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Study of the effect of alkali mixture on V–O bond length in Oxyfluoro Vanadate glasses using Raman spectroscopy

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ABSTRACT

Raman spectroscopic study on Oxyfluoro Vanadate glasses containing various proportions of lithium fluoride and rubidium fluoride was carried out to see an effect of mixture of alkali on vanadium–oxygen (V–O) bond length. Glasses with a general formula $40V_2O_5 - 30BaF_2 - (30 - x)\ LiF - xRbF\ (x = 0\text{–}30)$ were prepared. Room temperature Raman spectra of these glass samples were recorded in back scattering geometry. The data presented is in "reduced Raman intensity" form with maximum peak scaled to 100. We have used $\upsilon = A\exp(BR)$, where A and B are fitting parameters, to correlate the bond length R with Raman scattering frequency υ. We observed that variation in bond length and its distribution about a most probable value can be correlated to the alkali environment present in these glasses. We also observed that all rubidium environment around the network forming unit is more homogenous than all lithium environment.

1. Introduction

In glasses, the network forming units are arranged irregularly which leads to lack of long range order. These network forming units retain their polyhedral structures locally, but because of the random arrangement of the nearest neighbors the bond length of these units will have a distribution, for example, consider Zachariasen's well known diagram explaining continuous random network [1]. Raman or Infrared spectroscopy probe the molecular vibrations and therefore are better suited for local structure determination [2]. Variation in bond lengths can be estimated using these techniques. Raman scattering is often used to determine short range order in glasses [3–5].

Alkali elements in glasses behave as network modifier by breaking the network or by occupying voids created by network forming units. Incorporating alkali elements in glass imparts interesting properties, like increase in conductivity, lowering of glass transition temperature, and better stability. If one alkali element in a glass is gradually replaced with another alkali element, the glass shows dramatic variation in some of its physical properties, which is known as Mixed Alkali Effect (MAE) [6,7]. MAE happens to be one of the long standing problems in glass science.

In an alkali modified glasses, if one replaces an alkali with another alkali, a random distribution of different alkalis around the network forming units will cause its bond lengths to change from its previous values. Since Raman stretching frequency is sensitive to bond length variations, any change in bond length can be detectable using Raman spectroscopy.

Fluoride glasses have low phonon energy and are better suited for glass fibers with infra-red transmission capability [8]. But their chemical durability is poor [9–11]. On the other hand oxide glasses have good glass forming ability and are chemically durable but have large phonon energy. An oxyfluoride glass is both chemically durable and has low phonon energy. Vanadate glasses find interesting applications in memory switching [12].

Raman spectroscopy is used extensively to study both regular [13,14] and mixed alkali glasses [15–17]. Rouse et al. [15] and Swenson et al. [16] have studied mixed alkali phosphate glasses. There are a number of reports of Raman study on V_2O_5 [18,19] and V_2O_5 in Vanadate glasses [20,21]. A study of bond length variation as an effect of mixture of alkali is hitherto not attempted. In this communication we present a study of the effect of mixture of alkali on V–O bond length using Raman spectroscopy.

2. Experimental

2.1. Sample preparation and basic characterization

Glass samples having a general formula (in mol%), $40V_2O_5 - 30BaF_2 - (30 - x)\ LiF - xRbF\ (x = 0\text{–}30)$ (VB series) with varying amounts of LiF and RbF were prepared by usual melt quenching method. A little bit extra than the formula unit of the starting materials was taken to compensate any loss due to evaporation. All the samples were melted at ~700 °C for about 20 min and quenched between two brass plates. Final composition of glass samples was

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determined by EDS. Glass transition temperature, T_g (to an accuracy of ±0.05 °C) was determined by DSC using 10 °C/min heating rate. The samples were annealed at a temperature 30 °C below their T_g. Largest chunk of the samples thus prepared was used for density measurement by following Archimedes' principle. We used Xylene (density = 0.86 g/cm^3) as the immersion liquid. The weight of the samples measured was accurate to third decimal. Table 1 summarizes the starting material used (in mol%), T_g and density (to an accuracy of ±0.01 g/cm^3) of these samples.

2.2. Raman spectroscopy

Room temperature micro-Raman studies on VB series glasses were carried out in backscattering geometry using HORIBA JOBIN YVON LabRAM HR instrument equipped with a charge coupled device detector (CCD) at a working temperature of −70 °C. The samples were illuminated by the 514.5 nm line of an argon ion laser focused using a 100× objective on thin glass samples. Experiments were also carried out on finely powdered glass samples with 50× long working distance (LWD) focusing objective. The data obtained from both experiments were identical and in here we present data from thin glass samples. Experimental data were recorded using 3 mW of laser power (at the laser head) and for 10 s acquisition (per window) time. The spectral resolution is 0.4 cm^{-1}. Since laser intensity was small, laser burning was not observed.

3. Result and discussion

3.1. Raman data refinement and band assignment

The raw Raman data with a range 100 cm^{-1} to 1100 cm^{-1} was processed using the procedure applied by Wim J Malfait and Werner E Halter [22]. Then temperature–frequency correlation was applied [23], and the spectra were scaled to a maximum intensity of 100. The Raman data presented here is thus 'reduced Raman intensity' data. The 'reduced Raman' data were further de-convoluted using Gaussian line shape using Origin 9.0. Data in the range 600 cm^{-1} to 1100 cm^{-1} are considered because these correspond to various V–O bond vibrations. Three peaks were fitted corresponding to ~950 cm^{-1} (Q1 band); ~900 cm^{-1} (Q2 band) and ~780 cm^{-1} (Q3 band) which represent V=O vibration mode [18,19] VO_2 stretching vibration in meta Vanadate chains [21] and low energy vibrations of V_2O stretching [21] respectively. The parameters extracted from the fit include height of each peak, peak position and Full Width at Half Maximum (FWHM) with a reduced Chi-squared value less than or equal to 2.51. The uncertainties in Raman peak shift for Q1 band range from 0.07 cm^{-1} to 0.11 cm^{-1} while for Q2 band from 0.36 cm^{-1} to 1.27 cm^{-1}. For FWHM the uncertainties lie in the range 0.22 cm^{-1}–0.54 cm^{-1} for Q1 and 1.34 cm^{-1}–4.15 cm^{-1} for Q2. These uncertainties are shown as error bars in the respective plots. Fig. 1(a) shows a typical Raman spectrum of VB series glasses obtained using the above method. The Gaussian line shapes considered for de-convolution had large error for Q3 band in comparison with spectrometer resolution. Therefore it is not considered for analysis.

Table 1
Glass composition details, glass transition temperature T_g and density.

Sl. no.	Batch code	Content of the glass in mol%				T_g °C (±0.05)	Density g/cm^3 (±0.01)
		V_2O_5	BaF_2	LiF	RbF		
1	VBL	40	30	30	0	267.25	3.68
2	VBLR1	40	30	25	5	263.78	3.64
3	VBLR2	40	30	20	10	264.39	3.61
4	VBLR3	40	30	15	15	262.41	3.68
5	VBLR4	40	30	10	20	261.16	3.57
6	VBLR5	40	30	5	25	260.61	3.66
7	VBR	40	30	0	30	254.29	3.45

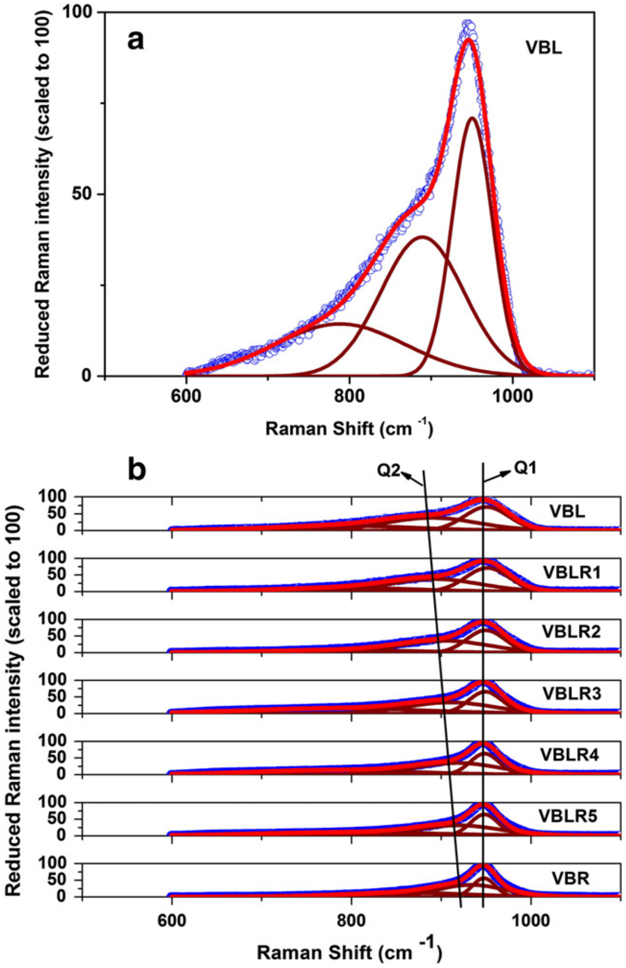

Fig. 1. (a): Representative Raman intensity plot showing scaled intensity and de-convoluted peaks. (Refer to text). (b): Variation of Raman Shifts of Q1 and Q2 bands with glass composition.

In Fig. 1(b), the variation of Raman shifts of Q1 and Q2 bands with glass compositions is shown. It is evident from the graph that peak corresponding to Q1 band has a slight shift whereas peak shift corresponding to Q2 band is quite large. Even FWHM corresponding to both the bands shows a variation. These features are separately studied with respect to variation in rubidium content.

Bulk V_2O_5 forms an orthorhombic layered crystal [24,19]. In glasses or in complexes, through Electron Spin Resonance study [25,26], it is assumed to be in octahedral structure with a tetragonal distortion. A sketch of V_2O_5 is shown in Fig. 2 [19]. Double bonded oxygen atom occupying terminal position is more strongly attached to vanadium atom than the planar oxygen atoms. Thus the strong Raman scattering peak at ~950 cm^{-1} is attributed to V=O vibrations. Scattering from planar O–V–O bonds is weaker compared to the V=O scattering and hence yields smaller Raman shift. Therefore ~900 cm^{-1} peak is attributed to this stretching vibration. V–O–V stretching vibrations require that the planar or lower polar oxygen of one unit be connected to vanadium atom of the other unit. This will have least Raman shift because it involves intra chain stretching with bond length greater than 2 Å and is attributed to peaks at ~780 cm^{-1}.

3.2. Interpretation of Raman data

Fig. 3 shows shift of peak position with respect to Rubidium (Rb) mole fraction for Q1 and Q2 bands. Peak shift observed is small