



Resonance structures of divalent cations in sodium phosphate glass

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Abstract. This research investigates the causes of abnormal phenomena that arise when alkaline earth elements are added to sodium phosphate glass, as network modifiers, through a structure-based study. Many studies have shown that the addition of MgO and ZnO to phosphate glass induces peculiarities in the physical properties, which are attributed to the structural changes caused by the added elements. In this work, sodium phosphate glass was prepared by adding alkaline earth oxides, such as CaO, BaO and CuO, all of which exhibit an inflection point, where the density changes. Abnormalities, similar to those observed in the previous studies, were observed in these cases also. X-ray diffraction was performed to analyse the structure of the prepared glass, and it was revealed that there was no change in the crystal structure, and an amorphous phase was identified. Fourier transform infrared spectroscopy (FT-IR) confirmed the difference in the short-range order of the glass structure. However, the reason for the resonance structure, when divalent cations added, was not fully confirmed through FT-IR. X-ray photoelectron spectroscopy was conducted to further confirm the abnormality in the glass. The abnormality caused by the addition of alkaline earth elements to phosphate glass was explained based on the results of these analyses.

Keywords. Phosphate glass; abnormality; resonance; cation; X-ray photoelectron spectroscopy; fourier transform infrared spectroscopy.

1. Introduction

Phosphate glass has a wide range of vitrification. The melting point of this glass can be reduced by adding a network modifier (NWM, typically metal ions); however, its commercialization is difficult because of its poor chemical properties such as low water resistance. In the recent years, phosphate glass has received much attention for use in applications that utilize its wide vitrification range and low melting point, such as glass-to-metal sealing, infrared transmission, laser technology, medical fields and display components. Several studies have also been conducted on phosphate glass [1–5]. Recent studies have focused on its chemical and physical properties rather than structural features, in various compositional systems [6,7]. The physical properties of glass are based on a structural perspective that makes it easy to predict the properties of glass. The structural analysis of phosphate glass involves techniques such as Fourier-transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy and nuclear magnetic resonance (NMR) imaging. Previous researches have mentioned that P and O have one non-bridging oxygen (NBO) in the form of a double bond, even in a PO₄ tetrahedron, which is a basic

structure in phosphate glass, with no alkali or alkaline earth ions added [8–12]. Studies have shown abnormalities such as the presence of an inflection point, which is difficult to explain in terms of the changes in the basic units (PO₄ tetrahedron), arising because of the resonance structures of Mg and Zn in the glass structures [13–15].

Thus, we investigated the above-described abnormality using FT-IR and XPS analyses [13,15,16]. Experiments were performed using Group 2 elements of the periodic table (belonging to the alkaline earth group), to determine the differences in the expression of abnormalities according to the atomic radius and presence of divalent cations in the structure.

2. Experimental

In this study, three-composition glass was prepared with varying concentrations of P₂O₅, from 50 to 70 mol%, in increments of 5 mol%. To compare the structural effects of MgO, CaO, BaO and CuO (in brief RO), three-composition glass consisting of [Mg]; P₂O₅–Na₂O–MgO, [Ca]; P₂O₅–Na₂O–CaO, [Ba]; P₂O₅–Na₂O–BaO and [Cu]; P₂O₅–Na₂O–CuO was fabricated.

For all samples, P_2O_5 ($NH_4H_2PO_4$, Junsei Chemical Co. Ltd., 99%) and Na_2O (Na_2CO_3 , Junsei Chemical Co. Ltd., 99%) were used as the starting materials. In the case of [R], MgO was substituted with CaO, BaO and CuO. The raw materials were mixed for 10 min in an alumina mortar, according to the compositions presented in table 1. The sample was calcined in an alumina crucible under air atmosphere at $500^\circ C$ for 1 h. After the mixture was melted sufficiently at $1300^\circ C$ for 1 h, it was cooled rapidly on a steel plate to produce the samples.

The densities of the manufactured samples were measured using the Archimedes' method with distilled water as the solvent. The structural changes in the glass were analysed through XRD (Rigaku, Ultima IV) and FT-IR spectroscopy (ThermoFisher, NiCOLET iS5). For XRD, the 2θ scan range was 10° – 90° , with a step size of 5° min^{-1} , and for FT-IR, scanning was performed in the 1800 – 500 cm^{-1} range using the KBr method with a scanning resolution of 4 cm^{-1} . Cross-validation of the binding energy of the O 1s peak was achieved through XPS (AXIS SUPRA) analysis.

3. Results and discussion

Figure 1 shows the glass-forming region for phosphate glass. The ternary systems of [Mg], [Ca], [Ba] and [Cu] have similar glass-forming regions because of the main network former (NWF) P_2O_5 . More than 50 mol% of P_2O_5 and less than 50 mol% of Na_2O produce a stable structure of glass; therefore, the prepared samples, which are greater than 50 mol%, [R] were selected to compare the resonance structures of MgO, CaO, BaO and CuO. As described previously, the samples had a large glass-forming region, even though the samples contained NWM. Generally, an NWM/NWF ratio less than 1 produces a well-linked structure, which is the reason for selecting the range of composition (more than 50 mol% of NWF) [17]. In addition, the glass composed of a three-composition system is chemically stable (this is the reason for selecting the three-composition system) [18–21]. We mentioned the structure of phosphate glass and the chemical durability (it has a stable structure), assuming only the physical effects of NWM, so that the samples could have stable structures, to observe the behaviours of the substances.

Table 1. Compositions (mol%) of P_2O_5 – Na_2O –RO glass.

Samples	P_2O_5	Na_2O	RO
[R]-1	70.0	15.0	15.0
[R]-2	65.0	17.5	17.5
[R]-3	60.0	20.0	20.0
[R]-4	55.0	22.5	22.5
[R]-5	50.0	25.0	25.0

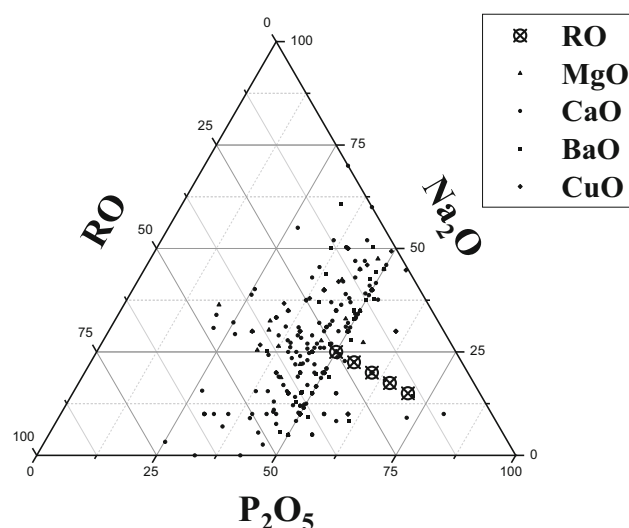


Figure 1. Glass-forming region of the three-composition system compared with RO.

The prepared samples are listed in table 1. The number of samples indicates the mol% of the divalent cations. The physical changes in the glass composition affect the resonance structures significantly. To identify the structure of glass, we analysed its physical properties. XRD is the most useful technique for this analysis, and the diffraction patterns are shown in figure 2, where the broad and diffused peaks correspond to those of typical amorphous materials, representing a non-crystalline structure. This indicates that the amorphous elements are arranged in a disordered fashion. When comparing [R]-5 in figure 2, it can be observed that they exhibit similar diffraction shapes. In addition,

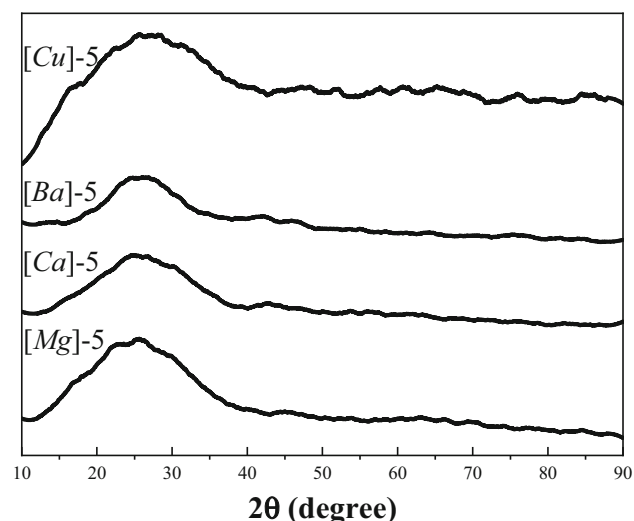


Figure 2. XRD patterns of sodium phosphate glass with 25 mol% of RO.

structural changes in the long-range order due to crystallinity will produce clear changes in the XRD pattern such as the appearance of a sharp peak. However, no sharp peaks were observed in figure 2, confirming that no change occurred in the crystal structure. Therefore, it is difficult to reliably resonance structure using XRD data, and it is necessary to perform a suitable analysis for amorphous materials.

The densities of the samples were then measured. The density of glass increases depending on the amount of *NWM* and not *NWF*, which satisfies the conditions of additivity of glass [22]. The samples are stable, owing to this property, and *NWM* has a great influence on the physical structure. In addition, *NWM* produces a structural change in the glass, and the density changes correspondingly [23]. Figure 3 shows the variation in the density of the three-composition glass with respect to the P_2O_5 content (mol%). In terms of the tendency of density, at P_2O_5 concentrations below 60 mol%, the slope of the graph changes, implying a change in the structure of the *RO*-containing glass. Thus, *RO*-containing glass exhibits a notable effect in the glass structure at *NWM* concentrations exceeding 40 mol%. The structural changes caused by various cations were compared through FT-IR analysis.

The band near 1320 cm^{-1} corresponds to the stretching mode of (P=O) double bonding, that near 1270 cm^{-1} corresponds to the $(PO_2)_{as}$ units (O-P-O) in the Q^2 tetrahedral site, and that near 1160 cm^{-1} corresponds to the $(PO_2)_s$ stretching mode. The band at 1100 cm^{-1} corresponds to the $(P-O^-)$ groups, that at 1000 cm^{-1} corresponds to the PO_3^{3-} group of symmetric stretching, that at 900, 780 and 720 cm^{-1} correspond to the stretching of (P-O-P) groups, and the band near 480 cm^{-1} corresponds to the deformation modes of the PO_4^{3-} groups [11,24,25].

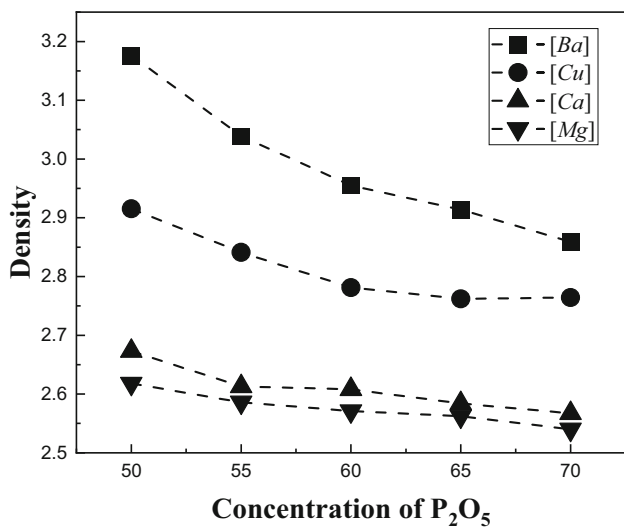


Figure 3. Density of glass as a function of the P_2O_5 content.

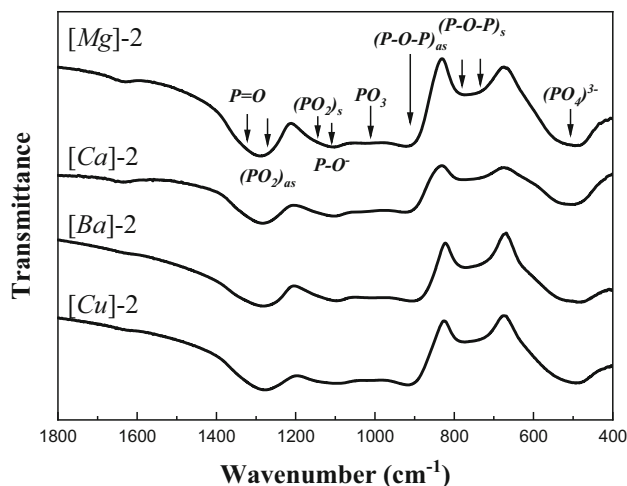


Figure 4. FT-IR spectra of selected glass with different P_2O_5 contents: [R]-2.

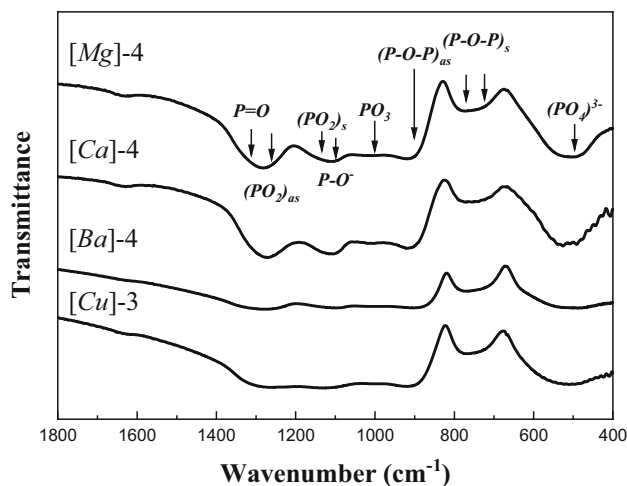


Figure 5. FT-IR spectra of some selected glass with different P_2O_5 contents: [R]-4 and [R]-3 (Cu).

Figures 4 and 5 show that the (P-O-P) band for [Mg] shifts towards longer wavenumbers as the amount of *NWM* increases. A band shift towards long wavenumbers occurs when a smaller-sized *NWM* is added or there is a decrease in the length of the (P-O-P) bonding [16]. The shift of a specific wavenumber towards longer wavenumbers, without any change in additives, can be interpreted to be due to a decrease in the (P-O-P) bonding length and structural changes. The $(P-O^-)$ peak also shows a similar tendency to shift towards a longer wavenumber as the amount of *NWM* increases, indicating that the bond length of $(P-O^-)$ also decreases. This reduction in the bond length indicates a contraction of the network structure and explains the variation in density, as shown in figure 3. Figure 6 shows the FT-IR spectra of [R]-5 and [R]-4 (Cu), where variations occurred in the density. Compared to the spectrum in figure 4, the (P=O) peak has disappeared, and the $(P-O^-)$ peak has shifted towards a longer wavenumber. Figure 7 shows

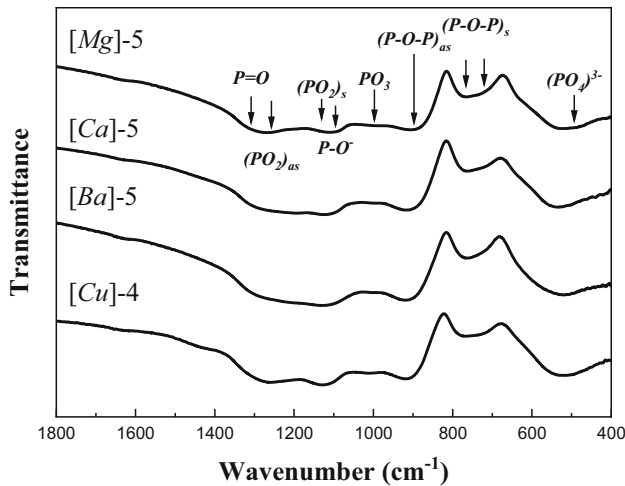


Figure 6. FT-IR spectra of some selected glass with different P_2O_5 contents: [R]-5 and [R]-4 (Cu).

the result, as described above, indicating the shift towards longer wavenumbers of all samples while the length of bonding decreases.

In phosphate glass, the bonds of (P=O), (P-O⁻) and (P-O-P) are present [17]. According to Dr Lee's study on

glass abnormalities [3], structural changes occur in the MgO-added phosphate glass, which shows a tendency to change its density, owing to the bond length. In the case of [Mg]-5, a structural change occurs, because of the bond length for (P-O⁻), as indicated by the bond length between (P=O) and (P-O⁻). Experiments were conducted to demonstrate phenomena similar to the expression of resonance structures depending on other elements. Similar phenomena occurred in [R]-5 and [R]-4 (Cu), and the resonance structures were identified. The strong band in the region of 1200–1100 cm^{-1} is considered to be longer than the double bonding of P and O in terms of the bond length and shorter than a single bonding of P and O. The length of the (P=O) bonding is $1.39 \pm 0.02 \text{ \AA}$, that of the (P-O) bonding is $1.62 \pm 0.02 \text{ \AA}$, and that of the (P-O⁻) bonding is 1.479 \AA [26,27]. It was observed that a resonance structure formed between (P=O) and (P-O⁻) [28]. Because of the resonance structure, the (P=O) bonding in the glass decreased and was formed a bond in the direction of (P=O) in the PO_4 tetrahedron, which is a basic unit of [R] glass. In the basic unit of phosphate glass, the (P=O) bonding exhibits different properties owing to NBO and has a negative charge. In addition, NWM breaks the cross-linking of the bridging oxygen (BO) and compensates for the charge of

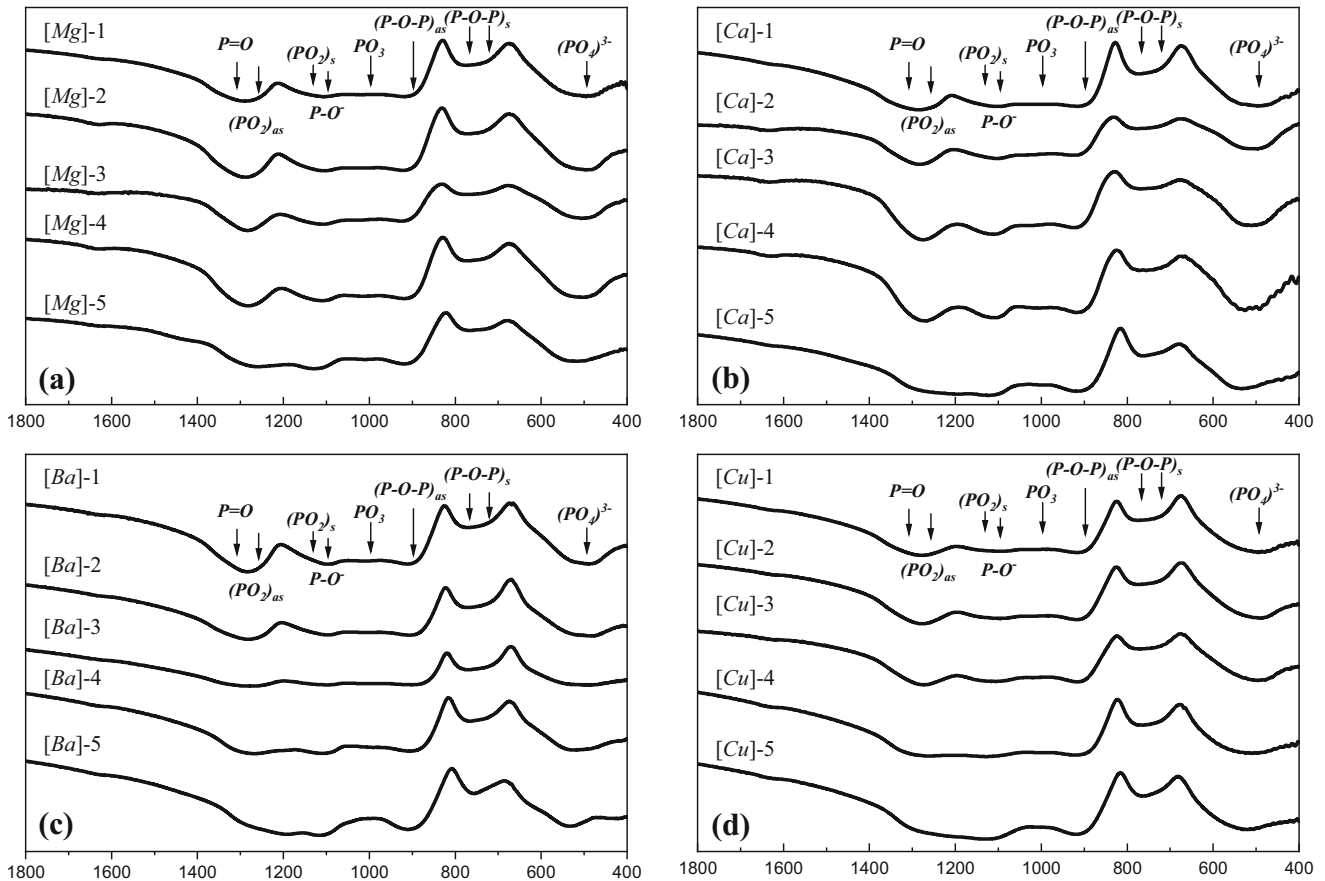


Figure 7. FT-IR spectra of glass with different P_2O_5 contents: [R]: (a) [Mg], (b) [Ca], (c) [Ba] and (d) [Cu] (70–50 mol%).

NBO. From [R]-2 to [R]-4 or [R]-3 (Cu), *NWM* acts as a common divalent cation and is not present around the (P=O) bonding, for example, cutting *BO*; structural deformation due to the addition of *NWM*, as described previously. A certain amount of *NWM*, especially [R]-5 or [R]-4 (Cu), is added such that a divalent cation seems to exist around the oxygen atom in the (P=O) bonding. That generates a force of attraction to compensate for the charge between the *NWM* and the oxygen atom in the (P=O) bonding. Based on these phenomena, the structure of glass contracts and the *NWM* is coordinated around the (P=O) bonding to form a resonance structure with the other *NBO*. In brief, divalent cations are difficult to find near the (P=O) bonding; however, the addition of a certain amount of *NWM* results in a charge compensation near the divalent cations and the oxygen atoms of the (P=O) bonding, resulting in the contraction of the network structure [13]. FT-IR confirmed the decrease in (P=O) bonding; however, to confirm that the oxygen atom of the (P=O) bonding compensated with the divalent cations, XPS was performed to prove that the O 1s peak decreased, indicating the shrinkage of the network structure.

Figures 8 and 9 show the results of the XPS analysis of the portion, where the inflection points occurred, owing to

the formation of resonance structures. Shih *et al* [15] and Onyiriuka [29] reported that divalent cations, such as Mg, Ca, Ba and Cu, participated in the structure through binding, shifting the P–O–[R] peak from 528.9 to 530.95 eV and yielding the (P–O–P) peak at 533.1 eV, thus exhibiting no resonance structure. However, when more than a certain amount of divalent cation was added, the intensity of the peak from 528.9 to 530.95 eV did not increase. Actually, the P–O–[R] and (P–O–P) peaks decreased and moved to a midpoint (~532 eV). As described in the FT-IR spectra, [R]-5 or 4 (Cu) has fewer (P=O) and (P–O–P) bonds than [R]-2. For the understanding, figure 10 shows XPS data of all samples. The thinnest and transparent graph, which is [R]-1, is located on the right side (low binding energy) and the thickest and clearest graph, which is [R]-5, is located on the left side (high binding energy). All samples have similar tendency, the P–O–[R] peak (straight line) tends to decrease as it moves towards high binding energy and the P–O–P peak (double line) changes either. So, the evidence of resonance structures occurs very clearly in the graph. In summary, the above results are listed as follows: the length of *BO* and *NBO* bonding decreases and the P–O–[R] moves towards 532 eV. To explain the second point, it means that the P–O–[R] bonding replaces both (P–O–P) and (P–O⁻)

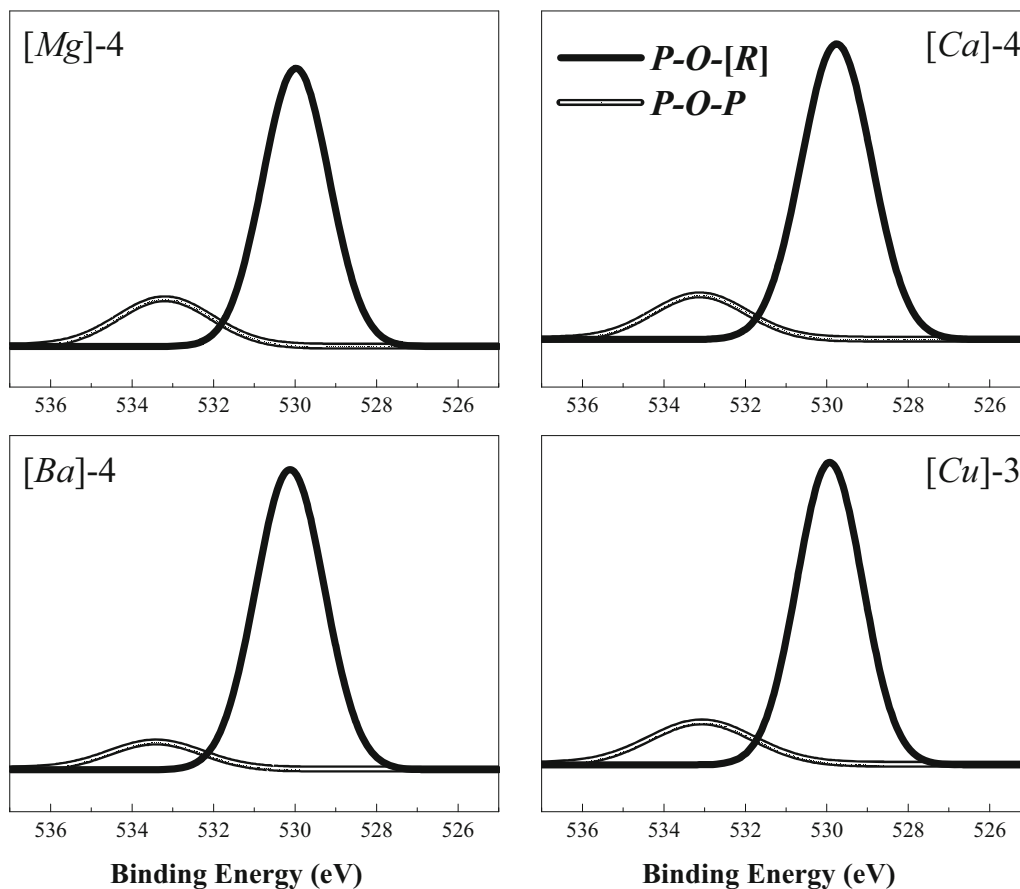


Figure 8. Decomposed O 1s binding energy of [R]-4 and [R]-3 (Cu).

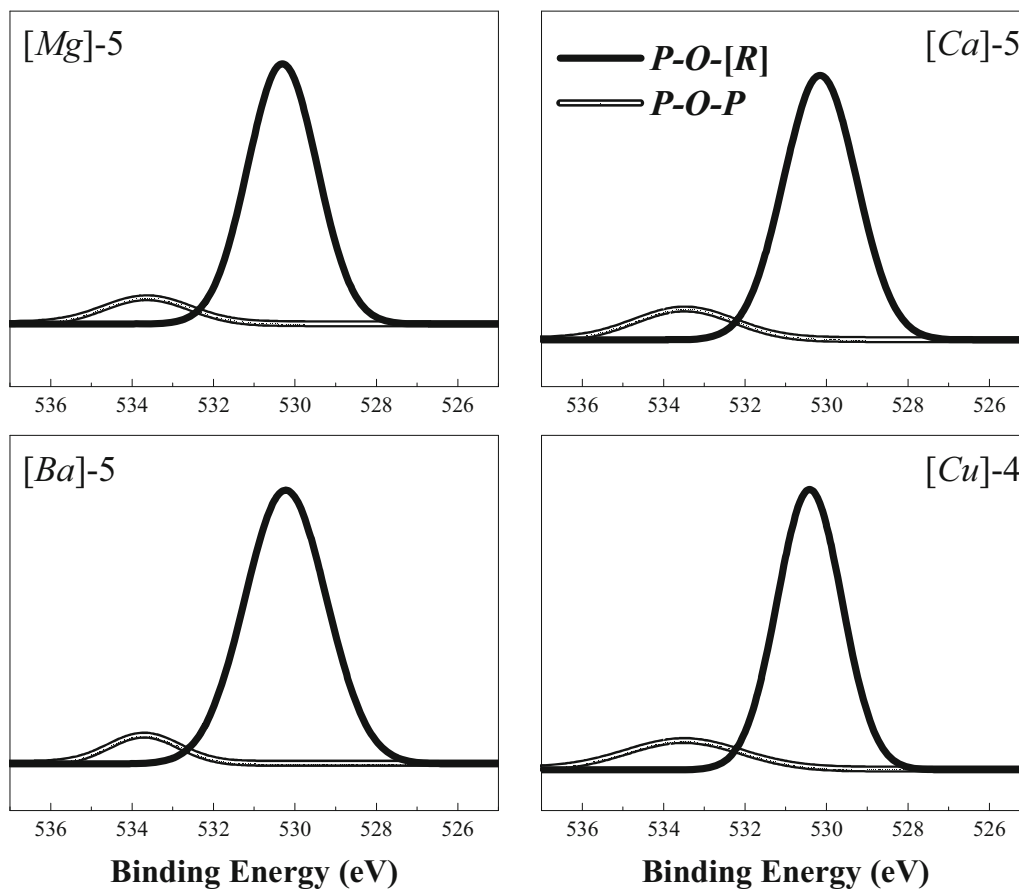


Figure 9. Decomposed O 1s binding energy of [R]-5 and [R]-4 (Cu).

bonding. These phenomena are because of the specific structural changes caused by the resonance structures. Additional divalent cations exist in the glass, resulting in resonance structures near the P=O and (P–O) bonding.

4. Conclusion

In this study, three-composition phosphate glass was fabricated using [Mg], [Ca], [Ba] and [Cu]. XRD was performed to determine the crystal structural changes during the experiment. The XRD analysis results revealed that the XRD patterns before and after the occurrence of abnormalities exhibited similar shapes. In addition, because no crystal phase was observed in the XRD pattern, it was confirmed that a structural change occurred in the short range, and that no change occurred in the long-range order. The structural changes were confirmed through FT-IR spectroscopy. Density measurements and FT-IR analysis showed that the addition of divalent cations other than MgO

also led to similar tendencies in abnormality and resulted in the same phenomena in structural changes. The results of XPS analysis also confirmed the occurrence of structural changes, consistent with the FT-IR results, which could be due to the formation of resonance structures of (P=O), (P–O[−]) and (P–O–P). The results of this study were similar to those obtained by Lee *et al* [3] and Shih *et al* [15]. It was confirmed through XRD analysis that abnormalities due to inflection in physical properties were not the result of changes in the long-range order. As a result of the cross-validation through FT-IR spectroscopy and XPS, structural changes in the short-range order were observed through resonance structures, which expressed the abnormality of having inflections even in the physical properties. In conclusion, the structural analysis results of phosphate glass containing *NWM* at the same molar ratio are as follows: double bonding oxygen coordinated with divalent cations generated from *NWM*, which probably caused shrinkage of the glass network structure. As a result, double bonding oxygen generated a resonance structure, together with

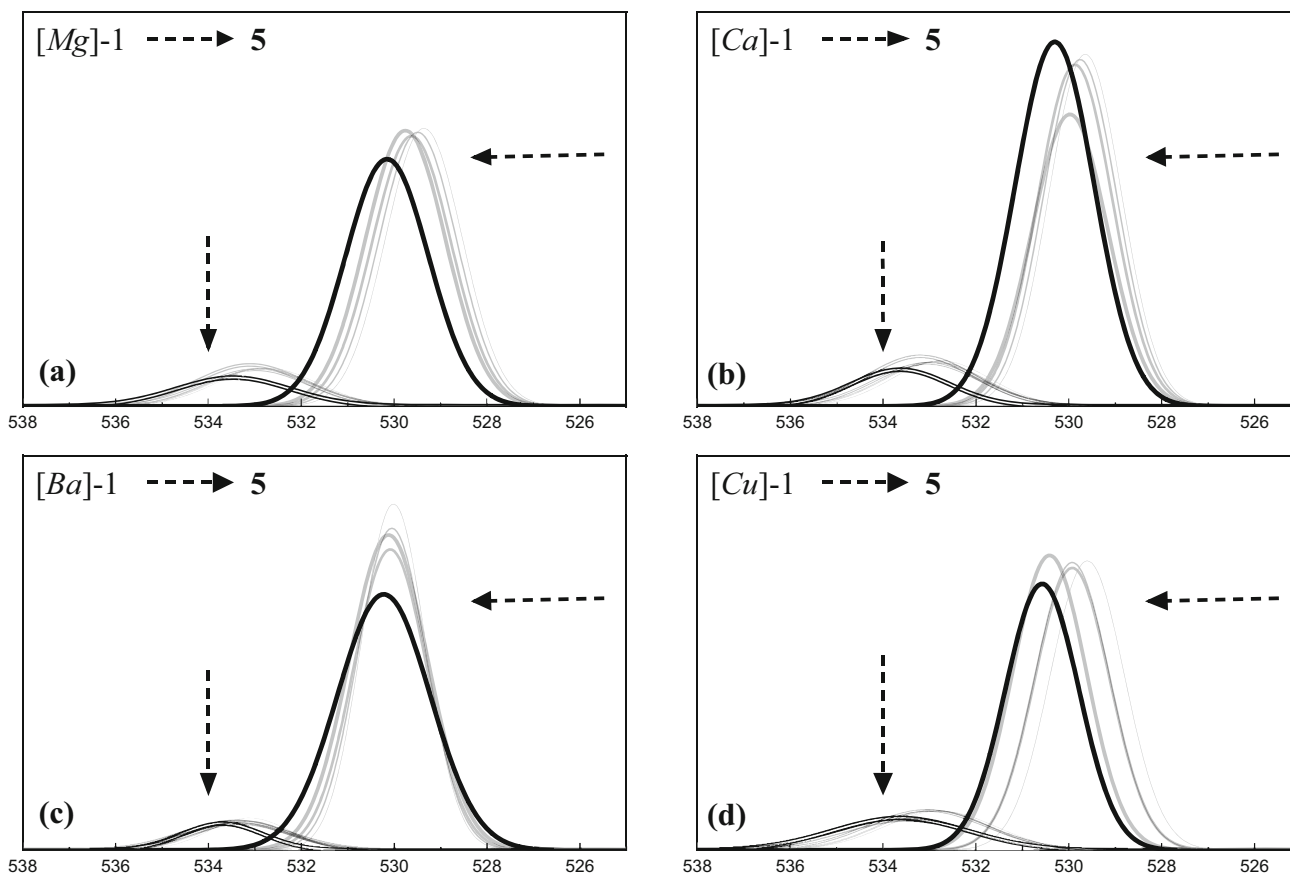


Figure 10. Decomposed O 1s binding energy of [R]: (a) [Mg], (b) [Ca], (c) [Ba] and (d) [Cu] (70–50 mol%).

another *NBO*. Resonance is a common feature that occurs when elements such as divalent cations are included in the composition of phosphate glass. The divalent cations generate a resonance structure in the phosphate glass.

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