Cadmium invert sodium phosphate glasses: A structural peculiarities

G. El-Damrawi¹, H. M. Zahran² and A. M. Abdelghany³,⁴

¹Department of Physics, Faculty of Science, Mansoura University, Mansoura, Egypt; ²Faculty of Basic Science, New-Mansoura University, New Mansoura, Egypt; ³Spectroscopy Department, Physics Research Institute, National Research Centre, 33 ElBehouth St., Giza, Dokki, Egypt; ⁴Basic Science Department, Horus University, International Costal Road, New-Damietta, Damietta, Egypt

ABSTRACT
xCdO.(100-x)(yNa2O.zP2O5) invert glasses, with CdO substituted for both Na2O and P2O5 were successfully prepared using a melt-quenching method. x changed up to 45 mol% and z equals y in all cases. ³¹P NMR studies show that CdO replaces both Na2O and P2O5, the total concentration of nonbridging oxygen atoms (NBO) increases. CdO switched its role of network intermediate to modifier with decreasing Na2O and P2O5 content Increasing NBO in the phosphate network causes a gradual decrease in density and increase in the molar volume of the glasses. Increasing CdO at expense of Na2O and P2O5 leads to the creation of more open spaces which can play the role of weakening in the structure that can be reflected by the increase of glass-free volume. Analysis based on NMR and FTIR spectroscopies confirmed that the Q2/Q1 ratio hardly decreased with increasing CdO at expense of equal concentration from P2O5 and Na2O.

1. Introduction

It was previously known that the introduction of modifier oxides like alkali or alkaline earth to P2O5 [1–3] or TeO2 and SiO2 [4–6] results in the creation of nonbridged oxygen bonds (NBO) in the network of the glasses [6,7]. Increased NBO can simply allow the development of crystalline or polycrystalline phases that are suitable for certain applications. For example, the wollastonite (CaSiO3) and apatite Ca3(PO4)2 (F, OH) crystalline phases could be formed only when the concentration of NBO in the glass network is high enough to form crystalline clusters from orthosilicate and orthophosphate units in both the silicate and phosphate networks [2,7]. Then, to get the greatest concentration from bio-crystal phases, continued production of NBO, particularly in the phosphate glass network, is necessary.

However, there is a difficulty that might cause the development of bio-crystalline phases in the host glass network to be delayed or limited. This issue is caused by an addition of large concentrations from monovalent modifiers such as Na2O, which are required to generate NBO in the glass network [7,8]. To create a crystalline clustered species from the beginning, a portion of the Na2O should be simply inserted as a modifier and the remainder as a former to form clusters from its own. These species can delay the development of bioactive phases. To solve such a problem, the benefits of substituting P2O5 and Na2O with any type of divalent oxides, such as CdO, should be studied. Because CdO acts as both a glass former and a modifier [9], substituting Na2O with CdO in most cases is likely to cause more problems. The component that consumed as a glass former should lower the concentration of NBO and, as a result, diminish the material’s capacity to crystallize. Therefore, different trials have been done to increase or enhance the content of NBO without any formation of crystalline clusters from the modifiers. This may be because of the mixing effect of the two modifiers (Na and Cd) which enhance the content of NBO without forming crystallized species. When the concentration of Na2O is high, most glass-forming units such as tellurite or silicate units containing NBO are electrically balanced with Na⁺ cation. But the reduction of both P2O5 and Na2O and increasing CdO may lead to the creation of an inverted process is in the glass structure and properties. The invert process means most of the NBO in the glass network are forced to be electrically balanced with Cd²⁺ ions instead of Na⁺. This process forces most of all added CdO to play a modifier role, that is consumed to create more and more NBO. This will be done by constructing what is called an inverted structure in which P2O5 and Na2O are both replaced step by step by CdO. Although CdO creates less concentration from NBO than that of Na2O, the exchange of both (P2O5 and Na2O) with CdO can play a role.

2. Experimental details

Glasses of nominal composition xCdO.(100-x) yNa2O.zP2O5 were prepared with mol fractions listed in
Table 1. Relative area of Q1, Q2, and Q2/Q1 ratio determined from the analyzed spectra of different samples.

| CdO (mol%) | Relative Area of Q2 | Relative Area of Q2 | Q2/Q1 |
|------------|--------------------|--------------------|-------|
| 0          | 0.98               | 0.02               | 49    |
| 10         | 0.78               | 0.22               | 3.54  |
| 20         | 0.61               | 0.39               | 1.56  |
| 30         | 0.40               | 0.60               | 0.67  |
| 40         | 0.23               | 0.77               | 0.30  |
| 42.5       | 0.10               | 0.90               | 0.11  |
| 45         | 0.03               | 0.97               | 0.03  |

Table 1 via the traditional melt quenching route. Analytical grade chemicals of cadmium carbonate, sodium carbonate, and ammonium dihydrogen orthophosphate supplied by Rayasan chemicals were used. Precalculated mole fractions were accurately weighed and mixed in porcelain mortar before melting. Weighted batches were placed in a muffle furnace for about 3 h at about 350°C to ensure complete emission of carbon dioxide and ammonia from constituents. The temperature was then raised gradually to about 1000°C until melting. The melts were then swirled at constant intervals to ensure homogeneity and formation of bubble-free glasses. The melts were then poured into stainless steel molds with the required dimensions.

Atomic arrangement within the studied matrix was studied via Shimadzu Dx-30 X-ray diffractometer within a Bragg angles extended between 5-70°. KBr disc route was adopted to explore FT-IR spectral that recorded with Nicolet is10 ThermoFisher within the spectral range extended from 4000 to 400 cm$^{-1}$ with resolution 2 cm$^{-1}$. Pulverized glass powders were mixed with spectroscopic grade KBr in a 1:100 ratio and subjected to about 5 tons/cm$^2$ until a clear transparent disc was formed. The deconvolution analysis technique (DAT) was accomplished using Jandel Scientific Peakfit4.12 software on the basis previously discussed [10]. Prepared discs that were measured directly after preparation. NMR measurements were conducted at room temperature with a JEOL resonance GSX-500 spectrometer adopting a magnetic field of 11.747 T. $^{31}$P NMR spectral data were measured at the resonance frequency of about 160.47 MHz using a 3.2 mm probe at rotor frequency 17kHz. The pulse length was 2.5 µs with 60 s delay to ensure relaxation. From which the distribution of Q$^2$ of phosphate units can be determined.

3. Results and discussion

Phosphate glasses modified with modifier oxides like CaO and Na$_2$O [11,12], as well as additional glass formers like silica (SiO$_2$) [11], can be used as bioactive and biocompatible materials [13,14]. In this case, the as-prepared glass system must be used with the requirement that the molar ratio of (Na$_2$O and CaO)/(P$_2$O$_5$) should be higher than unity ($>$ 1). As a result, anionic groups such as PO$_4^{3–}$ can be connected through (Ca$^{2+}$) ions to form apatite Ca$_3$(PO$_4$)$_2$ and can also connect with SiO$_2$ to form wollastonite (CaSiO$_3$). In this situation, the concentration of the modifier such as (CaO) should be higher than that of P$_2$O$_5$.

The modifier oxide should then be raised until the orthophosphate crystallizes into PO$_4^{3–}$ groups to form Ca$_3$(PO$_4$)$_2$ units which are highly recommended to be formed. In this scenario, the greater concentration of NBO might alter the network of the obtained glass, which may comprise several crystalline phases [9–14]. This action may be considered in terms of invert glasses, since adding another type of intermediate oxide, such as PbO, ZnO, or CdO at the expense of (Na$_2$O + P$_2$O$_5$) results in invert structure since most of the negative charges on NBO should be balanced with positive charges on Cd$^{2+}$ cation. Modification of NBO with Cd without formation of crystalline phases leads to glass
structure modified mainly with CdO instead of Na$_2$O which is called invert glasses structure.

3.1. XRD diffraction

Figure 1 showed XRD spectra for all the investigated glasses. It can be noticed that the amorphous structure is the characteristic feature for all the examined compositions. There is no tendency toward crystallization even in the composition of the highest concentration from a modifier oxide. Only a broad hump has appeared in the XRD spectra in the region between 15° and 35° which characterizes the amorphous glass network [13–15]. XRD measurement to ensure that there is no tendency...
for crystallization and since no sharp peaks are appearing in the higher concentration authors only describe the behaviour (qualitative measure).

### 3.2. NMR spectroscopy

Figure 2 depicts the $^{31}$P NMR resonance spectra of all investigated glasses. The resonance spectrum of glasses with 0 mol% CdO, Figure 2, is nearly identical to metaphosphate composition (phosphate units containing two NBO, called Q2) [7,9,15]. The differences between the NMR spectra of CdO free glass and glasses containing relatively high concentration from CdO Figure 2, indicates that CdO plays an effective role since the substitution of CdO for P$_2$O$_5$ and Na$_2$O induces a strong effect on the characteristic feature of the measured $^{31}$P NMR spectra. The spectral feature is highly modified in glasses containing CdO. The resonance peak centred at $-16.8$ ppm is continuously decreased with increasing CdO content. In addition, a new resonance peak appears at about 2 ppm, and its area increases to reach its maximum value at 45 mol% CdO. The main resonance peaks centred at $-16.8$ ppm could be assigned to phosphate units containing two nonbridging bonds (2NBO) per each phosphate building unit, noted as Q2[9,15,16].

Decreasing of this peak and the formation of a new one at 2 ppm is attributed to an increase of concentration of NBO atoms around phosphate units. Furthermore, the appearance of additional resonance peaks at (2 ppm) in most of the investigated glasses confirms the formation of phosphate units with more NBO (Q1 and Q0) [6,15]. In general, increasing CdO content results in increasing the amount of NBO in the phosphate glass structure.

As shown in Figure 3a:g, the percentage of various Q$^n$ species in the phosphate network can be quantitatively determined using line shape simulations or deconvolution processes. The $^{31}$P MAS NMR analyzed spectra generally consist of three phosphate units Q0, Q1, Q2, in which the superscript indicates the number of bridging oxygen per PO$_4$ tetrahedron. After peak deconvolution, each Q$^n$ fraction can be calculated and listed in Table 1. Figure 4 shows the changes of Q$^n$ fraction as a function of the CdO fraction. The fraction of Q2 units decreases with increasing CdO fraction, whereas the fractions of Q1 and Q1 increase. We use Q$^n$ fractions as structural factor constraints the investigate glasses. Q2/(Q1+Q0) ratios are represented in Figure 4. Then in the situation, of sodium-rich glass, a structure with the highest Q2/(Q1+Q0) (49) ratio is formed. While the distorted local environment is maintained which leads to a decrease of Q2/(Q1+Q0) due to cadmium invert glass.

Then from Table 1 and Figures 4 and 5, it can be concluded that the changes of the percentage of Q2 and (Q1+Q0) with increasing CdO content is mainly due to the creation of more NBO associated with CdO addition. This conclusion is highly evidenced from the reverse changes in the peak intensity of the two main resonance lines situated at $-16.8$ and 2 ppm (Figures 3a:g). It can be shown that the intensity and relative area of a peak centred around $-16.8$ ppm is sharply decreased and in the same type the resonance peak around 2 ppm becomes more resolved and its relative area is increased. These changes are related to the decreasing concentration of the phosphate units in the metaphosphate (Q2) and increasing phosphate units of orthophosphate structure which contains the highest amount of NBO atoms [13–15].

### 3.3. FTIR spectroscopy

As shown in Figure 6, the percentage of various Q$^n$ species in the phosphate network can be quantitatively determined using line shape simulations or deconvolution processes. The FTIR analyzed spectra generally consist of several absconded. After peak deconvolution, each Q$^n$ fraction can be calculated. We use Q$^n$ fractions
Figure 6. FTIR analyzed spectra for glasses containing different CdO concentration.

as structural factor constraints the investigate glasses. Q^2/Q^1 ratios are represented in Figure 7. Then in the situation, of sodium-rich glass, a structure with the highest (Q^2/Q^1 + Q^0) ratio is formed. Replaces of Na_2O and P_2O_5 with CdO leads to a decrease of Q^2/Q^1. Then the changes of the percentage of Q^2 and (Q^1 + Q) with increasing CdO content is mainly due to the creation of more NBO associated with CdO addition as confirmed from data based on NMR spectroscopy which presented above. The change of the relative area of Q^2 with CdO is related to the decreasing concentration of the phosphate units in the metaphosphate (Q^2) and increasing phosphate units of orthophosphate structure which contains the highest amount of NBO atoms \[13–15\]. This argument is further supported by decreasing molar volume V_m in the glasses network with increasing CdO content, Figure 8. The decrease of V_m is related to the breaking of the phosphate chains of higher volumes and the formation of a phosphate ring-like structure that contains more free volumes due to increasing NBO atoms.

Studied glass composition consists mainly of P_2O_5 as an essential glass-forming oxide that forms PO_4 as structural building units in combination with alkali oxide (Na_2O) that act as a modifier result in the conversion of the three-dimensional network, to linear phosphate chains \[13,15–18\]. Linear phosphate chain structure consequences in the cleavage of P-O-P linkages and the formation of nonbridging oxygens (NBOs) in the glass structure. The identified FTIR spectral vibrational bands observed at 480 and 530 cm\(^{-1}\) can be correlated with the bending vibrations of O-P-O bonding and the vibration of modifier ions (Na) in their sites. While the two peaks at 740 and 771 cm\(^{-1}\) are attributed to symmetric stretching of P-O-P bonding. Bands at 890, 1095, 1200, and 1280 cm\(^{-1}\) may be related to different phosphate vibrational groups. Water, POH, and OH vibrations can be observed at 1640, 2840, 2940 cm\(^{-1}\) respectively.
Cd-O- vibrations were also observed within the region extended from 400-600 cm$^{-1}$ [19–20–21].

4. Conclusions

Different glass compositions in the glass system of the chemical formula: xCdO.(100-x) (yNa$_2$O.zP$_2$O$_5$), x changed from 0 to 45 mol% and z equals to y in all cases have been studied XRD, NMR, and FTIR spectroscopies. The amorphous structure of all samples was confirmed by XRD spectra. NMR as well as FTIR studies show that when CdO replaces both Na$_2$O and P$_2$O$_5$, the total concentration of nonbridging oxygen atoms (NBO) increases. CdO switched its role of network intermediate to a strong modifier. Analysis based on NMR and FTIR spectroscopies confirmed that the Q$^2$/Q$^1$ ratio hardly decreased with increasing CdO at expense of equal concentration from P$_2$O$_5$ and Na$_2$O. The molar volume of the glasses is decreased due to the breaking of phosphate chains with increasing NBO atoms.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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