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1997 J. Phys.: Condens. Matter 9 10977

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Vibrational study of the superionic–protonic phase transition of $\text{CsH}(\text{SO}_4)_{0.76}(\text{SeO}_4)_{0.24}$

M Gargouri, T Mhiri and A Daoud

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

Received 14 May 1997, in final form 26 August 1997

Abstract. Raman spectra ($10\text{--}1300\text{ cm}^{-1}$) of polycrystalline samples of $\text{CsH}(\text{SO}_4)_{0.76}(\text{SeO}_4)_{0.24}$ were studied from 300 to 500 K. The first-order phase transitions were previously detected at 333 and 408 K. These transitions are believed to be governed by librations of the AO_4^{2-} ion and the A–OH (A = S, Se) stretching mode. The transition at 333 K is characterized by the conversion of infinite $(\text{HAO}_4^-)_n$ with (A = S, Se) chains to cyclic $(\text{HAO}_4^-)_2$ dimers. The transition at 408 K corresponds to a superprotonic phase transition (SPT) where proton and AO_4^{2-} (A = S, Se) ions contribute to the unusual high conductivity. The activation energy was determined from the plot of $\Delta\nu_{1/2}$ as a function of temperature for the $\nu_{\text{Se-OH}}$ bands. It is of the same order of magnitude as that estimated from conductivity.

1. Introduction

Hydrogenosulphate and selenate compounds of general formula MHAO_4 (M = Cs, Rb, Li, K, A = S, Se) are known for their superionic phase transitions [1–3]. They are interesting since the high-temperature phase above 400–420 K exhibits an unusually high conductivity of the order of $10^{-2}\ \Omega\ \text{cm}^{-1}$. In the mixed compound $\text{CsH}(\text{SO}_4)_{0.76}(\text{SeO}_4)_{0.24}$, it has been established that a partial substitution of sulphate by selenate spreads out the superionic conductor transition. Many papers have reported on the high-temperature phase transition, mainly in CsHSO_4 ($T = 417\text{ K}$) [4].

In this work we discuss the results concerning the determination of the activation energy from the Raman spectroscopic studies compared to the activation energy by electrical conductivities.

2. Experimental details

$\text{CsH}(\text{SO}_4)_{0.76}(\text{SeO}_4)_{0.24}$ alloys have been synthesized by slow evaporation above 300 K of stoichiometric $\text{Cs}_2\text{SO}_4/\text{H}_2\text{SO}_4/\text{H}_2\text{SeO}_4$ aqueous solutions [5]. Crystals and polycrystalline pieces of this material are isolated. Raman spectra of polycrystalline samples sealed in glass tubes were recorded on an RTI DILOR instrument using the 514.5 nm exciting line of a Spectra-Physics argon ion laser and a cryostat SMC (TBT) in the temperature range 100–500 K.

3. Structure

At room temperature, mixed crystals $\text{CsH}(\text{SO}_4)_{0.76}(\text{SeO}_4)_{0.24}$ belong to the monoclinic space group $P2_1/a$ with the parameters $a = 7.8340\ \text{\AA}$, $b = 8.2147\ \text{\AA}$, $c = 7.444\ \text{\AA}$, $\beta = 110.91^\circ$

and four formula units per unit cell [5]. The hydrogen sulphate or hydrogen selenate groups are connected by hydrogen bonds. The separated chains of asymmetric hydrogen bonds run parallel to the c -axis. The length of the O–H \cdots O bond is 2.608 Å compared to 2.603 Å for CsHSeO₄. The proton seems to be disordered between two equivalent positions with the (0.23, 0.27, 0.06) and (0.17, 0.77, –0.06) coordinates along the O–H \cdots O bond. The structure is very open: half the oxygen anions belonging to AO₄^{2–} (A = S, Se) groups are H bonded so that half the possible proton sites are actually occupied. The structure consists of infinite (HAO₄[–])_n (with A = S, Se) chains.

4. Results and discussion

4.1. Assignment

Raman spectra of both internal and external modes of a polycrystalline sample CsH(SO₄)_{0.76}(SeO₄)_{0.24} were recorded at different temperatures between 300 and 500 K (figure 1). This study was restricted to the 10–1300 cm^{–1} spectral region because it includes lattice vibrations and mainly $\nu_{(A-O)}$ and $\nu_{(A-OH)}$ (with A = S, Se) stretching modes which are most sensitive to phase transitions and crystal changes. In previous work [6, 7] we considered the splitting $\Delta\nu = \nu_{(A-O)} - \nu_{(A-OH)}$ to discriminate between the chains (HAO₄[–])_n or dimers of (HAO₄[–])₂.

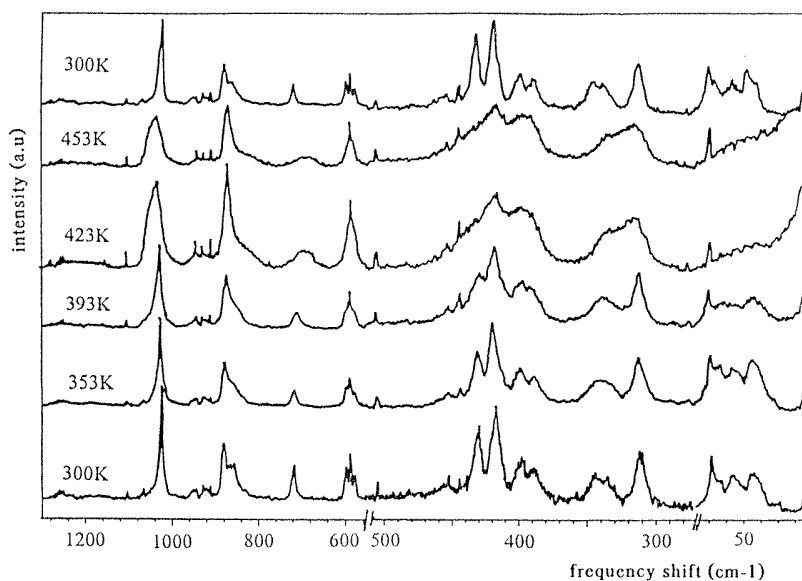


Figure 1. Raman spectra of a polycrystalline sample of CsH(SO₄)_{0.76}(SeO₄)_{0.24} in the range 10–1300 cm^{–1} at different temperatures.

If $\Delta\nu \leq 160$ cm^{–1} the AO₄^{2–} (A = S, Se) ions are associated with (HAO₄[–])_n chains, and if $\Delta\nu > 160$ cm^{–1} the AO₄^{2–} (A = S, Se) are associated with (HAO₄[–])₂ dimers [3, 5]. In our case, $\Delta\nu \leq 160$ cm^{–1} (figure 2). This observation shows that (HAO₄[–]) are associated with chains at room temperature.

The observed Raman bands at selected temperatures and their assignments are given in (table 1). The rotational and translational motions of different groups are given in the

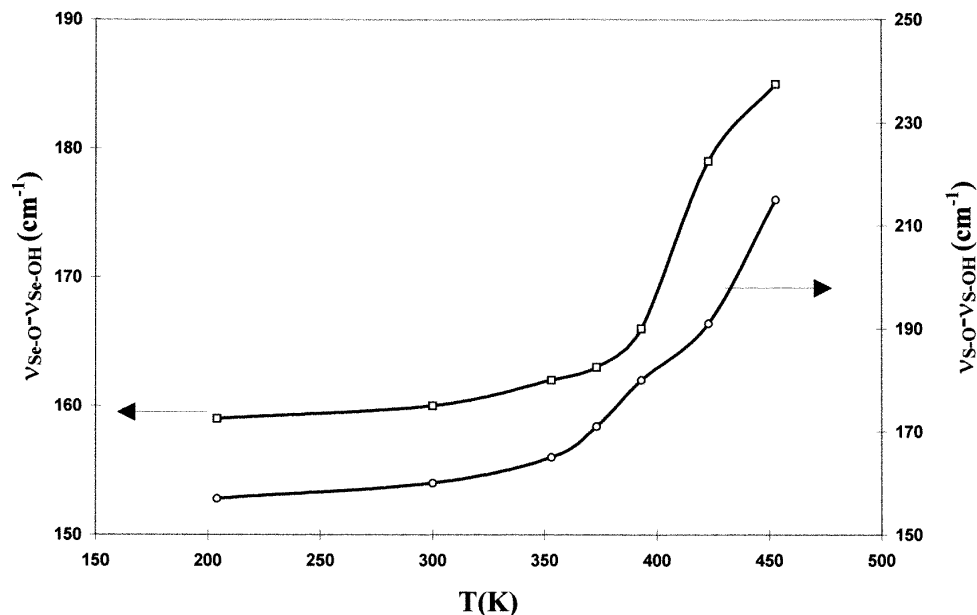


Figure 2. Temperature variation of the splitting ($\nu_{\text{S-O}} - \nu_{\text{S-OH}}$) and ($\nu_{\text{Se-O}} - \nu_{\text{Se-OH}}$).

frequency range $10\text{--}300\text{ cm}^{-1}$. By comparison with the homologous compounds (CsHSO_4) and CsHSeO_4 [1, 2] we can distinguish between the bands assigned to the cation motions and those corresponding to $(\text{HAO}_4^-)_n$ chains (table 1).

Raman lines between 300 and 1300 cm^{-1} are unambiguously assigned to the internal modes of sulphate and selenate ions (table 1). At room temperature we note that the large band at the frequency 862 cm^{-1} , has two peaks which characterize respectively $\nu(\text{S-O-H}\cdots\text{O-S})$ and $\nu(\text{S-O-H}\cdots\text{O-Se})$. The intense band at 878 cm^{-1} is attributed to $\nu_{\text{Se-O}}$. Based on this idea we can deduce that the internal Se-OH stretching mode have an important role in the disorder mechanism governing both transitions.

4.2. Phase transition

Raman spectra of $\text{CsH}(\text{SO}_4)_{0.76}(\text{SeO}_4)_{0.24}$ alloys between 10 and 1300 cm^{-1} at different temperatures are shown in figure 1. They allow us to characterize unambiguously the phase transitions in this material.

These transition temperatures are close to those found by differential scanning calorimetry and conductivity measurements [5].

4.2.1. Transition I-II. The transition which is observed at 333 K for $\text{CsH}(\text{SO}_4)_{0.76}(\text{SeO}_4)_{0.24}$ has been interpreted in terms of the conversion of infinite chains $(\text{HAO}_4^-)_n$ ($A = \text{S}, \text{Se}$) into cyclic dimers $(\text{HAO}_4^-)_2$ [8, 9].

At room temperature the $\Delta\nu = \nu_{\text{S-O}} - \nu_{\text{S-OH}} = 160\text{ cm}^{-1}$ and $\Delta\nu = \nu_{\text{Se-O}} - \nu_{\text{Se-OH}} = 160\text{ cm}^{-1}$ for $\text{CsH}(\text{SO}_4)_{0.76}(\text{SeO}_4)_{0.24}$ alloys which indicates that the HAO_4^- groups are associated with chains. However, on increasing the temperature across the I-II phase transition $\Delta\nu$ increases abruptly to values $> 160\text{ cm}^{-1}$ (figure 2). This indicates that a conversion of $(\text{HAO}_4^-)_n$ chains into $(\text{HAO}_4^-)_2$ dimers takes place [8].

Table 1. Observed Raman frequencies (cm^{-1}) and band assignment for $\text{CsH}(\text{SO}_4)_{0.76}(\text{SeO}_4)_{0.24}$.

Phase I 300 K		Phase II 393 K		Phase III 453 K		Assignment
Raman	<i>I</i>	Raman	<i>I</i>	Raman	<i>I</i>	
40	s	40	m,b	40	w	TCs^+
50	s					
60	s	60	w			
73	s	73	s	73	s	$\text{R}', \text{T}' (\text{HSO}_4)$
81	w	81	w			
308	s	310	s	310	s,b	$\nu_2\text{SeO}_4$
330	s	328	m			
340	s	340	m	340	w	$\nu_4\text{SeO}_4$
380	s	380	m,b	380	w	
390	s	390	m,b	390	w	$\nu_2\text{SO}$
410	s	410	s	410	s,b	
422	s	422	s	422	m,b	
477	m	477	w	477	w	
575	s	575	sh			$\nu_4\text{SO}_4$
585	s	585	s	585	s,b	
591	s	591	sh			
718	s	709	s,b	688	w	$\nu(\text{Se-OH})(\text{donor})$
862	s	850	vs	840	w	$\nu(\text{S-OH})$
878	s	875		873	vs	$\nu(\text{S-O})(\text{donor})$
943	m	943	m	943	m	$\nu_3(\text{Se-O}_4)$
1022	vs	1030	vs,b	1055	vs,b	
1063	w	1063	w	1063	w	
1160	w	1160	w	1165	w	
1222	w	1222	w			
1247	w	1247	w	1247	w	

vs = very strong; s = strong; m = medium; w = weak; sh = shoulder.

4.2.2. Superionic transition II–III. The appearance of a substantial disorder above the SPT at 408 K for $\text{CsH}(\text{SO}_4)_{0.76}(\text{SeO}_4)_{0.24}$ is evident from the band broadening (figure 1). This indicates that the orientational disorder of (HAO_4^-) with (A = S, Se) species takes place at the superionic phase transition. Figure 2 shows the temperature variation of the splitting $\nu_{\text{A-O}} - \nu_{\text{A-OH}}$. The splitting shows an increase of about 10 cm^{-1} for the two components, which characterizes the conversion of $(\text{HAO}_4^-)_2$ dimers into ‘quasi-free’ AO_4^{2-} ions and protons. This transition corresponds to the melting of the proton sublattice to a ‘quasi-liquid’ state where protons and AO_4^{2-} ions contribute to the unusually high conductivity previously reported [8]. The S–OH band is masked by the Se–O band so we cannot use the Porto model for this band; however we can use it for $\nu_{\text{Se-OH}}$. The line assigned to the $\nu_{\text{Se-OH}}$ mode (at 718 cm^{-1}) has a remarkable evolution across the transition. It shows a considerable broadening and decreases in intensity on increasing the temperature

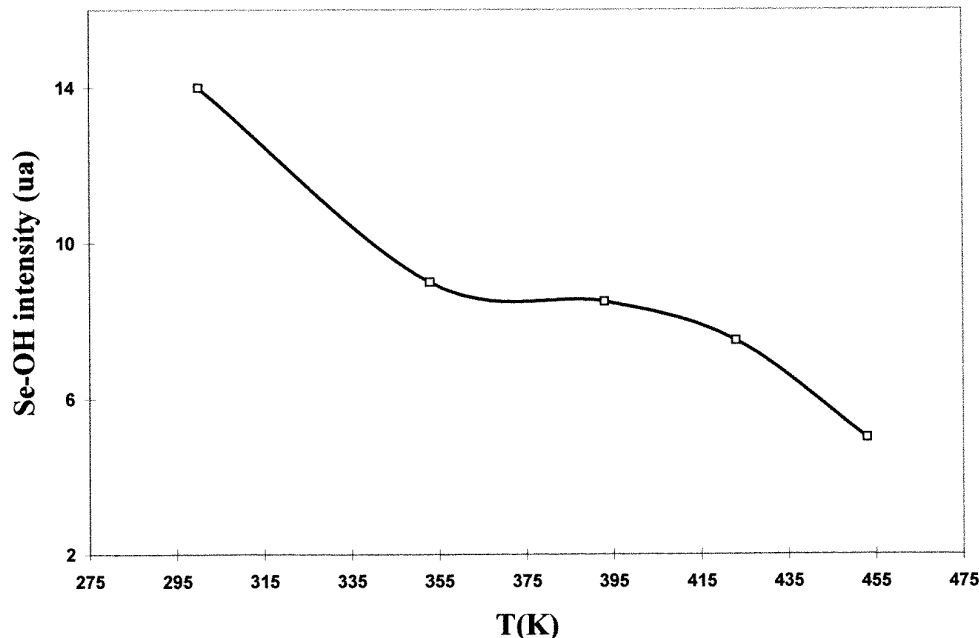


Figure 3. Temperature variation of relative intensity of $\nu_{\text{Se-OH}}$.

(figures 3 and 4). This is interpreted as a results of the large amplitude of oscillation of the proton between two groups AO_4^{2-} and to the weakness of the $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bonds. From the dynamic point of view this phonon may be considered as an internal mode of $(\text{HAO}_4^-)_2$ dimers. When the proton oscillates between two neighbouring AO_4^{2-} groups, the dimer oscillates between two energetically equivalent configurations. Based on work of Andrade and Porto [10, 11] over a broad range of temperature, the dependence of the line width of a non-dispersive phonon associated with an order–disorder mechanism and with a self-diffusive process is a function of the correlation time, τ_c , given by:

$$\Delta\nu_{1/2} = (a + bT) + c \left(\frac{\tau_c}{(1 + \omega^2\tau_c^2)} \right) \quad (1)$$

where ω is the phonon frequency. The time-dependent statistical behaviour of the disorder mechanism is described by the correlation time of the form:

$$\tau_c = \tau_0 \exp(E_0/kT) \quad (2)$$

where E_0 is the activation energy corresponding approximately to the height of the potential barrier between equivalent molecular positions governing the disorder mechanism [12]. According to an earlier microwave measurement [3], the order of magnitude of the correlation time τ_c is 10^{-12} s. Based on the fact that $\omega^2\tau_c^2 \gg 1$ and if we combine the two equations (1) and (2) we obtain:

$$\Delta\nu_{1/2} = (a + bT) + c' \exp(-E_0/kT) \quad (3)$$

where $c' = c/\omega^2\tau_0$. The first term presents the influence of the anharmonicity and the second term represents the thermally active process of a diffusive nature. The experimental curve $\Delta\nu_{1/2}(\text{Se-OH})$ was fitted by the above equation (3) in the temperature range 300–425 K and

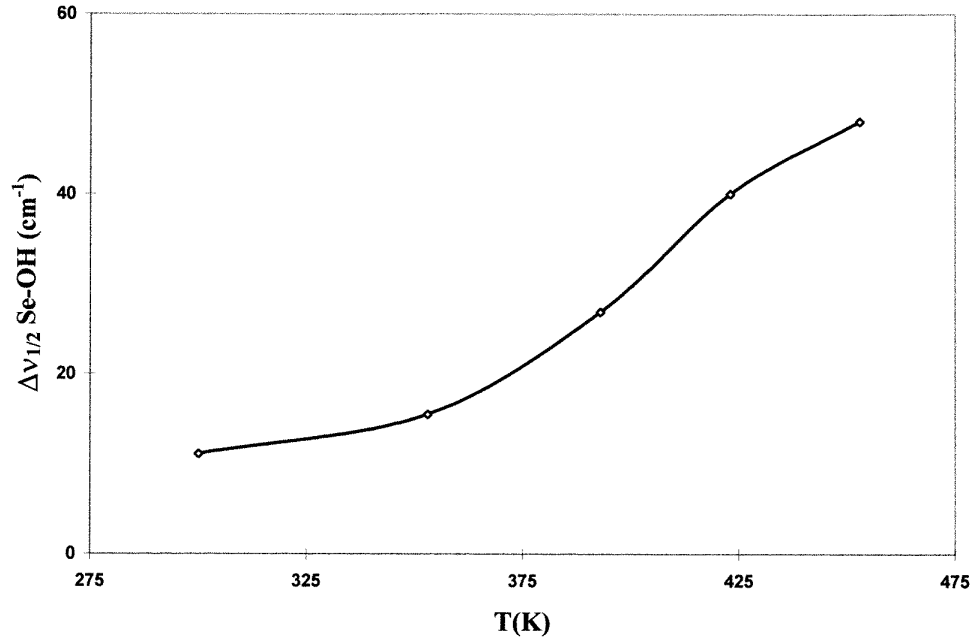


Figure 4. Temperature variation of full width at half-height of $\nu_{\text{Se-OH}}$.

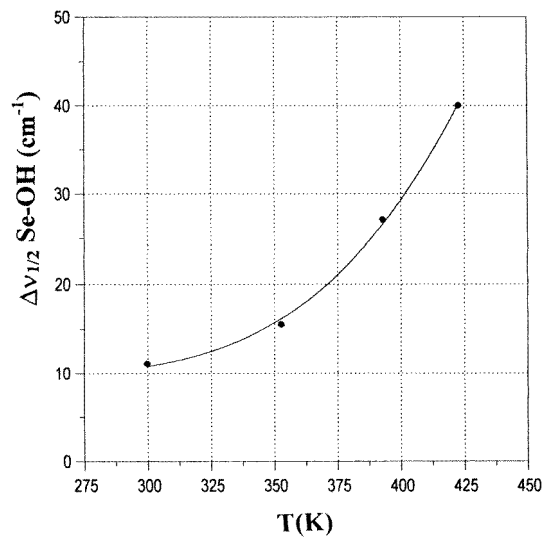


Figure 5. Temperature variation of full width at half-height of $\nu_{\text{Se-OH}}$ with best-fitted curve according to (3).

is illustrated in figure 5. According to this method the E_0 value 0.26 eV. This value of the activation energy is surprisingly close to that estimated from conductivity measurements which is 0.24 eV [13]. We note also the estimated parameters are $a = 9.4 \text{ cm}^{-1}$, $b = 27.499 \times 10^{-5} \text{ cm}^{-1} \text{ K}^{-1}$ and $c' = 67184 \text{ cm}^{-1}$.

5. Conclusion

This mixed compound exhibits two first-order phase transitions. These transitions are of order–disorder type. The evolution of the ν_{A-OH} band across the transitions is very characteristic. This phonon may be considered as an internal mode of the $(HAO_4^-)_2$ (A = S, Se) dimer: when the proton oscillates between two neighbouring AO_4^{2-} (A = S, Se) groups, the dimer oscillates between two energetically equivalent configurations. Based on these properties we have applied the Andrade and Porto theory on this line.

The activation energy value obtained from the Raman studies for this compound and that obtained from conductivity measurements is in good agreement between the two techniques.

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