FTIR investigations of solid precursor materials for sol-gel deposition of WO$_3$ based electrochromic films

M. DEEPA, N. SHARMA, P. VARSHNEY, S. P.VARMA, S. A. AGNIHOTRY
National physical Laboratory, Dr. K. S. Krishnan Road New Delhi, 110012, India
E-mail: agni@csnpl.ren.nic.in

Peroxypolytungstic acid derivative (APTA) and peroxypolytungstic acid derivative coupled with a dicarboxylic acid additive i.e., oxalic acid dihydrate (APTA + OAD) in xerogel form, synthesized by a wet chemistry route were the solid sol-gel precursors for casting WO$_3$ films. These bulk materials have a complex structure owing to the presence of several groups such as acetate, peroxy anions and water molecules in their basic matrix. Additionally, oxalate ions constitute an integral part of the structure in the APTA + OAD xerogel. Detailed FTIR analysis of these coordination compounds has thrown light on the modes of association of the various anions or groups with tungsten metal ion. The mode of coordination of the acetate ion as a bidentate as well as a monodentate ligand enabling chelate formation and the several other chemical linkages prevalent in APTA have been established. Upon the incorporation of OAD in APTA, the net ramifications are drastic changes in the structure inclusive of changes in the nature and strength of metal - ligand bonding, which is exemplified by FTIR studies of (APTA + OAD) xerogel. © *2000 Kluwer Academic Publishers*

1. Introduction

Electrochromic (EC) coatings by virtue of their ability to undergo reversible colouration induced by an electric field, when incorporated in electrochromic devices (ECDs) offer dynamic reflection/transmission modulation of radiant energy. As a result, ECDs have fascinating possibilities to be used as solar control windows modulating transmission and contributing significantly to save energy in buildings [1, 2]. Antidazzling mirrors in automobiles and large area information displays are the other potential applications based on reflection modulation [3].

Large area uniform, thick and cost effective EC coatings play an important role in ECD fabrication. Sol-gel deposition, rather than the conventional physical and chemical deposition techniques, in this regard is advantageous being less capital intensive and thus less expensive. Amongst different precursor materials, alkoxides are most popular for their known properties. Precursor materials for tungsten oxide based EC coatings include colloidal polytungstic acid sol (PTA) [4, 5], peroxypolytungstic acid (PPTA) [6], peroxypolytungstic acid derivative (APTA) and peroxopolytungstic acid derivative coupled with dicarboxylic acid additive such as oxalic acid dihydrate (APTA + OAD) [7]. Liquid precursor materials as such and the solid precursor materials dissolved in suitable solvents are generally deposited by spinning, spraying or dip-coating technique on substrates. Appropriate post deposition thermal treatment depending on the decomposition temperatures of various functionalities trapped in, converts the coatings into EC oxide coatings.

The nature of chemical bonding inclusive of complexation, chelation (acetylation), water absorption (both chemisorbed and physisorbed), condensation polymerization etc. that prevails in these polyanionic acidic products of tungsten and the chemical changes that occur in them during annealing, resulting in their final transformation into a pure tungsten-oxygen network is accompanied by retention of an optimum amount of water crucial for electrochromism. The elucidation of these diverse chemical phenomena is found to be within the scope of FTIR studies. Moreover, an analogy on the basis of these FTIR investigations pertaining to the bulk materials, can be drawn for the as deposited and heat treated WO$_3$ films, which is the fundamental objective for the detailed study undertaken. We report here, a comprehensive and a comparative FTIR analysis of the as prepared as well as that of the annealed bulk peroxo based precursor materials mentioned above.

2. Experimental

Details of preparation of solid peroxypolytungstic acid derivative (APTA) is reported in our earlier publication [8]. APTA + OAD xerogel was prepared by adding OAD in an amount equivalent to 5 wt% of ethanolic solution of APTA, followed by drying under ambient conditions. Annealing treatment given to both these precursor materials was in line with that followed for EC films deposited by using solutions of the same

precursor materials. The first step involved annealing at 100°C for 1 hr and the subsequent step comprised annealing at 250°C for the same time. FTIR spectra were recorded for the aforementioned unannealed and annealed (at 100°C and 250°C) precursors as KBr pellets using Perkin Elmer GX 2000 OPTICA FTIR spectrophotometer.

3. Results and discussion
3.1. FTIR investigations of APTA

Fig. 1a illustrates the FTIR spectrum of untreated APTA in the region 4000–400 cm^{-1}. As can be observed, there is a very broad band peaking at around 3455 cm^{-1} and another sharp and strong one at around 1626 cm^{-1}. The former band can be assigned to the antisymmetric and symmetric stretching frequencies ν(OH) of (both physisorbed and chemisorbed) water molecules and the latter can be assigned to δ (H$_2$O) – in plane bending vibration mode of water molecules [9]. The broadness of this band can be attributed to the several ways in which adsorbed (physisorbed) and structural (chemisorbed) water molecules coordinate [10]:

a) they can directly coordinate with W as hydroxyl groups or as water molecules i.e. W – OH or W-OH$_2$

b) they may form intermolecular hydrogen bonds with hydroxyl groups already associated with tungsten i.e. W - OH - - - OH$_2$

This manifests itself in unequal W-OH bond lengths or bond strengths which are dispersed throughout the molecular structure and is reflected in the broadness and intensity of the band at 3455 cm^{-1}. The expansive nature of this band also illustrates that a good amount of water is retained by the structure.

A series of three bands comprising of a sharp and narrow peak at 2922 cm^{-1} along with two sharp but weak ones at 2955 cm^{-1} and 2844 cm^{-1} are observed that correspond to the stretching vibration ν (CH) of the aliphatic CH$_3$ group which is in accordance with Nakamoto's [11] assignment for acetate ion. An interesting feature of the 2000–1000 cm^{-1} region is the set of two sharp, strong bands observed at 1545 cm^{-1} and 1460 cm^{-1}. According to Nakamoto [11], the acetate ion may coordinate to the metal ion [(M≡W), in the present case], in any one of the following modes:

Structure 1   Structure 2   Structure 3

The ν_{asymm}(COO^{-1})/ν(C=O) and ν_{symm}(COO$^-$)/ ν(C - O) of the free acetate ion have been reported to be 1560 cm^{-1} and 1416 cm^{-1} respectively and the frequency separation between the two ν(COO$^-$), represented by $\Delta\nu$ is 144 cm^{-1}. When the acetate ion coordinates as a bi-dentate chelating ligand involving the participation of both the oxygens as potential donor atoms with tungsten (the acceptor central metal ion), the carbonyl C=O bond (labelled as 'a' in structure 4) weakens. This is due to the formation of W-O bond through the carbonyl oxygen and the extensive delocalization of the π electrons over the adjacent C-O bond (labelled as 'b' in structure 4) which is also linked to W through oxygen. These factors collectively manifest in further strengthening of the non carbonyl C-O bond whose ν_{symm}(COO$^-$)/ν(C - O) shifts to a higher frequency from 1416 cm^{-1} (for free acetate) to 1460 cm^{-1} (see Table I). A net repercussion of this chelate or four membered ring formation (due to resonance stabilization of electrons over the $C{<}^O_O$ bonds) is the weakening of the C=O bond resulting in a shift of ν_{asymm}(COO$^-$)/ ν (C=O) to a lower frequency 1545 cm^{-1}, in comparison with 1560 cm^{-1} for the free acetate. Thus in a
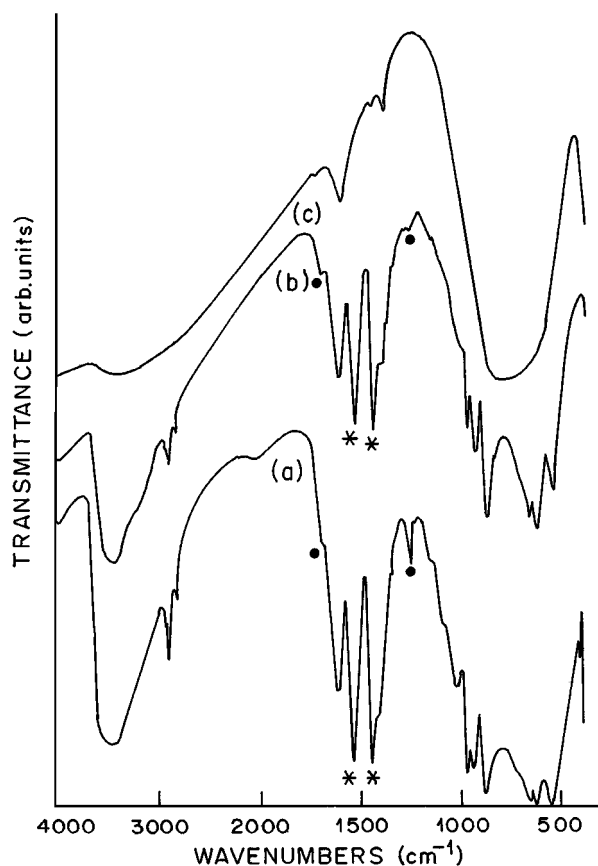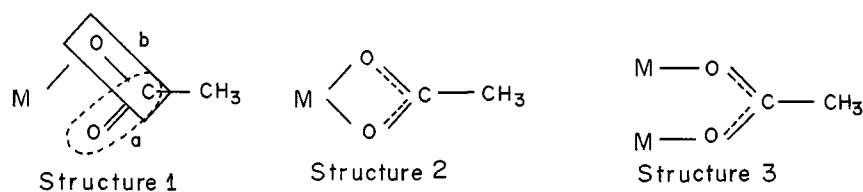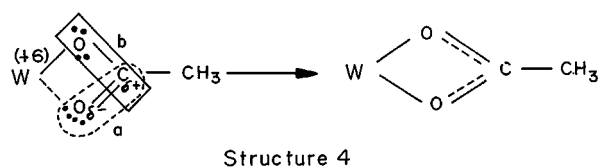

Figure 1 Infrared Spectra of APTA : a) unannealed b) annealed at 100°C for 1 hr. c) annealed at 250°C for 1 hr. [* & • representing bidentate and monodentate coordination modes of acetate ion].

Structure 4

Coordination mode of acetate ion	ν(C $-$ O) or ν_{symm}(COO$^-$) (cm^{-1})	ν(C$=$O) or ν_{asymm}(COO$^-$) (cm^{-1})	$\Delta\nu$ (cm^{-1})
Free acetate	1416	1560	144
Bidentate	1460	1545	105
Monodentate	1250	1700	450

bidentate chelating complex (structure 4), ν_{asymm}(COO$^-$) for bound acetate is less than ν_{asymm}(COO$^-$) for free acetate and ν_{symm}(COO$^-$) of bound acetate is greater than ν_{symm}(COO$^-$) of free acetate [11]. Also, the frequency separation $\Delta\nu$ is expected to be much smaller than that of the free ion. Thus the frequency separation $\Delta\nu$ of 105 cm^{-1} between ν_{asymm}(COO$^-$) at 1545 cm^{-1} and ν_{symm}(COO$^-$) at 1460 cm^{-1} strongly indicates that the acetate ion predominantly acts as a bidentate chelating ligand rather than a bridging ligand (structure 3) as bridging ligands usually give rise to larger $\Delta\nu$ ranging between 120–160 cm^{-1} [12].

When the acetate ion coordinates with tungsten metal ion as a monodentate ligand through the non-carbonyl oxygen (structure 5), the W-O bond becomes stronger and the C-O bond coordinated to the
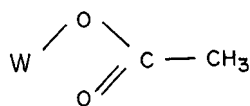
Structure 5

metal becomes weaker. As a result ν_{symm}(COO$^-$) shifts to a lower frequency in comparison with the free acetate and the free C$=$O bond (carbonyl group) becomes stronger. Consequently a shift of ν_{asymm}(COO$^-$)/ν(C$=$O) to a higher frequency in comparison with free acetate ion is expected. So in a monodentate complex (structure 5) ν_{asymm}(COO$^-$) for bonded acetate is higher than ν_{asymm}(COO$^-$) of free acetate and ν_{symm}(COO$^-$) for bonded acetate is lowered with respect to ν_{symm}(COO$^-$) of free acetate and the frequency separation $\Delta\nu$ lies around 400 cm^{-1} [12].

Two additional bands are encountered in the FTIR spectrum of APTA (Fig. 1), one of them appears as a weak shoulder at around 1700 cm^{-1} and the other as a sharp isolated band at 1250 cm^{-1}. These could be attributed to the ν(COO$^-$) vibrations of the acetate monodentate ligand and the extremely large frequency separation ($\Delta\nu = 450$ cm^{-1}) suggests that the acetate ion not only acts as a bidentate ligand as established earlier but also as a monodentate ligand [11]. This is also corroborated by the presence of quite a number of weak shoulders in the 1700–1250 cm^{-1} frequency range. Thus, two different coordination modes for the acetate ion with tungsten metal have been unambiguously identified and distinguished. Table I summarizes positions of carboxyl bands as reported for free acetate ion [11] and those observed for mono and bidentate coordination modes of acetate ion in APTA.

A couple of two weak bands are seen as shoulders at 1437 cm^{-1} and 1415 cm^{-1} and may be assigned to the asymmetric deformation vibration modes δ (CH$_3$) of the methyl group [11, 12]. Another set of two consecutive bands appearing as weak shoulders are observed at 1160 cm^{-1} and at 1091 cm^{-1}. These correspond to the W-O-C vibrations of the acetate group bonded directly to W. A set of two bands, a sharp and strong one at 1023 cm^{-1} and the other which appears as a weak shoulder at 1045 cm^{-1} can be assigned to the rocking vibrational modes (ρ_r) of the CH$_3$ group [11].

The low energy side of the spectrum (1000–400 cm^{-1}) is predominantly characterized by W-O vibrational modes. Two strong bands are observed at 990 cm^{-1} and at 960 cm^{-1}. The band at 960 cm^{-1} is less intense and much broader than the band at 990 cm^{-1} and corresponds to the stretching frequency of W$=$O$_t$, O$_t$ representing the terminal oxygen atom [13, 14]. Hibino et al. [14] have reported that the lesser the degree of polymerization prevalent in these polyanions of tungsten, the sharper and narrower is the band corresponding to the stretching frequency of W$=$O$_t$. In APTA, the extent of polymerization is significantly reduced when compared with PPTA [14] or PTA [15]. This is evidenced by the presence of two bands : a highly intense one at 990 cm^{-1} and another slightly broad one at 960 cm^{-1} unambiguously proving the existence of two types of W$=$O$_t$ bonds in APTA, as two different molecular environments persist for W$=$O$_t$ bonds.

Two distinct bands observed at 890 cm^{-1} and at 551 cm^{-1} can be attributed to the W (O)$_2$ {bidentate peroxy group} stretching and O-O stretching vibrations of peroxo linkage respectively [13, 16, 6]. Three medium strong bands are seen at 688, 665 and 630 cm^{-1}. Assigning these bands is rather difficult as a large number of bands corresponding to the vibrational modes of different bonds such as the π (CH) or π (COO) at around 620 cm^{-1} i.e. out of plane bending modes of –CH or –COO groups, δ (O-C$=$O) at around 650 cm^{-1} [11] and the antisymmetric [W(O)$_2$] stretching modes [16] are expected to appear in this region. Immense complexity is rendered to this region of the spectrum due to excessive overlapping of bands within a narrow frequency range, thus making it virtually impossible to make precise band assignments.

3.2. FTIR investigations of APTA + OAD

The precursor (APTA + OAD) in xerogel form consists of both physisorbed and chemisorbed water molecules, acetate groups (as acetic acid is incorporated during synthesis and due care is taken to decompose only excess acetic acid), hydrogen peroxide (but may not continue to exist as such) and oxalate ions [as oxalic acid dihydrate (OAD), a pre-film deposition additive, is added to the precursor APTA solution in alcohol for excellent EC properties].

Fig. 2a displays the FTIR spectrum of APTA + OAD xerogel in the region 4000–400 cm^{-1}. The broad, strong band observed at $\sim$3444 cm^{-1} is attributable to the stretching vibration ν (OH) of water molecules and the sharp, intense band at 1635 cm^{-1} is basically due to in plane bending δ (HOH) of the same [9, 10]. A cluster of
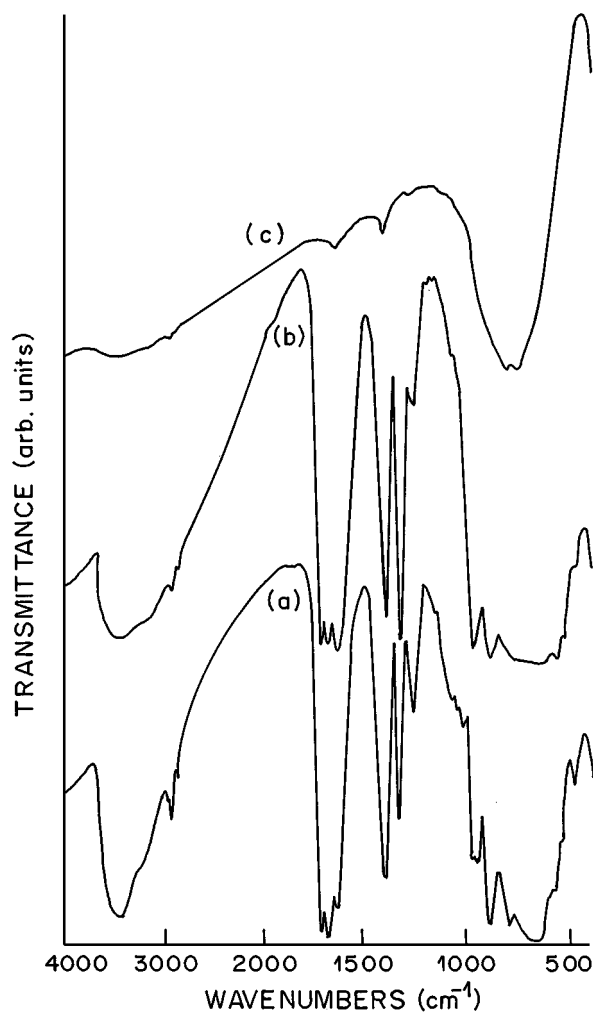
Figure 2 Infrared Spectra of APTA + OAD : a) unannealed b) annealed at 100°C for 1 hr. c) annealed at 250°C for 1 hr.

three bands in the frequency range 2900–2800 cm^{-1} are observed similar to that shown by APTA (Fig. 1a), with their relative intensities also continuing to be similar. However, their positions have undergone a slight shift, as they now appear at 2944, 2911 and 2822 cm^{-1} respectively. These three bands correspond mainly to the stretching vibration ν (CH) of the aliphatic CH$_3$ group [11] of the acetate ion.

Nakamoto [11] had shown that the oxalate anion coordinates to transition metal ions as a monodentate (Structure 6) or a bidentate (Structure 7) ligand or it may act as a bridging group between metal atoms. In fact, according to Scott *et al.* [17] it can assume four types of bridging structures.
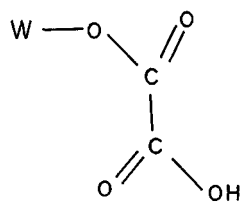
Structure 6   Structure 7
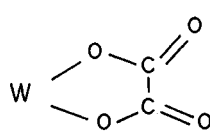
The ν (CO) frequencies of an oxalato bridging ligand and a bidentate one lie very close to each other and it is therefore difficult to distinguish them on the basis of their frequencies. But IR spectra of peroxy-

oxalato complexes of tungsten studied by Griffith [18] have revealed that oxalate ions predominantly act as bidentate ligands, an observation that is strongly corroborated by Nakamoto [11] who states that the bidentate chelate structure formed by oxalate ions is most common. According to Bellamy [19], the ν (C=O) frequencies of free oxalic acid dihydrate (OAD) appear at 1710 cm^{-1} and 1690 cm^{-1}. Rao's [20] studies on IR spectra of several oxalate complexes have shown that all the fundamental vibrations of the oxalate ion are affected by coordination. The general feature of the spectra were: 1) a strong doublet around ~1700 cm^{-1} due to modified C=O groups 2) a strong band around 1400 cm^{-1} mainly due to C-O stretching vibration. The only prominent difference that persists between the "peroxy – oxalate complexes with tungsten" studied by Griffith [18] and the complexes we synthesized is that in these APTA + OAD chelates apart from peroxo and oxalato groups, acetate groups are also an integral part of the matrix.

On the basis of the band assignments made by Griffith [18] for peroxyoxalates of tungsten, it can be confirmed that the doublet comprising of two strong bands at 1713 cm^{-1} and 1687 cm^{-1} are primarily due to the antisymmetric ν_{asymm}(C=O) stretching vibration of carboxyl group of the oxalate anion. Similarly, a second doublet consisting of very strong bands at 1401 cm^{-1} and 1335 cm^{-1} can be attributed to stretching vibrational modes ν(CC) and ν_{symm}(CO) of the oxalate ion. Moreover the characteristic bands corresponding to ν_{asymm}(C=O) and ν_{symm}(CO) of the acetate were also expected to be seen in 1400–1700 cm^{-1} region. However, the ligand strength and chelating tendency of oxalate ion is much superior to that of acetate ion by the virtue of oxalate's larger size and greater number of nucleophilic electron donating oxygen atoms. This might enable a) the substitution of a substantial number of acetate groups by oxalate ions b) direct linkages between tungsten and oxalate anion which are also facilitated by the electrophilic tungsten's ability to easily assume a higher coordination number and expand its coordination matrix. This distinct property of the oxalate ion is clearly reflected in the spectrum, as all bands characteristic of acetate acting as bidentate or as a monodentate ligand are heavily superimposed or have simply merged with the bands of the oxalate ion which are characteristic of its tendency to act as a bidentate ligand. This reaffirms that the associative power or complexing ability of the oxalate ion is considerably greater than that of the acetate ion. Griffith has summarized the vibrational modes of K$_2$[WO(O$_2$)$_2$ (OX)] and K$_2$[WO$_2$(O$_2$)(OX)(H$_2$O)]. H$_2$O in the lower wavenumber region [18]. From his assignments, it can be confirmed that the doublet at ~983 cm^{-1} and ~958 cm^{-1} corresponds to stretching ν(W=O$_t$) vibrational modes of terminal W-O bond [16, 18]. The reason for the appearance of a doublet instead of a single band is that the structure of the compound is highly irregular at molecular level. This is evidenced by the fact that the degree of polymerization that prevails in these compounds is strongly dependant on 1) the nature of additives incorporated during synthesis and 2) processing parameters. Although

extensive hydrogen bonding through water molecules and hydroxyl groups plays a vital role in the formation of a continuous, basic tungsten- oxygen network, complexation inhibits polymerization (W-O-W bond formation) to a very great extent which results in 1) a high concentration of terminal $W{=}O$ groups 2) prominent differences in the vicinal chemical environment of these $W{=}O$ bands. These two factors are thus responsible for the doublet observed for the $W{=}O_t$ band.

The two bands at 894 and 854 cm^{-1} can be assigned to the ν(O-O) stretching vibration of peroxo group [13, 18]. The broadness of the band appearing in the 600–660 cm^{-1} illustrates the overlapping of several bands which were expected to lie in this region at the following positions $\nu_{sym}[W(O_2)]$ at $\sim$661 cm^{-1}, π(CH) or π(COO) of acetyl groups at 620 cm^{-1} [11], fundamental symmetric and antisymmetric stretching modes of W-O-W network. The weak shoulder at 539 cm^{-1} is basically due to the combination band of the two stretching modes ν(WO) + ν(CC) and the strong sharp band peaking at 483 cm^{-1} is characterized by ν(WO) + ring deformation [21, 11].

3.3. FTIR spectra of APTA and APTA + OAD annealed at 100 °C

The spectra for bulk materials a) APTA and b) APTA + OAD each annealed at 100 °C for one hour are exhibited in Figs 1b and 2b respectively. Unlike the spectrum of unheated samples, which comprised of a smattering of weak shoulders, the spectrum for heated samples [Figs 1b and 2b] are much cleaner as the number of weak shoulders have depleted significantly. In Fig. 1b, most of the peaks have shown slight positional shifts and have also exhibited a decrement in their absorption intensities. However in Fig. 2b, apart from the positional variations displayed by the peaks, the relative intensities for peaks in the range 1720–1330 cm^{-1} have changed remarkably but their individual intensities haven't shown any drastic decrement. This is indicative of thermally induced rearrangements at molecular level which promote structural evolution – a process whose occurrence can be correlated to the presence of OAD. Moreover the doublet corresponding to ν(W=O$_t$) [at 958 & 983 cm^{-1} in Fig. 2a] has transformed into a single, intense peak at 989 cm^{-1} [in Fig. 2b], thereby reaffirming the preceding statement.

Another noticeable aspect observed in the spectra of heated materials is that the absorption intensities for peaks at a) 1250 cm^{-1} [Fig. 1a, attributed to ν_{symm}(COO) of acetate] and b) 1262.5 cm^{-1} [Fig. 2a, assigned to ν(CO) + ν(OCO) {for oxalate} and ν_{symm}(COO) {for acetate}], have diminished by an unusually large extent upon heating and appear as weak shoulders [in Figs 1b and 2b]. This suggests that thermal decomposition at low temperatures causes an enormous reduction in the concentration of acetate groups, especially the acetate ions bound as monodentate ligands. Corroborating this, is the decrease in the intensities of the three bands corresponding to ν(CH) of methyl groups of acetate at $\sim$2900 cm^{-1}. Since the peaks cor-

responding to acetate ions acting as bidentate ligands haven't been perturbed strongly, it is apparent that excessive degradation of these groups occurs at higher temperatures.

3.4. FTIR spectra of APTA and APTA + OAD annealed at 250 °C

Figs 1c and 2c show the spectra for a) APTA and b) APTA + OAD bulk materials heated at 250 °C. In both spectra, it is interesting to note that most of the peaks attributable to the various vibrational modes of acetate or oxalate have completely vanished or appear as weak peaks with poor intensities; indicating that the concentration of these groups is reduced to trace amounts in the heated materials.

Only a broad band at wavenumbers superseding 3000 cm^{-1} and peaks at 1618 cm^{-1} [Fig. 1c] / [Fig. 2c] corresponding to stretching and bending vibrational modes of water molecules remain. In both spectral patterns, a broad band is observed in the 1000–500 cm^{-1} region. Fig. 1c illustrates a peak developing at $\sim$819 cm^{-1} and Fig. 2c shows a similar peak at 815 cm^{-1} along with an additional peak at 763 cm^{-1}. These peaks can be attributed to the stretching frequency of O-W-O, which is characteristic of WO$_3$ framework [22]. The spectrum of commercially available orthorhombic WO$_3$ also shows two such distinct peaks. These two peaks are well developed for APTA + OAD sample [Fig. 2c] and not at all well formed for APTA without OAD [Fig. 1c]. Perhaps this is an indirect evidence, establishing the onset of crystallization for APTA (with an acid additive) at 250 °C as was revealed from the XRD patterns of the films of APTA + OAD under similar heating treatment [8].

Annealing of bulk materials at elevated temperatures i.e., at 250 °C enables a) almost complete elimination of acetates or oxalates by thermal and oxidative decomposition, b) absolute removal of peroxo ligands or deoxidation (as W(O$_2$) → W=O, W-O-O-W → W-O-W etc), c) dehydration and d) polymerization or aggregation to form W-O-W linkages [6]. Eventually these processes lead to the formation of highly condensed species such as a complex, cross-linked, hydrated and hydroxylated tungsten trioxide network.

4. Conclusion

Our FTIR investigations of peroxypolytungstic acid derivatives APTA and APTA + OAD – the precursors for depositing WO$_3$ films – have revealed important information about the modes of association of acetate, oxalate ions, peroxo groups and water molecules with tungsten metal ion. Oxalate ions predominantly coordinate as bidentate ligands whereas acetate ions act as monodentate as well as bidentate ligands. The associative power of oxalate is shown to be far more superior to that of acetate ion and how these complexation phenomena inhibit extensive polymerization and control the condensation pathway for the evolution of final tungsten – oxygen network has been demonstrated. Excessive decomposition of mono and bidentate ligands occurring at 100 °C and 250 °C respectively, accompanied

by the initiation of crystallization in the APTA + OAD sample at 250 °C explains the two step annealing treatment of the films deposited by using these precursor materials for EC applications.

Acknowledgment

References

1. C. M. LAMPERT, *Solar Energy Mater* **11** (1984) 1.
2. C. G. GRANQVIST, in "Materials Science for Solar Energy Conversion Systems" edited by C. G. Granqvist (Pregamon, Oxford, 1991) p. 106.
3. S. A. AGNIHOTRY and S. CHANDRA, *Ind J Mater Sci & Eng* **1** (1994) 320.
4. A. CHEMSEDDINE, T. D. R. MORINEAU and J. LIVAGE, *Solid State Ionics* **9/10** (1983) 357.
5. PRADEEP, NIDHI, R. RAMCHANDRAN and S. A. AGNIHOTRY, *Ind J Pure & Appl Physics* **37** (1999) 262.
6. K. YAMANAKA, H. OKAMOTO and H. KIDOU and T. KUDO, *Jpn. J. Appl. Phys* **25** (1986) 1420.
7. J. P. CRONIN, A. AGRAWAL, D. J. TARICO and J. C. L. TONAZI , US Patent no **5, 525, 264** (1996).
8. S. A. AGNIHOTRY, NIDHI SHARMA, M. DEEPA, RAM KISHORE, K. N. SOOD and S. K. SHARMA, *Proceedings of SPIE* **3788** (1999) 111.
9. L. J. BELLAMY, "The Infrared Spectra of Complex Molecules" (John Wiley &, Inc. Sons, 1954) Ch. 6, p. 85.
10. B. GERAND, G. NOVOGROCKI and M. FIGLARZ, *J. Solid State Chemistry* **38** (1981) 312.
11. K. NAKAMOTO, "Infrared & Raman Spectra of Inorganic & Coordination Compounds" (Wiley Interscience Publication, 1978).
12. S. DOEUFF, M. HENRY, C. SANCHEZ and J. LIVAGE, *J. Non Crystalline Solids* **89** (1987) 206.
13. H. OKAMOTO, K. YAMANAKA and T. KUDO, *Materials Research Bulletin* **21** (1986) 551.
14. M. HIBINO, T. KUSAKABE and T. KUDO, in "Solid State Ionics: Science & Technology," edited by B. V. R. Chowdari, K. Lal, S. A. Agnihotry, N. Khare, S. S. Sekhon, P. C. Srivastava and S. Chandra (World Scientific Publishing Co, 1998). p. 275
15. M. F. DANIEL, B. DESBAT, J. C. LASSEGUES, B. GERAND and M. FIGLARZ, *J. Solid State Chem.* **67** (1987) 235.
16. W. P. GRIFFITH and T. D. WICKINS, *J. Chem. Soc (A)* (1968) 397.
17. K. L. SCOTT, K. WIEGHARDT and A. G. SYKES, *Inorg. Chem.* **12** (1973) 655.
18. A. C. DENGEL, W. P. GRIFFITH, R. D. POWELL and A. C. SKAPSKI, *J. Chem. Soc. Dalton Trans* (1987) p. 991.
19. L. J. BELLAMY, "The Infrared Spectra of Complex Molecules" (John Wiley &, Inc. Sons, 1954) Ch. 10, p. 145.
20. C. N. R. RAO, "Chemical Applications of Infrared Spectroscopy" (Academic Press, 1963).
21. W. P. GRIFFITH and T. D. WICKINS, *J. Chem. Soc.* (*A*) (1967) 590.
22. W. P. GRIFFITH, *ibid.* (1963) 5345.