Indonesian Physics Communication

Department of Physics, Universitas Riau, Pekanbaru, Indonesia
p-ISSN 1412-2960 | e-ISSN 2579-521X

Vol. 21 | No. 3
November 2024

Web: https://kfi.ejournal.unri.ac.id
E-mail: kfi@ejournal.unri.ac.id

FTIR and Raman studies of manganese phosphate glasses

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ABSTRACT

Raman and infrared (IR) spectra of $xMn_2O_3(1\text{-}x)P_2O_5$ glasses (x = 5 mol% – 25 mol%) are reported. The spectral shift is related to changes in the coordination of the neodymium ion. The changes observed are consistent with an elongation of P–O$^-$ terminal and P–O–P bridging bonds in the PO_4 tetrahedra.

Keywords: Infrared; PO_4 tetrahedra; Raman

Received 05-09-2023 | Revised 02-10-2023 | Accepted 15-10-2024 | Published 30-11-2024

INTRODUCTION

Glasses are widely used mainly because they are transparent in the visible spectral range. We are now entering an era when it has become at least as significant to process and transmit information rapidly [1]. Phosphate glasses have very interesting molecular structures and some unique physical properties such as high thermal expansion coefficients, low transition and softening temperatures and low preparation temperatures. Metaphosphate glasses containing rare earth ions have potentially important applications in optical communications and laser technologies [2, 3]. Glasses of the $R(PO_3)_3$ formula (where R represents one of the lanthanide ions) have been reported to exhibit the largest magnetic contributions to the low temperature specific heats known in oxide glasses [4]. Sm and Eu phosphate glasses are unusual in having a negative hydrostatic pressure dependence of bulk modulus and a negative coeeficient of thermal expansion [5]. The promising physical properties of the rare earth phosphate glasses have initiated many studies of their structure including EXAFS and Neutron diffraction [6], and Mossbaur spectroscopy [7]. Raman and IR spectroscopy have been used for investigation of the molecular structure of phosphate glasses [8]. However for phosphate glasses having band gaps in visible or near infrared, the intrinsic optical transitions of the glass overlap some of the intra 4f-shell transitions of the rare-earth dopants. The relevant optical transitions of host glass can be summarize in terms of the optical spectrum [9].

In this paper we report our results and interpretation on IR and Raman spectra of Mn_2O_3-P_2O_5 glasses. Previous investigations on d.c. electrical conduction of neodymium phosphate glasses showed that the electronic conduction is due to hopping of an electron from lower valence state (Nd^{2+}) to higher valence state (Mn^{3+}) of manganese ions [10].

EXPERIMENTAL

Preparation of Sample

Neodymium phosphate glasses of general formula $x(Mn_2O_3)1\text{-}x(P_2O_5)$ were prepared by melting mixtures of high-purity dry manganese oxide with phosphorus pentoxide P_2O_5 in a closed platinum crucible of 80 cm^3 capacity. To react the constituents, the mixture of manganese oxide and phosphorus pentoxide in the crucible was heated in an electrical furnace at a temperature was progressively increased, reaching a maximum of approximately 1500ºC. To ensure proper mixing and homogeneity, the molten liquid was shaken frequently and vigorously. After being checked, the melt was cast by pouring as fast as possible into a hot

©Author(s) | DOI: 10.31258/jkfi.21.3.257-260

steel split mould to quench to form a glass. The glass was immediately transferred to an annealing furnace at 500ºC where it was kept for 3 h to relieve any residual stress which could cause embrittlement. At the end of this annealing process, the furnace was switched off and the glass left to cool down to the room temperature gradually by controlled thermal treatment at cooling rate of 0.5ºC/min. The sample were selectively cut, ground, and polished. After preparation, samples were stored in plastic containers in a dessicator.

Measurements of IR Spectra

A Perkin Elmer 1600 Fourier-transform infrared (FTIR) have been used to investigate to all sample prepared using the KBr pellet technique. Typically around 2 mg of the finely ground sample is mixed with 200 mg of KBr powder and the mixture then pressed for 4 minutes, in evacuable die under 10 tons of pressure to give a transparent disk with a surface area of 1 cm^3. The FTIR spectra were recorded in the spectral range of 4000 – 400 cm^{-1} resolution and 64 scans to ensure a good signal to noise ratio.

Raman Spectroscopy

Powder samples were used for measurement of Raman spectroscopy (2000R NIR FT-Raman). An Nd:YAG laser (an yttrium aluminum garnet crystal doped with triply-ionized neodymium) at the wavelength 810 nm was used for sample excitation. Power of the laser at the sample was typically ~300 mW. Spectra of the samples were taken in the frequency region between 100 cm^{-1} and 3500 cm^{-1} at a spectral bandpass of 1 cm^{-1}.

RESULTS AND DISCUSSION

Infrared absorption

The IR spectra of x(Mn_2O_3)1-x(P_2O_5) are shown in Figure 1 and Table 1. The spectra of glasses show five major peak vibration bands at around 1251, 1072, 915, 776.5, and 481 cm^{-1}. Significant changes occur in both intensities and band shapes as a function of composition. These bands can be assigned to $v_{as}PO_2$, v_aPO_2, $v_{as}POP$, v_aPOP, and δPO_2 modes of $(PO_3)_n$ chain groups, respectively [11].

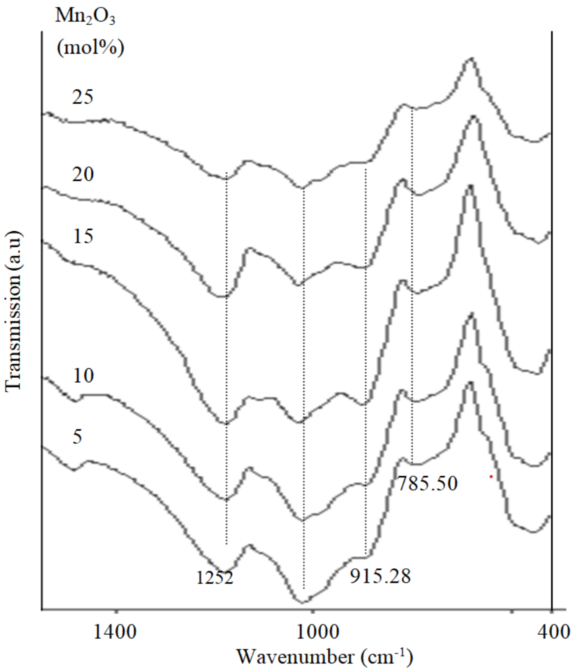

Figure 1. IR spectra of xMn_2O_3(1-x)P_2O_5 glasses, with $0.05 \leq x \leq 0.25$.

The results are very similar to those of the metaphosphate glasses studied by Corbridege [12], Exarhos et al. [13], Karabulut [14], and Hudgens [15]. The band frequency shifts continuously from 1251 cm^{-1} at $(Mn_2O_3)_{0.05}(P_2O_5)_{0.95}$ to 1262.46 cm^{-1} at $(Mn_2O_3)_{0.2}(P_2O_5)_{0.8}$ sample. However there are no significant structural changes to the network and there is no evidence for presence of significant concentrations of terminal groups ($v_{as}PO_3$ at 1255.51 cm^{-1}). These observations are consistent with the analyzed compositions which yield O/P ratio of ≈ 2.69 [16] and so PO_3 groups as indicated by the presence of the IR band at 1255.51 cm^{-1}. In addition to the relatively low frequency position of the band at 481 cm^{-1}, are in part due to cross linked three dimensional phosphate structure. This observation is an agreement with results obtained [17]. The band at 776.5 cm^{-1} is assigned to P–O–P ring frequency in the part of three dimensional network relatively free of chain. Generally the structure of the v_sPOP band is considered as the most characteristic one in the spectra of metaphosphate since it appears in a frequency range free from other vibrational frequencies [18]. In addition, the v_sPOP bands are very sensitive to changes since the frequency is strongly dependent on POP bond angle.

Table 1. Infrared spectra of glasses in the region 1500 – 400 cm^{-1}.

Glass	Position of prominent absorption maxima (cm^{-1})				
$5Mn_2O_3 + 95P_2O_5$	1251_s	1072_s	915_{ms}	776.5_m	481_m
$10Mn_2O_3 + 90P_2O_5$	1254.29_s	1062.23_s	898.3_{ms}	780.5_m	490.37_m
$15MN_2O_3 + 85P_2O_5$	1254.26_s	1062.22_s	898.3_s	779.45_m	487.33_m
$20MN_2O_3 + 80P_2O_5$	1262.46_s	1068.49_{ms}	912.85_{ms}	774.66_m	484.57_m
$25MN_2O_3 + 75P_2O_5$	1255.51_{ms}	1060.49_{ms}	912.54_{sh}	-	492.58_m

Note: s, strong; ms, medium strong; m, medium; sh, shoulder

Raman Spectra

The Raman spectra of all glasses were obtained. For binary manganese phosphate glasses, the spectra exhibit major variations as a function of manganese concentration, x, over the x = 5 mol% to x = 25 mol%. These are evident in the 1170 – 1250 cm^{-1}, 970 – 1100 cm^{-1}, and 730 – 780 cm^{-1}, as well as lower frequency regions of the Raman spectra in Figure 2 and Table 2.

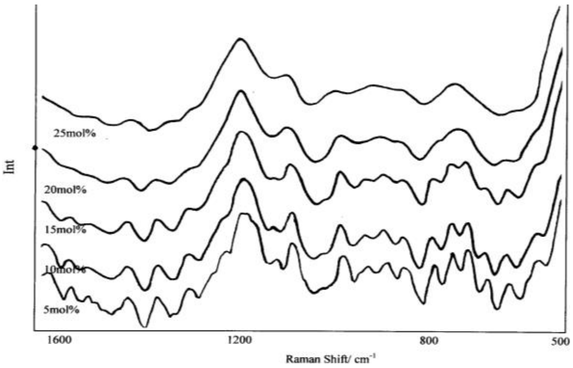

Figure 2. Raman spectra of xMn_2O_3–$(1-x)P_2O_5$ glasses, with $5 \leq x \leq 25$.

The change in frequency and relative intensity of the band maximum at 1360 cm^{-1} to shoulder at 1177.87 cm^{-1} with a change in x = 25 mol% is quite dramatic. Band contour analysis shows that this feature is not due to one band shifting but to the change in relative intensity of two bands at 1085.95 cm^{-1} and 1177.87 cm^{-1}, whose convoluted band maximum shifts. These bands are due to the asymmetric PO_2 stretch of PO_2 units in the chain but with different bonding configurations relative to the rare earth ions [19]. As x increases a shoulder at 1360 cm^{-1}, due to stretch of uncoordinated P=O units disappears, and the strongest band due to the PO_2 symmetric stretch broadens and shift from 977.02 cm^{-1} to lower frequency.

The Raman band at 731.91 – 710.65 cm^{-1} is assigned to predominately P–O–P stretching mode involving imperturbed chain and residual ring units in the P_2O_5 rich glasses. It decreases in intensity and is replaced by the band 710.65 cm^{-1} when x exceeds 10 mol%.

Several bands have been observed in the region of the spectrum containing out of chain PO_2 vibration. Two main bands at around 1270 cm^{-1} and 1420 cm^{-1} in this region are present in the spectra of metaphosphate glasses and assigned to the asymmetric stretch of PO_2 and P=O, respectively [20].

Table 2. The Raman peak positions for xMn_2O_3–$(1-x)P_2O_5$ glasses.

Sample	Absorption peak (cm^{-1})				
S_1	706.38	746.38	985.10	1142.55	1189.36
S_2	708.21	748.26	988.34	1144.23	1192.42
S_3	710.52	754.63	989.21	1149.41	1194.62
S_4	716.36	-	992.46	1152.36	1198.21
S_5	721.27	-	1021.27	1163.13	202.36

For all the glasses, the broad bands are observed in the wavenumber region between 400 – 600 cm^{-1}. Their assignment is not unambiguous because these bands are due to complicated internal vibration such as the skeletal deformation vibration of phosphate chains and PO_3.

CONCLUSION

Stable phosphate glasses containing up to 25 mol% Mn_2O_3 can be obtained by ordinary melt quenching. IR spectroscopy reveals that the glass networks are dominated by bridging P-tetrahedra that constitute the metaphosphate chains, with some chain-terminating sites in glasses with O/P ratio 2.69. The Raman bands reveal that the manganese ion interacts more covalently with phosphate anions in glasses leading to a redistribution of PO_2 (POP) bond angels and lengths. Minor variations in the concentration of Mn_2O_3 around the metaphosphate composition lead to different structures and oxygen environment for the rare-earth ion in glass.

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