Infrared and Raman spectra of new molybdenum and tungsten oxyfluoride glasses

I. Z. HAGER, R. EL-MALLAWANY
Physics Department, Faculty of Science, Menoufia Univ., Shebin El-Koom, Egypt

M. POULAIN
Lab. Mater. Photoniques, Univ. des Rennes 1, 35042 Rennes, France

The infrared (400–1200 cm^{-1}) and Raman (200–1150 cm^{-1}) spectra are reported for the new AO_3-BaF_2-RF glasses where A is molybdenum or tungsten and RF is the alkali fluoride LiF, NaF and mixed LiF-NaF respectively. The observed absorption bands of each glass series were assigned to their vibrational modes. This study has shown that structural units formed in these glasses include [MoO_4] and [WO_4] tetrahedra, [MoO_6], [WO_6], [MoF_6] and [WF_6] octahedra groups. © *1999 Kluwer Academic Publishers*

1. Introduction

The previous studies of the oxyfluoride glasses have been concentrated on the glass forming behaviour, thermal and optical properties [1–4]. So that it is interesting that the structure of these glasses is very important to be investigate. The IR absorption is a dominant factor for determining the intrinsic minimum losses. In general IR spectrum can be devided into the fundamental resonance which provide intense absorptions. While Raman spectra can be used to obtain a deeper understanding of the glass structure.

The fundamental modes of the halide glasses are found in the 10–15 μm region. A comparison between various materials was given by Parker and France [5] which show IR and Raman spectra for vitreous SiO_2, BeF_2 and $ZnCl_2$ and compare the results with a HfF_4-BaF_2-ThF_4 glasses. The main features in the IR spectra of these glasses are two major broad peaks, whose positions depend on glass composition. The spectra of SiO_2 and BeF_2 are remarkably similar, except that the peaks in BeF_2 are shifted to the IR, indicating similar structure. In conjunction with IR; spectra, Raman scattering can reveal useful data on glass structure. Although IR absorption and Raman scattering both involve the same set of energy levels, different selection rules allows different transitions. For example, in the vibrational modes of SiO_2, ν_1 and ν_2 are only Raman active while ν_3 and ν_4 are both Raman and IR active. Consequently the techniques are complementary and can be used to obtain a deeper understanding of glass structure.

A more details account of Raman spectra as to halide glasses is given by Bendow *et al.* [6]. The Raman scattering spectra of rare-earth fluoride glasses differ markedly from those of fluorozirconate-type [7, 8] and transition-metal fluoride glasses [9]. In the latter glasses, the spectrum is dominated by a strong relatively narrow and highly polarized peak at high frequencies. Both fluorozirconate and transition metal fluoride (TMF) glasses display two-mode behaviour in Raman and IR, i.e. both spectra are dominated by strong peaks.

The purpose of this work is to report the complete IR and Raman spectra for a series of new oxyfluoride glasses based on the AO_3-BaF_2-RF systems (where A is Mo or W and RF is the alkali fluoride LiF, NaF and the mixed LiF-NaF respectively) with the goal of obtaining a better understanding of the structure of these glasses.

2. Experimental procedure
2.1. Glass preparation

Anhydrous fluorides are commercial products: BaF_2 and LiF are from Prolabo, NaF is from Ridel de Haen. MoO_3 and WO_3 were supplied by Strem. Calculated amounts of starting materials are mixed and heated up to melting temperature. That is around 500–550 °C and 650–700 °C for molybdenum and tungsten oxyfluoride glass respectively. Melting is carried out in a deep platinum crucible for 30–45 min. Then the melt is poured into a brass mould preheated around 200–250 °C, which allows a thick parallelipipedic samples of $10 \times 15 \times 3$ mm in size and their colour is brown for molybdenum and yellow for tungsten oxyfluoride glasses were obtained. And their Compositions are tabulated in Table I. Samples are annealed near the glass transition temperature for one hour, then the furnace is switched off. Then the samples were polished and prepared for the measurements.

2.2. Infrared measurement

For infrared investigations, glass sample was ground in a clean mortar to fine powder. Glass powder and KBr (from Prolabo) were mixed and ground. Then transparent pellets were formed by pressing the mixture at 15 tons for a few minutes under vacuum. IR absorption spectra of the present glass systems were determined by using a Bomem Michelson 100 spectrophotometer. All measurements were carried out at room temperature over the range of wavenumbers from 400–1200 cm^{-1}.

TABLE I The composition in mol % of MoO_3-BaF_2-RF and WO_3-BaF_2-Rf oxyfluoride glasses

Sample no.	MoO_3	WO_3	BaF_2	LiF	NaF
MBL1	65		30	5	
MBL2	60		30	10	
MBL3	55		30	15	
MBL4	50		30	20	
MBL5	45		30	25	
MBN1	75		20		5
MBN2	70		20		10
MBN3	65		20		15
MBN4	60		20		20
MBN5	55		20		25
MBNL1	65		20	10	5
MBNL2	60		20	10	10
MBNL3	55		20	10	15
MBNL4	50		20	10	20
MBNL5	45		20	10	25
WBL1		42	30	28	
WBL2		40	30	30	
WBL3		38	30	32	
WBL4		36	30	34	
WBL5		34	30	36	
WBN1		46	30		24
WBN2		44	30		26
WBN3		42	30		28
WBN4		40	30		30
WBNL1		42	30	10	18
WBNL2		40	30	10	20
WBNL3		38	30	10	22
WBNL4		36	30	10	24
WBNL5		34	30	10	26

2.3. Raman spectroscopy

Raman spectra of the present parallellepipedic glass samples with two polished faces and approximately 1 mm in thickness were measured in the range of 200–1150 cm^{-1} using Raman DILOR XY 1 accu. CCD spectrometer with excitation light of argon ion laser of 514.53 nm wavelength and output power of 200 mW were used (at Rennes University). All the experimental conditions kept constant during the measurements and the measurements were performed in the air at room temperature.

3. Results and discussion
3.1. IR spectra

The infrared absorption spectra of the present glasses are shown in Figs 1 and 2 and the corresponding absorption bands are displayed in Table II. The absorption bands of the Mo-oxyfluoride glass observed at 470, 695 and 885 cm^{-1} for MBL3, 485, 685, 885 cm^{-1}

for MBN3 and 475, 695 and 885 cm^{-1} for MBNL3 glasses respectively. While for W-oxyfluoride the absorption bands lies in the range 430, 495, 658, 865 and 945 cm^{-1} for WBL3, 430, 480, 655, 865 and 945 cm^{-1} for WBN3 and 430, 480, 640, 860 and 940 cm^{-1} for WBNL3 glasses respectively.

According to these figures fluoromolybdate and fluorotungstate glasses exhibit similarities with three major absorption bands. However, the relative intensities are somewhat different. And there are only two active vibration modes for a [MoO$_4$] and [WO$_4$] tetrahedra: ν_3 and ν_4. Interpretation of IR spectra may be implemented on the basis of the following hypothesis. Firstly, if we assume that coordination polyhedra are octahedra, then major absorption bands in MoO_3 and WO_3 based glasses are identified as follows: ν_3 in the range of 860–890 cm^{-1}, ν_4 in the range 640–695 cm^{-1} and ν_5 in the range of 470–495 cm^{-1} respectively. The small band at 945 cm^{-1} in the fluorotungstate glass would be ν_1 which has the highest frequency in the [WO$_4$] tetrahedron vibration modes. Secondly, analysis of IR spectra is the tetrahedral hypothesis. There are four vibrations modes with only two active modes in IR ν_3 and ν_4 (see Table I). The bands in 640–695 cm^{-1} range could be interpreted as the result of the coupling of tetrahedra in chain-like arrangements. In order to collect additional information, a Raman study was implemented on these glasses.

3.2. Raman spectra

The Raman spectra of the present glasses are shown in the Figs 3–6 and reported in Table III. These figures show the effect of different alkali fluorides RF and transition metal oxides MoO_3 or WO_3 on Raman spectra. It is seen that, the increase in RF concentration does not induce notable shifts or changes in the band frequency position for certain modes. Raman spectra of the Mo-oxyfluoride glasses revealed six bands: very strong higher frequency bands at 930–945 cm^{-1},

TABLE II Observed infrared absorption band positions in cm^{-1} for molybdenum and tungsten oxyfluoride glasses

Sample no.	[AO$_4$]	ν_3 [AO$_6$]	ν_2 [AO$_4$]	ν_5 [AO$_6$]	ν_4 [AO$_6$]
MBL3		885	695	470	
MBN3		885	685	485	
MBNL3		885	695	475	
WBL3	945	865	658	495	430
WBN3	945	865	655	480	430
WBNL3	940	860	640	480	430

TABLE III Frequencies in cm^{-1} in Raman spectra of molybdenum and tungsten oxyfluoride glasses

Sample no.	ν_1 [AO$_4$]	ν_3 [AO$_4$]	ν_3 [AF$_6$]	ν_5 [AO$_6$]	ν_2 [AO$_4$]	Ba-F
MBL1	940	855	715	460	370	228
MBL3	935	860	710	470	370	235
MBL5	930	860	745	468	366	236
MBN1	935	845	720	440	360	236
MBN3	945	860	710	470	370	234
MBN5	935	845	780	460	350	223
MBNL1	935	840	735	455	365	235
MBNL3	945	865	725	465	370	235
MBNL5	930	850	730	465	365	230
WBL1	930	845	740		365	240
WBL3	930	850	720		370	240
WBL5	925	850	740		365	240
WBN1	925	845	735		370	245
WBN3	930	850	730		370	255
WBN4	925	855	725		370	245
WBNL1	925	850	730		370	240
WBNL3	930	855	720		375	250
WBNL5	925	860	725		370	245
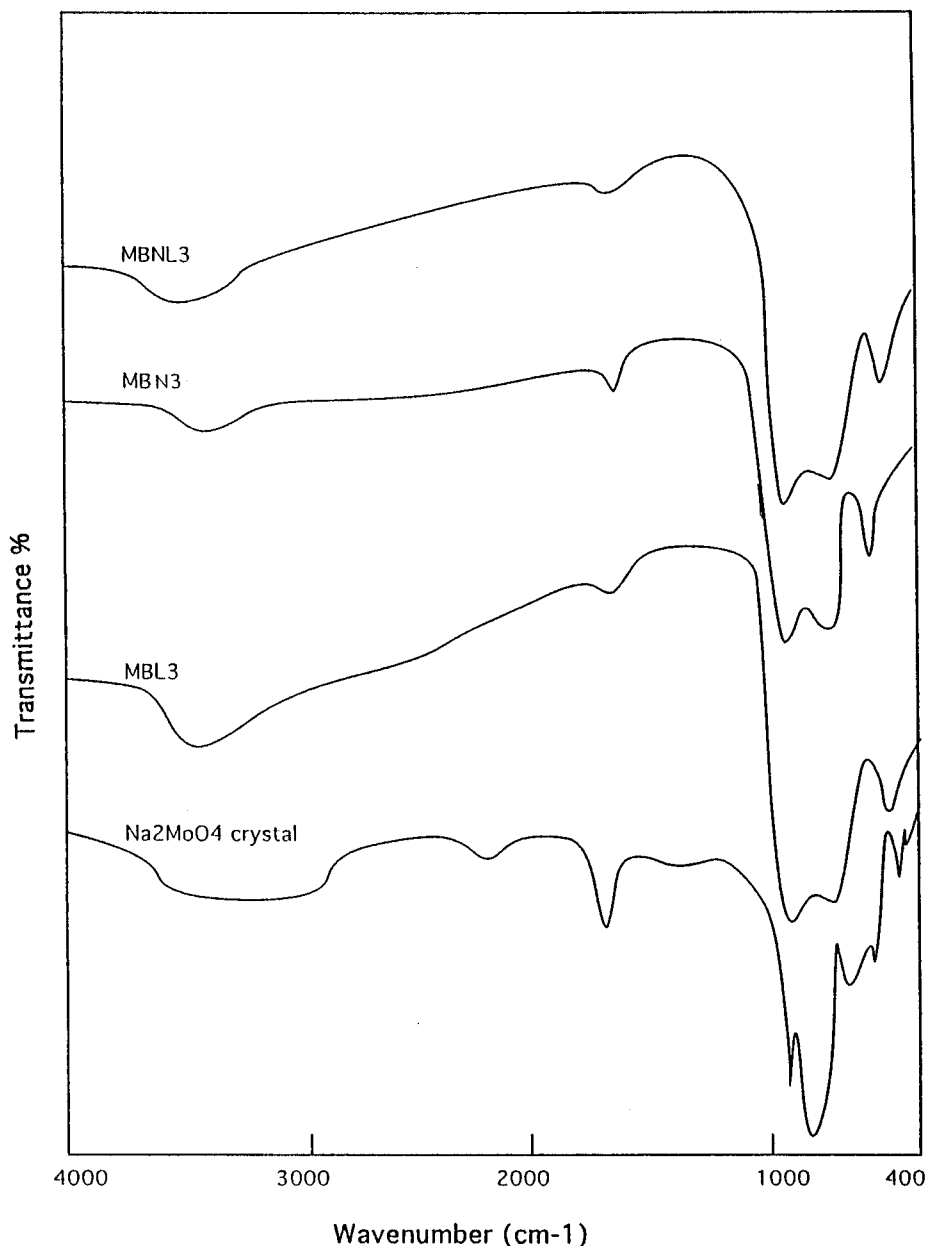
Figure 1 The IR spectra of some of the MoO$_3$-BaF$_2$-RF glasses.

shoulder one at 840–865 cm^{-1}, very weak broader two bands at 710–745 cm^{-1} and 440–470 cm^{-1}, two weak bands at 350–375 and 225–240 cm^{-1} respectively. The Raman spectra of Na$_2$MoO$_4$ crystalline compound have also been shown for comparison in Figs 3 and 4. Their absorption bands observed to be at 900, 875 and 315 cm^{-1} respectively. In tungsten oxyfluoride glasses their spectra revealed five main bands: very strong one at 925–930 cm^{-1}, weak band at 845–860 cm^{-1}, very weak and shoulder one at 720–740 cm^{-1} and two weak bands at about 365–375 cm^{-1}, 240–255 cm^{-1} respectively as shown in Figs 5 and 6. The Raman spectra of Na$_2$WO$_4$ crystalline gives strong similarities between it's spectra and those of fluorotungstate glasses, with ν_1 at 920 cm^{-1}, ν_3 around 850 cm^{-1} and ν_2 near 370 cm^{-1}.

The Raman spectra of crystalline compounds has been reported for comparison as illustrated in Figs 3, 4 and 5. Crystal structure of Na$_2$MoO$_4$ and Na$_2$WO$_4$ is of spinel type with isolated [AO$_4$] tetrahedra (where A: Mo or W) [10, 11]. Strong similarities appear between Raman spectra of Na$_2$WO$_4$ and those of fluorotungstate glasses with ν_1 at 925–945 cm^{-1}, ν_3 around 850 cm^{-1} and ν_2 near 370 cm^{-1}. These bands are characteristics of [WO$_4$] tetrahedra, which suggests strongly that they make the predominant structural unit in the glass. In this respect, the other bands correspond to the coupling between tetrahedra connected in the glass structure. Fluoromolybdates may be compared to fluorotungstates. However, there is a significant shift in the position of ν_1 band around 940 cm^{-1} with respect to the position of this band in Na$_2$MoO$_4$. This could be indicate shoulder Mo—O bonds in the glass. Shorter Mo—O bonds could be the result of the anion mixing, as highly charged cations attract highly anions in a medium which contain a large number of monovalent fluorine anions. From Raman data it appears that tetrahedra [MoO$_4$] and [WO$_4$] are the major structural units
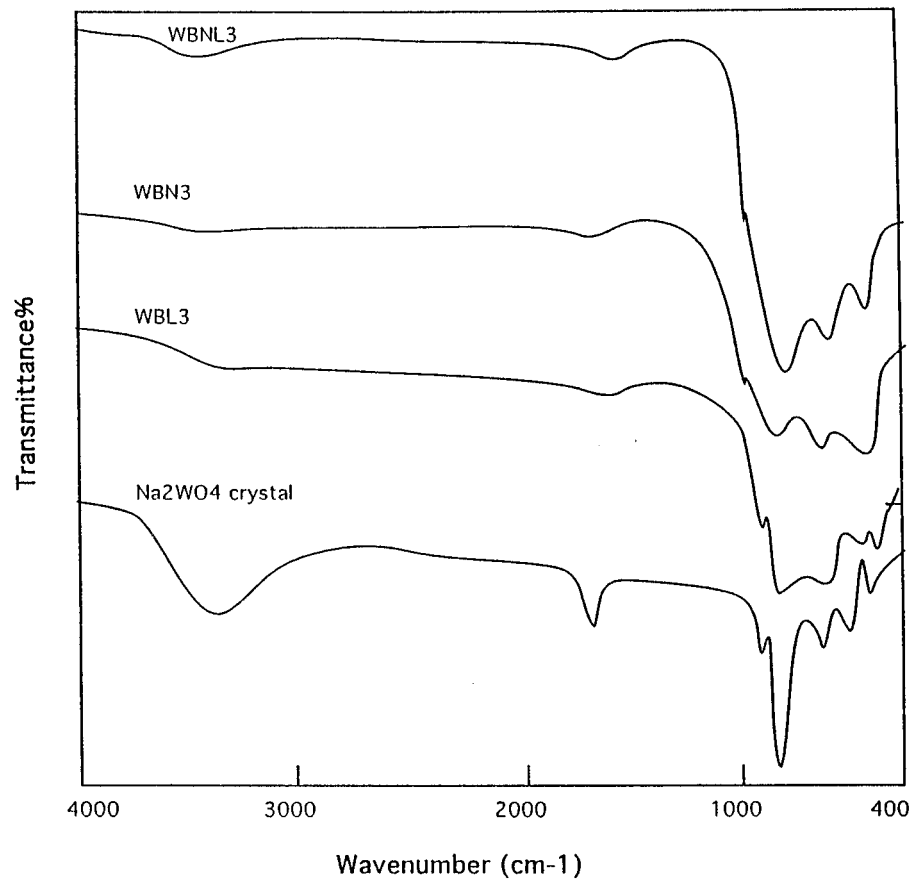
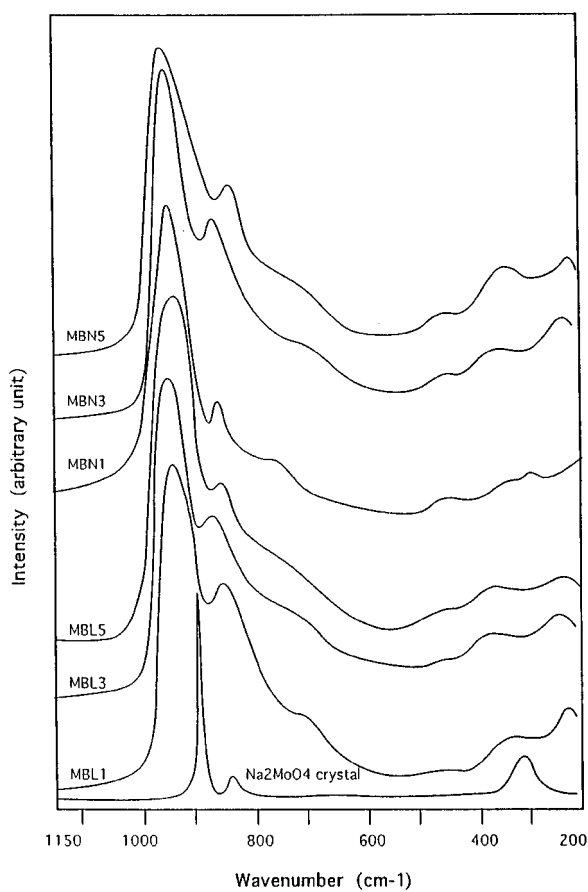*Figure 2* The IR spectra of some of WO_3-BaF_2-RF glasses.

Figure 3 Raman spectra of Na_2MoO_4 crystal and some of MoO_3-BaF_2-RF glasses.
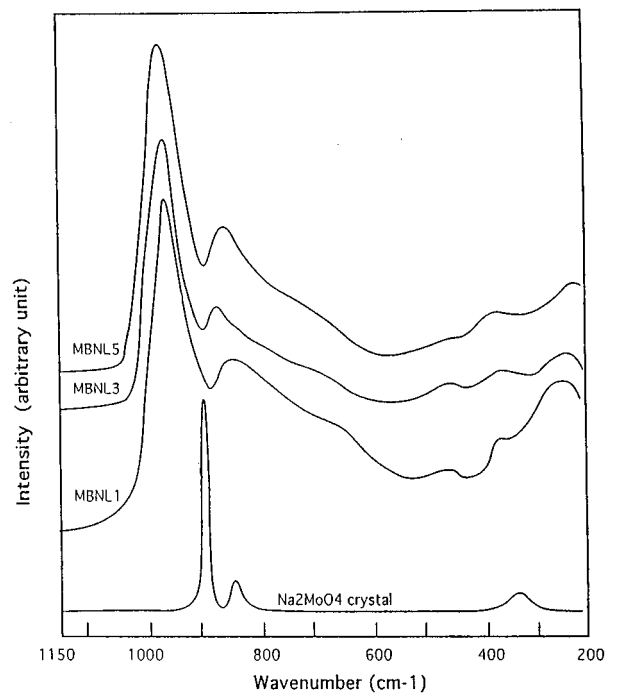

Figure 4 The Raman spectra of Na_2MoO_4 crystal and some of MoO_3-BaF_2-RF glasses.

in these new oxyfluoride glasses. While the occurrence of a limited number of octahedra remains, these glasses may be described as a hybrid glasses in which the ionic disordered packing of fluorine anions and Ba^{++} and alkali cations are prevented from crystallization by the
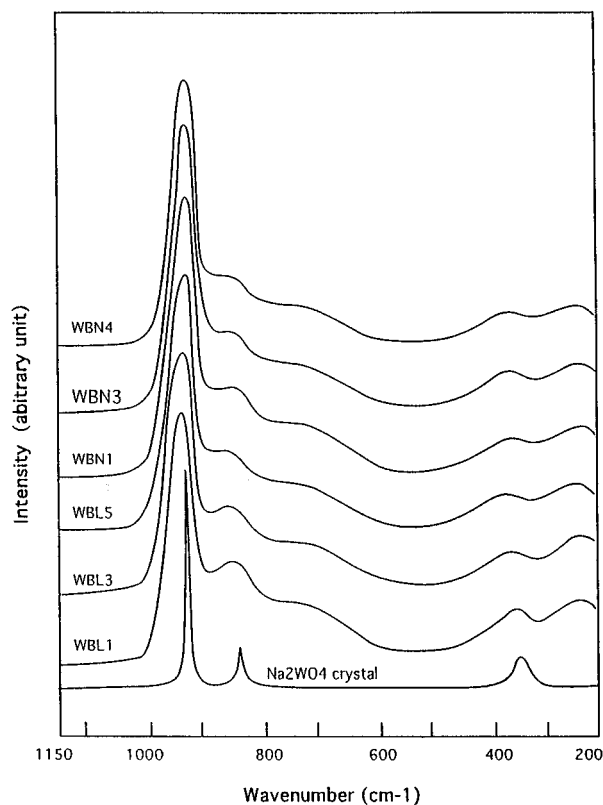
Figure 5 The Raman spectra of Na_2WO_4 crystal and some of WO_3-BaF_2-RF glasses.
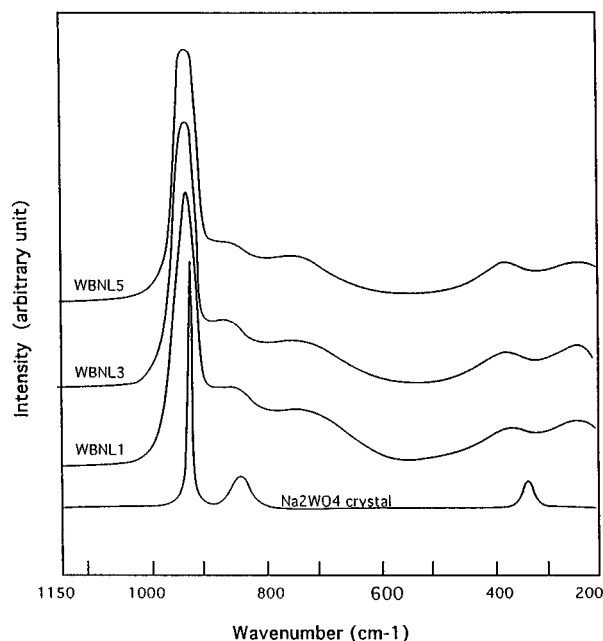

Figure 6 The Raman spectra of Na_2WO_4 and some of WO_3-BaF_2-RF glasses.

impregnation of polymeric-like tetrahedra chains. They cannot be described classical as an oxide network with alkali and earth alkali cations as modifiers. In addition, the presence of fluorine anion in the present glasses may create also vibrational modes related to the octahedra groups. For example the bands at 720–740 cm^{-1} and 710–780 cm^{-1} may be interpreted as ν_3 of [WF$_6$] and [MoF$_6$] octahedra [12] and the low frequency bands at 255–240 cm^{-1} and 228–235 cm^{-1} may due to nonsym-
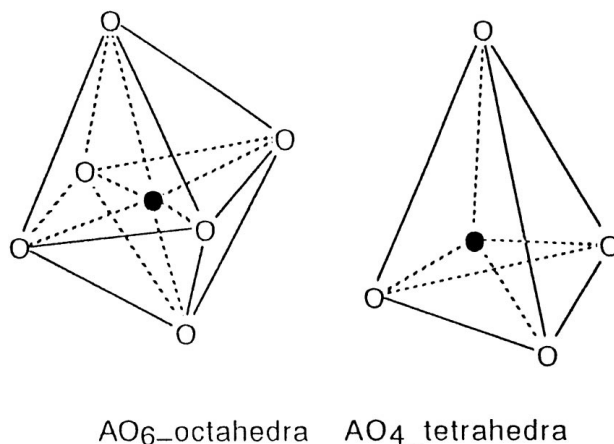

AO$_6$_octahedra   AO$_4$_tetrahedra

Figure 7 Basic metal-oxygen structural groups building up the glass network of MoO_3 and WO_3 based glasses. (a) AO$_6$ octahedra (b) AO$_4$ tetrahedra.

metric Ba-F bond [7, 8]. The above discussion may be understood by reference with infrared and Raman spectra of crystalline compounds and from the assumption that absorption bands in far infrared are characteristics of vibration modes of the coordination polyhedra of Mo and W. Molybdenum and tungsten are introduced in glass as trioxides MoO_3 and WO_3. The structure of these oxides is described as a tridimensional network of [AO$_6$] octahedra (where A: Mo or W) sharing corners. On the other hand, alkali molybdates and tungstates, such as Na_2MoO_4 and Na_2WO_4 contain unconnected tetrahedra [10, 11]. Considering chemical formula, glass structure could be constructed either from [MoO$_4$] and [WO$_4$] tetrahedra sharing two corners in a chain like arrangement, or from [MoO$_6$] and [WO$_6$] octahedra sharing corners as shown in Fig. 7.

4. Conclusion

The structure of the present new oxyfluoride glasses was interpreted by using IR absorption and Raman scattering techniques. The spectra of Mo-based glasses are very similar to those of W-based glasses. This means that the structure of both glasses is not different. The major structural unit of the present glasses is [MoO$_4$] and [WO$_4$] tetrahedra which defined from the Raman spectra. Also there are some of [MoO$_6$] and [WO$_6$] octahedra in the glass structure. Therefore, the structure of these glasses are a hybrid of [AO$_4$] tetrahedra and [AO$_6$] octahedra. In addition the presence of [MoF$_6$] and [WF$_6$].

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