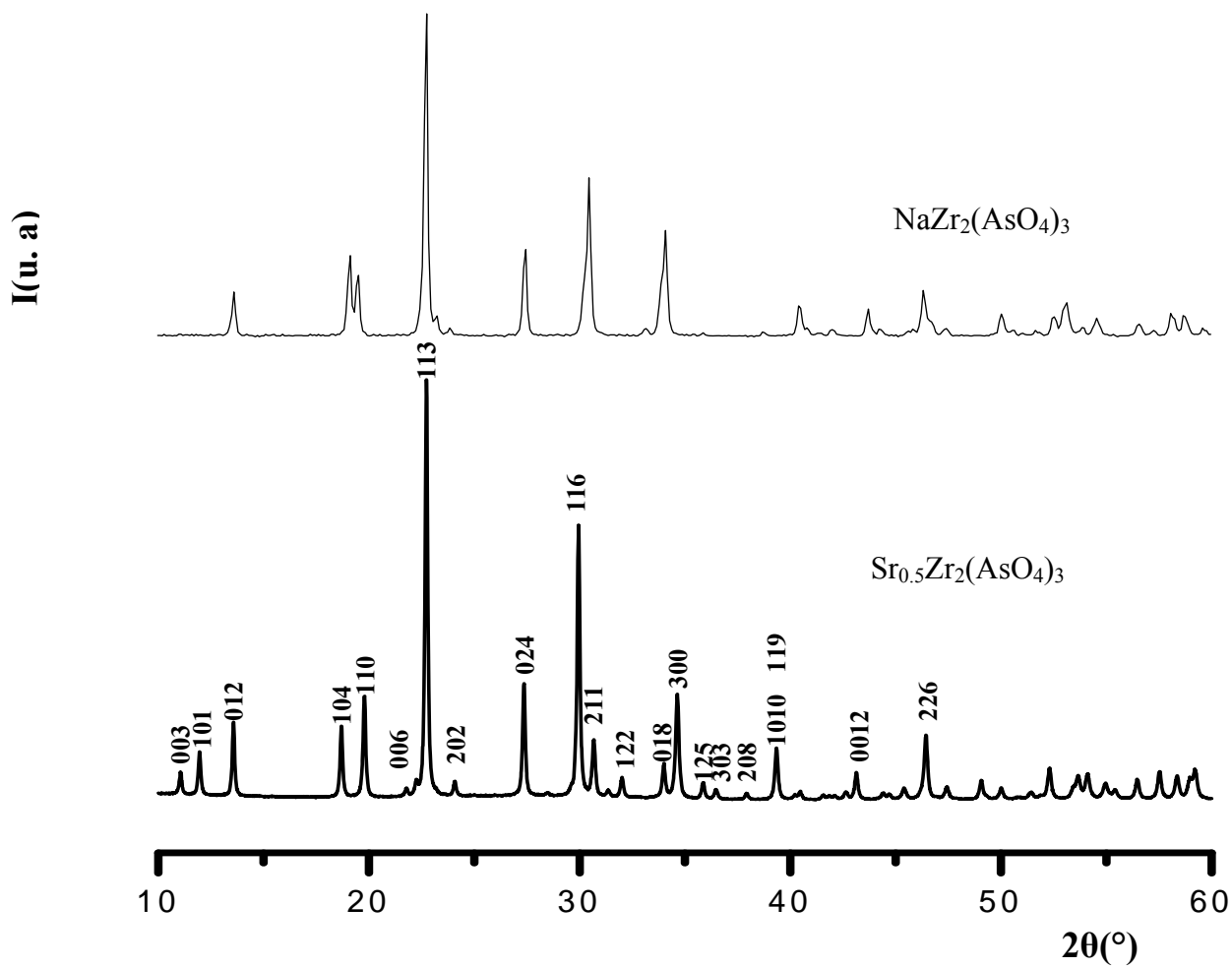


Figure 1. Powder X-ray diffraction of  $\text{NaZr}_2(\text{AsO}_4)_3$  and  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ .

### Sr<sub>0.5</sub>Zr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub>

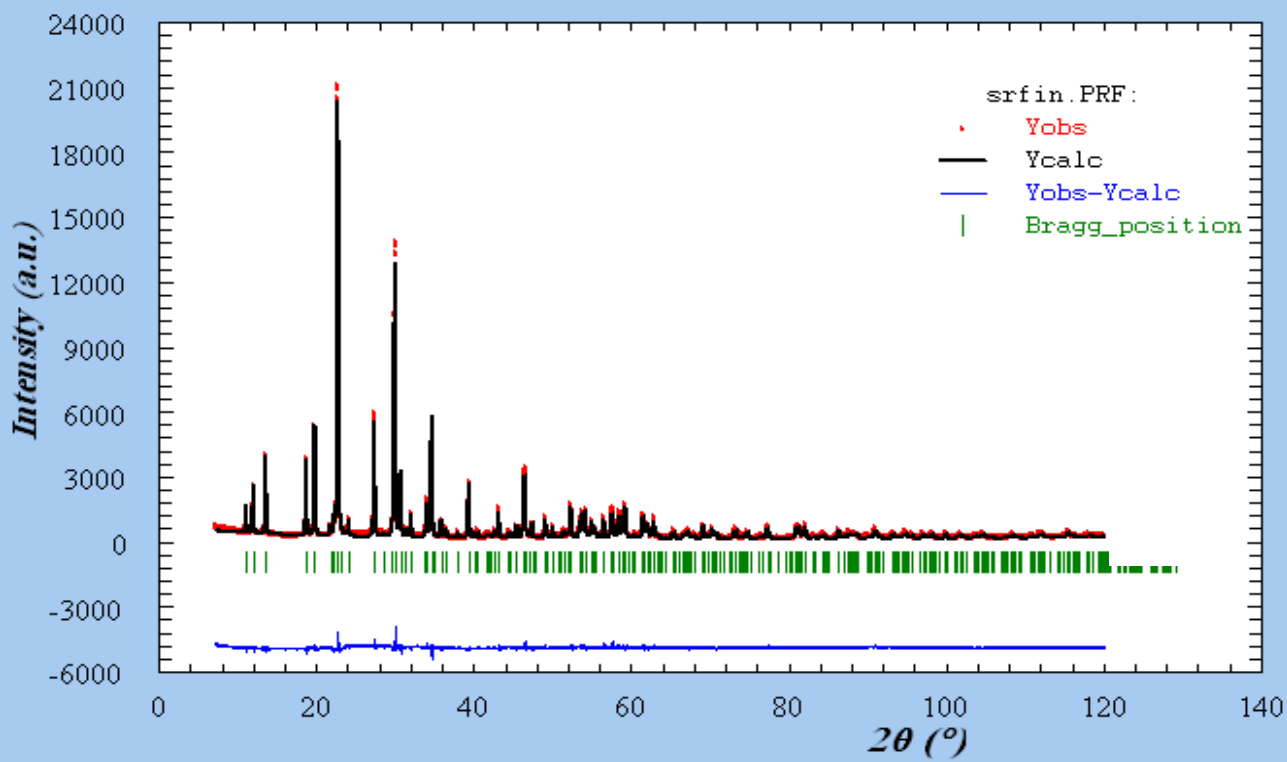


Figure 2. Observed (•), calculated (—) and difference X-ray profiles for Sr<sub>0.5</sub>Zr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub>.

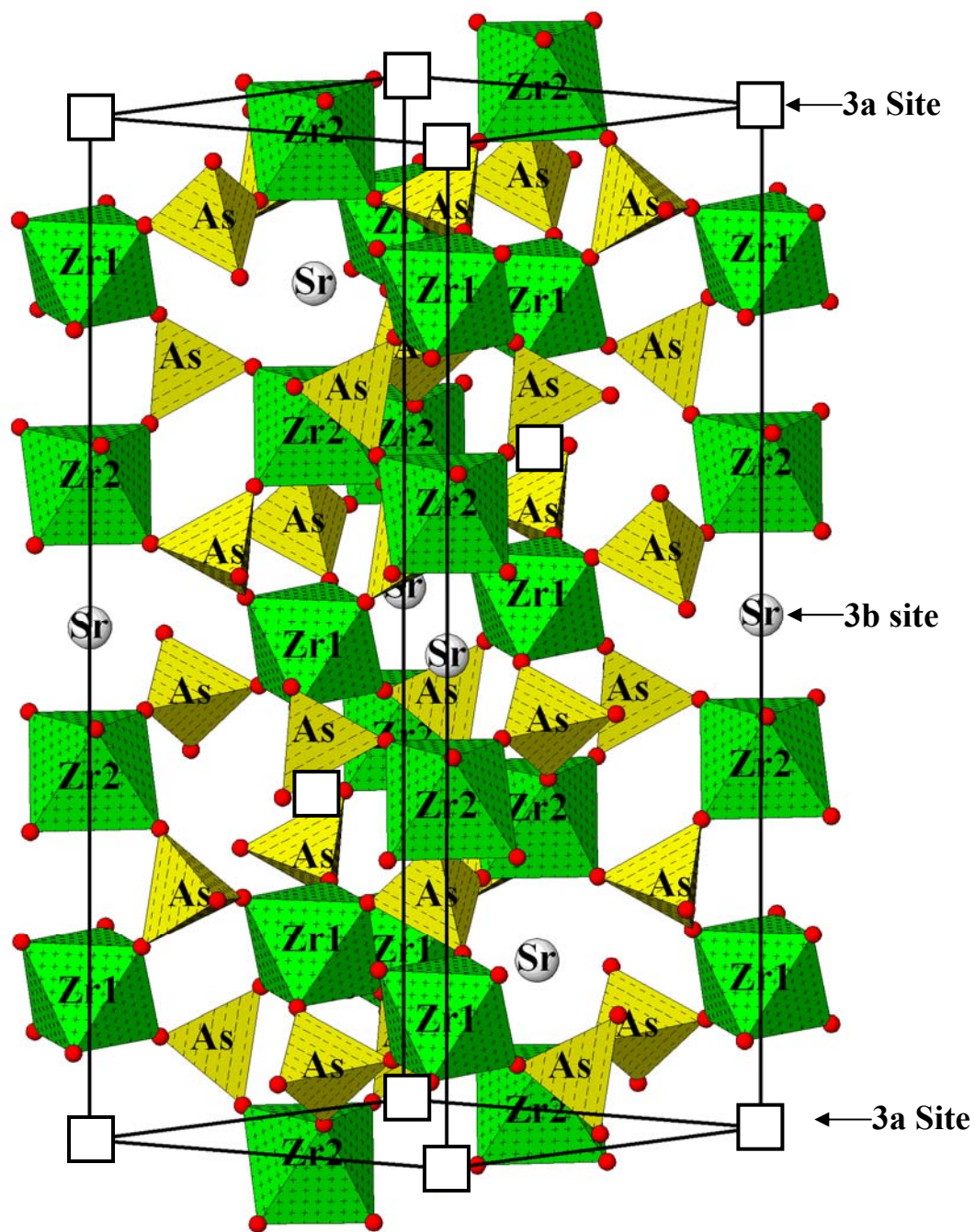


Figure 3. Structure of  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$  (Drawn by ATOMS, Dowty, E., 1997)



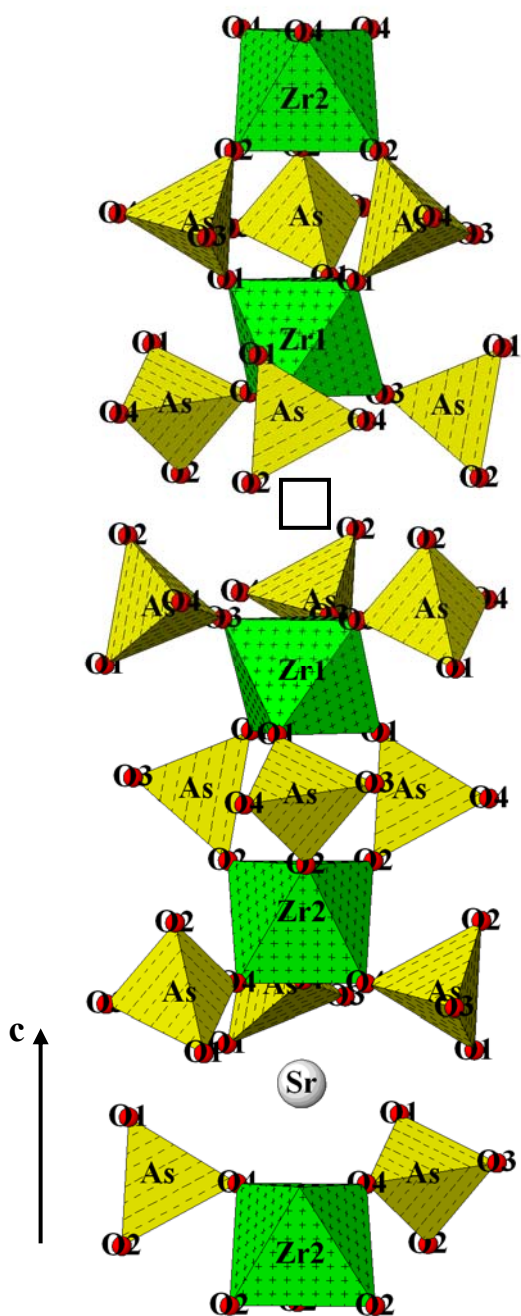


Figure 4. Fragment of the structure of  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$  showing a row along c axis.

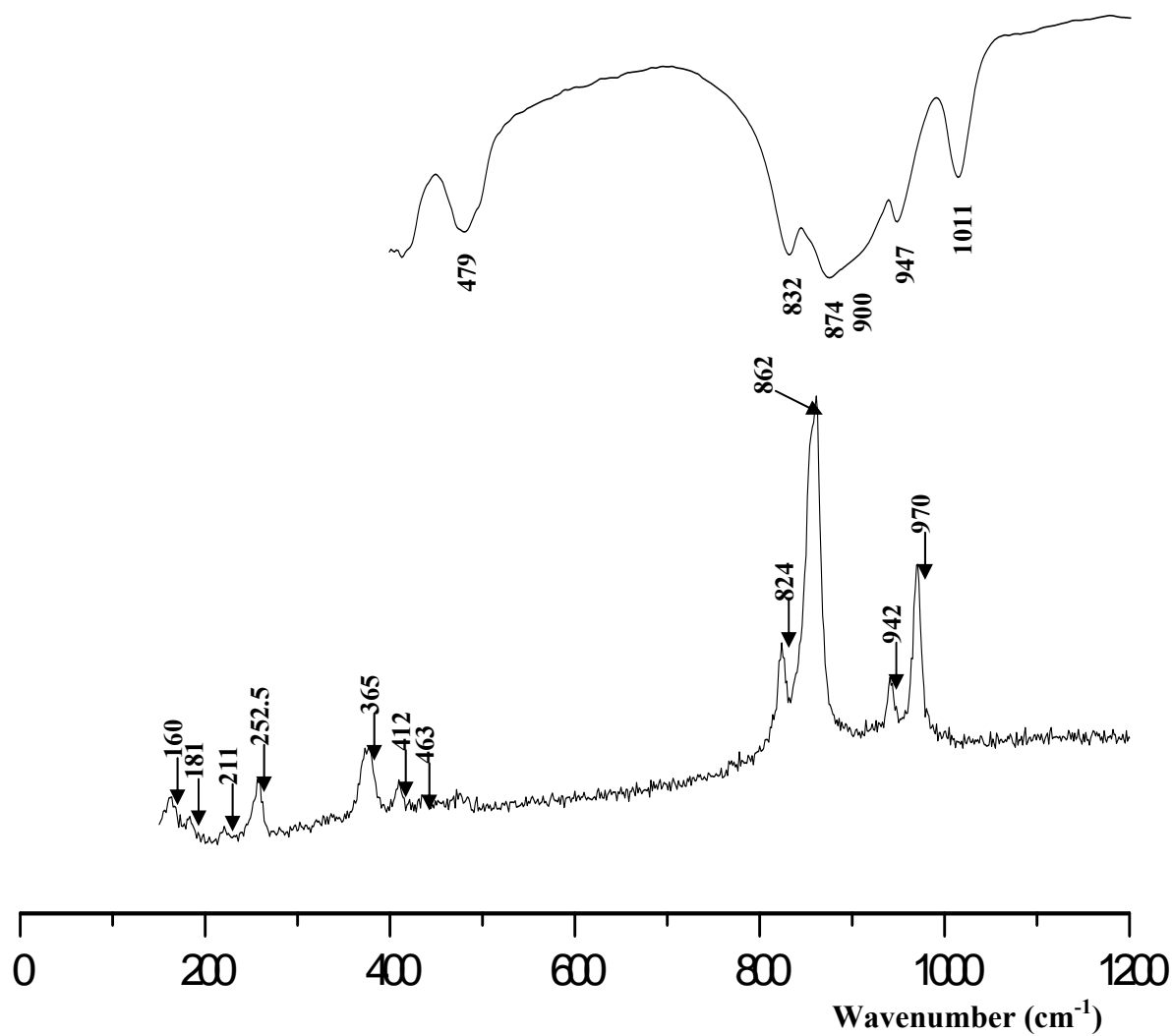


Figure 5. Raman and infrared spectra of  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ .

**TABLE I. Conditions and Rietveld refinement results of Sr<sub>0.5</sub>Zr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub>.**

Wavelength (Å)	$\lambda_{K\alpha 1}=1.5406$ ; $\lambda_{K\alpha 2}=1.5444$
Step width(°); counting time(s)	0.008; 30
Angular range(°)	7.008-119.992
Zero point	-0,023(1)
Pseudo-voigt function	PV= $\eta$ L+(1- $\eta$ )G; $\eta=0,790(6)$
Caglioti law parameters	U=0,121(5); V=-0,037(4); W=0,020(1)
Number of refined parameters	44
System; Space group, Z	Hexagonal; R-3; 6
a(Å); c(Å); V(Å <sup>3</sup> );	8.965(2) ; 23.955(6) ; 1667.43(6)
R <sub>F</sub> ; R <sub>B</sub> ; R <sub>P</sub> ; R <sub>WP</sub> ; $\chi^2$	0.036; 0.067; 0.082; 0.106; 5.34

**TABLE II. Atomic coordinates, isotropic temperature factors, occupancy and bond valence sums for  $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ .**

Atom	Wyckoff Site	x	y	z	$B_{\text{iso}}(\text{\AA}^2)$	Occupancy	Valence sums (Exp.) (Th.)	
Sr	3b	0	0	1/2	2.60(11)	1	1.62	2
Zr(1)	6c	0	0	0.1436(8)	0.51(9)	1	4.23	4
Zr(2)	6c	0	0	0.6474(8)	0.12(8)	1	4.11	4
As	18f	0.2809(2)	0.9941(3)	0.2475(7)	0.47(4)	1	5.13	5
O(1)	18f	0.1398(9)	0.9312(8)	0.1973(3)	0.3(2)	1	2.05	2
O(2)	18f	0.0116(8)	0.8102(8)	0.6903(3)	0.9(2)	1	2.00	2
O(3)	18f	0.2142(7)	0.1406(8)	0.0954(3)	2.6(3)	1	2.03	2
O(4)	18f	0.8198(7)	0.8293(8)	0.5883(2)	1.2(3)	1	2.10	2

**TABLE III. Bond distances (Å) and angles (°) for Sr<sub>0.5</sub>Zr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub>.**

Bond distances (Å)		Bond Angles (°)
Sr – O(4) x 6	2.604(7)	O(4) – Sr – O(4) : 61.8(3); 118.2(5); 180.0(5)
Zr(1) – O(1) x 3	2.072(8)	O(1) – Zr(1) – O(1) : 86.3(6); O(3) – Zr(1) – O(3) : 92.9(6)
Zr(1) – O(3) x 3	2.036(8)	O(1) – Zr(1) – O(3) : 90.6(6); 90.1(6) ; 175.3(7)
Zr(2) – O(2) x 3	2.030(7)	O(2) – Zr(2) – O(2) : 95.9(6); O(4) – Zr(2) – O(4) : 78.6(5)
Zr(2) – O(4) x 3	2.111(7)	O(2) – Zr(2) – O(4) : 90.3(6); 94.0(6); 167.7(8)
As – O(1)	1.648(8)	O(1) – As – O(2): 111.8(8); O(1) – As – O(3): 103.1(7)
As – O(2)	1.685(10)	O(1) – As – O(4): 107.3(9); O(2) – As – O(3): 105.4(8)
As – O(3)	1.672(9)	O(2) – As – O(4): 107.4(10); O(3) – As – O(4): 111.8(10)
As – O(4)	1.691(11)	