Research Article

Synthesis, Crystal Structure, and Electrical Properties of a New Molybdylarsenate $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$

Hamadi Hamza, Mohamed Faouzi Zid, and Ahmed Driss

Laboratoire de Matériaux et Cristallochimie, Faculté des Sciences de Tunis, Université de Tunis El Manar, Manar II, 2092 Tunis, Tunisia

Correspondence should be addressed to Hamadi Hamza; hamadi.hamza@hotmail.com

Received 29 December 2013; Accepted 24 April 2014; Published 13 July 2014

Academic Editor: Baoyuan Man

Copyright © 2014 Hamadi Hamza et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

$\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$ is a new inorganic compound. It was synthesized by a solid state method. The crystal structure has been studied by single crystal X-ray analysis. The R -values reached 2.8%. The title compound crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 10.550$ (2) Å, $b = 11.723$ (2) Å, $c = 17.469$ (3) Å, $\alpha = 102.35$ (3)°, $\beta = 87.61$ (2)°, and $\gamma = 111.03$ (3)°. The anionic unit $[\text{Mo}_{11}\text{As}_3\text{O}_{45}]^{9-}$ is formed by nine MoO_6 octahedra, two MoO_5 trigonal bipyramids, and three AsO_4 tetrahedra. The association of $[\text{Mo}_{11}\text{As}_3\text{O}_{45}]^{9-}$ units, running along $[010]$, leads to a one-dimensional framework. Li, K, and Na are located in the space surrounding the anionic ribbons. This material was characterized by SEM microscopy, IR spectroscopy, and powder X-ray diffraction. The electrical conductivity was investigated from 528 K to 673 K by impedance complex followed by DSC spectroscopy.

1. Introduction

The search for new materials, based in arsenic and molybdenum, with an open framework formed by octahedra and tetrahedra showing multiple modes of connections and containing alkali gives a big interest in solid state chemistry [1]. This kind of material shows important energetic property which is the ionic conductivity. We are interested in this field and we have explored the $\text{A}_2\text{O}-\text{MoO}_3-\text{As}_2\text{O}_5$ systems ($A =$ alkali or silver) in which many compounds were characterized: $\text{K}_2\text{MoO}_2(\text{MoO}_2\text{As}_2\text{O}_7)_2$ [2], $\text{Na}_2(\text{MoO}_2)_3(\text{As}_2\text{O}_7)_2$ [3], and $\text{NaAg}_2\text{Mo}_3\text{O}_9\text{AsO}_4$ [4]. We have succeeded in the synthesis of a new material $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$. It was prepared by a solid state method.

2. Experimental Details

2.1. Synthesis. The $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$ compound was obtained from a mixture of $(\text{NH}_4)_2\text{Mo}_4\text{O}_{13}$ (Fluka 69858), $\text{NH}_4\text{H}_2\text{AsO}_4$ (ASTM 01-775), Na_2CO_3 (Prolabo 27778), K_2CO_3 (Pan 121490) and $\text{LiOH}\cdot\text{H}_2\text{O}$ (Fluka 62530). The mixture was grinded and preheated in air at 673 K to remove NH_3 , H_2O , and CO_2 . Then, it was grinded and heated again to 808 K. The mixture was left at this temperature for 2 weeks

to promote germination and growth of crystals. The final residue was subjected at a first slow cooling (5 K/24 h) in an interval of 50 K and then at a second faster cooling (50 K/h) to reach room temperature. The yellowish crystals obtained by spontaneous crystallization were separated by flow of hot water to do the preliminary identification.

2.2. Single Crystal X-Ray Data Collection. It was performed with a CAD-4 Enraf-Nonius X-ray diffractometer [5] at 298 K with graphite monochromator using MoK_α wavelength. All calculations were performed using the Wingx-98 crystallographic software package [6]. An empirical correction of absorption by PSI scan [7] was applied. The structure was solved and refined using, respectively, SHELXS-97 and SHELXL-97 [8] by full-matrix least squares based on F^2 . The graphs of the structure were drawn with diamond 2.1 supplied by Crystal Impact [9]. The crystal data and the refinements details are summarized in Table 1. Table 2 contains the main bond distances.

2.3. Powder XRD Analysis. The polycrystalline powder was prepared from a stoichiometric mixture of reagents forming the single crystal. In the beginning, the mixture was heated

TABLE 1: Crystal data and the refinements details.

Empirical formula	LiNa ₅ K ₃ Mo ₁₁ As ₃ O ₄₅
Crystal system/space group/Z	Triclinic/P-1/2
<i>a</i> (Å)	10.550(2)
<i>b</i> (Å)	11.723(2)
<i>c</i> (Å)	17.469(3)
α (°)	102.35(3)
β (°)	87.61(2)
γ (°)	111.03(3)
<i>V</i> (Å ³) <i>Z</i>	1986.46(2)
μ (mm ⁻¹)	6.39
ρ_x (g·cm ⁻³)/formula weight (g/mol)	3.78/2247.34
Crystal size (mm)/Color	0.2 × 0.3 × 0.5/yellow
Tmin/Tmax	0.7026/0.8745
Measured reflections	9789
Independent reflections/ <i>rint</i>	8557/0.0157
Observed refl. with <i>I</i> > 2 σ (<i>I</i>)	7730
Data/restraints/parameters	8557/2/619
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.028
<i>wR</i> (<i>F</i> ²)/ <i>S</i> / <i>F</i> (000)	0.071/1.22/2072
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e·Å ⁻³)	1.56/−1.39

FIGURE 1: Experimental XRD pattern of LiNa₅K₃Mo₁₁As₃O₄₅.

at 473 K to remove volatile compounds. Then, it was grinded and heated to 673 K and it was rigorously grinded again before heating up to 773 K. The residue was maintained for 48 hours at this temperature. Then, it was cooled down rapidly to room temperature. Obtained powder was characterized using X-ray diffraction. XRD analysis was performed with a PANalytical X'PertPro diffractometer with CuK α radiation (λ = 1.5406 Å). The comparison of obtained pattern (Figure 1) with reference pattern (Figure 2) shows that powder is pure. The obtained pattern was indexed in Table 3 by the programs X'pert Highscore plus [10] and Diamond 3.2 [11].

The confidence factor calculated by the formula $\sum(|2\theta_{\text{cal}} - 2\theta_{\text{exp}}|) / \sum ni$ is 1.27%.

2.4. Scanning Electron Microscopy. One single crystal was selected by means of polarizing microscope. Then, it was analyzed by dispersive energy spectroscopy (model FEI type Quanta 200). The SEM analysis was used to observe the crystal morphology (Figure 3). The EDS local microanalysis (Figure 4) confirms the presence of expected chemical

TABLE 2: Main bond distances.

Bond distances (Å)			
As1–O30	1.669 (4)	Mo10–O9	2.313(4)
As1–O25	1.677 (4)	Mo10–O14	2.360(4)
As1–O9	1.691 (4)	Mo11–O39	1.707(4)
As1–O10	1.696 (4)	Mo11–O45 ⁱⁱⁱ	1.714(5)
As2–O15 ⁱⁱⁱ	1.663 (4)	Mo11–O21	1.835(4)
As2–O24	1.679 (4)	Mo11–O35	1.915(4)
As2–O13	1.690 (4)	Mo11–O37	2.285(4)
As2–O37	1.695 (4)	K1–O41	2.751(4)
As3–O23	1.675 (4)	K1–O38 ^{vi}	2.759(4)
As3–O20	1.677 (4)	K1–O12 ⁱ	2.802(4)
As3–O14	1.698 (4)	K1–O17 ^{vii}	2.823(4)
As3–O4	1.699 (4)	K1–O43 ^{viii}	2.906(4)
Mo1–O28	1.701 (4)	K1–O15	2.912(4)
Mo1–O26	1.731 (4)	K1–O17 ⁱ	2.958(5)
Mo1–O6	1.826 (4)	K1–O5	3.115(4)
Mo1–O19	1.923 (4)	K2–O7	2.755(4)
Mo1–O10	2.273 (4)	K2–O28 ^v	2.770(4)
Mo2–O22	1.706 (4)	K2–O34 ^v	2.803(4)
Mo2–O41	1.735 (4)	K2–O32 ^x	2.852(4)
Mo2–O5	1.869 (4)	K2–O45	2.867(5)
Mo2–O18 ⁱ	1.972 (4)	K2–O1	2.932(5)
Mo2–O30	2.217 (4)	K2–O31 ⁱ	2.979(5)
Mo2–O14	2.285 (4)	K2–O20	3.019(4)
Mo3–O16 ⁱⁱ	1.685 (4)	K3–O29	2.615(4)
Mo3–O32	1.724 (4)	K3–O2 ^{vii}	2.713(4)
Mo3–O29	1.943 (4)	K3–O33	2.726(4)
Mo3–O19	1.972 (4)	K3–O22 ^{vii}	2.932(5)
Mo3–O24	2.239 (4)	K3–O36 ⁱⁱ	2.964(4)
Mo3–O10	2.266 (4)	K3–O30	3.063(4)
Mo4–O11	1.700 (4)	Na1–O4	2.409(4)
Mo4–O40	1.731 (4)	Na1–O32	2.444(5)
Mo4–O8	1.916 (4)	Na1–O11 ⁱ	2.522(5)
Mo4–O3 ⁱⁱⁱ	1.924 (4)	Na1–O26	2.530(5)
Mo4–O4 ⁱⁱⁱ	2.263 (4)	Na1–O33	2.608(5)
Mo4–O13	2.317 (4)	Na1–O10	2.719(5)
Mo5–O38 ⁱⁱ	1.705 (4)	Na1–O23	2.861(5)
Mo5–O33	1.714 (4)	Na1–O30	2.995(5)
Mo5–O5	1.918 (4)	Na2–O43	2.400(6)
Mo5–O8 ⁱ	1.943 (4)	Na2–O18 ⁱ	2.468(5)
Mo5–O15	2.205 (4)	Na2–O41 ^{viii}	2.521(5)
Mo5–O4	2.308 (4)	Na2–O22	2.642(5)
Mo6–O1	1.702 (5)	Na2–O44 ^{viii}	2.710(6)
Mo6–O27	1.710 (4)	Na2–O2	2.812(6)
Mo6–O7	1.936 (4)	Na2–O25	2.882(5)
Mo6–O6	1.963 (4)	Na3–O40 ^{xi}	2.483(4)
Mo6–O9	2.220 (4)	Na3–O1	2.527(6)
Mo6–O23	2.237 (4)	Na3–O39 ^v	2.628(5)
Mo7–O17	1.697 (4)	Na3–O3	2.737(4)
Mo7–O2	1.710 (4)	Na3–O27 ^v	2.749 (5)

TABLE 2: Continued.

	Bond distances (Å)		
Mo7–O29	1.922 (4)	Na3–O31 ⁱ	2.786(5)
Mo7–O12	1.964 (4)	Na3–O23	2.845(4)
Mo7–O24	2.252 (4)	Na4–O14	2.313(5)
Mo7–O25	2.280 (4)	Na4–O36	2.401(6)
Mo8–O43	1.712 (4)	Na4–O44	2.412(6)
Mo8–O44 ⁱⁱⁱ	1.712 (4)	Na4–O45	2.416(6)
Mo8–O12	1.889 (4)	Na4–O37 ⁱ	2.436(5)
Mo8–O35	1.933 (4)	Na4–O20	2.671(5)
Mo8–O37	2.301 (4)	Na4–O41	2.910(6)
Mo8–O25	2.450 (4)	Na5–O16	2.373(5)
Mo9–O31	1.702 (4)	Na5–O8 ^x	2.401(4)
Mo9–O34	1.721 (4)	Na5–O27	2.439(6)
Mo9–O3 ⁱⁱⁱ	1.929 (4)	Na5–O42	2.468(5)
Mo9–O21	1.949 (4)	Na5–O35	2.474(5)
Mo9–O20 ⁱⁱⁱ	2.224 (4)	Na5–O39	2.734(5)
Mo9–O13	2.227 (4)	Li–O19	2.037(12)
Mo10–O42	1.710 (4)	Li–O40	2.041(12)
Mo10–O36	1.725 (4)	Li–O34	2.053(13)
Mo10–O18 ⁱ	1.894 (4)	Li–O26 ^{xi}	2.075(12)
Mo10–O7	1.927 (4)		

Symmetry codes: (i) $x, y-1, z$; (ii) $x-1, y, z$; (iii) $x, y+1, z$; (iv) $x-1, y-1, z$; (v) $-x+1, -y+1, -z$; (vi) $-x+1, -y, -z+1$; (vii) $-x, -y+1, -z+1$; (viii) $-x+1, -y+1, -z+1$; (ix) $-x, -y, -z+1$; (x) $x+1, y, z$; (xi) $-x, -y+1, -z$; (xii) $x+1, y+1, z$.

FIGURE 2: Calculated XRD pattern of $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$.

elements, particularly: sodium, potassium, molybdenum, arsenic, and oxygen.

2.5. Infrared Spectroscopy FTIR. For this analysis, sample was prepared from a mixture of 2 mg of pure powder of $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$ and 200 mg of KBr and compressed with hydraulic press under 100 kg/cm^2 in order to obtain a little pellet. In the transmission spectrum (Figure 5) obtained by spectrometer model Nicolet-IR 200, we have found two main strong and well-resolved bands around 490 and 830 cm^{-1} characterizing, respectively, the stretching of MoO_6 [12, 13] and AsO_4 [14] and two absorption bands at 425 and 625 cm^{-1} arising from the vibration of MoO_6 [15]. A peak around 952 cm^{-1} might be assigned to the stretching and

TABLE 3: Indexation of powder XRD pattern.

h	k	l	$I/I_0 \%$	$2\theta_{\text{ref}} (^\circ)$	$2\theta_{\text{exp}} (^\circ)$
-1	1	0	6.4	09.786	09.791
-1	0	1	100	10.196	10.199
0	0	2	77.8	10.367	10.369
1	-2	1	49.9	15.567	15.621
-1	2	0	11.8	15.764	15.758
0	2	0	87	16.571	16.574
-1	0	3	11.4	17.703	17.696
1	0	3	10.9	18.309	18.308
0	2	1	10.2	18.409	18.393
-1	2	2	16.2	20.603	20.620
2	0	2	12.8	21.177	21.113
-1	-2	1	14.4	21.243	21.249
2	1	0	13.1	22.420	22.422
1	2	1	11.9	23.096	23.090
3	-1	1	30.1	25.758	25.754
2	-1	4	16.4	26.075	26.077
2	-2	4	15.8	26.574	26.608
-2	1	4	41.3	27.783	27.777
-1	-1	5	45.5	27.890	27.896
-1	2	4	19.6	28.713	28.712
-1	-3	1	19.9	28.976	28.890
-2	-2	2	8.2	29.067	29.069
-3	2	2	7.1	29.246	29.256
-1	-3	2	25.6	29.372	29.466
2	-3	4	22.9	29.573	29.579
-2	-2	3	13.7	30.651	30.650
-3	-1	1	10.9	31.199	31.194
0	3	3	11.5	32.348	32.333
3	-4	1	10.8	34.308	34.305
3	-4	3	11.3	35.677	35.682
-3	1	5	11.5	37.266	37.263
-1	-1	7	10.9	37.577	37.523
-3	-1	5	4.8	39.189	39.184
2	-2	8	5.9	44.250	44.251
4	-3	6	12.6	45.773	45.780
-1	-5	4	2.4	47.146	47.140
2	-5	8	2.7	52.161	52.155
-1	2	9	0.8	54.077	54.076
5	-3	7	2.5	55.893	55.895
-4	-4	1	6.5	58.832	58.836
4	0	9	2.4	63.020	63.018
2	-8	5	2.7	65.199	65.194

the bending of AsO_4 [14] and little band, at 995 cm^{-1} , is the result of the vibration of MoO_5 [12, 16].

2.6. Complex Impedance Analysis. The electrical properties of the $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$ material have been investigated using complex impedance spectroscopy. The sample is prepared by pressing the crystal powder at 100 kg/cm^2 and sintering at 673 K for 24 hours. The thickness and the surface of

FIGURE 3: Crystal morphology.

FIGURE 4: EDS analysis spectrum.

the obtained pellet are respectively, 0.136 cm and 1.40 cm². This pellet was placed between two blocking platinum electrodes in order to ensure good electric contacts in a tubular oven to undergo the measurements of complex impedance by using a Hewlett-Packard 4192-A impedance analyzer in the temperature range from 523 K to 673 K and in the frequency range from 5 Hz to 13000 Hz.

2.7. Differential Scanning Calorimetric Analysis. To examine thermal transitions in $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$ compound, a sample of 10.3 mg was analyzed by using a differential scanning calorimeter 822-E made by Mettler Toledo.

3. Results and Discussion

3.1. Structure Description. The asymmetric unit of $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$ compound (Figure 6) consists of

- (i) three Mo_3O_{14} motifs; each one is formed by three octahedra sharing edges;
- (ii) two MoO_5 bipyramids which are inserted between the three Mo_3O_{14} motifs. They are linked by edges and corners;

FIGURE 5: IR spectrum of $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$.

FIGURE 6: The asymmetric unit.

- (iii) three AsO_4 tetrahedra; each one is linked by sharing corners with four octahedra.

The association of two MoO_5 bipyramids and one Mo_3O_{14} motif leads to a Mo_5O_{20} semicyclic group.

The charge compensation is ensured by Na^+ , K^+ , and Li^+ . The molybdenum atom Mo (11) is delocalized. It occupies two positions with the distance of 0.949 (8) Å with various occupancies 93.3% and 6.7%.

The combination of asymmetric units by sharing corners between octahedra and tetrahedra leads to $(\text{Mo}_{11}\text{As}_3\text{O}_{45})^{9-}$ ribbons (Figure 7). The structure of $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$ can be described as a one-dimensional framework of ribbons disposed along [010] direction. Na^+ , K^+ , and Li^+ are situated in the space surrounding the ribbons (Figures 8 and 9).

In the structure of $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$, the polyhedra are distorted because of the existence of

- (i) short atomic bonds of molybdenyl group in MoO_6 octahedra and MoO_5 bipyramids;
- (ii) short atomic bonds in AsO_4 tetrahedra.

FIGURE 7: View of $(\text{Mo}_{11}\text{As}_3\text{O}_{45})^{9-}$ ribbon. FIGURE 8: Projection of the structure of $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$. FIGURE 9: Projection of the structure along $[010]$.

FIGURE 10: Arrangements of cations.

TABLE 4: Angles and distances distortion factors (%).

Polyhedra	D_dF	A_dF
As(1)-O ₄	0.15	2.33
As(2)-O ₄	0.15	2.54
As(3)-O ₄	0.16	3.70
Mo(1)-O ₅	1.75	13.64
Mo(2)-O ₆	1.64	7.49
Mo(3)-O ₆	1.58	8.45
Mo(4)-O ₆	1.77	9.39
Mo(5)-O ₆	1.64	8.25
Mo(6)-O ₆	1.51	10.61
Mo(7)-O ₅	1.66	9.03
Mo(8)-O ₆	2.09	9.37
Mo(9)-O ₆	1.51	7.49
Mo(10)-O ₆	1.94	9.79
Mo(11)-O ₆	1.76	9.29

The distortion factors of angles and distances of atomic bonds (resp., A_dF and D_dF), obtained by the following formula, are summarized in Table 4:

$$D_dF = \left[\frac{\sum (|d_i - d_m|)}{n_1 \cdot d_m} \right], \quad (1)$$

$$A_dF = \left[\frac{\sum (|a_i - a_m|)}{n_2 \cdot a_m} \right]$$

(see [17]). d_i is real distance value, d_m is moyen distance value, n_1 is coordination number, a_i is real angle value, a_m is moyen angle value, and n_2 is angles number.

Moreover, the calculation of the various valence sums of atomic bonds (BVS), using empirical formula of Altermatt and Brown [18], confirms that they are the expected values of ions charges. All bond valence sums are represented in Table 5.

FIGURE 11: Spectrum of complex impedance of $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$.

3.2. Structure Comparison. The studied phase reveals some structure affiliations with the phases found in the literature. In fact, the structures of $\text{K}_2\text{Mo}_3\text{O}_{10}$ [19] and $\text{K}_2\text{Mo}_4\text{O}_{13}$ [20] are one dimensional. Their basic units are formed by MoO_6 octahedra and MoO_5 bipyramids. The ribbons forms are helicoidal, as the ribbon forms of $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$ compound. In the three-dimensional framework of $\text{Na}_6\text{Mo}_5\text{P}_2\text{O}_{23} \cdot 14\text{H}_2\text{O}$ [21], we have found a cyclic group Mo_5O_{21} , but, in the structure of $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$, the Mo_5O_{20} group is linear. So, the structure of $\text{Na}_6\text{Mo}_5\text{P}_2\text{O}_{23} \cdot 14\text{H}_2\text{O}$ differed from the structure of $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$.

In the one-dimensional framework of $\text{Na}_2\text{AgMo}_3\text{AsO}_{13}$ [4] and the framework of $\text{Ag}_{12.4}\text{Na}_{1.6}\text{Mo}_{18}\text{As}_4\text{O}_{71}$ [1], there are two motifs similar to those found in $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$

compound that are Mo_3O_{14} , formed by three MoO_6 octahedra linked by sharing edges, and $\text{Mo}_3\text{AsO}_{17}$, composed by Mo_3O_{14} motif and AsO_4 tetrahedron.

3.3. Ionic Conductivity. The geometric data analysis shows that a few interstitial sites are adjacent to those occupied by cations (Figure 10). Furthermore, on the basis of the arrangement of cations in the one-dimensional framework, $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$ compound could be a good ionic conductor. Figure 11 shows the spectrum of complex impedances of $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$ in the various temperatures.

The radius of semicircles decreases when temperature increases signifying an ionic conduction with activated mechanism. The intercepts of the semicircles with the real

TABLE 5: Bond valence sums.

Polyhedra	BVS
As(1)-O ₄	4.904
As(2)-O ₄	4.924
As(3)-O ₄	4.859
Mo(1)-O ₅	5.963
Mo(2)-O ₆	6.101
Mo(3)-O ₆	6.042
Mo(4)-O ₆	6.087
Mo(5)-O ₆	6.117
Mo(6)-O ₆	6.117
Mo(7)-O ₆	6.083
Mo(8)-O ₆	5.991
Mo(9)-O ₆	6.142
Mo(10)-O ₆	6.007
Mo(11)-O ₅	5.988
K(1)-O ₈	0.927
K(2)-O ₈	0.966
K(3)-O ₆	0.976
Na(1)-O ₈	1.001
Na(2)-O ₈	0.905
Na(3)-O ₇	0.715
Na(4)-O ₇	1.052
Na(5)-O ₆	0.915
Li-O ₄	0.727

TABLE 6: Conductivity value at various temperatures.

T° (C)	Z (Ω)	$\sigma = (e/s)/z$ (Ω ⁻¹ ·cm ⁻¹)
255	4.500 10 ⁵	2.14 10 ⁻⁷
280	2.550 10 ⁵	3.78 10 ⁻⁷
310	1.400 10 ⁵	6.90 10 ⁻⁷
340	8.650 10 ⁴	1.11 10 ⁻⁶
370	4.100 10 ⁴	2.35 10 ⁻⁶
400	2.050 10 ⁴	4.71 10 ⁻⁶

axis give the estimated values of the material's resistances by using the Zview software [22]. The measured impedance can be modeled as that of an equivalent electrical circuit composed of a resistor R connected in parallel with a nonideal capacitor usually known as constant phases elements CPE [23]. After determination of the resistance values at various temperatures and the dimensions of the sample, we have calculated the conductivity values (Table 6).

Figure 12 shows the variation of $\log(\sigma T)$ (S·K·cm⁻¹) versus $10000/T$ (K⁻¹). The values of activation energies (E_{a1} and E_{a2}) of cations migration deduced from the slopes are equal to

(i) $E_{a1} = 0.559$ eV before 340°C;

(ii) $E_{a2} = 0.871$ eV after 340°C.

The change of activation energy is assigned to a change of cation migration process or a thermal transition.

FIGURE 12: Variation of $\log \sigma T$ versus $10^4/T$. FIGURE 13: Variation of $Z''/Z''_{\max}$ versus $(\ln f)$.

Figure 13 shows the variation of the resistance imaginary part versus the relaxation frequency ($Z''/Z''_{\max}$ versus $(\ln f)$). All curvatures in various temperatures have the same wide at midheight which is equal to 60.34 Hz ($\ln f = 4.1$); this confirms that the variation of activation energy is not due to the change of cation migration process [24, 25]. The DSC diagram in Figure 14 shows the change of baseline from 340°C. Therefore, $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$ compound is the subject of a thermal transition from this temperature and this is the real reason of change of activation energy. This compound shows a medium electric conductivity, compared with the compounds found in literature [1, 15, 26].

FIGURE 14: DSC diagram of $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$ compound.

4. Conclusion

$\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$ compound was prepared by solid state reaction. The structure has been resolved by single crystal X-ray diffraction and characterized by dispersive energy spectroscopy, powder X-ray diffraction, FTIR spectroscopy, and DSC. The compound crystallizes in the triclinic system (space group P-1) with the following unit cell parameters: $a = 10.550$ (2) Å, $b = 11.723$ (2) Å, $c = 17.469$ (3) Å, $\alpha = 102.35$ (3)°, $\beta = 87.61$ (2)°, and $\gamma = 111.03$ (3)°. This material has one-dimensional structure. The electrical properties are investigated using complex impedance spectroscopy. The conductivity value at 673 K is $4.71 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ and the activation energy value is 0.559 eV. $\text{LiNa}_5\text{K}_3\text{Mo}_{11}\text{As}_3\text{O}_{45}$ presents medium electric properties.

Disclosure

The CIF file corresponding to the studied structure has been deposited in the database of FIZ Karlsruhe no. CSD 426635.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

- [1] M. Hajji and M. F. Zid, "Synthesis, structure and ionic conductivity of the molybdenum arsenate: $\text{Ag}_{12.4}\text{Na}_{1.6}\text{Mo}_{18}\text{As}_4\text{O}_{71}$," *Solid State Sciences*, vol. 14, no. 9, pp. 1349–1354, 2012.
- [2] M. F. Zid, " $\text{K}_2\text{MoO}_2(\text{MoO}_2\text{As}_2\text{O}_7)_2$," *Acta Crystallographica C*, vol. 52, pp. 2947–2949, 1996.
- [3] R. Jouini, M. F. Zid, and A. Driss, "Disodium tris-(dioxidomolybdenum) bis-(diarsenate)," *Acta Crystallographica E: Structure Reports Online*, vol. 68, part 4, pp. i24–i25, 2012.
- [4] H. Hamza, M. F. Zid, and A. Driss, " $\text{NaAg}_2\text{Mo}_3\text{O}_9\text{AsO}_4$," *Acta Crystallographica E*, vol. 66, no. 10, pp. i69–i70, 2010.
- [5] A. J. M. Duisenberg, "Indexing in single-crystal diffractometry with an obstinate list of reflections," *Journal of Applied Crystallography*, vol. 25, no. 2, pp. 92–96, 1992.
- [6] L. J. Farrugia, "WinGX and ORTEP for windows: an update," *Journal of Applied Crystallography*, vol. 45, no. 4, pp. 849–854, 2012.
- [7] A. C. T. North, D. C. Phillips, and F. S. Mathews, "A semi-empirical method of absorption correction," *Acta Crystallographica Section A*, vol. 24, pp. 351–359, 1968.
- [8] G. M. Sheldrick, "A short history of SHELX," *Acta Crystallographica A*, vol. 64, no. 1, pp. 112–122, 2007.
- [9] K. Brandenburg and M. Berndt, *Diamond Version 2.1 Crystal Impact*, GBR, Bonn, Germany, 2001.
- [10] X'pert Highscore Plus, "Version 2.1 PANalytical B.V.," Almelo, Netherlands, 2004.
- [11] K. Brandenburg, *Diamond Version 3.2 Crystal Impact*, Bonn, Germany, 1998.
- [12] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, NY, USA, 3rd edition, 1978.
- [13] R. Marzouki, A. Guesmi, M. F. Zid, and A. Driss, "Electrical properties and Na^+ mobility in $\text{Na}_4\text{Co}_{5.63}\text{Al}_{0.91}(\text{AsO}_4)_6$ material," *Journal of Inorganic Chemistry*, vol. 1, pp. 9–16, 2013.
- [14] K. Viswanathan, V. Nayar, U. G. Aruldas, and V. Ramakrishnan, "Vibrational spectra of $\text{Te}(\text{OH})_6 \cdot 2\text{NH}_4\text{H}_2\text{PO}_4 \cdot (\text{NH}_4)_2\text{HPO}_4$," *Journal of Solid State Chemistry*, vol. 77, no. 2, pp. 394–400, 1988.
- [15] W. Frigui, F. B. Amor, M. F. Zid, A. Madini, and A. Driss, "Synthesis and physico-chemical study of $\text{Na}_{0.5}\text{K}_{0.865}\text{Mn}_{3.435}(\text{AsO}_4)_3$ compound," *Jordan Journal of Chemistry*, vol. 6, pp. 295–305, 2011.
- [16] H. Siebert, "Kraftkonstante und strukturchemie," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 275, p. 225, 1954.
- [17] B. Renner and G. Lehmann, "Correlation of angular and bond length distortions in TO_4 units crystals," *Zeitschrift für Kristallographie*, vol. 175, pp. 43–59, 1986.
- [18] D. Altermatt and I. D. Brown, "The automatic searching for chemical bonds in inorganic crystal structures," *Acta Crystallographica*, vol. B41, no. 4, pp. 240–244, 1985.
- [19] B. M. Gatehouse and P. Leverett, "The crystal structure of dipotassium trimolybdate, $\text{K}_2\text{Mo}_3\text{O}_{10}$: a compound with five-coordinate molybdenum (VI)," *Journal of the Chemical Society A*, pp. 1398–1405, 1968.
- [20] K. Eda, K. Chin, N. Sotani, and M. S. Whittingham, " $\text{K}_2\text{Mo}_4\text{O}_{13}$ phases prepared by hydrothermal synthesis," *Journal of Solid State Chemistry*, vol. 177, no. 3, pp. 916–921, 2004.
- [21] B. Hedman, "Multicomponent polyanions. 16. The molecular and crystal structure of $\text{Na}_6\text{Mo}_5\text{P}_2\text{O}_{23}(\text{H}_2\text{O})_{14}$, a compound containing sodium-coordinated pentamolybdodiphosphate anions," *Acta Crystallographica B*, vol. 24, pp. 3083–3090, 1977.
- [22] D. Johnson, *Zview version 3.1c*, Scribner Associates, 1990.
- [23] A. K. Jonscher, "The interpretation of non-ideal dielectric admittance and impedance diagrams," *Physica Status Solidi A*, vol. 32, no. 2, pp. 665–676, 1975.
- [24] A. Kumar, B. P. Singh, R. N. P. Choudhary, and A. K. Thakur, "A.C. impedance analysis of the effect of dopant concentration on electrical properties of calcium modified BaSnO_3 ," *Journal of Alloys and Compounds*, vol. 394, no. 1–2, pp. 292–302, 2005.

- [25] P. Muralidharan, M. Venkateswarlu, and N. Satyanarayana, "Sol-gel synthesis, structural and ion transport studies of lithium borosilicate glasses," *Solid State Ionics*, vol. 166, no. 1-2, pp. 27-38, 2004.
- [26] N. Ouerfelli, A. Guesmi, D. Mazza, A. Madani, M. F. Zid, and A. Driss, "Synthesis, crystal structure and mono-dimensional thallium ion conduction of $\text{TlFe}_{0.22}\text{Al}_{0.78}\text{As}_2\text{O}_7$," *Journal of Solid State Chemistry*, vol. 180, no. 4, pp. 1224-1229, 2007.