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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 $40\text{V}_2\text{O}_5 - 30\text{BaF}_2 - (30 - x)\text{LiF} - x\text{RbF}$ ($x = 0-30$) 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 $\nu = A \exp(BR)$, where A and B are fitting parameters, to correlate the bond length R with Raman scattering frequency ν . 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.

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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%), $40\text{V}_2\text{O}_5 - 30\text{BaF}_2 - (30 - x)\text{LiF} - x\text{RbF}$ ($x = 0-30$) (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 $\sim 700^\circ\text{C}$ 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/cm³) 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/cm³) 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 \times objective on thin glass samples. Experiments were also carried out on finely powdered glass samples with 50 \times 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] VO₂ stretching vibration in meta Vanadate chains [21] and low energy vibrations of V₂O 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

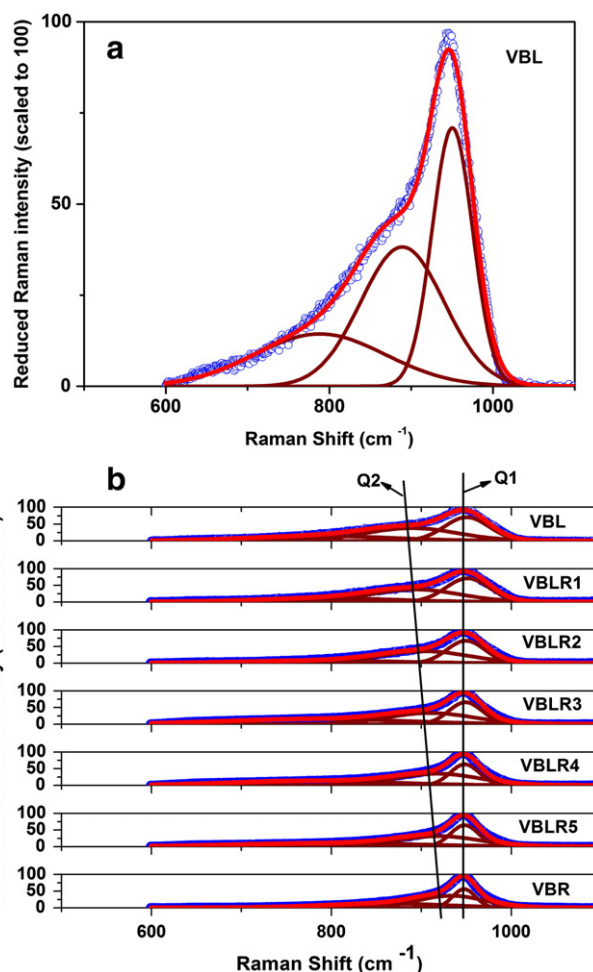


Fig. 1. (a): Representative Raman intensity plot showing scaled intensity and de-convoluted peaks. (Refer to text). (b): Variation of Raman Shifts of Q1 and Q2 bands with glass composition.

with spectrometer resolution. Therefore it is not considered for analysis.

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 V₂O₅ 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 V₂O₅ 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

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 ₂ O 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

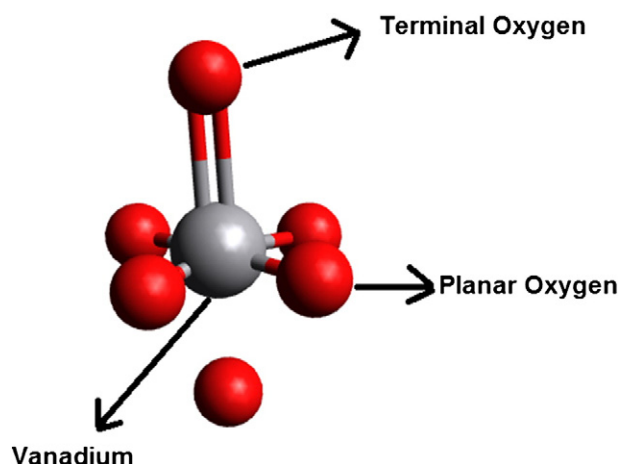


Fig. 2. A sketch of V_2O_5 showing terminal and planar oxygen positions.

($\sim 4 \text{ cm}^{-1}$) for Q1 band and it first shows an increase at 17% of Rb content and then decreases to its lowest value at 100% of Rb content. Shift is quite large ($\sim 40 \text{ cm}^{-1}$) for Q2 band and increases monotonically.

When an alkali is introduced in glass matrix as a modifier, it can break the network producing non-bridging oxygen or it can sit in voids of the network. This introduces a particular strain in the network which is felt by V–O bonds. Lithium has a smaller ionic radius compared to rubidium. Replacing lithium by rubidium increases this strain. Raman scattering of a particular bond depends on the bond length and a shift in Raman peak is a measure of bond length variation. The strain introduced when lithium is replaced by rubidium brings about a change in V–O bond length. Since polar $V=O$ is a strong covalent bond, variation in nearest neighbor environment affects it only a little. Therefore Raman peak shift is small (Fig. 3(a)).

On the other hand, planar V–O bonds are not so strong and can be easily stretched. This explains the larger Raman shifts observed in Fig. 3(b). We also observe that the value of the peak shift increases as lithium is gradually replaced by rubidium.

Badger's rule relates bond lengths to force constant in a diatomic molecule. The general form of the rule is given below.

$$k^{-1/3} = (a_{ij} - d_{ij})^{-1} (R - d_{ij}) \quad (1)$$

where k (mdyn/Å) is the force constant for a particular bond and R (Å) is the equilibrium bond length. a_{ij} and d_{ij} are constants [27,28]. Since $k^{-1/3}$ is not a linear function of R , the above rule does not adequately correlate bond distance to stretching frequencies in vanadium oxide crystals. By trial and error, Hardcastle and Wachs [27] applied an exponential function to fit V–O bond length/stretching frequency data. This requirement of exponential function was also used in Herschbach and Laurie's treatment [28]. The equation that relates Raman stretching frequency (ν) of V–O to the bond length R is given in general as,

$$\nu = A \exp(BR) \quad (2)$$

where A and B are fitting parameters.

From Eq. (2) it is evident that a slight variation in bond length gives rise to a large shift in Raman stretching frequency. A slight shift in terminal V–O stretching frequency in Fig. 3(a) shows that even though $V=O$ is a strong covalent bonding, the replacement of lithium with rubidium has an effect of slightly shortening this bond. On the other hand planar V–O bond gets elongated with an increase in rubidium concentration (Fig. 3(b)). Perhaps a compression at terminal V–O results in an elongation of planar V–O. But the extent of compression is not proportional to the extent of elongation; otherwise peak shift in both cases should have been comparable. We think that this non-proportionality retains the slightly deformed octahedral structure of V_2O_5 in the glass matrix. The fact that both graphs in Fig. 3 vary slightly non-monotonically has to do with the random mixture of both alkalis around the network forming unit. This can be attributed to MAE.

In Fig. 4, FWHM is plotted against Rb content. Glasses inherently have a non-periodic nature with random distribution of network forming units and network modifiers. Because of this irregular arrangement of network units, in VB glasses the VO_6 polyhedra will have a distribution of V–O bond lengths around a most probable value. The width of Raman spectral peaks can be attributed to distribution of a particular bond length.

FWHM of Q1 and Q2 bands in Fig. 4 has been seen to decrease gradually indicating that the distribution of bond length in both cases of terminal $V=O$ and planar V–O decreases. This can be interpreted as bonds becoming homogeneous or well defined as lithium is replaced by rubidium. Since the distribution in bond length is an indication of randomness of the coordination surrounding a particular bond, a decrease in FWHM can be interpreted as an increase in homogeneity of the surrounding. As we are replacing Li with Rb and the FWHM is seen to decrease with increase in Rb content, we can conclude that

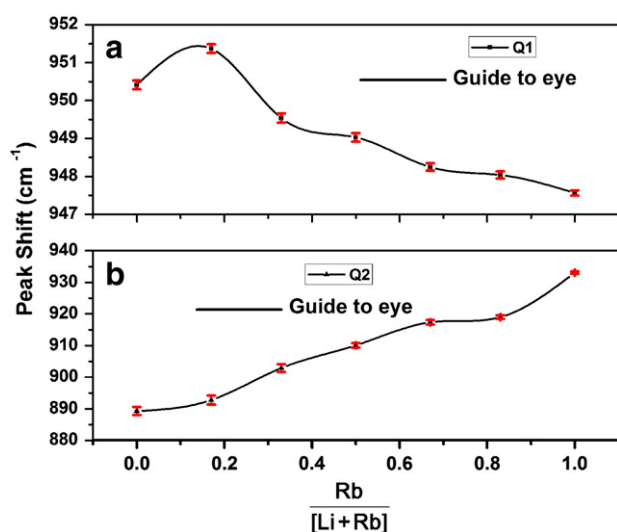


Fig. 3. (a) & (b): Raman peak shift of Q1 and Q2 bands vs Rubidium content.

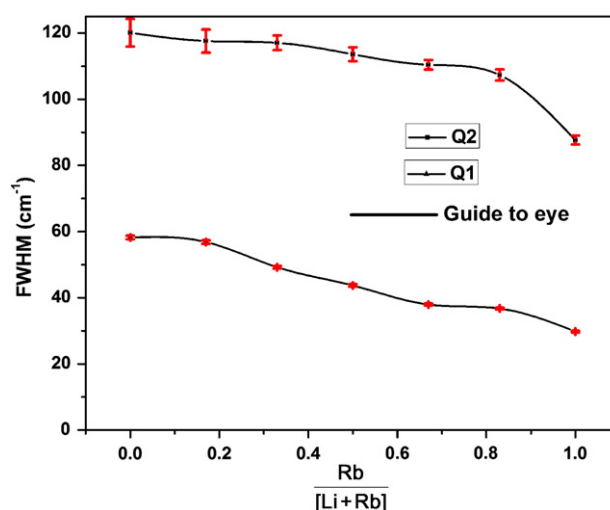


Fig. 4. Variation of FWHM of Q1 and Q2 bands with Rubidium content.

Table 2

Approximate distribution of V=O bond length around 950 cm^{-1} (as the de-convolution in Fig. 1(a), (b) is for minimum Chi-square, no explicit errors are mentioned).

Composition	Most probable value in Å	Bond length distribution in Å	Width in bond length distribution in Å
VBL	1.623	1.605–1.639	0.34
VBLR1	1.623	1.605–1.639	0.34
VBLR2	1.624	1.607–1.637	0.30
VBLR3	1.624	1.608–1.636	0.28
VBLR4	1.624	1.614–1.635	0.21
VBLR5	1.625	1.615–1.634	0.019
VBR	1.625	1.617–1.632	0.017

Rb–Rb coordination is more well defined than Li–Li or Li–Rb coordination. A similar kind of conclusion was made by Kamitsos in his study of alkali modified borate glasses using far IR [29] and by Swenson et al. using neutron diffraction [30].

An estimate of most probable bond length and distribution in bond length can be made using Eq. (2) mentioned above. In [27], the best fit for the experimental values was obtained by taking $A = 21,349$ and $B = -1.9176$ so that Eq. (2) becomes,

$$\nu = 21,349 \exp(-1.9176R). \quad (3)$$

Tables 2 and 3 gives a summary of the bond length and distribution in bond length calculated using above the formula for Q1 and Q2 bands respectively.

Raman intensity of a vibrational mode can be related to phonon density of that particular mode. Fig. 5 shows the variation of the ratio of intensities of Q2 to Q1 modes with Rb concentration. We observe that this ratio has a value about 0.54 when VB series glass has only Li as alkali element suggesting that planar VO_2 vibrations are 54% of that of terminal V=O vibration. The ratio increases to 0.65 when the glass has Rb as alkali element. Since this ratio also gives a hint of the surrounding environment of these particular vibrational modes, a higher value of the ratio is an indication that the surrounding environment is tending towards more homogeneity. The non-monotonous variation of this ratio tells that the surrounding environment goes through a non-homogeneous trend to settle into a more homogeneous environment.

Further studies such as Electron Paramagnetic Resonance (EPR), AC conductivity and X-ray Photoelectron Spectroscopy (XPS) are being pursued on the same glass systems for a comprehensive understanding of the alkali environment.

4. Conclusion

The effect of mixed alkali on the V–O bond length in the glassy system having a general formula $40\text{V}_2\text{O}_5 - 30\text{BaF}_2 - (30 - x)\text{LiF} - x\text{RbF}$ (with $x = 0-30$), was investigated. The de-convoluted Raman peaks corresponding to V=O, VO_2 were considered for the study. Considering a distorted octahedral structure of V_2O_5 in glass, V=O and VO_2 form the terminal and planar V–O bonds respectively. It is observed that as Li is replaced by Rb, terminal V–O bond gets less

Table 3

Approximate distribution of V–O bond length around 900 cm^{-1} (as the de-convolution in Fig. 1(a), (b) is for minimum Chi-square, no explicit errors are mentioned).

Composition	Most probable value in Å	Bond length distribution in Å	Width in bond length distribution in Å
VBL	1.658	1.624–1.694	0.072
VBLR1	1.656	1.622–1.692	0.07
VBLR2	1.650	1.618–1.686	0.068
VBLR3	1.646	1.616–1.679	0.063
VBLR4	1.642	1.612–1.674	0.062
VBLR5	1.641	1.612–1.673	0.061
VBR	1.633	1.610–1.657	0.047

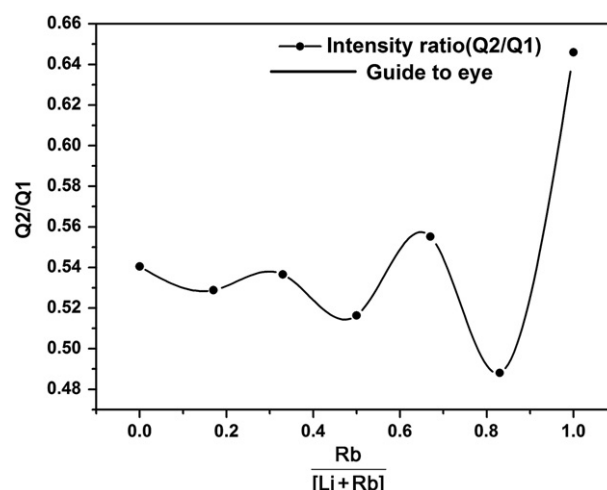


Fig. 5. Variation of ratio of Q2 and Q1 band intensities with Rubidium content.

affected than planar one which we think is the cause to retain the distorted octahedral structure. A study of FWHM and ratio Q2/Q1 reveals that all Rb environment is more homogeneous than all Li environment.

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References

- [1] R. Zallen, The Physics of Amorphous Solids, John Wiley & Sons, USA, 1983. 64–65.
- [2] D. N. Satyanarayana, Vibrational Spectroscopy: Theory and Applications, New Age International Publishers, New Delhi, 2004.
- [3] J. Wong, C. A. Angell, Glass: Structure by Spectroscopy, Marcel Dekker Inc., USA, 1976.
- [4] B. Bendow, in: C. J. Simmons, O. El-Bayoumi (Eds.), Experimental Techniques of Glass Science, 1993, pp. 33–76.
- [5] R.M. Almeida, J. Non-Cryst. Solids 106 (1988) 347.
- [6] J.O. Isard, J. Non-Cryst. Solids 1 (1969) 235.
- [7] D.E. Day, J. Non-Cryst. Solids 21 (1976) 343.
- [8] F. Gan, J. Non-Cryst. Solids 184 (1995) 9.
- [9] C.J. Simmons, J.H. Simmons, J. Am. Ceram. Soc. 69 (1986) 661.
- [10] M. Poulain, A. Soufiane, Y. Messaddeq, M.A. Aegerter, Braz. J. Phys. 22 (1992) 205.
- [11] J.M. Parker, Annu. Rev. Mater. Sci. 19 (1989) 21.
- [12] A. Ghosh, J. Appl. Phys. 64 (1988) 2652.
- [13] J. Lorösch, M. Couzi, J. Pelous, V.R., A. Levasseur, J. Non-Cryst. Solids 69 (1984) 1.
- [14] F.L. Galeener, A.J. Leadbetter, M.W. Stringfellow, Phys. Rev. B 27 (1983) 1052.
- [15] G.B. Rouse, P.J. Miller, W.M. Risen, J. Non-Cryst. Solids 28 (1978) 193.
- [16] J. Swenson, A. Matic, A. Brodin, L. Börjesson, W. Howells, Phys. Rev. B 58 (1998) 11331.
- [17] C. Karlsson, E. Zanghellini, J. Swenson, B. Roling, D. Bowron, L. Börjesson, Phys. Rev. B 72 (2005) 064206.
- [18] S. Lee, H.M. Cheong, M. Je, P. Liu, C.E. Tracy, A. Mascarenhas, J.R. Pitts, S.K. Deb, Solid State Ionics 165 (2003) 111.
- [19] B. Zhou, D. He, J. Raman Spectrosc. 39 (2008) 1475.
- [20] G.W. Anderson, J.L. Verble, J. Appl. Phys. 50 (1979) 2765.
- [21] N. Vedeau, et al., Vib. Spectrosc. 48 (2008) 259.
- [22] W.J. Malfait, W.E. Halter, Phys. Rev. B 77 (2008) 014201.
- [23] D. A. Long, Raman Spectroscopy, McGraw-Hill, New York, 1977.
- [24] R. Enjalbert, J. Galy, Acta Crystallogr. C42 (1986) 1467.
- [25] C. Ballhausen, H.B. Gray, Inorg. Chem. 1 (1962) 111.
- [26] G. Hochstrasser, Phys. Chem. Glasses 7 (1966) 178.
- [27] F.D. Hardcastle, I.E. Wachs, J. Phys. Chem. 95 (1991) 5031.
- [28] D.R. Herschbach, V.W. Laurie, J. Chem. Phys. 35 (1961) 458.
- [29] E.I. Kamitsos, J. Phys. Chem. 93 (1989) 1604.
- [30] J. Swenson, A. Matic, C. Karlsson, L. Bo, C. Meneghini, W.S. Howells, Phys. Rev. B 63 (2001) 132202.