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

A. Jriifi¹, A. El Jazouli^{1,a)}, J. P. Chaminade² and M. Couzi³

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

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

³ 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, $V=1667.43(6)$ Å³, and $Z=6$. The structure is formed by an ionic three-dimensional network of AsO_4 tetrahedra and ZrO_6 octahedra linked by corners with 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 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

^{a)} 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 PO_4 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_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 AsO_4 tetrahedra and 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 AsO_4^{3-} tetrahedra were made. Substitution of 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 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°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 $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$.

Powder X-ray diffraction data were collected on a Philips PW 3040 (θ - θ) 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 AsO_4 tetrahedra and ZrO_6 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 ($2.604 \text{ \AA}$)

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_6 octahedra: Zr(1)O_6 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^{2+} ions. The AsO_4 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_{ij} : distance between i and j atoms, R_{ij} is relative to O^{2-} : 1.928 Å for Zr^{4+} , 2.118 Å for Sr^{2+} and 1.767 Å for As^{5+}), (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 $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ ($a_h = 8.965(2)$ Å, $c_h = 23.955(6)$ Å) are greater than those of the phosphate $\text{Sr}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ ($a_h = 8.6937(7)$ 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 $(\text{O}_3\text{ZrO}_3\text{M1O}_3\text{ZrO}_3)_\infty$ infinite rows

connected by XO_4 tetrahedra ($\text{X} = \text{As}, \text{P}$) in three dimensions. As the ionic radii of As^{5+} ($r_{\text{As}^{5+}} = 0.335 \text{ \AA}$) is larger than that of P^{5+} ($r_{\text{P}^{5+}} = 0.17 \text{ \AA}$), the lengths of the O-O tetrahedron edges increase when $\text{X}=\text{As}$, and consequently the cell parameters of arsenate $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ are larger than those found for phosphate $\text{Sr}_{0.5}\text{Zr}_2(\text{PO}_4)_3$.

B. Vibrational spectroscopy

Vibrational analysis for the isolated AsO_4^{3-} anion with point group Td leads to four modes: $\text{A}_1(\nu_1)$, $\text{E}(\nu_2)$, $2\text{F}_2(\nu_3 \text{ and } \nu_4)$. All of them are Raman active, whereas only ν_3 and ν_4 are infrared active. The ν_1 mode is the totally symmetric stretching vibrational mode of the AsO_4^{3-} anion, ν_2 is the doubly degenerate bending mode, ν_3 is the triply degenerate stretching mode and ν_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 $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ (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, $2\nu_1(\text{A}_g+\text{E}_g) + 6\nu_3(3\text{A}_g+3\text{E}_g)$, and eight IR-active modes, $2\nu_1(\text{A}_u+\text{E}_u) + 6\nu_3(3\text{A}_u+3\text{E}_u)$, for the stretching vibrations and for the bending vibrations, we expect ten Raman-active modes, $4\nu_2(2\text{A}_g+2\text{E}_g) + 6\nu_4(3\text{A}_g+3\text{E}_g)$, and ten IR-active modes, $4\nu_2(2\text{A}_{1u}+2\text{E}_u) + 6\nu_4(3\text{A}_u+3\text{E}_u)$. 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 $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ (Figure 5) are similar to those obtained previously for $\text{NaZr}_2(\text{AsO}_4)_3$ (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 cm^{-1} , whereas five infrared bands are observed at 832, 874, 900, 947, and 1011 cm^{-1} . The distinction between the ν_1 and ν_3 modes is no longer possible since the 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 cm^{-1} (i.e., 365, 412, 463 and 480 cm^{-1}) are assigned to the different components of the ν_2 and ν_4 bending vibrations, whereas the predicted ones are ten. The peaks situated below 300 cm^{-1} are attributed to the external modes; four Raman peaks are observed between 150 and 300 cm^{-1} (i.e., 160, 181, 211 and 252.5 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 ZrO_6 octahedra and AsO_4 tetrahedra linked by corners. The strontium ions occupy half of antiprismatic sites (i.e., the M1 sites) located between two ZrO_6 octahedra. Assignments of internal modes of the 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.

ACKNOWLEDEMENT

The authors would like to thank P. Graveriau (ICMCB) for fruitful discussions.

REFERENCES

- Aatiq, A., Delmas, C., and El Jazouli, A., **(2001)**. "Structural and Electrochemical Study of $\text{Li}_{0.5}\text{Mn}_{0.5}\text{Ti}_{1.5}\text{Cr}_{0.5}(\text{PO}_4)_3$," J. Solid State Chem. **158**(2), 169-174.
- Breese, N.E., and O'Keeffe, M. **(1991)**. "Band valence parameters for solids," Acta Crystallogr. B **47**, 192–197.
- Brian, L., Cushing, B.L., and Goodenough, J.B., **(2001)** " $\text{Li}_2\text{NaV}_2(\text{PO}_4)_3$: A 3.7 V Lithium-Insertion Cathode with the Rhombohedral NASICON Structure," J. Solid State Chem. **162**(2), 176-181.
- Brown, I.D., and Altermatt, D. **(1985)**. "Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database," Acta Crystallogr. B **41**(4), 244–247.
- Bussereau, I., Olazcuaga, R., Dance, J.M., Delmas, C., Le Flem, G., and El Jazouli, A., **(1992)**. "Lithium intercalation in $\text{Cu}^{\text{II}}_{0.5}\text{Ti}_2(\text{PO}_4)_3$, J. Alloys and Compounds, **188**, 110-112.
- Caglioti, G., Paoletti, A., and Ricci, F. P., **(1958)**. "Choice of collimators for a crystal spectrometer for neutron diffraction," Nucl. Instrum. **3**, 223–228.
- Chakir, M., El Jazouli, A., and de Waal, D. **(2003)**." Structural and vibrational studies of $\text{NaZr}_2(\text{AsO}_4)_3$," Mat. Res. Bull. **38**(13), 1773-1779.
- Cherkaoui, F., Viala, J.C., Delmas, C., and Hagenmuller, P., **(1986)**. "Crystal chemistry and ionic conductivity of a new Nasicon-related solid solution $\text{Na}_{1+x}\text{Zr}_{2-x/2}\text{Mg}_{x/2}(\text{PO}_4)_3$," Solid State Ionics **21**(4), 333-337.

Delmas, C., Nadiri, A., and Soubeyroux, J.L., **(1988)**. "The nasicon-type titanium phosphates $\text{ATi}_2(\text{PO}_4)_3$ ($\text{A}=\text{Li}, \text{Na}$) as electrode material," *Solid State Ionics* **28-30** (part1), 419-423.

Dowty, E. **(1997)** ATOMS 3.2. A Computer Program for Displaying Atomic Structures, Kingsport, TN 37663.

El Brahimi, M., and Durand J., **(1990)**. "Structure Cristalline de l'Arseniate Double de Potassium et de Zirconium: $\text{KZr}_2(\text{AsO}_4)_3$," *Z. Anorg. Allg. Chem.* **584**(1), 178-184.

Fischer, W., and Singheiser, L., Basu, D., and Dasgupta, A., **(2004)**. "Crystal structure of $\text{Ca}_{1-x}\text{Sr}_x\text{Zr}_4(\text{PO}_4)_6$, ($0 \leq x \leq 1$)" *Powder Diffraction* (2004), 19(2), 153-156.

Goodenough, J.B., Hong, H. Y. P., and Kafalas, J.A., (1976) "Fast Na^+ -ion transport in skeleton structures " *Mater. Res. Bull.* **11**(2), 203-220.

Hagman, L. O., and Kierkegaard, P. **(1968)**. "The crystal structure of $\text{NaMe}^{\text{IV}}(\text{PO}_4)_3$, $\text{Me}^{\text{IV}} = \text{Ge}, \text{Ti}, \text{Zr}$," *Acta Chem. Scand.* **22**, 1822-1832.

Harrison, W.T.A, and Philips, M.L.F. (2001)." Sodium scandium arsenate, $\text{Na}_3\text{Sc}_2(\text{AsO}_4)_3$," *Acta Cryst. C* **57**, 2-3.

Hong, H. Y. -P., **(1976)** "Crystal structures and crystal chemistry in the system $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ " *Mater. Res. Bull.* **11**(2), 173-182.

Khorari, S., Rulmont, A., and Tarte, P., **(1997)**. "Alluaudite-Like Structure of the Arsenate $\text{Na}_3\text{In}_2(\text{AsO}_4)_3$," *J. Solid State Chem.* **134**(1), 31-37.

Krimi, S., Mansouri, I., El Jazouli, A., Chaminade, J.P., Gravereau, P., and Le Flem, G., **(1993)**. "The Structure of $\text{Na}_5\text{Ti}(\text{PO}_4)_3$," *J. Solid State Chem.* **105**(2), 561-566.

Krimi, S., El Jazouli, A., Lachgar, A., Rabardel, L., de Waal, D., and Ramos-Barrado, J.R., **(2000)**. "Glass-crystal transformation of $\text{Na}_{5-2x}\text{Ca}_x\text{Ti}(\text{PO}_4)_3$ phosphates," *Ann. Chim. Sc. Mat.* **25** (Suppl.), S75-S78.

- Lii, K. and Ye, H., J., **(1997)**. “Hydrothermal Synthesis and Structures of $\text{Na}_3\text{In}_2(\text{PO}_4)_3$ and $\text{Na}_3\text{In}_2(\text{AsO}_4)_3$: Synthetic Modifications of the Mineral Alluaudite,” J. Solid State Chem. **131**(1), 131-137.
- Masquelier, C., d’Yvoire, F., and Collin, G., **(1995)**. “Crystal Structure of $\text{Na}_7\text{Fe}_4(\text{AsO}_4)_6$ and $\alpha\text{-Na}_3\text{Al}_2(\text{AsO}_4)_3$, Two Sodium Ion Conductors Structurally Related to $\text{II-Na}_3\text{Fe}_2(\text{AsO}_4)_3$,” J. Solid State Chem. **118**(1), 33-42.
- Masquelier, C., Padhi, A.K., Nanjundaswamy, K.S., and Goodenough, J.B., **(1998)**. “New Cathode Materials for Rechargeable Lithium Batteries: The 3-D Framework Structures $\text{Li}_3\text{Fe}_2(\text{XO}_4)_3$ ($\text{X}=\text{P}, \text{As}$),” J. Solid State Chem. **135**(2), 228-234.
- Masse, R., Durif, A., Guitel, J.C, and Tordjman, I. **(1972)**, “Crystal structure of the lacunary monophosphate potassium titanium triphosphate. Lacunary monophosphates niobium germanium triphosphate and $\text{M}^{5+}\text{Ti}(\text{PO}_4)_3$ where $\text{M}^{5+} =$ antimony, niobium, tantalum.” Bull. Soc. Mineral. Crystallogr. **95**, 47-55
- Mazza, D., Lucco-Borlera, M., and Ronchetti, S., **(1998)**. “Powder diffraction study of arsenic-substituted nasicon structures $\text{MeZr}_2\text{As}_{(3-x)}\text{P}_x\text{O}_{12}$ ($\text{Me}=\text{Na}^+, \text{K}^+$),” Powder Diffraction **13**(4), 227-231.
- Nakamoto, K., **(1986)**. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", Fourth Edition, John Wiley & Sons Ed.
- Rodrigo, J.L., Carrasco, P., and Alamo, J. **(1989)**. “Thermal expansion of $\text{NaTi}_2(\text{PO}_4)_3$ studied by Rietveld method from X-ray diffraction data”. Mater. Res. Bull. **24**(5), 611-618.
- Rodriguez Carvajal, J., **(1990)**. “Fullprof: a program for Rietveld refinement and pattern matching analysis,” Collected Abstract of Powder Diffraction Meeting, vol. **127**. Toulouse, France.

Shannon, R. D. (1976). "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Cryst.* A32, 751-767.

Winand, J. M., Rulmont, A., and Tarte, P., (1990). "Synthèse et étude de nouveaux arsénates $(M^I)_3(N^{III})_2(AsO_4)_3$ et de solutions solides $(M^I)_3(N^{III})_2(AsO_4)_x(PO_4)_{3-x}$ ($M = Li, Na; N = Fe, Sc, In, Cr$)," *J. Solid State Chem.* **87**(1), 83-94.

Yaakoubi, A., Jouini, T., and Jouini, N., (1991) "Preparation and radiocrystallographic data of two new families of titanium arsenates $A^I Ti_2(AsO_4)_3$ ($A =$ lithium, sodium, silver, potassium) and $A^{II}_{0.5} Ti_2(AsO_4)_3$ ($A =$ magnesium, calcium, strontium). *C. R. Acad. Sci. Paris* **312**(5), 451-453.

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

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

.

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

Figure 2. Observed (...), calculated (---) and difference X-ray profiles for Sr_{0.5}Zr₂(AsO₄)₃.

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

Wavelength (Å)	$\lambda_{\text{K}\alpha 1}=1.5406$; $\lambda_{\text{K}\alpha 2}=1.5444$
Step width(°); counting time(s)	0.008; 30
Angular range(°)	7.008-119.992
Zero point	-0,023(1)
Pseudo-voigt function	PV= η L+(1- η)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 ³);	8.965(2) ; 23.955(6) ; 1667.43(6)
R _F ; R _B ; R _P ; R _{WP} ; χ^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 $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$.

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)	