Journal of Solid State Chemistry **145**, 612–618 (1999)
Article ID jssc.1999.8254, available online at http://www.idealibrary.com on IDEAL®

Structural and Vibrational Study of $K_2SeO_4 \cdot Te(OH)_6$ Material

M. Dammak, H. Khemakhem, T. Mhiri,[1] A. W. Kolsi, and A. Daoud

Laboratoire de l'Etat Solide (LES), Faculté des Sciences de Sfax, 3038 Sfax, Tunisia

Received December 24, 1998; in revised form February 22, 1999; accepted February 26, 1999

At room temperature, the new compound $K_2SeO_4 \cdot Te(OH)_6$ was synthesized from water solutions of H_6TeO_6/K_2SeO_4. The potassium selenate tellurate (KTSe), $M_m = 480.81$ g, possesses a monoclinic structure with *Cc* space group. The crystal and refinement cell parameters are: $a = 11.552(2)$ Å, $b = 6.432(1)$ Å, $c = 13.919(2)$ Å, $\beta = 105.92(1)$, $V = 994.5(3)$ Å^3, $Z = 4$, $D_x = 3.011$ g/cm^3, and $F(000) = 840$. The residuals are $R1 = 0.023$ and $WR2 = 0.069$ for 1139 observed reflections (1108 with $I > 2\sigma(I)$) refined with 152 parameters. The main interest of this structure is the presence of two different and independent anionic groups (TeO_6^{6-} and SeO_4^{2-}) in the same crystal. Raman and IR spectra of $K_2SeO_4 \cdot Te(OH)_6$, recorded at room temperature in the frequency range 200–4000 cm^{-1}, show that both SeO_4^{2-} and TeO_6^{6-} groups coexist in the crystal independently. © 1999 Academic Press

Key Words: **KTSe material; structure; Raman; infrared.**

I. INTRODUCTION

Telluric acid can form stable adducts with a large variety of organic and inorganic compounds of considerable importance as $Te(OH)_6$ acts as both acceptor and donor of hydrogen bonds. In most of these, like the sulfate tellurate salts (2, 20, 23), we study here the effects of anionic substitution (SO_4^{2-} by SeO_4^{2-}) in $K_2AO_4 \cdot Te(OH)_6$ (A = S, Se) crystals. A dielectric study performed on some compounds of this family as $K_2SO_4 \cdot Te(OH)_6$ (1) shows that they present a ferroelectric–paraelectric phase transition accompanied by a superionic protonic conduction at high temperature. The structure of KTSe is different from both $K_2SO_4 \cdot Te(OH)_6$ (KTS) and $K_2HPO_4 \cdot KH_2PO_4 \cdot Te(OH)_6$. The structure of potassium sulfate tellurate is triclinic $P\bar{1}$, whereas the structure of the potassium phosphate tellurate is monoclinic *Pn* (2, 3).

In the present work, we describe the crystal structure of $K_2SeO_4 \cdot Te(OH)_6$ and we present vibrational spectra of this new material. To justify the ferroelectric–paraelectric type of the phase transition in this material, we need just the dielectric measurements because a detailed work on physical properties is under study and will be published at a later date.

II. EXPERIMENTAL DETAILS:

A crystal of $K_2SeO_4 \cdot Te(OH)_6$ is synthesized by slow evaporation at room temperature of an aqueous solution of telluric acid (H_6TeO_6) and potassium selenate (K_2SeO_4) in the stoichiometric ratio. Schematically the reaction is

$$H_6TeO_6 + K_2SeO_4 \rightarrow K_2SeO_4 \cdot Te(OH)_6.$$

Several recrystallizations were necessary to obtain single crystals suitable for the study of physical properties and X-ray analysis. Infrared absorption spectra of suspensions of crystalline powders in KBr were recorded using a IR-470 Shimadzu spectrophotometer in the 400–4000 cm^{-1} region. Raman spectra of polycrystalline samples sealed in a glass tube were performed employing a Perkin Elmer 2000.

Unit cell parameters were refined using sets of 25 reflections in the range $10.77 \leq \theta \leq 16.53°$. The crystal had the parallelipipedic form with a size of about $(0.3 \times 0.3 \times 0.4)$ mm^3. A small specimen was selected with an Enraf–Nonius CAD-4 diffractometer using Mo$K\alpha$ radiation ω–2θ scan mode. The scan width was $0.65 + 0.60\ \mathrm{tg}\theta)°$ and counter slit width $1.3 + 1.6\ \mathrm{tg}\theta$ mm; 2460 reflections with miller indices $-14 \leq h \leq 14$; $0 \leq k \leq 8$; $-17 \leq l \leq 0$ were collected. The empirical absorption corrections were applied using Ψ scan data force reflections (4). Two standard reflections (2 2 6 and 2 2 −6) with no systematic variation were observed. Equivalent reflections averaged as $I/\sigma(I) > 4$ to give 1146 unique reflections ($R_{\mathrm{int}} = 0.0056$). The systematic absences $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$ were consistent with the space groups *Cc* and $C2/c$ with intensity statistics suggesting the first (N°9).

The structure was solved by the patterson method using SHELXS 86(5). Refinement was done by full-matrix least squares methods (SHELXL 93) (6).

The crystal data and details of data collection and refinement for our compound are summarized in Table 1. The

---

[1] To whom correspondence should be addressed.

0022-4596/99 $30.00

TABLE 1
Main Crystallographic Features, X-Ray Diffraction Data Collection Parameters, and Final Results for KTSe

Formula	$K_2SeO_4 \cdot Te(OH)_6$
Formula weight	480.81
Crystal system	Monoclinic
a (Å)	11.552 (2)
b (Å)	6.432 (1)
c (Å)	13.919 (2)
β (°)	105.92 (1)
V (Å^3)	994.5(3)
Z	4
Space group	Cc
T(K)	298 (2)
Diffractometer	Enraf-Nonius CAD4
$\theta_{\max}$. (deg.)	26.96
λ (Mo$K\alpha$) (Å)	0.71073
ρ_{cal} (g cm^{-3})	3.011
μ (cm^{-1})	75.2
Total reflections	1139
Reflection with $I > 2\sigma(I)$	1108
Reference reflections (2)	2 2 6 and 2 2 $\bar{6}$
Parameters	152
min., max., $\Delta\rho$(e Å^{-3})	-1.20, $+0.79$
$R(F)^a$	2.3
Rw $(F)^a$	6.9

^{a}R values are defined as $wR_2 = (\sum[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2])^{1/2}$ and $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

final positional and equivalent isotropic thermal parameters are given in Table 2.

Hydrogen atoms were not determined or calculated but were refined anisotropically (SHELXL 93(6)).

III. RESULTS AND DISCUSSIONS

III.1. X-Ray Diffraction Study

Figure 1 shows a projection on the *ac* plane of (KTSe). A projection on the *ab* plane is depicted in Fig. 2. The KTSe is not isomorphous with the corresponding sulfate because the first is monoclinic *Cc* and the second $K_2SO_4 \cdot Te(OH)_6$ (KTS) is triclinic $P\bar{1}$ (2).

The main feature of this structure is the coexistence of two different anions (TeO_6^{6-} and SeO_4^{2-}) in the same crystal. This structure type can be the origin of the ferroelectric polar phase in this material, (7) which is why we need to perform dielectric measurements to justify this statement. It can be regarded as being built of planes of pure SeO_4 tetrahedra alterning with planes of pure TeO_6 octahedra, both families being parallel to the *bc* plane. The Te atom in TeO_6 octahedral occupies a general position whereas in the KTS material the Te atom occupies two special positions (2). In consequence, we observe in the KTS structure two types of TeO_6 octahedra. The main interatomic distances and bond angles for the TeO_6 octahedron and the SeO_4 tetrahedron are given in Table 3. The TeO_6 octahedra are more regular in KTS (the distances of Te–O vary from 1.914 to 1.928 Å and angles O–Te–O vary from 89.3 to 90.6° (2)) than in KTSe material (distances of Te–O are between 1.867 and 1.946 Å and angles O–Te–O vary from 88 to 92.8°). The Se–O distances in KTSe are similar to those of K_2SeO_4 (8) and the Te–O distances are similar to those of H_6TeO_6 (9). The potassium atoms are distributed on two sites. The K–O distances are given in Table 3. The interesting point is that in the corresponding sulfate (KTS), the environment of the K atom is octahedral (2) whereas in KTSe, the cation K^+ is coordinated by nine oxygen atoms. Every cation K^+ is coordinated by two oxygen atoms belonging to a SeO_4 tetrahedron, four to a $Te(OH)_6$ octahedron, one to another octahedron, one to a third TeO_6 group, one to another SeO_4 group, and one other oxygen atom to a third SeO_4 tetrahedron.

The distances K–O vary from 2.755 to 3.391 Å for the first potassium atom, whereas the distances K–O are between 2.787 and 3.318 Å for the second potassium atom but in the KTS structure the K–O distances vary from 2.713 to 2.987 Å (2).

In an attempt to locate the H atoms of the OH groups belonging to the Te octahedra, we have used the results of Brown and Shannon (10) and Novak (11) concerning the

TABLE 2
Fractional Atomic Coordinates and Temperature Factors (U_{iso} for H Atoms) for $K_2SeO_4 \cdot Te(OH)_6$ (Standard Deviations Are in Parentheses)

	X	Y	Z	U_{eq} (Å^2)^a
Te	– 0.3416(6)	– 0.2496(1)	0.2378(4)	0.0132(2)
Se	– 0.0921(1)	– 0.2125(9)	– 0.0115(1)	0.0140(2)
K_1	– 0.4425(2)	– 0.2013(6)	– 0.1189(2)	0.0277(5)
K_2	– 0.2401(2)	0.3010(6)	0.0988(2)	0.0330(6)
O_1	– 0.1911(6)	– 0.3828(13)	0.2911(6)	0.0223(15)
O_2	– 0.3552(6)	– 0.2061(14)	0.3692(5)	0.0264(12)
O_3	– 0.4179(6)	– 0.5077(11)	0.2282(5)	0.0260(13)
O_4	– 0.2591(5)	0.0166(12)	0.2478(4)	0.0229(13)
O_5	– 0.3216(6)	– 0.2777(11)	0.1041(6)	0.0185(12)
O_6	– 0.4922(6)	– 0.1028(5)	0.1852(5)	0.026(2)
O_7	0.0232(5)	– 0.3633(11)	0.0356(6)	0.031(2)
O_8	– 0.0587(5)	– 0.0672(9)	– 0.0987(5)	0.0204(12)
O_9	– 0.1264(6)	– 0.0686(12)	0.0728(6)	0.036(2)
O_{10}	– 0.2112(6)	– 0.3554(10)	– 0.0614(5)	0.030(2)
H_1	– 0.1836(70)	– 0.2854(106)	0.3170(54)	0.009(18)
H_2	– 0.3950(57)	– 0.3238(105)	0.3809(38)	0.008(14)
H_3	– 0.4690(54)	– 0.5220(104)	0.1896(44)	0.011(12)
H_4	– 0.1690(51)	0.0214(104)	0.3084(40)	0.010(14)
H_5	– 0.2403(94)	– 0.2620(108)	0.1137(56)	0.033(27)
H_6	– 0.4863(53)	– 0.0108(121)	0.1442(44)	0.016(14)

$$^aU_{\mathrm{eq}} = \frac{1}{3}\sum_i \sum_j U_{ij} a_j^* a_i^* a_i a_j.$$

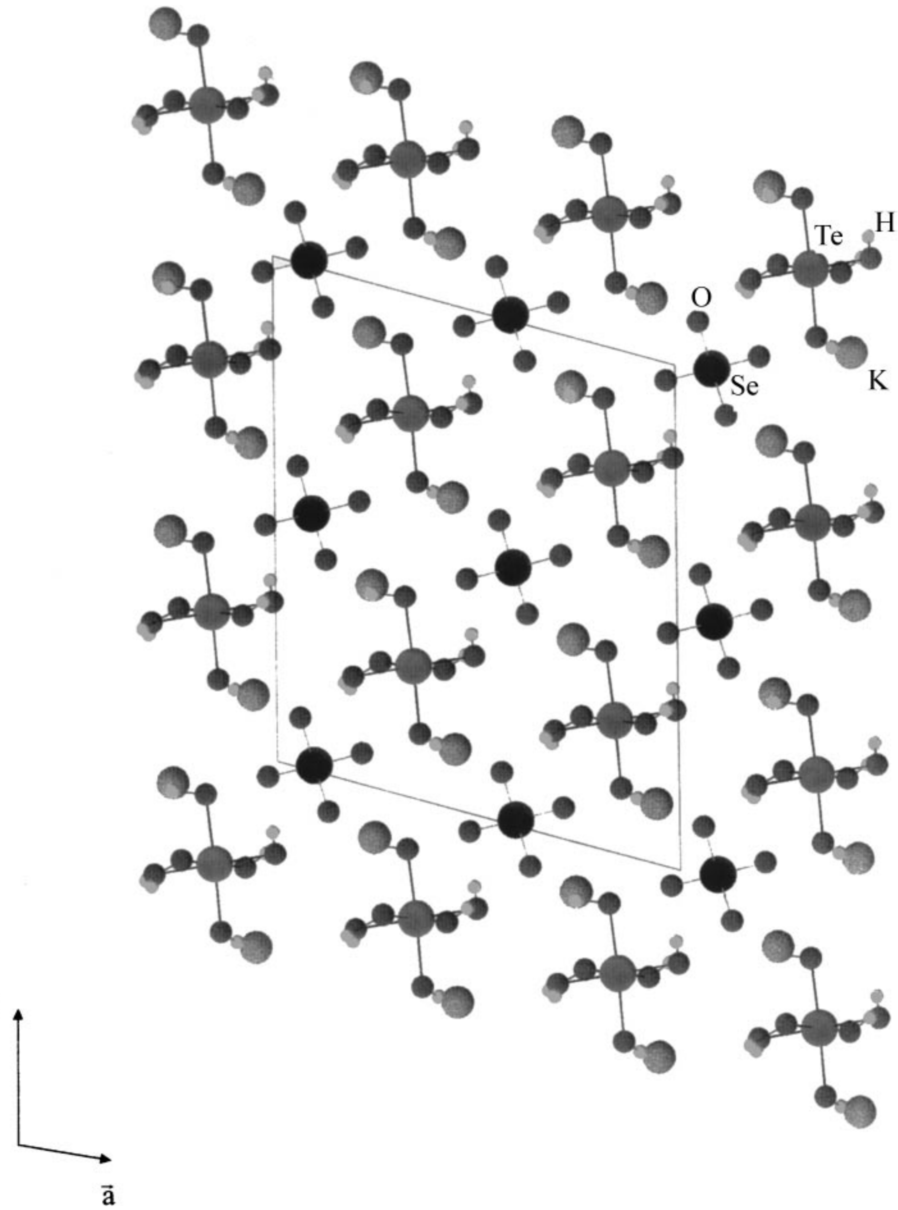

FIG. 1. Projection of $K_2SeO_4 \cdot Te(OH)_6$ crystal structure on the *ac* plane.

bond strength. In the structure of KTSe, the selenate tetrahedrons are connected with tellurate octahedrons by hydrogen bonds O–H ··· O assured by protons belonging to a hydroxide groups. In consequence, five hydrogen atoms participate in the formation of hydrogen bonding. In the selenate group, one oxygen atom is tied to one hydrogen atom but to two other oxygen atoms; every one is tied to two hydrogen atoms. The distances O ··· H vary from 1.75 to 2.10 Å and the O ··· H ··· O angles have values between 138.84 and 179.18°. All these values of O ··· H and O ··· H ··· O distances can favor the appearance of the superionic–protonic phase transition at high temperature. This deduction was confirmed by conductivity and dielectric measurements. In consequence the materials present a superprotonic phase transition at 480 K characterized by the brinking of hydrogen bonds which link SeO_4^{2-} to TeO_6^{6-} and the protons become free between the potential hole SeO_4^{2-} and/or TeO_6^{6-} (21). On the other hand, the thermal evolution of ε_r' shows an important peak at 433 K corresponding to a minimum of the dissipation factor (tan δ) and this behavior characterizes very well a ferroelectric–paraelectric phase transition in this material (21) and the fact that we have a noncentrosymmetric structure (*Cc*) is a second justification of a polar room phase.

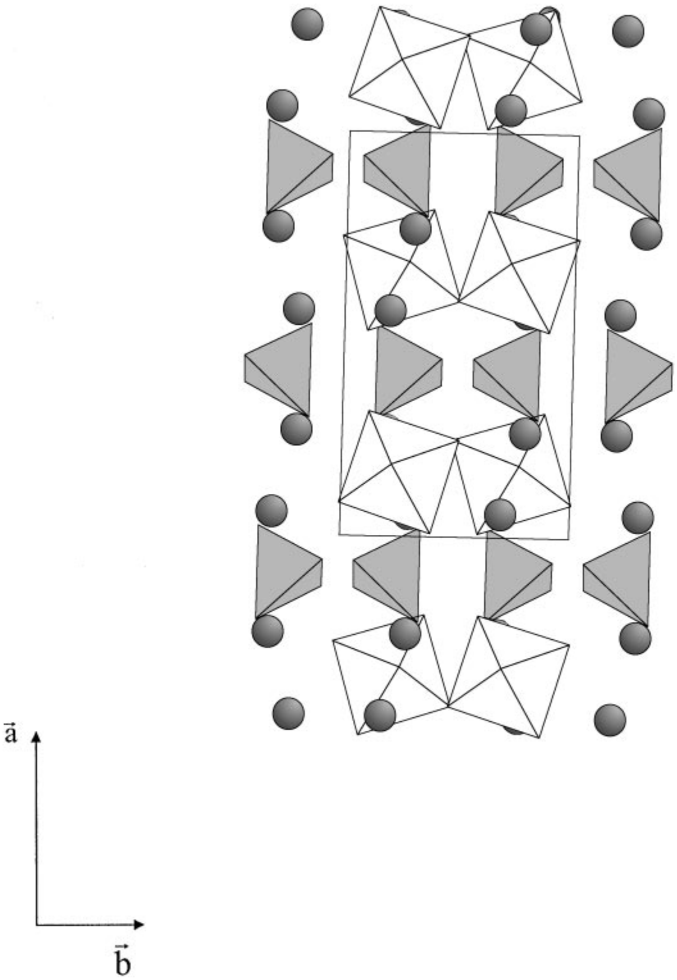

FIG. 2. Projection of $K_2SeO_4 \cdot Te(OH)_6$ crystal structure on the *ab* plane.

III.2. Vibrational Study

Adducts with $Te(OH)_6$ of different types of organic and inorganic compounds are of considerable importance (12–14). In most of these, the different groups are found to vibrate independently. The IR and Raman spectra of $K_2SeO_4 \cdot Te(OH)_6$ contain two different types of anions reported here, in order to study the vibrational nature of the $Te(OH)_6$ group when it is in coexistence with another anion in the same crystal. At room temperature KTSe exhibits a monoclinic symmetry with space group (Cc, $Z = 4$). Raman spectra of the polycrystalline sample of KTSe have been recorded in the frequency range 200–1300 cm^{-1} (Table 4). We shall not give a detailed assignment but we intend as far as possible to identify the external and internal modes. Figures 3 and 4 and Table 4 show IR and Raman spectra of KTSe and give frequencies. The observed frequencies are attributed on the basis of the characteristic frequencies of the $Te(OH)_6$ and SeO_4 groups.

III.2.1. Vibrations of $Te(OH)_6$ groups. The $Te(OH)_6$ group consists of TeO_6 and hydrogenic vibrations. The octahedral TeO_6 group has the following vibrational

TABLE 3
Atomic Distances (Å) and Angles (°)

Distance (Å)	Distance (Å)
a. Potassium coordination	
K_1	K_2
O_{10}..........2.755(7)	O_9..........2.787(9)
$O_8{}^c$..........2.762(7)	O_4..........2.818(7)
$O_2{}^b$..........2.829(10)	$O_7{}^b$..........2.838(7)
$O_1{}^e$..........2.852(7)	$O_6{}^h$..........2.853(8)
$O_3{}^d$..........2.906(7)	$O_5{}^a$..........2.876(8)
O_5..........3.074(9)	$O_2{}^h$..........3.166(8)
$O_7{}^b$..........3.159(8)	$O_{10}{}^a$..........3.221(7)
$O_6{}^b$..........3.276(10)	$O_1{}^a$..........3.285(9)
$O_4{}^h$..........3.391(6)	$O_3{}^a$..........3.318(7)
b. Selenate groups	
$Se–O_9 = 1.627(7)$	$O_9–Se–O_7 = 112.4(5)$
$Se–O_7 = 1.633(6)$	$O_9–Se–O_{10} = 106.4(4)$
$Se–O_{10} = 1.641(7)$	$O_7–Se–O_{10} = 109.5(2)$
$Se–O_8 = 1.659(7)$	$O_9–Se–O_8 = 111.0(2)$
	$O_7–Se–O_8 = 107.5(4)$
	$O_{10}–Se–O_8 = 110.0(4)$
c. Tellurate groups	
$Te–O_3 = 1.867(7)$	$O_3–Te–O_2 = 92.2(3)$
$Te–O_2 = 1.898(7)$	$O_3–Te–O_1 = 89.5(3)$
$Te–O_1 = 1.897(7)$	$O_2–Te–O_1 = 89.9(3)$
$Te–O_6 = 1.938(7)$	$O_3–Te–O_6 = 92.8(4)$
$Te–O_4 = 1.946(7)$	$O_2–Te–O_6 = 89.4(3)$
$Te–O_5 = 1.946(7)$	$O_1–Te–O_6 = 177.7(4)$
	$O_3–Te–O_4 = 178.8(4)$
	$O_2–Te–O_4 = 88.3(3)$
	$O_1–Te–O_4 = 89.5(3)$
	$O_6–Te–O_4 = 88.2(3)$
	$O_3–Te–O_5 = 91.5(3)$
	$O_2–Te–O_5 = 176.3(4)$
	$O_1–Te–O_5 = 89.7(3)$
	$O_6–Te–O_5 = 90.8(3)$
	$O_4–Te–O_5 = 88.0(3)$
d. Hydrogen bonds	
$O_9....O_3{}^g = 2.789(9)$	$O_9....H_3{}^g = 2.10(6)$
$O_8....O_4{}^h = 2.705(6)$	$O_8....H_4{}^g = 1.57(5)$
$O_8....O_2{}^f = 2.902(7)$	$O_8....H_2{}^f = 2.10(6)$
$O_9....O_5 = 2.761(9)$	$O_9....H_5 = 2.00(9)$
$O_7....O_9{}^i = 2.634(9)$	$O_7....H_6 = 1.81(7)$
$O_9....H_3{}^g–O_3{}^g = 179.28(9)$	$O_1–H_1 = 0.71(7)$
$O_8....H_4{}^h–O_4{}^h = 167.4(5)$	$O_2–H_2 = 0.92(6)$
$O_8....H_2{}^f–O_2{}^f = 143.6(5)$	$O_3–H_3 = 0.79(6)$
$O_9....H_5–O_5 = 138.8(6)$	$O_4–H_4 = 1.14(5)$
$O_7....H_6{}^i–O_6{}^i = 166.6(7)$	$O_5–H_5 = 0.91(10)$
	$O_6–H_6 = 0.84(7)$

Note. Symmetry code: ${}^a -x, y+1, z$; ${}^b x-\frac{1}{2}, y+\frac{1}{2}, z$; ${}^c x-\frac{1}{2}, y-\frac{1}{2}, z$; ${}^d x, -y-1, z-\frac{1}{2}$; ${}^e x-\frac{1}{2}, -y-\frac{1}{2}, z-\frac{1}{2}$; ${}^f x+\frac{1}{2}, y+\frac{1}{2}, z$; ${}^g x+\frac{1}{2}, -y-\frac{1}{2}, z-\frac{1}{2}$; ${}^h x, -y, z-\frac{1}{2}$; ${}^i x+\frac{1}{2}, y-\frac{1}{2}, z$.

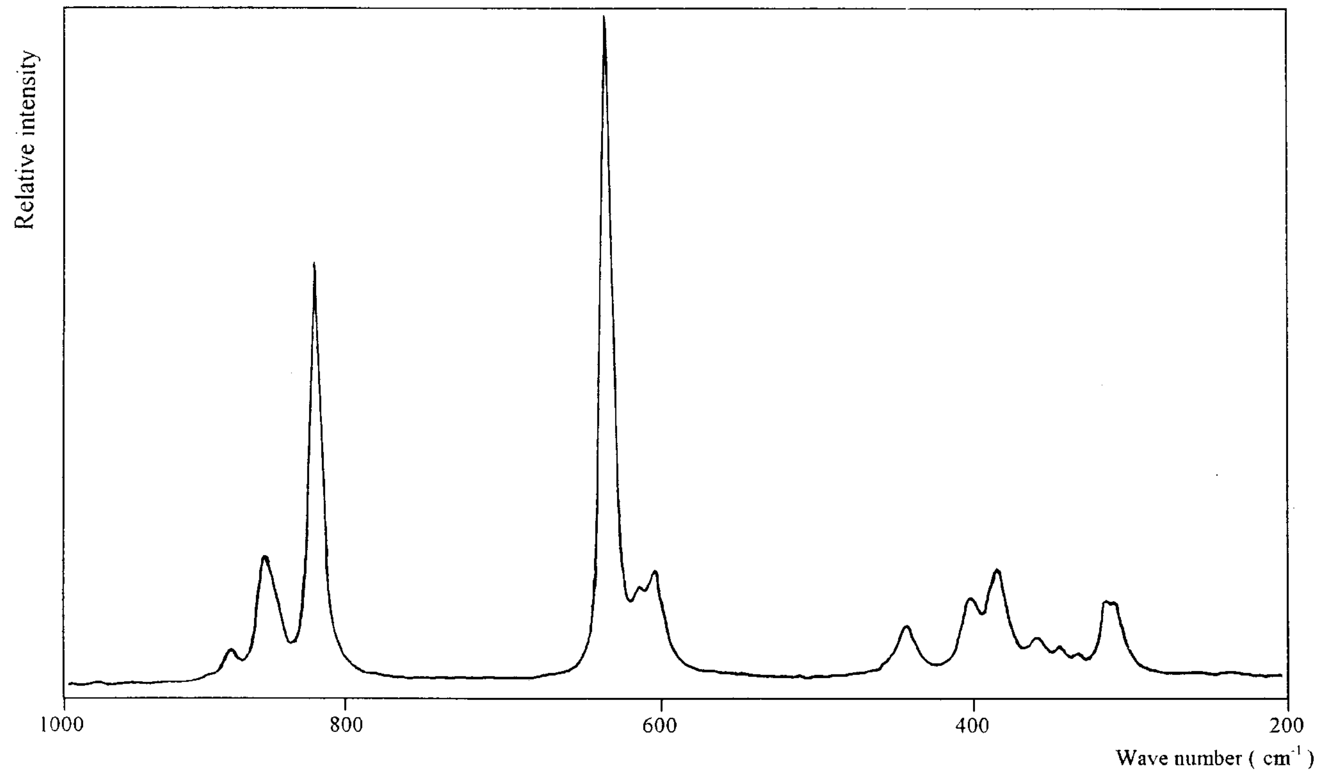

FIG. 3. Raman spectra of $K_2SeO_4 \cdot Te(OH)_6$ (200–1000 cm^{-1}).

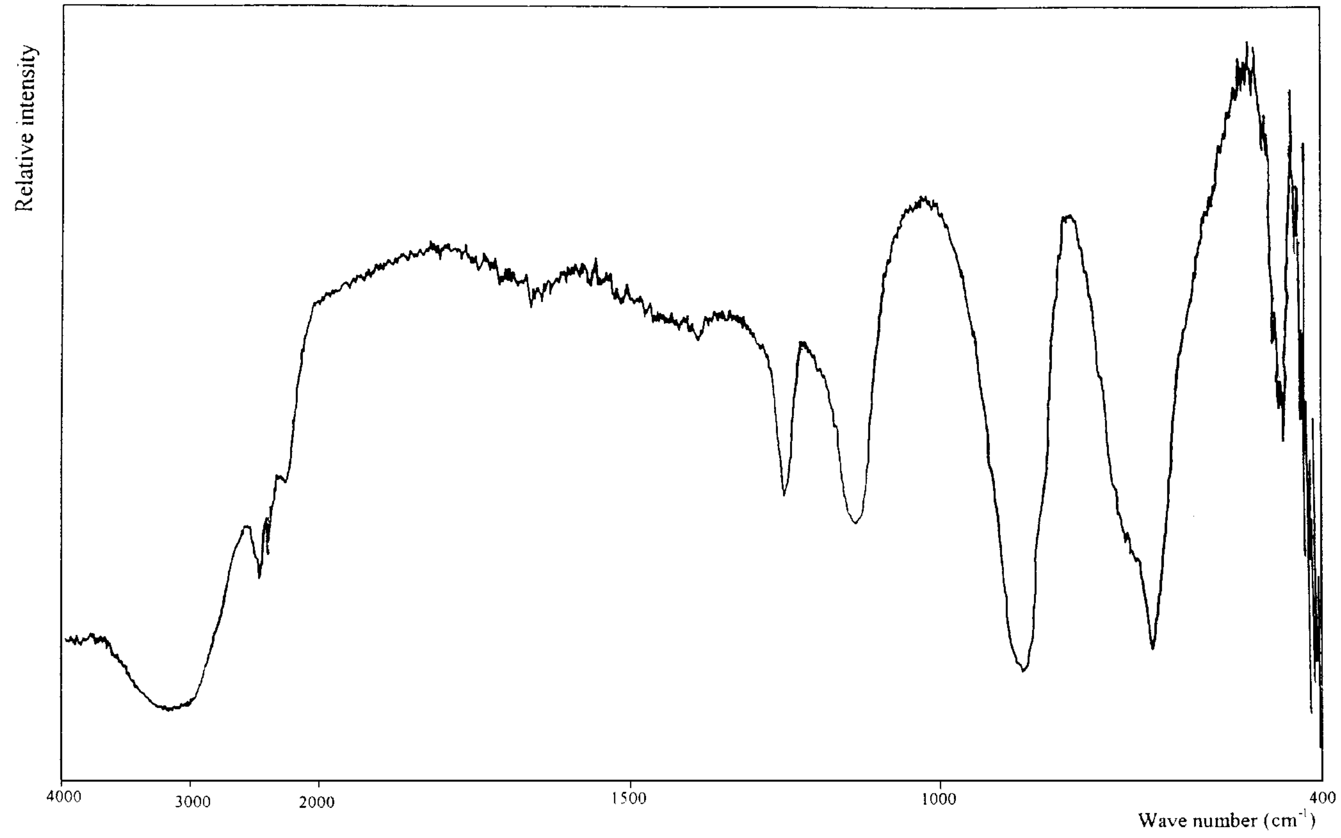

FIG. 4. IR spectra at room temperature of $K_2SeO_4 \cdot Te(OH)_6$.

TABLE 4
Infrared and Raman Frequencies of $K_2SeO_4 \cdot Te(OH)_6$

IR	*I*	Raman	*I*	Assignment
—		245	sh	$\nu_6(TeO_6)$
—		328	mb	$\nu_2(SeO_4) + \nu_4(TeO_6)$
—		347	sh	$\nu_5(TeO_6)$
—		357	sh	
—		369	wb	
		397	s	$\nu_4(SeO_4)$
412	m	—		
—		414	m	
432	m			
456	vs	456	m	
—		618	m	$\nu_2(TeO_6)$
—		627	m	
—		648	vs	$\nu_1(TeO_6)$
665	vs	—		$\nu_3(TeO_6)$
698	wb	—		
—		836	vs	$\nu_1(SeO_4)$
870	vs	870	s	$\nu_3(SeO_4)$
—		894	w	
1139	s	—		
1251	s	—		
1332	b	—		
1654	b	—		
2156	sh	—		
2384	w	—		O–H Stretching
2448	m	—		
3152	vb	—		$\nu(OH)$ of $Te(OH)_6$

Note. Relative intensities: vs, very strong; s, strong; m, medium; w, weak; mb, medium broad; wb, weak broad; vb, very broad, sh, short.

modes: ν_1, ν_2, and ν_5 (Raman active) and ν_3 and ν_4 (IR active). The vibration ν_6 is inactive in both IR and Raman spectra. The stretching and bending vibrations for compounds containing the TeO_6 group normally occur in the range 350–750 cm^{-1} (15). The intense band around 648 cm^{-1} in Raman spectra is assigned to the symmetric stretching (ν_1) mode of TeO_6. The ν_3 mode is observed at 698 cm^{-1} (14, 19, 20). The shoulder peaks at 627 and 618 cm^{-1} are tentatively assigned to the ν_2 vibration of TeO_6 (16). The weak band at 328 cm^{-1} is attributed to ν_4 (TeO_6) and the peaks at 369, 357, and 347 cm^{-1} are assigned to ν_5 (TeO_6) (14). The IR band at 1139 cm^{-1} is attributed to the vibration in the plane bending (16). The short line at 259 cm^{-1} is attributed to the ν_6 (TeO_6) (16).

III.2.2. Vibration of SeO_4 group. The Raman and IR bands in the 870 to 894 cm^{-1} range are assigned to an IR active vibration $\nu_3(SeO_4)$ (17), whereas the Raman line at 836 cm^{-1} is attributed to ν_1 of SeO_4 tetrahedral groups (18). The lines in the 397 to 414 cm^{-1} range in both Raman and IR spectra involve the $\nu_4(SeO_4)$ and $\nu_2(SeO_4)$. The very weak and broad line at 2384 cm^{-1} in IR can be assigned to the O–H stretching vibration but the line at 3152 cm^{-1} is attributed to $\nu(OH)$ of $Te(OH)_6$ (16).

CONCLUSION

The interest of this structure is the presence of two different SeO_4^{2-} and TeO_6^{6-} anions in the same crystal which can be the cause of the appearance of the ferroelectric phase in this type of material. The $Te(OH)_6$ octahedra belong to a number of sheets perpendicular to the *a* axis alternating with planes of SeO_4 tetrahedra also perpendicular to the *a* axis. Both SeO_4 tetrahedra and $Te(OH)_6$ octahedra are connected by a hydrogen bond. A preliminary electric study shows that the presence of hydrogen bonds are in the origin of superprotonic phase transition that appears in a strong jump in the conductivity plot at 480 K (21).

The vibrational study of the KTSe was necessary to observe the coupling of different vibrating groups. The fact that splitting due to the interaction between the two anions was not observed, suggests that both anions vibrate independently in the crystal.

The substitution of the sulfate group in KTS by the selenate group in KTSe changes the space group from $P\bar{1}$ to Cc in spite of the two anions in each compound vibrating independently. This structural change can be due to the cell volume evolution ($V = 472(2)$ Å^3 in KTS and $V = 994.5(3)$ Å^3 in KTSe). In order to deduce the effect of the presence of three anions in the same crystal, we considered studies of the $K_2(SO_4)_{1-x}(SeO_4)_x \cdot Te(OH)_6$ solid solution (22). From these studies we hope to obtain from classic ferroelectric $K_2SO_4 \cdot Te(OH)_6$ and $K_2SeO_4 \cdot Te(OH)_6$ a relaxor ferroelectric in the solid solution $K_2(SO_4)_{1-x}(SeO_4)_x \cdot Te(OH)_6$. The second reason for this study is to determine a relationship between the *x* composition of SO_4/SeO_4 and the variation of the curie temperature T_c. The third reason is to obtain some compositions with high levels of conductivity.

ACKNOWLEDGMENTS

The authors are grateful to Dr. A. Driss, Prof. T. Jouini for access to the CAD4 diffractometer, and Dr. R. Ben Hassen for his help.

REFERENCES

1. H. Khemakhem, M. Gargouri, M. Dammak, R. Ben Hassen, T. Mhiri, and A. Daoud in "Proc. SSPC 9, Bled, Slovenia, 1998," p. 127.
2. R. Zilber, A. Durif, and M. T. Averbuch-Pouchot, *Acta Crystallogr. B* **36,** 2743 (1980).
3. M. T. Averbuch-pouchot and A. Durif, *Ferroelectrics* **52,** 271 (1984).
4. A. C. T. North, D. C. Philips, and F. S. Mattews, *Acta Crystallogr. A* **39,** 351 (1968).
5. G. M. Sheldrick, SHELXS 86, program for the solution of crystal structures, Univ. Of Göttingen, Germany, 1990.
6. G. M. Sheldrick, SHELXL 93, program for crystal structure determination, Univ. Of Göttingen, Germany, 1993.
7. H. Khemakhem, submitted, 1998.
8. A. Kalman, J. S. Stephens, and D. W. J. Cruickshank, *Acta Crystallogr. B* **26,** 1451 (1970).

9. D. F. Mullik, J. D. Korp, W. O. Milligan, G. W. Beall, and I. B. R. Zilber, *Acta Crystallogr. B* **36,** 2565 (1980).
10. I. D. Brown and R. D. Shannon, *Acta Crystallogr. A* **29,** 266 (1973).
11. A. Novak "Hydrogen Bonding in Solids," p. 177. Springre-Verlag, Berlin, 1974.
12. X. Mathew and V. U. Nayer, *J. Raman Spectr.* **20,** 633 (1989).
13. R. Haresh, P. Rajagopal, G. Aruldhas, and G. Keresztury, *Spectrochim. Acta A. Mol. Spectrosc.* (*UK*) **48A,** 1153 (1992).
14. D. Philip, S. Abraham, and G. Aruldhas, *J. Raman Spectr.* **21,** 521 (1990).
15. Allman and W. Hasse, *Inorg. Chem.* **15,** 804 (1976).
16. K. Viswanathan, V. U. Nayar, and G. Aruldhas, *Infrared Phys.* **26,** 89 (1986).
17. M. Kamoun, M. Halouani, and A. Daoud, *Phase Transitions* **9,** 327 (1987).
18. M. Gargouri, R. B. Hassen, T. Mhiri, and A. Daoud, *Phys. Stat. Sol. B* **206,** 535 (1998).
19. M. Gargouri, T. Mhiri, A. Daoud, and T. Jouini, *Phys. Stat. Sol. B* **200,** 3 (1997).
20. M. Dammak, H. Khemakhem, T. Mhiri, A. W. Kolsi, and A. Daoud, *J. Alloys Compounds* **280,** 107 (1998).
21. M. Dammak, H. Khemakhem, T. Mhiri, and A. W. Kolsi, under study.
22. M. Dammak, H. Khemakhem, T. Mhiri, and A. Daoud, in preparation.
23. R. Zilber, I. Tordjman, and J. C. Guitel, *Acta Crystallogr. B* **36,** 2741 (1980).