

RAMAN STUDY OF LEAD VANADATES GLASSES

D. MANIU, T. ILIESCU, S. AȘTILEAN

Molecular Spectroscopy Dept., Faculty of Physics, Babes-Bolyai University, Cluj-Napoca, Romania e-mail: dmaniu@phys.ubbcluj.ro

Abstract. Vanadates glasses are relatively new class of vitreous materials belonging to the amorphous oxide semiconductors.

In this work the influence of lead oxide on the structure of xV_2O_5 (1-x) PbO glasses was investigated by Raman spectroscopy. The Raman bands of studied glasses can be related to stretching frequencies for V-O bonds, found in 1050-750 cm^{-1} ranges.

The vibrational modes of VO_4 tetrahedra as well as VO_5 species are present in the mentioned range. The characteristic bands of PbO appear at low frequencies ($< 350 cm^{-1}$) only at high PbO content.

The addition of PbO in vanadium glasses involves changing of vanadium coordination. At low PbO content, vanadium ions are fivefold coordinate, while at high PbO content vanadium ions are fourfold coordinate.

Key words: lead vanadates glasses, Raman spectroscopy

1. INTRODUCTION

Vanadates glasses are a relatively new class of vitreous materials belonging to the amorphous oxide semiconductors. Since electron transport depends on the structure, we started a study of the short-range order.

Any experimental method giving direct or indirect insight into morphology and short-range order in these solids is very valuable. One such method, used in this work is Raman spectroscopy. Raman spectroscopy may be regarded as a powerful and efficient tool in studying the structure of local arrangements of the atoms in glasses.

Two basic approaches are proposed in the literature for the description of disordered structures. The random network hypothesis [1, 2] assumes the fundamental polyhedra present in crystals to appear also in the corresponding glasses. On the other hand, the crystallite model [3] considers the glass to consist of local order regions, which are connected to each other by a disordered structure. This latter model has not found much support by experimental data [2]. According to the Krong-Moe hypothesis [4] the structural units present in oxide glasses resemble the units of the groups present in the corresponding crystalline compounds. This hypothesis has been taken into account for the analysis of Raman spectra of vanadates lead glasses.

Binary vanadium glasses form an interesting system because the glass phase can be obtained over a large range of vanadium oxide. Vanadates glasses are relatively new class of vitreous materials belonging to the amorphous oxide semiconductors.

In the present paper the influence of lead oxide on the structure of $xV_2O_5 \cdot (1-x)PbO$ glasses was investigated by Raman spectroscopy.

2. EXPERIMENTAL

The samples were prepared by mixing, in suitable proportions, V_2O_5 and PbO having reagent grade purity and melting this admixture in a corundum crucible at the temperature of 1523 °C. Vitrification was achieved by rapid cooling of the melts on stainless steel plates at room temperature and atmospheric pressure. All the samples were equilibrated at the above temperature for 30 minutes.

Vanadium lead glasses in the 40-90 mol % range for V_2O_5 were obtained.

The Raman spectra were obtained using the micro-Raman technique. The Raman spectra have been recorded on a Spex 1404 double monochromator, with a spectral slit width of 2 cm^{-1} , using a Spectra Physics 166 Ar^+ laser (514.5 nm) with 350 mW power at the sample. A 180° geometry was used. The laser excitation was coupled to an optical microscope. The laser excitation was coupled to an optical microscope Olympus U-CMAD-2 with two objectives (DPLAN 20 160/0.17 and ULWD MSPLAN 80/0.75), used to focus the laser light and collect the Raman scattering radiation. The Raman spectra were recorded without polarizer in the collection optics.

3. RESULTS AND DISCUSSION

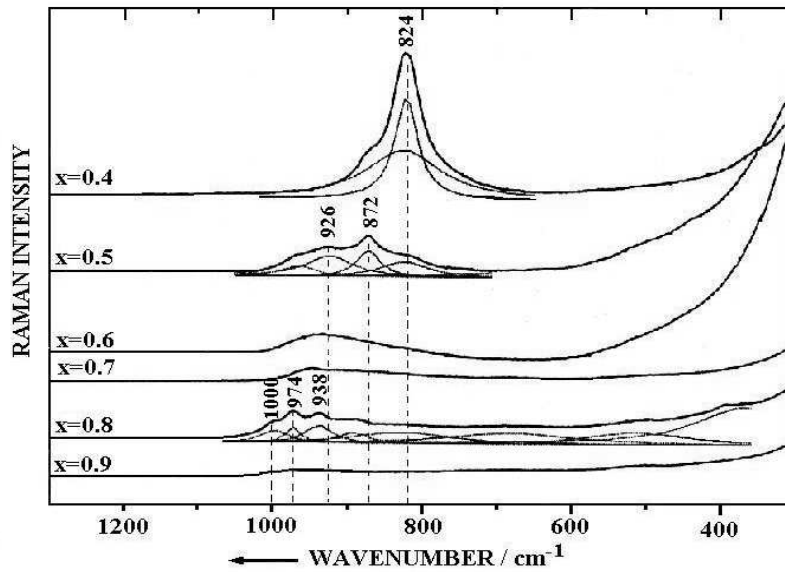
The Raman spectra of $xV_2O_5 \cdot (1-x)PbO$ glass samples with various contents of lead oxide ($0.4 \leq x \leq 0.9$) are presented in Fig. 1.

The following bands are present in these Raman spectra: 824 cm^{-1} , 872 cm^{-1} , 926 cm^{-1} , 938 cm^{-1} , 974 cm^{-1} and 1000 cm^{-1} . All these bands can be related to stretching frequencies for V-O bonds, found in 1050-750 cm^{-1} range [5].

Nabavi et al. [6] have concluded that vanadium ions exhibit fourfold and fivefold coordination states. In the case of transition the frequency of vanadium oxygen bond decreases and this is related to the decrease in the coordination number of vanadium.

Different structural models are developed for these vanadates glasses [6]:

- VO_5 and VO_4 basis units;
- metavanadate groups $M(VO_3)_2$ or MV_2O_6 ;
- pyrovanadates $M_2V_2O_7$;



-orthovanadates $M_3(VO_4)_2$.

Fig. 1- Raman spectra of $xV_2O_5 (1-x)PbO$ glasses with $0.4 \leq x \leq 0.9$.

The mechanisms of incorporation of modifying ions in these structures are:

i) M^{n+} ions rest between vanadates chains and may affect the isolated $V = O$ bonds. As a result they are markedly elongated and the vibrations frequency shift toward low number.

ii) M^{n+} ions can occupy a position in the chain itself and their influence of the $V = O$ bond is limited. If $V = O$ mode position at around 1020 cm^{-1} is preserved it can be concluded that $V = O$ bond is not directly influenced and the coordination number and symmetry of the VO_4 or VO_5 polyhedra do not change

The vibrational modes of VO_4 tetrahedra as well as VO_5 species are present in $1050\text{-}750 \text{ cm}^{-1}$ range.

For glasses having high content of V_2O_5 three bands centred at 1000 cm^{-1} , 974 cm^{-1} and 938 cm^{-1} characterize the Raman spectrum.

The stretching modes of $V = O$ terminal bond having frequencies in $970\text{-}1000 \text{ cm}^{-1}$ range in Raman spectra, is consider as a fingerprint of fivefold coordinated vanadium [7]. The band centred at 1000 cm^{-1} can be found in all vitreous structure form by vanadium oxide: meta-; pyro-; and ortho-vanadate glasses. This band is assigned to $V = O$ stretching modes in VO_5 group [5, 7]. Thus, VO_5 units are present in the structure of studied glasses, at high content of V_2O_5 .

Dimitrov et al [8] has find in Raman spectra of $20RO\ 80V_2O_5$ ($R = Ba, Sr$) a band centred at 970 cm^{-1} and has attributed this band to $V\text{-}O$ stretching mode in VO_4 groups. In our Raman spectra, as is observed; the intensity of 970 cm^{-1} is quite significant when vanadium oxide content is high.

The bands from 970 cm^{-1} regions are related to stretching vibrations of vanadates with fourfold coordination of oxygen atoms around the vanadium atom [9].

The Raman bands centred at 1000 cm^{-1} decrease in intensity when lead oxide content increases. This behaviour suggests that in studied glasses the VO_5 polyhedra is changed to VO_4 deformed polyhedra when lead oxide content rises.

Further increases of lead oxide content the band centred at 970 cm^{-1} decrease in intensity and shift to low number. In the same time, the band centred at 938 cm^{-1} became significant.

In according with the mechanism suggested above the Pb^{2+} ions rest between vanadates chains and their influence on the $\text{V}=\text{O}$ bond is important. In this case we have a metavanadate structure where two of the $\text{V}=\text{O}$ bond are shorter and non-bridged forming a VO_2 group. The main unit for such a structure is $(\text{VO}_3)_n^-$. The analysis of the vibrations in alkaline crystal metavanadates has been carried out by Botto et al [10]. There are two symmetrical and two asymmetrical stretching vibrations of the VO_2 groups. These bands are found in our Raman spectra at 938 cm^{-1} for symmetrical stretching and 886 cm^{-1} for asymmetrical stretching.

The band within the $910\text{-}935\text{ cm}^{-1}$ range is usually assigned to the stretching vibrations of VO_3 units from metavanadate groups [7]. Thus we can ascribe the 938 cm^{-1} peak to the metavanadate network vibrations.

Further decrease in the V_2O_5 content leads to the shift of 938 cm^{-1} band at 926 cm^{-1} and to the appearing of two bands at 872 cm^{-1} and 824 cm^{-1} .

The band about $810\text{-}825\text{ cm}^{-1}$ has been assigned to stretching vibrations of the V-O-V bridges from pyrovanadate [7].

These changes can be explained only if we admit that the coordination number of vanadium decrease and for our sample the metavanadate structure is changed in pyrovanadate structure.

The characteristic bands of PbO appear at low frequencies [11] (90 cm^{-1} , 140 cm^{-1} , 315 cm^{-1}) at high PbO content and they are not included in the wavenumbers range of discussed Raman spectra. These bands are specific for lead and seem to be independent of the oxygenated glass former. In the same time these bands are characteristic for yellow β -PbO and this may be indicate that the lead, in these samples, is involved in some structural arrangements in the crystalline oxide: Lead is the apex of the tetragonal PbO_4 pyramid. These bands correspond to the symmetric vibrations of these units.

Therefore, we conclude that lead oxide acts as network modifier in studied glasses. At high content PbO could act as network former, as indicate the spectra shape from low wavenumbers (under 400 cm^{-1}). As a result, the studied glasses consist of different kind of network. The dominant network is given by V_2O_5 and consists of VO_5 units for high content of vanadium oxide. While the vanadium oxide content decrease, the VO_5 units are transformed in VO_4 units and then in VO_3 units from metavanadate structure. Further decrease of vanadium oxide content determines a conversion from metavanadate structure in pyrovanadate structure.

4. CONCLUSIONS

We conclude that the addition of lead oxide in vanadium glasses determine the changing of vanadium coordination.

The increase of lead oxide determines the changing of VO_5 polyhedra in VO_4 deformed polyhedra and than in VO_3 units from metavanadate groups.

Further increase of lead oxide determines the change of metavanadate structure in pyrovanadate structure.

At low lead oxide content, vanadium ions are fivefold coordinate, while at high lead oxide content vanadium ions are fourfold coordinate.

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