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#### Synthesis, crystal structure and vibrational spectra of Sr<sub>0.5</sub>Zr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub>

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#### Abstract

 $Sr_{0.5}Zr_2(AsO_4)_3$  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 AsO<sub>4</sub> tetrahedra and ZrO<sub>6</sub> octahedra linked by corners with Sr<sup>2+</sup> 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 AsO<sub>4</sub><sup>3-</sup> 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:

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#### **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 NaZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (Hagman and Kierkegaard, 1968), consists of a three-dimensional (3D) network formed by PO<sub>4</sub> and  $ZrO_6$  polyhedra linked by corners. The site occupied by sodium ions is an elongated trigonal antiprism formed by triangular faces of two ZrO<sub>6</sub> 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 NbTi(PO<sub>4</sub>)<sub>3</sub> (Masse et al., 1972), partially occupied as in NaZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (Hagman and Kierkegaard, 1968) and Na<sub>3</sub>CaTi(PO<sub>4</sub>)<sub>3</sub> (Krimi *et al.*, 2000), or fully occupied as in Na<sub>5</sub>Ti(PO<sub>4</sub>)<sub>3</sub> (Krimi et al., 1993). In contrast to the extensive studies of the Nasicontype 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 MTi<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> (M=Li, Na, Ag, K), M<sub>0.5</sub>Ti<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> (M=Mg, Ca, Sr) (Yaakoubi et al., 1991) and MeZr<sub>2</sub>(As<sub>1-x</sub>P<sub>x</sub>O<sub>4</sub>)<sub>3</sub> (Me=Na, K) (Mazza et al., 1998). The structures of KZr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> (El Brahimi and Durand, 1990) and Na<sub>3</sub>Sc<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> (Harrison and Philips, 2001) have been determined from single-crystal X-ray diffraction data. Structural, electrochemical and vibrational studies of A<sub>3</sub>M<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> (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 NaZr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> (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 AsO<sub>4</sub> tetrahedra and ZrO<sub>6</sub> 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 AsO<sub>4</sub><sup>3-</sup> tetrahedra were made. Substitution of Na<sup>+</sup> by divalent ions in NaZr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> led to the synthesis of new arsenates M<sub>0.5</sub>Zr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> (M = Ca, Cd, Sr,...). The present paper reports the synthesis, crystal structure and vibrational spectra of Sr<sub>0.5</sub>Zr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub>.

#### **II EXPERMENTAL**

Crystalline powder of  $Sr_{0.5}Zr_2(AsO_4)_3$  was prepared from solutions of  $SrCO_3$  (or  $SrCl_2.H_2O$ ) (I),  $ZrOCl_2.8H_2O$  (II) and  $(NH_4)H_2AsO_4$  (III). Stoichiometric proportions of these reagents (amounts necessary to obtain 2 g of  $Sr_{0.5}Zr_2(AsO_4)_3$ ) 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°C until complete evaporation, the white solid obtained was successively sintered at 100, 300, 500 and 700°C, for 24 hours with intermediate grinding, to obtain microcrystalline powder of  $Sr_{0.5}Zr_2(AsO_4)_3$ .

Powder X-ray diffraction data were collected on a Philips PW 3040 ( $\theta$ - $\theta$ ) diffractometer (40kV, 40mA). The structure of Sr<sub>0.5</sub>Zr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> 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 NaZr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> (R-3c space group) (Chakir *et al.*, 2003) and Sr<sub>0.5</sub>Zr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub>. 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 premited in R-3 and R32 space groups. As the isostructural phosphate Sr<sub>0.5</sub>Zr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (Fischer *et al.*, 2004) crystallizes in the R-3 space group, the structure of Sr<sub>0.5</sub>Zr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> was refined in this space group. The initial atomic coordinates used for the refinement were those of Sr<sub>0.5</sub>Zr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (Fischer *et al.*, 2004). The refinement, using 44 parameters, resulted in the conventional reliability factors Rp = 0.082, Rwp = 0.106, R<sub>F</sub> = 0.036 and R<sub>B</sub> = 0.067. The formula calculated from the occupancy values of Sr and Zr is "Sr<sub>0.495</sub>Zr<sub>1.985</sub>(AsO<sub>4</sub>)<sub>3</sub>". The parameters of the equivalent hexagonal cell are:  $a_h = 8.965(2)$  Å,  $c_h = 23.955(6)$  Å. 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  $Sr_{0.5}Zr_2(AsO_4)_3$  (Figures 3 and 4) is similar to that of  $Sr_{0.5}Zr_2(PO_4)_3$  (Fischer *et al.*, 2004). It consists of a three-dimensional (3D) network of AsO<sub>4</sub> tetrahedra and ZrO<sub>6</sub> octahedra linked by corners. The divalent ion  $Sr^{2+}$  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 Å)

is slightly larger than that calculated (2.54 Å) from the ionic radii of  $Sr^{2+}$  and  $O^{2-}$ (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  $Zr(2)O_6$  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  $Zr^{4+}$  and  $O^{2-}$  (Shannon, 1976). The zirconium is off centered in the octahedron. Within the  $Zr(2)O_6$  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  $Zr(1)O_6$ 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 ( $\sigma_i = \sum \exp[(R_{ii}-d_{ii})/b]$  with b=0.37 Å,  $d_{ii}$ : distance between i and j atoms,  $R_{ij}$  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  $Zr^{4+}$  and  $As^{5+}$  (Table II). The low value in the case of  $Sr^{2+}$  may be due to the relatively high isotropic temperature factor of this ion.

The cell parameters of the arsenate  $Sr_{0.5}Zr_2(AsO_4)_3$  ( $a_h = 8.965(2)$  Å,  $c_h = 23.955(6)$  Å) are greater than those of the phosphate  $Sr_{0.5}Zr_2(PO_4)_3$  ( $a_h = 8.6937(7)$  Å;  $c_h = 23.299(1)$  Å) (Fischer *et al.*, 2004). This variation can be explained in the context of the Nasicon-type structure, which is built of  $(O_3ZrO_3M1O_3ZrO_3)_{\infty}$  infinite rows

connected by XO<sub>4</sub> tetrahedra (X = As, P) in three dimensions. As the ionic radii of As<sup>5+</sup> ( $r_{As5+} = 0.335$  Å) is larger than that of P<sup>5+</sup> ( $r_{P5+} = 0.17$  Å), the lengths of the O-O tetrahedron edges increase when X=As, and consequently the cell parameters of arsenate Sr<sub>0.5</sub>Zr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> are larger than those found for phosphate Sr<sub>0.5</sub>Zr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>.

#### B. Vibrational spectroscopy

Vibrational analysis for the isolated  $AsO_4^{3-}$  anion with point group Td leads to four modes:  $A_1(v_1)$ ,  $E(v_2)$ ,  $2F_2(v_3 \text{ and } v_4)$ . All of them are Raman active, whereas only  $v_3$ and  $v_4$  are infrared active. The  $v_1$  mode is the totally symmetric stretching vibrational mode of the  $AsO_4^{3-}$  anion,  $v_2$  is the doubly degenerate bending mode,  $v_3$  is the triply degenerate stretching mode and  $v_4$  is the triply degenerate bending mode. In the free  $AsO_4^{3-}$  anion, they are found at 837, 349, 878, and 463 cm<sup>-1</sup>, 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,  $2v_1(A_g+E_g)$ +  $6v_3(3A_g+3E_g)$ , and eight IR-active modes,  $2v_1(A_u+E_u) + 6v_3(3A_u+3E_u)$ , for the stretching vibrations and for the bending vibrations, we expect ten Raman-active modes,  $4v_2(2A_g+2E_g) + 6v_4(3A_g+3E_g)$ , and ten IR-active modes,  $4v_2(2A_{1u}+2E_u) + 6v_4(3A_u+3E_u)$ . 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<sup>-1</sup>) of these spectra correspond to the stretching vibrations of the  $AsO_4^{3-1}$  tetrahedra. The Raman bands observed in the 800-1100 cm<sup>-1</sup> region could be

decomposed into five peaks located at 824, 854, 862, 942 and 970 cm<sup>-1</sup>, whereas five infrared bands are observed at 832, 874, 900, 947, and 1011 cm<sup>-1</sup>. The distinction between the  $v_1$  and  $v_3$  modes is no longer possible since the AsO<sub>4</sub><sup>3-</sup> 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 cm<sup>-1</sup> (i.e., 365, 412, 463 and 480 cm<sup>-1</sup>) are assigned to the different components of the  $v_2$  and  $v_4$  bending vibrations, whereas the predicted ones are ten. The peaks situated below 300 cm<sup>-1</sup> are attributed to the external modes; four Raman peaks are observed between 150 and 300 cm<sup>-1</sup> (i.e., 160, 181, 211 and 252.5 cm<sup>-1</sup>).

#### **IV. CONCLUSIONS**

The arsenate  $Sr_{0.5}Zr_2(AsO_4)_3$  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 ZrO<sub>6</sub> octahedra and AsO<sub>4</sub> tetrahedra linked by corners. The strontium ions occupy half of antiprismatic sites (i.e., the M1 sites) located between two ZrO<sub>6</sub> octahedra. Assignments of internal modes of the AsO<sub>4</sub> 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 NaZr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> and 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

 $Sr_{0.5}Zr_2(AsO_4)_3$ .

Figure 3. Structure of  $Sr_{0.5}Zr_2(AsO_4)_3$ .

Figure 4. Fragment of the structure of  $Sr_{0.5}Zr_2(AsO_4)_3$  showing a row along c axis.

Figure 5. Raman and infrared spectra of Sr<sub>0.5</sub>Zr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub>.

#### Table's legend

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Table 1. Conditions and results of the Rietveld refinement of  $Sr_{0.5}Zr_2(AsO_4)_3$ .

Table 2. Atomic coordinates, isotropic temperature factors and bond valences for

 $Sr_{0.5}Zr_2(AsO_4)_3$ 

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



Figure 1. Powder X-ray diffraction of NaZr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> and Sr<sub>0.5</sub>Zr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub>.

Sr0.5Zr2(AsO4)3



Figure 2. Observed (...), calculated (---) and difference X-ray profiles for  $Sr_{0.5}Zr_2(AsO_4)_3$ .



Figure 3. Structure of Sr<sub>0.5</sub>Zr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> (Drawn by ATOMS, Dowty, E., 1997)



Figure 4. Fragment of the structure of  $Sr_{0.5}Zr_2(AsO_4)_3$  showing a row along c axis.



Figure 5. Raman and infrared spectra of Sr<sub>0.5</sub>Zr<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub>.

	TABLE I.	Conditions	and Rietveld	refinement	results o	f Sr <sub>0.5</sub> Zr <sub>2</sub> (	(AsO <sub>4</sub> ) <sub>3</sub> .
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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 Caglioti law parameters	PV=ηL+(1-η)G; η=0,790(6) U=0,121(5); V=-0,037(4); W=0,020(1)
Number of refined parameters	44
System; Space group, Z a(Å); c(Å); V(Å <sup>3</sup> );	Hexagonal; R-3; 6 8.965(2) ; 23.955(6) ; 1667.43(6)
$R_F; R_B; R_P; R_{WP}; \chi^2$	0.036; 0.067; 0.082; 0.106; 5.34

Atom	Wycko	ff x	У	Z	$B_{iso}(Å^2)$	Occupancy	Valence	sums
	Site		-				(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 II. Atomic coordinates, isotropic temperature factors, occupancy and bond valence sums for  $Sr_{0.5}Zr_2(AsO_4)_{3.}$ 

Bond distances (Å)		Bond Angles (°)		
$Sr - O(4) \ge 6$	2.604(7)	O(4) – Sr – O(4) : 61.8(3); 118.2(5); 180.0(5)		
$Zr(1) - O(1) \ge 3$	2.072(8)	O(1) - Zr(1) - O(1) : 86.3(6); O(3) - Zr(1) - O(3) : 92.9(6)		
$Zr(1) - O(3) \ge 3$	2.036(8)	O(1) – Zr(1) – O(3) : 90.6(6); 90.1(6) ; 175.3(7)		
$Zr(2) - O(2) \ge 3$	2.030(7)	O(2) - Zr(2) - O(2) : 95.9(6); O(4) - Zr(2) - O(4) : 78.6(5)		
$Zr(2) - O(4) \ge 3$	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)			

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