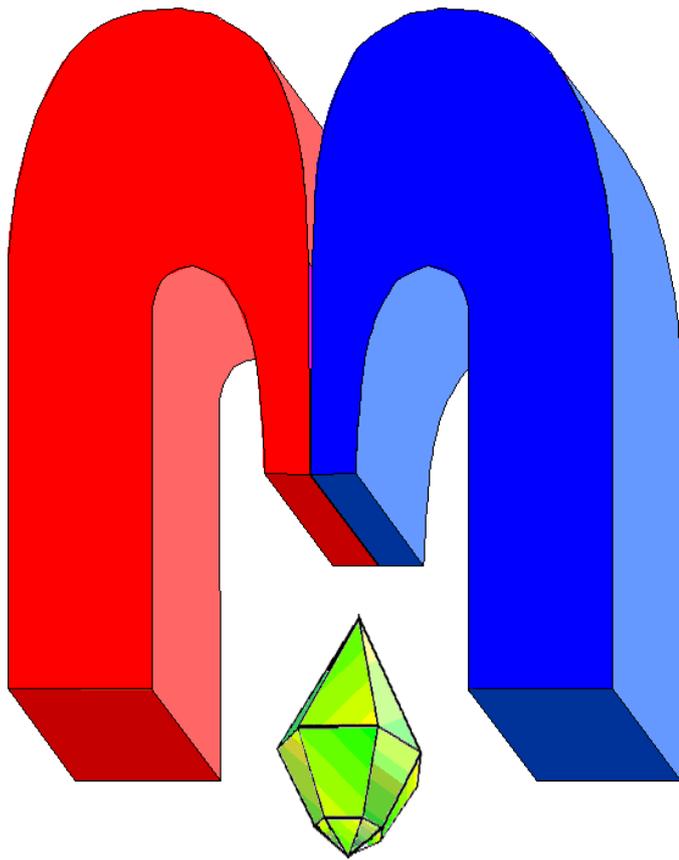


ISSN 2072-5981
doi: 10.26907/mrsej



***magnetic
Resonance
in Solids***

Electronic Journal

Volume 21

Issue 5

Paper No 19504

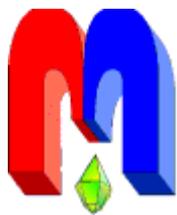
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2019

doi: 10.26907/mrsej-19504

<http://mrsej.kpfu.ru>

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Established and published by Kazan University
Endorsed by International Society of Magnetic Resonance (ISMAR)
Registered by Russian Federation Committee on Press (#015140),
August 2, 1996
First Issue appeared on July 25, 1997

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"Magnetic Resonance in Solids. Electronic Journal" (MRSej) is a peer-reviewed, all electronic journal, publishing articles which meet the highest standards of scientific quality in the field of basic research of a magnetic resonance in solids and related phenomena.

Indexed and abstracted by
Web of Science (ESCI, Clarivate Analytics, from 2015), Scopus (Elsevier, from 2012), RusIndexSC (eLibrary, from 2006), Google Scholar, DOAJ, ROAD, CyberLeninka (from 2006), SCImago Journal & Country Rank, etc.

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Nuclear magnetic resonance studies on vanadium phosphate glasses

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(Received May 16, 2019; revised August 9, 2019;
accepted September 4, 2019; published September 11, 2019)

The structures of a single V_2O_5 , binary $CdO-V_2O_5$ and ternary $CdO-V_2O_5-P_2O_5$ glass systems have been investigated by means of ^{51}V and ^{31}P MAS-NMR spectroscopy. NMR spectrum of pure V_2O_5 glass has showed that the network structure is made up of VO_5 groups, as in crystalline V_2O_5 . This means that only 5-fold coordination of the vanadium atom, $V(5)$, is the predominant type in this glass. Substitution of V_2O_5 with CdO in the glass network leads to destruction of the layered VO_5 structure and as a result VO_4 tetrahedral units are formed. Vanadium is located in this situation at $V(5)$ and $V(4)$ sites. The difference between the feature of NMR spectra of the sample containing 30 mol% CdO and the glass of pure V_2O_5 is considered to be due to formation of both $V(4)$ and $V(5)$. On the other hand, cadmium orthovanadate $Cd_3(VO_4)_2$ building units are the main constituent of CdO rich glass (60 mol% CdO). The local structure of the ternary $CdO-P_2O_5-V_2O_5$ glasses contains three types of vanadium sites, which are pentavalent vanadate units ($V5$), tetrahedral ($V4$) and mixed vanadate and phosphate units ($V4-O-P4$). The latter represents V atoms coordinated with P atoms as the second neighbor (VO_4) P . ^{31}P NMR results have showed that the concentration of nonbridging oxygen atoms (NBOs) is increased in the phosphate network with increasing CdO contents.

PACS: 76.60.Cq., 74.25.nj., 71.23.Cq., 76.60.-k

Keywords: Glass structure, Cadmium vanadate, Vanadium coordination, ^{31}P and ^{51}V NMR Spectroscopy

1. Introduction

Growing attention has been devoted in the last few decades to glasses containing V_2O_5 [1-6]. There is a considerable practical interest in these glasses due to their optical and electrical properties. Generally, investigation based on the structure of an amorphous network containing V_2O_5 is a difficult task and usually requires a combination of different experimental techniques. Thus, for the complicated amorphous glasses containing vanadate and phosphate structural units, XRD diffraction, and both ^{51}V and ^{31}P NMR spectroscopies are considered the most suitable tools. Mixed former glasses containing P_2O_5 and V_2O_5 have shown the presence of PO_4 , VO_4 and/or VO_5 units which are connected to each other via bridging oxygen to form a three dimensional network [7-9].

V_2O_5 plays a dual structural role in many oxide glasses both as a network modifier and simultaneously as a network former [7-9]. When V_2O_5 is mixed with a stronger glass former like B_2O_3 or P_2O_5 or TeO_2 [10-13], it can form stable network in comparatively wide range of compositions. This is because vanadium and phosphorus atoms are considered glass-formers cations, which exhibit the extended mixed network peculiarities. They are commonly studied using ^{31}P and ^{51}V NMR spectroscopy. The vanadium-oxygen bonds which can be occurred by V_2O_5 in the mixed glass matrix can vary between ionic to highly covalent or metallic [8, 9].

V_2O_5 has unusual characteristics due to its different valence states and coordination numbers in the glass network. In addition, the nature of the outer d-electrons has also play a role [14-16].

The valence states and coordination number of vanadium depend on the ratio of modifiers to formers, the size of the ions, their field strength and mobility [14-16].

The role of any network-modifying oxide such as CdO or alkali oxides is appeared in the formation of ionic bonds [7, 9-18]. The modifier oxide is consumed to form non-bridging oxygen atoms (NBOs) in the main glass network. In addition, the modifier cation enters into the glass network interstitially to balance the negative electric charge of NBO atoms. This leads to change the structure of glass samples [9, 15, 17] upon its addition.

The studies on glasses containing CdO, P₂O₅ and V₂O₅ together, to our knowledge, are limited [19-21]. Therefore, it is aimed in this work to account and determine the structural role of vanadium ions in both binary and ternary glass systems. The obtained data are discussed in comparison with glasses containing alkali and alkaline earth oxides as modifiers [9, 17, 18, 22-24].

2. Experimental details

Binary CdO-V₂O₅ and ternary CdO-P₂O₅-V₂O₅ glass systems have been prepared by mixing the basic raw chemicals which include V₂O₅, CdO and, NH₄H₂PO₄ as a source of P₂O₅. The used chemicals were all of analytical grade with the purity of 99.9%. Glasses were prepared by the melt quenching method [4-6,13]. The mixture was melted in an electric furnace in silica crucibles. The melting time and temperature are dependent on the glass composition. The applied melting temperature is ranged between 1100-1350 °C. The melt is then quenched by pouring it between two stainless steel plates. To remove the internal stresses and strains, the glass samples were annealed at a temperature slightly less than their own glass transition temperature (*T_g*) i.e. at 350 °C. The amorphous nature for the prepared samples was checked by X-ray diffraction.

NMR measurements have been carried out at ambient temperature on a JEOL RESONANCE GSX-500 spectrometer (Mansoura University) operating at 11.747 T. ⁵¹V NMR spectra were collected at the resonance frequency of 131.2 MHz. A 3.2 mm MAS NMR probe operated at a rotor frequency of 15 kHz has been used. Typical pulse lengths were 2.5 μs and 60 seconds delay time was sufficient to enable relaxation. A total numbers of 200 scans were accumulated. ³¹P MAS NMR experiments were also conducted at resonance frequency (202.4 MHz) using a 3.2 mm diameter rotor spinning at 15 kHz. Solid NH₄H₂PO₄ was used as a secondary reference compound and the signal from this set to 0.8 ppm. A pulse length of 2.5 μs and a recycle delay of 5 s was applied. Delta NMR software, version 5.04 (Japan), has been used for NMR analysis, simulation and integration of the area under each specific peak.

3. Results and Discussions

3.1. Cadmium vanadate glasses

Figure 1 (a) presents the solid state ⁵¹V NMR spectra of the pure V₂O₅ glass. There is a strong signal at about -304 ppm. This resonance peak is attributed to V₂O₅ of the square pyramid coordination [22]. Comparisons with NMR data from known crystalline compounds are beneficial for understanding data from glasses [22]. The increase of CdO concentration as a glass modifier and decreasing of V₂O₅ concentration as an intermediate oxide lead to a reduction in the -304 ppm peak intensity to reach its minimum in the spectra of glass of 60 mole% CdO and 40 mole% V₂O₅, figure 1 (c). In addition, a more intense peak at -734 ppm is formed and becomes more resolved in the glass of 30 mol% CdO (spectra (b)). The decrease of -304 ppm resonance peak and the shift in the peak position indicate the destruction of the square pyramidal units of V₂O₅, which are usually formed in the layered structure [22-24]. As a result, vanadate tetrahedral units VO₄ with different concentrations form (NBO) are alternatively formed [23-

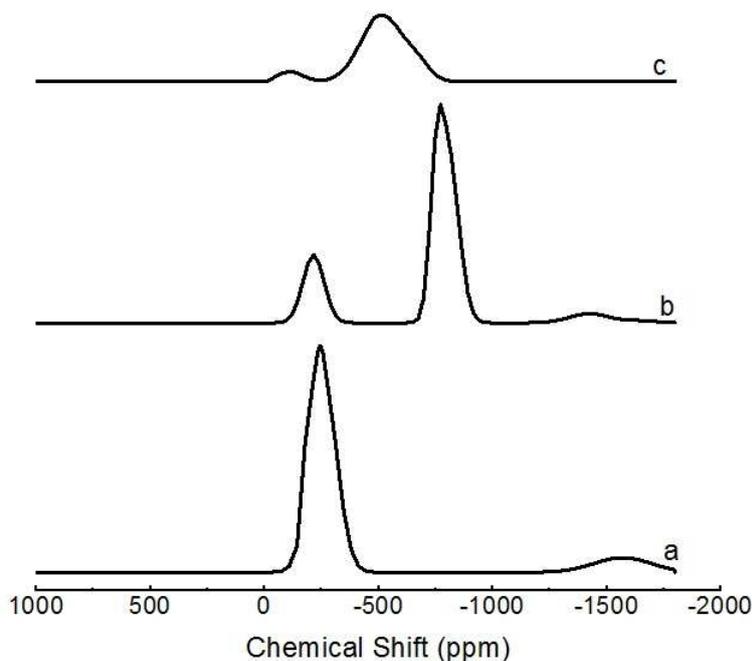


Figure 1. ^{51}V MAS NMR spectra for CdO- V_2O_5 glasses with composition (a) the vitreous (V_2O_5), (b) and (c) for the binary CdO- V_2O_5 glasses containing 30 and 60 mol% CdO, respectively.

25]. Formation of V(4) at expense of V(5) is considered the main reason for the appeared shift in position represented in figure 1. The presence of the V(4) groups is further confirmed by the appearance of a more intense resonance peak at about -734 ppm.

A series of the binary CdO vanadate glasses was examined by ^{51}V NMR spectroscopy, and there is a clear development of ^{51}V chemical shifts in terms of Q^n notation (where, Q is V or P atom and n is the number of bridging oxygen atoms) with increasing CdO content. In addition to distinct resonance at -304 ppm, there are additional peaks in these spectra e.g., -734 ppm (spectrum (b)) and around -507 ppm (spectra (c)). Presence of more than one spectral peak in glasses containing CdO reflects the formation of Q^n environments with different next-nearest neighbor polyhedral [22-25]. The spectra of glass samples containing 30 and 60 mol% CdO (figure 1(b) and (c)) show multiple Q^n environments, attributed to tetrahedral VO_4 in the form of Q^4 neighbors which is represented by -734 ppm in the glass of 30 mol% CdO. The presence of a broader peak around -507 ppm in a glass of the higher CdO content (60 mol%), figure 1(c), suggests that most of VO_4 tetrahedral units are found in orthovanadate, $\text{Cd}_3(\text{VO}_4)_2$ units due to the presence of an extremely high concentration from modifier oxide which in turn increases the content of NBOs [23-25].

There is an additional weak resonance in spectra represented by figure 1 (a), (b). The ^{51}V NMR peak is appeared around -1600 ppm. This weak peak is related to the formation of surface hydrated vanadium oxide (SHV) in the form of six-fold coordination [26]. This SHV structure differs from that of bulky V_2O_5 presented in both 4 and 5-fold coordination units. It contains $\text{VO}_2\text{O}_{2/2}$ (metavanadate groups) and V_2O_7 (pyrovanadate units). The 6-coordinated and hydrated vanadium are considered as modifiers in the network of the glass and therefore the limited area of such peak didn't consider in the calculations. This may because the analysis presented in tables 1 and 2 represent the content of the former species only. The percentage of different Q^n species in vanadate network can be quantitatively determined by using line shape simulations or deconvolution process as shown in figure 2. The quantitative assessments of

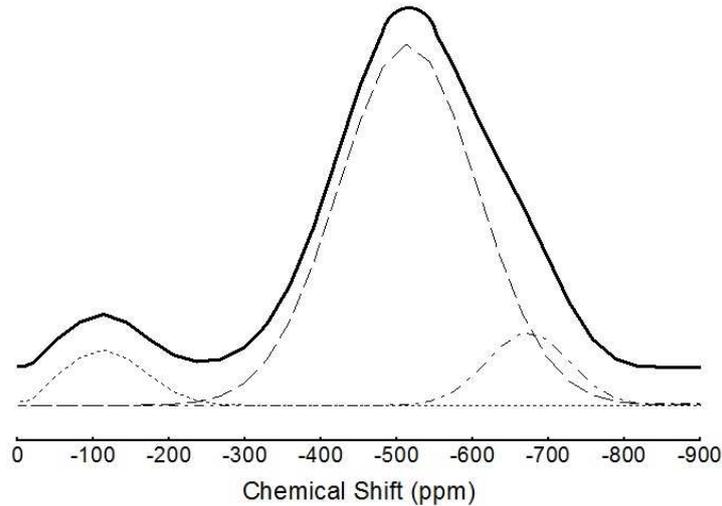


Figure 2. Deconvolution of NMR spectra for glass of 60 mol% CdO, solid lines denote experimental ^{51}V MAS NMR data, and filled curves or dashed lines represent fitting of the data using Gaussian line shapes.

the V species, indicates that the V(5) is maximum in pure V_2O_5 glass, whereas a mixture of VO_4 and VO_5 is found in glass of 30 mol% CdO. Vanadate units containing NBOs as a main species has been found in CdO rich glass. Thus, a mixture from Q^1 and Q^0 are the predominant species in the cadmium rich glass (60 mol%). The percentage of each vanadium type is listed in table 1. The above arguments suggest that cadmium orthovanadate $\text{Cd}_3(\text{VO}_4)_2$ units dominantly control the structure of the CdO rich glass. In such a case, structure with greater distorted local environment compared with V_2O_5 is retained. From the simulated spectra presented in figure 2,

Table 1. Fraction of V5 and V4 in glasses of 0, 30 and 60 mol% CdO.

Content	Fraction		
	0 mol%	30 mol%	60 mol%
V5	100	78	8
V4	0	22	92

there are two separated peaks of different values of chemical shift (-507 ppm and -730 ppm). The presence of the two resonances is assigned to presence of different local environments of vanadium nuclei [22-27] in the studied glass network. In this situation, (Q^1 and Q^0) are the two suggested types of tetrahedral vanadium complexes with different oxygen environments.

3.2. Cadmium phosphovanadate glasses

Modification of both phosphate and vanadate glass networks with CdO as a network modifier leads to the formation of a common mixed network structure consisting of both phosphate and vanadate structural units. The structures of the ternary $\text{CdO-V}_2\text{O}_5\text{-P}_2\text{O}_5$ glasses are investigated by means of ^{31}P and ^{51}V MAS NMR spectroscopies. The local structures around both P and V atoms are discussed in detail from the corresponding NMR spectra. Previous studies based on modified vanadate and phosphate glasses have showed that the fraction of NBO atoms increases in both vanadate and phosphate network with increasing modifier oxide [9, 13]. In addition, the fraction of VO_4 tetrahedral units increases and that of VO_5 trigonal bipyramids decreases with increasing the modifier content [9, 13, 22].

In the mixed glass former, the nearest environment of vanadium differs significantly from that of a single glass former [9,13]. This suggests a distribution of second or higher order atomic environments (PO_4) around different vanadate structural units. As a consequence, P-O-V bonds are formed [22-24] and their effects were appeared in changing the spectral feature of the mixed vanadium phosphate network relative to V-O-V bonds. Figure 3 represents ^{51}V MAS NMR spectra for the ternary $x\text{CdO}-(70-x)\text{V}_2\text{O}_5-30\text{P}_2\text{O}_5$ glasses as a function of CdO. Three

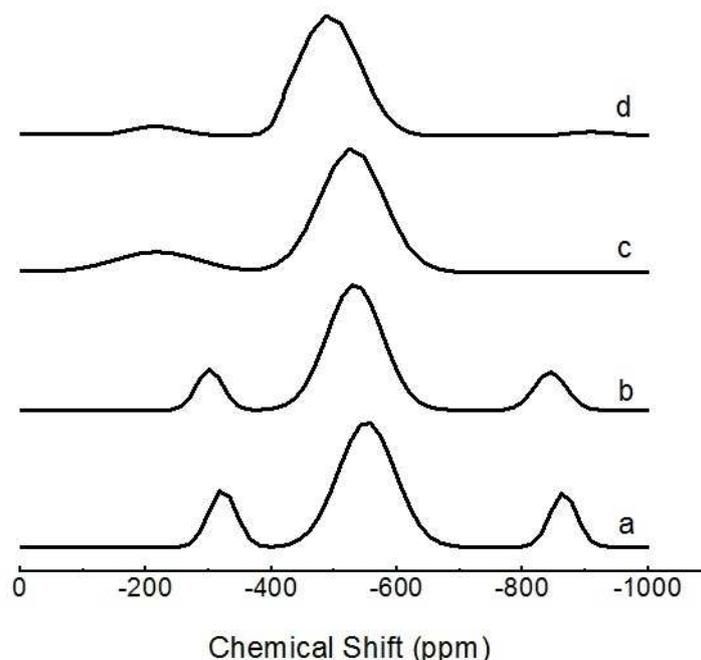


Figure 3. ^{51}V MAS NMR spectra for ternary $\text{CdO-V}_2\text{O}_5\text{-P}_2\text{O}_5$ glasses containing 0, 20, 30 and 50 mol% CdO represented by spectrum (a), (b), (c), and (d), respectively.

vanadium resonances were observed in the spectra of the investigated glasses with changing glass compositions. The resonant bands which have been appeared at -329 ppm represents vanadium in square pyramids, -550 ppm represents distorted tetrahedral coordinated vanadium and at -866 ppm represents oxygen coordination environments connected between V and P units [22-27]. It can be seen from figure 3 that both intensity and area of resonance peaks at -329 ppm and -866 ppm decrease and the signal intensity at -555 ppm slightly changes with increasing CdO at expense of V_2O_5 . This trend leads to suggest that the vanadate structural units in both VO_4 tetrahedra and VO_5 trigonal bipyramids are decreased due to decreasing V_2O_5 concentration in the glasses with increasing CdO contents. Increasing the latter results in increasing depolymerization in Q^n units. The obvious shift in the resonance peak at about -550 ppm toward less negative values may refer to increase the concentration of average V-O-P mixed species [22,25]. Then both NBO atom offered by the modifier oxide and deshielding of some vanadate units by phosphorus linkage are the main reasons for decreasing band area at -329 ppm and -866 ppm and increasing the peak shift of the middle resonance line, respectively. This leads that some of phosphorus units are found as a second neighbor for V one. The phosphor nuclei which are the nearest neighbors to the vanadium atom produce an extra resonance on the low field side of the ^{51}V spectrum. The relative area and intensity of the peak located at -866 ppm is vanished with increasing CdO (figure 3 (c) and (d)). The small hump in spectrum (c) may be considered as a result of increasing coordination of non-bridged phosphate units

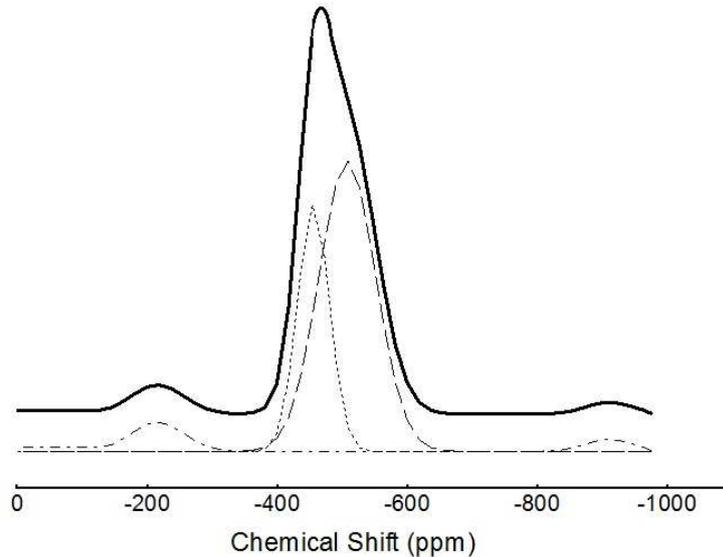


Figure 4. ^{51}V MAS NMR deconvoluted spectra for glass containing 50 mol% CdO as an example.

around vanadate species. Figure 4 shows the analyzed spectra of glass containing 50 mol% CdO presented as an example.

3.3. ^{31}P NMR results

Figure 5 represents ^{31}P MAS NMR spectra for a series of ternary $x\text{CdO}-(70-x)\text{V}_2\text{O}_5-30\text{P}_2\text{O}_5$ glasses. Exchange of V_2O_5 with CdO exhibits changes in chemical shielding of the ^{31}P nucleus with glass composition. In these glasses, phosphorus is primarily found in Q^2 tetrahedra, and the change in chemical shift in figure 5 is a reflective of mixing between Q^4 vanadate and these Q^2 phosphate groups. Both the phosphorus and vanadate structural groups are sensitive to glass composition and exhibit concentrations that depend on the amount of VO_4 , which associates with PO_4 tetrahedra to form mixed VPO_4 similar to BPO_4 -like associated polyhedral in oxide glasses [25-28].

Based on the ^{31}P MAS-NMR spectrum of a binary $30\text{P}_2\text{O}_5-70\text{V}_2\text{O}_5$ glass (figure 5 (a)), two resonances are observed at different values of chemical shift (-4 and -18 ppm). They are attributed to Q^1 and Q^2 phosphate site [13, 23]. The absence of Q^3 in the binary vanadium phosphate glass leads that some of V_2O_5 enter the glass network as modifier consumed in degradation of Q^3 which would be transformed to Q^2 and Q^1 [13]. This means that some of V_2O_5 could play the role of creation of NBO in both the phosphate and vanadate networks. On the other hand, ^{31}P NMR spectral peaks of glasses of lower V_2O_5 concentrations (50 and 40 mol% V_2O_5) are shown to be shifted to higher values of chemical shifts. The resonance peak located at about 14 ppm (figure 5 (b)) shows a growing behavior at the expense of the main peaks at -3 and -18 ppm (figure 5 (a)). In addition, the resonance at -18 ppm is totally disappeared. This behavior may be attributed to increasing of Q^0 and Q^1 sites at expense of Q^2 ones, as presented in table 2. The small envelope located at -8 ppm may be assigned to formation of a small separated concentration from Q^1 units. This limited peak may be due to the limited modifier concentration, since CdO is not added to this composition. In glasses of high CdO concentration, there is no any tendency for formation of both Q^3 and Q^2 sites in this composition. This argument is correlated to the structure role of CdO which plays the role of a glass modifier. In addition, decreasing V_2O_5 concentration from 70 to 40 mol% due to increasing

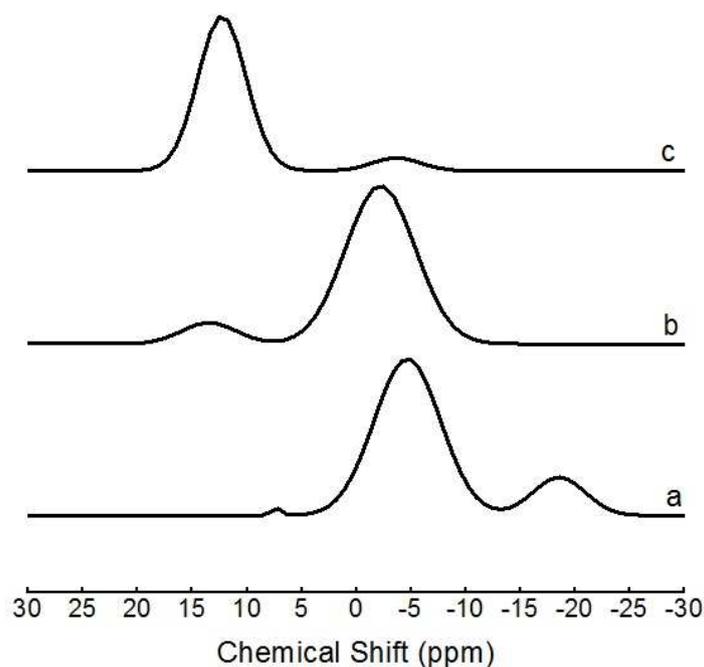


Figure 5. ^{31}P MAS NMR spectra for ternary CdO- V_2O_5 - P_2O_5 glasses containing 0, 20 and 30 mol% CdO represented by spectra (a), (b), and (c) respectively.

Table 2. Fraction of Q^2 , Q^1 and Q^0 in glasses of 0, 20, 30 (present glasses) and 49 mol% alkali oxide [29].

CdO mol%	Q^2	Q^1	Q^0
0	0.35	0.60	0.05
20	0.07	0.64	0.35
30	0	0.28	0.72
49	0	0.13	0.87

CdO from 0 to 30 mol% results in decreasing the bonds between vanadium units and between phosphate and vanadate species. This behavior results in increasing nonbridging oxygen atoms in the whole glass network. As a result Q^1 are the main phosphate sites in the CdO rich glass. More NBO atoms are progressively formed in the glass of a higher modifier oxide (30 mol%), since Q^0 is the specific units characterize high modified glasses. The value of chemical shift and the intensity of the resonance line representing Q^0 were found to depend on the concentration of the modifier oxide. In such situation formation of isolated Q^0 sites is very recommended to be present. Increasing chemical shift with composition means decreasing shielding process around both vanadate and phosphate atoms [22-25].

Figure 6 represents deconvolution of NMR spectra for a glass of 20 mol% CdO. The solid lines denote the experimental data, and filled curves or dashed lines represent the fitting of the data.

Each type of vanadium coordination, V(5) and V(4), has specific range of chemical shift value. Then the area under each peak can represent the total number of resonating species such as V(4) or V(5). In such case there are two types for the quantitative analysis they: (1) by integration using NMR analytical program or (2) by using deconvolution processes using the peak fit program. The fraction of various vanadate species are calculated by means of the two above given methods. All the NMR parameters are automatically adjusted by the modified

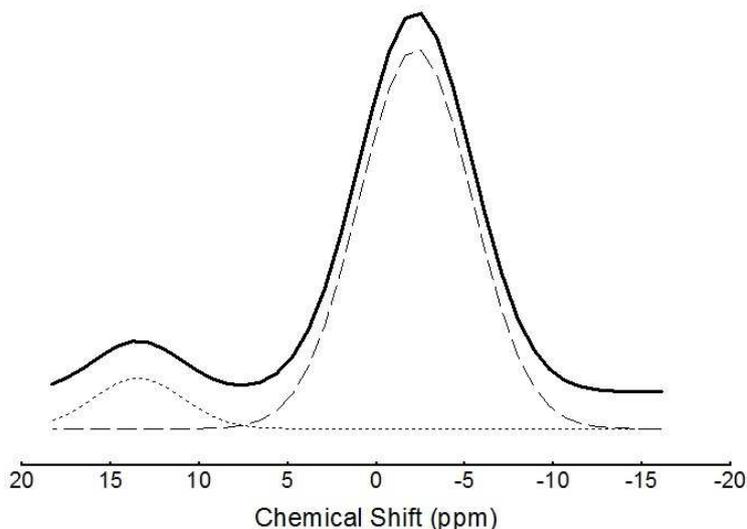


Figure 6. Deconvolution of NMR spectra for glass of 20 mol % CdO. solid lines denote experimental ^{51}V MAS NMR data, and filled curves or dashed lines represent fitting of the data using Gaussian line shape.

applied NMR program responsible for ^{51}V NMR measurements. The data in tables 1 and 2 are calculated from the area under each resonance peak representing by Q^2 , Q^1 and Q^0 structural species.

4. Summary

Structural role of V_2O_5 has been studied in the single V_2O_5 , binary $\text{CdO-V}_2\text{O}_5$ and ternary $\text{CdO-V}_2\text{O}_5\text{-P}_2\text{O}_5$ glass systems. ^{51}V and ^{31}P MAS NMR measurements have been carried out to determine the changes in the network structure of the investigated systems. NMR data has indicated that only 5-fold coordination of the vanadium atom, V(5), is the predominant type in the pure V_2O_5 glass. Vanadium in the modified CdO glasses exists in more than one coordination states which are V(5) and V(4). The local vanadate structure unit in the CdO rich glass (60 mol%) is mainly consisted of VO_4 units in the form of orthovanadate $\text{Cd}_3(\text{VO}_4)_2$. ^{31}P NMR results have showed that concentration of (NBOs) is increased in the phosphate network with increasing CdO contents.

Acknowledgments

We wish to acknowledge Professor R. Hassan (Leeds University, UK) for the critical review and editing of the text.

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