Correlation between structure, chromaticity, and dielectric properties of calcium copper pyrophosphates, Ca$_{2-x}$Cu$_x$P$_2$O$_7$

Rattanai Baitahe$^{1,2}$, Chuchai Sronsri$^{1,2}$, Somphob Thompho$^{3,4}$, Kittichai Chaiseda$^4$, Nattaya Montri$^{5}$ & Banjong Boonchom$^{1,2}$

The solid-state reaction was employed to synthesize Ca$_{2-x}$Cu$_x$P$_2$O$_7$ by varying the mole ratio between Ca and Cu. The structure and crystallography of the pyrophosphate compounds were identified and confirmed by using X-ray diffraction (XRD). The Rietveld refinement method and the extended X-ray absorption fine structure (EXAFS) least-squares fitting technique were also applied to refine the sample crystal structure. The single phases of the obtained Ca$_2$P$_2$O$_7$, CaCuP$_2$O$_7$, and Cu$_2$P$_2$O$_7$ samples and the mixing phases of the obtained Ca$_{1.5}$Cu$_{0.5}$P$_2$O$_7$ and Ca$_{0.5}$Cu$_{1.5}$P$_2$O$_7$ samples were identified, and then only a single phase of the samples was subjected to structural and dielectrical analyses. The structural results exhibit the tetragonal crystal system with the P4$_1$ space group for Ca$_2$P$_2$O$_7$, the monoclinic crystal system with the P2$_1$/c space group for CaCuP$_2$O$_7$, and the C2/c space group for α-Cu$_2$P$_2$O$_7$. The dielectric constant ($\varepsilon_r$) of the single metal pyrophosphates (Ca$_2$P$_2$O$_7$ and Cu$_2$P$_2$O$_7$) was higher than that of binary metal pyrophosphates (CaCuP$_2$O$_7$). The image sensor result of the Cu$_2$P$_2$O$_7$ sample ($x = 2.00$) illustrated a yellowish-green color, while other compounds ($x = 0.50$–1.50) presented color tones that changed from blue-green to bluish-green. Raman and Fourier transform infrared (FTIR) spectrophotometers were employed to characterize and confirm the vibrational characteristics of the P$_2$O$_7^4$ group, which contains the O−P−O radical ([PO$_2$]−) and the P−O−P bridge ([PO$_4$]) and approximate M−O stretching modes. Furthermore, this work reports for the first time that the change in the crystal structure of Ca$_{2-x}$Cu$_x$P$_2$O$_7$ (i.e., bond angle of P−O−P in P$_2$O$_7^4$ and distortion phenomena in the M−O$_6$ octahedral site) are the cause of the correlation between the structure, chromaticity, and dielectric properties of calcium copper pyrophosphates, Ca$_{2-x}$Cu$_x$P$_2$O$_7$.

Currently, metal phosphate materials show interesting properties because they are used in many applications. For example, they have been applied as microwave dielectric materials, corrosion-resistant coatings, biomedical cements, chelating agents, glass ceramics, and high-quality fertilizers$^{1,3}$. Bian et al.$^2$ reported that metal pyrophosphates (M$_2$P$_2$O$_7$, M = divalent cations) show low-loss dielectric properties as well as a relatively low sintering temperature. When the ionic radius of M in the M$_2$P$_2$O$_7$ structure is higher than 0.97 Å (M = Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, Pb$^{2+}$, Cd$^{2+}$), M$_2$P$_2$O$_7$ compounds crystallize in the dichromate (Cr$_2$O$_7^{2−}$) form, in which a pair of P$_2$O$_4^{4−}$ groups in eclipsed are the center of symmetry and bridging oxygen (O) atoms spread to each other. However, when the ionic radius of M is lower than 0.97 Å (M = Ni$^{2+}$, Mg$^{2+}$, Zn$^{2+}$, Co$^{2+}$, Cu$^{2+}$, Mn$^{2+}$), the M$_2$P$_2$O$_7$ structure is a thortveitite type$^4$ (scandium yttrium silicate (Sc$_2$Y)$_2$Si$_2$O$_7$ with the monoclinic crystal system, prismatic crystal class (2/m), and C2/m space group$^6$). Based on this thortveitite structure, P$_2$O$_4^{4−}$ groups occur in a staggered conformation. Moreover, compared to metal oxides (i.e., MO, M = divalent metals), thortveitite-type pyrophosphates, such as

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$^1$Material Science for Environmental Sustainability Research Unit, School of Science, King Mongkut’s Institute of Technology Ladkrabang, Bangkok 10520, Thailand. $^2$Municipal Waste and Wastewater Management Learning Center, School of Science, King Mongkut’s Institute of Technology Ladkrabang, Bangkok 10520, Thailand. $^3$Pharmaceutical Research Instrument Center, Faculty of Pharmaceutical Sciences, Chulalongkorn University, Pathumwan, Bangkok 10330, Thailand. $^4$Organic Synthesis, Electrochemistry and Natural Product Research Unit (OSEN), Department of Chemistry, Faculty of Science, King Mongkut’s University of Technology Thonburi, Bangkok 10140, Thailand. $^5$Department of Plant Production Technology, School of Agricultural Technology, King Mongkut’s Institute of Technology Ladkrabang, Bangkok 10520, Thailand. $^6$email: somphob@hotmail.com; banjong.bo@kmitl.ac.th
α-Cu₃P₂O₇ and α-Mg₂P₂O₇ exhibit a rather low sintering temperature. However, the single metal pyrophosphate groups, such as Cu₃P₂O₇, Mg₂P₂O₇, Zn₂P₂O₇, and Co₂P₂O₇, still show a phase transition with changing sintering temperature. Therefore, the first aim of this research is to modify the crystal structures of some metal pyrophosphate compounds to decrease the loss of the dielectric value, manipulate the relative permittivity with various temperatures, and improve the stability of the crystal structure in the high-temperature range.

The crystal structures of M₃P₂O₇ compounds have been extensively investigated, and some metal pyrophosphates exhibit the allotropic property (a property of some compounds to exist in two or more crystal forms). For example, β-Ca₂P₂O₇ is tetragonal, whereas α-Ca₂P₂O₇ is monoclinic. Ca₃P₂O₇ is also an important material in the luminescence and biomaterial fields. The thortveitite form undergoes a reversible phase transformation below 600 °C from the α-form (occurring at low temperature) to the β-form (occurring at high temperature). However, the dichromite form undergoes irreversible transformation at temperatures above 700 °C. The thortveitite-form M₃P₂O₇ (M = Mg²⁺, Mn²⁺, and Zn²⁺) compounds are difficult to sinter into dense ceramics. SrZnP₂O₇, CaZnP₂O₇, α-Zn₂P₂O₇, SrCuP₂O₇, MnP₂O₇, and CaCuP₂O₇ are effective glass-low-temperature co-fired ceramic (LTCC) materials. These metal pyrophosphates react with silver (Ag), but CaZnP₂O₇ and SrZnP₂O₇ do not react with copper (Cu)⁶.

Unary metal pyrophosphate, such as Mg₂P₂O₇, was thermally synthesized by using minerals such as dittmarite (NH₄MgPO₄·H₂O), struvite (NH₄MgPO₄·6H₂O), and newberyite (MgHPO₄·3H₂O) as precursors. Binary metal pyrophosphates, such as Mn₄Co₀₅P₂O₇, were synthesized from the thermal decomposition of manganese cobalt hydrogen phosphate trihydrate (Mn₀₉Co₀₅HPO₄·3H₂O)¹³. Another binary metal compound, CaCuP₂O₇, was synthesized by using a mixture of diammonium hydrogen phosphate [(NH₄)₂HPO₄], calcium carbonate (CaCO₃), and copper oxide (CuO) with the losses of carbon dioxide (CO₂) and ammonia (NH₃) gases based on the following equation (Eq. (1))¹⁴:

\[
2(\text{NH}_4)_2\text{HPO}_4(s) + \text{CaCO}_3(s) + \text{CuO}(s) \rightarrow \text{CaCuP}_2\text{O}_7(s) + 3\text{H}_2\text{O}(g) + 4\text{NH}_3(g) + \text{CO}_2(g)
\]  

To decompose the carbonate (CO₃²⁻) and condense the phosphate (PO₄³⁻), resulting in the formation of pyrophosphate (P₄O₁₀⁺), the solid-state starting materials [(NH₄)₂HPO₄ + CaCO₃ + CuO] were homogeneously mixed first and kept at 700 °C. The obtained mixture was ground and then kept at 1060 °C for nine days. Using this thermal decomposition reaction, CaCuP₂O₇ was successfully synthesized. In addition, manganese cobalt magnesium hydrogen phosphate trihydrate (Mn₀₉Co₀₅HPO₄·3H₂O)¹³, manganese cobalt magnesium pyrophosphate dihydrate (Mn₉Co₅Mg₁₀P₂O₇·2H₂O)¹⁵, and ammonium cobalt zinc manganese monohydrate (NH₄Co₉Zn₄Mn₇P₂O₇·H₂O)¹⁶ were employed as precursors to synthesize ternary metal pyrophosphates, namely, Mn₉Co₅Mg₁₀P₂O₇, Mn₉Co₅Mg₁₀P₂O₇, and Co₉Zn₄Mn₇P₂O₇, respectively. Most studies of different metal phosphate and metal pyrophosphate compounds have focused on both the syntheses and the characterizations of bulk and nano particles, the kinetics and thermodynamics of the reaction, and their properties. For example, the photoluminescence of the LiMg₀.⁷₄Mn₀.₂₆PO₄ phosphor was investigated, and the results revealed that the luminescent property of this phosphor depended on its surface area. Nevertheless, the relationship between crystal structures and dielectric properties is not widely understood. Therefore, the second aim of this work is to investigate the influence of the crystal structure on the dielectric phenomena of binary metal pyrophosphate compounds. Furthermore, substitutional solid solutions (binary metal compounds) based on the Hume-Rothery rules can be formed if the solute (Ca²⁺) and solvent (Cu²⁺) have similar valency (Ca = Cu = 2+) and the same crystal structure (β-Ca₂P₂O₇ = α-Ca₂P₂O₇ = monoclinic). This information shows a high possibility of substitutional metals between Cu and Ca ions forming a binary metal solid solution in pyrophosphate compounds, i.e., Ca₉₋ₓCuₓP₂O₇.

The dielectric properties of metal pyrophosphates occur due to two effects. They comprise the movement of M⁺ ions in the MO₆ octahedral and the shifting of O atoms in the collinear P−O−P bridge of the O₃P−O−PO₃ or P₂O₇ anion. If the collinear P−O−P bond of P₂O₇⁺ is destroyed, some distortions will also occur in the MO₆ octahedra. This phenomenon will improve the dielectric properties of materials by polarization production. It is well known that the highly relative permittivity of BaTiO₃ tetragonal perovskite occurs from the Ti⁴⁺ ion off-centered in the TiO₆ octahedral. The atomic radii of Cu²⁺ and Ca²⁺ are 0.73 and 1.00 Å, respectively, whereas their electronegativities are 1.90 and 1.00, respectively. Doping the large cationic species, i.e., Ca²⁺, into the crystal structure of the Cu₃P₂O₇ host resulted in the formation of Ca₉₋ₓCuₓP₂O₇ solid solutions. Both distortion of the MO₆ octahedral and O shifting in the collinear P−O−P bond phenomena may occur. These phenomena may then improve the dielectric properties of Caₓ⁺-doped Cu₃P₂O₇ compounds at low sintering temperatures. Consequently, to investigate this doubt, this research synthesized Ca₉₋ₓCuₓP₂O₇ (x = 0.00−2.00) by using conventional and uncomplicated methods. Then, various scientific methods were used to characterize and confirm the synthesized Ca₉₋ₓCuₓP₂O₇ samples. Raman and Fourier transform infrared (FTIR) spectrophotometers were employed to characterize the vibrational spectra of the synthesized samples. X-ray diffraction (XRD) was used to investigate the crystal structure of the samples. The dielectric properties of the samples were also investigated by using an LCR meter, an effective technique for material measurement. The polarization phenomena in the crystal structure of the samples were studied to characterize the bond length and bond angle of Ca₉₋ₓCuₓP₂O₇. The chromaticity property was studied by applying the image sensor with a spatially multiplexed exposure-high dynamic range (SME-HDR) imaging function. The results were then compared to the CIE (International Commission on Illumination) chromaticity diagram (standard database). Consequently, these synthesized Ca₉₋ₓCuₓP₂O₇ compounds can be applied as effective optical materials. In addition, synchrotron light technology was also employed to analyze the Ca₉₋ₓCuₓP₂O₇ samples by using X-ray absorption spectroscopy (XAS) mode at the Cu and Ca K edges.
Materials and methods
Preparation. Binary metal pyrophosphate samples with various Ca/Cu ratios (Ca$_{2-x}$Cu$_x$P$_2$O$_7$, $x = 0.00$, 0.50, 1.00, 1.50, and 2.00) were synthesized via the solid-state method. To avoid contamination, high-purity starting materials, namely, (NH$_4$)$_2$HPO$_4$ (99%), CuO (99.9%), and calcium oxide (CaO, 99.9%), were selected in this preparation process. All starting materials were weighed according to the stoichiometric ingredients and then homogenized by vibratory milling with 10 mm spherical yttria (yttrium oxide, Y$_2$O$_3$)-stabilized zirconia (zirconium dioxide, ZrO$_2$) (YSZ) grinding beads in ethanol media for 4 h. The dried powders were transferred to crucibles and directly heated at 1000 °C for 24 h for Ca$_{2-x}$Cu$_x$P$_2$O$_7$, when $x = 0.00$−1.50, and 800 °C for 24 h for Ca$_{2-x}$Cu$_x$P$_2$O$_7$, when $x = 2.00$. After that, the calcined powders were ball-milled anew, pressed uniaxially into small pellets at a pressure of 1000 kg·cm$^{-2}$ and then sintered at 950 °C for 24 h for Ca$_{2-x}$Cu$_x$P$_2$O$_7$, when $x = 0.00$−1.50, and 1030 °C for 24 h for Ca$_{2-x}$Cu$_x$P$_2$O$_7$, when $x = 2.00$. The observed densities of all prepared metal pyrophosphates, in theory, were investigated by Archimedes’ principle and found to be in the range of 95−98% (Fig. 1). The preparation of the target powder samples (Ca$_{2-x}$Cu$_x$P$_2$O$_7$) was carried out according to the following reaction (Eq. (2)),

$$x\text{CuO}(s) + (2 - x)\text{CaO}(s) + 2(\text{NH}_4)_2\text{HPO}_4(s) \rightarrow \text{Ca}_{2-x}\text{Cu}_x\text{P}_2\text{O}_7(s) + 4\text{NH}_3(g) + 3\text{H}_2\text{O}(g) \quad (2)$$

where $x = 0.00$−2.00.

Characterization. The room temperature FTIR spectra of the samples were recorded by using a Perkin Elmer Spectrum GX FTIR spectrometer. The measured wavenumber range was 4000−400 cm$^{-1}$, whereas the selected scan number and resolution were 8 scans and 4 cm$^{-1}$, respectively. A Thermo Scientific DXR Raman microscope was used to record the Raman spectra in the Raman shift of 1300−100 cm$^{-1}$ using a scan number of 8 scans. A Raman spectrum was observed by irradiating each synthesized sample with an intense beam of an argon ion (Ar$^+$) laser with a wavenumber of 20,492 cm$^{-1}$ (wavelength of 488 nm). The power of the incident beam was 12.5 mW. The XRD patterns of all prepared samples were recorded by using a D8 Advance X-ray diffractometer (XRD, Bruker AXS, Karlsruhe, Germany) with Cu K$_\alpha$ radiation ($\lambda = 0.1546$ nm) to analyze and confirm the crystal structures of the samples. The dielectric properties were analyzed as a function of the frequency (1−1000 kHz) and temperature (room temperature to 150 °C) using an Agilent/HP 4284A precision LCR meter (an effective technique for the material measurement with a wide frequency range (20 Hz−1 MHz) and superior signal performance to test materials to the most commonly used test standards). The Sony IMX214 CMOS image sensor (CIS, 13 MP “stacked” CIS with a spatially multiplexed exposure-high dynamic range (SME-HDR) imaging function) was applied to focus the colors of the samples. The results were then compared to the CIE (International Commission on Illumination) chromaticity diagram (standard database) to estimate the trend of the absorption wavelength. X-ray absorption spectroscopy (XAS) was performed at the Beamline 8 (BL8) Station of the National Synchrotron Research Center (NSRC, Nakhon Ratchasima, Thailand). BL8 of the NSRC is routinely operated for the XAS in an intermediate photon energy range from 1.25 to 10 keV$^{29}$. The double crystal Ge(220) was used for the extended X-ray absorption fine structure (EXAFS) monochromator. The XAS spectra were detected in transmission mode at the copper (Cu) and calcium (Ca) K-edge.
Ethics declarations.

- The datasets generated and/or analyzed during the current study are not available in the other repository.
- The datasets used and/or analyzed during the current study available from the corresponding author on reasonable request.
- All data generated or analyzed during this study are included in this published article.
- The datasets generated and/or analyzed during the current study are not publicly available due to 
  REASON WHY DATA ARE NOT PUBLIC but are available from the corresponding author on reasonable request.
- The data that support the findings of this study are available from the corresponding author but restrictions apply to the availability of these data, which were used under license for the current study, and so are not 
  publicly available. Data are however available from the authors upon reasonable request and with permission 
  of the corresponding author.

Results and discussion

Structural, optical, and dielectric analyses. After applying the D8 Advance X-ray diffractometer, the 
resulting XRD patterns of the synthesized $\text{Ca}_2$-$\text{Cu}_x\text{P}_2\text{O}_7$ powders ($x=0.00$–$2.00$) are displayed in Fig. 2. The 
structures of $\text{Ca}_2$-$\text{Cu}_x\text{P}_2\text{O}_7$ were analyzed through the Rietveld refinement analytic technique\(^{30}\) using the Full-
Prof package\(^{31}\). A pseudo-Voigt function (a linear combination between the Lorentzian and Gaussian functions) 
was adequate at all times for obtaining good fits of the experimental data. The initial model for the refinement 
of the single phase structure ($\text{Ca}_2\text{P}_2\text{O}_7$, $\text{CaCuP}_2\text{O}_7$ and $\text{Cu}_2\text{P}_2\text{O}_7$) was taken from parameters described well in 
the Calvo research\(^{32}\).

In addition, Fig. 3 shows the corresponding Rietveld refinement results of $\text{Ca}_2$-$\text{Cu}_x\text{P}_2\text{O}_7$ when 
$x=0.00$, $1.00$, and $2.00$. Figure 3 shows the calculated ($Y_{\text{cal}}$) and observed ($Y_{\text{obs}}$) diffraction patterns as well as the different 
values between them ($Y_{\text{obs}}$–$Y_{\text{cal}}$) of the samples. The refinement plots gave the evolution of the XRD patterns in 
the various ratios between Ca and Cu ($\text{Ca}_2$-$\text{Cu}_x\text{P}_2\text{O}_7$, $x=0.00$, $1.00$ and $2.00$). The Rietveld refinement analysis 
and the XRD data of powders confirmed the formation of metal pyrophosphate compounds ($\text{Ca}_2$-$\text{Cu}_x\text{P}_2\text{O}_7$).

The crystallographic information of the synthesized compounds is briefly described. When $x=0.00$, the 
single metal pyrophosphate phase, $\beta$-$\text{Ca}_2\text{P}_2\text{O}_7$, was obtained with the tetragonal crystal system, space group of 
$P4_1$, space group number of 76, Schoenflies symbol of $C_{2h}^{6}$, and number of formula units per unit cell or 
$Z=8$. When $x=1.00$, the binary metal pyrophosphate phase, $\text{CaCuP}_2\text{O}_7$, was obtained with the monoclinic crystal 
system, space group of $P2_1/c$, space group number of 14, Schoenflies symbol of $C_{2h}^{5}$, and $Z=4$. Finally, when $x= 
2.00$, another single metal pyrophosphate phase, $\alpha$-$\text{Cu}_2\text{P}_2\text{O}_7$, was obtained with the monoclinic crystal system, 
space group of $C2/c$, space group number of 15, Schoenflies symbol of $C_{2h}^{6}$, and $Z=4$. For other $\text{Ca}_2$-$\text{Cu}_x\text{P}_2\text{O}_7$ 
samples, when $x=0.50$, there were two phases between $\text{CuCuP}_2\text{O}_7$ and $\alpha$-$\text{Cu}_2\text{P}_2\text{O}_7$, whereas when $x=1.50$, two 
phases between $\text{CuCaP}_2\text{O}_7$ and $\beta$-$\text{Ca}_2\text{P}_2\text{O}_7$ were then observed. The P–O–P bond angles (of the $\text{O}_3\text{P}–\text{O}–\text{PO}_3$ 
bridge of $\text{P}_2\text{O}_7^{4−}$) and $\text{M}$–$\text{O}_6$ bond lengths ($\text{M}=\text{Ca} \text{or Cu}$) were determined by using refinement analysis, and 
the obtained values are summarized in Table 1.

X-ray absorption near-edge structure (XANES) is very sensitive to both the change in the local geometry 
-especially the ligand environment of the metal- and the oxidation state\(^{34}\). Therefore, the spectra were collected 
at both the Ca and Cu K-edges. They could help to understand the Fourier transform evolutions\(^{34}\). The X-ray 
absorption edge energies ($E_\text{b}$) of the synthesized $\text{Ca}_2$-$\text{Cu}_x\text{P}_2\text{O}_7$ compounds at the Ca and Cu K-edges are listed in 
Table 2.

The $E_\text{b}$ values of the various Cu valences ($\text{Cu}^{0}$, $\text{Cu}^{1+}$, and $\text{Cu}^{2+}$) obtained in this work are in line with the information 
reported by Yano and Yachandra\(^{34}\). They reported that the $E_\text{b}$ values increase with increasing oxidation.

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**Figure 2.** X-ray diffraction (XRD) patterns of the $\text{Ca}_2$-$\text{Cu}_x\text{P}_2\text{O}_7$ powders ($x=0.00$–$2.00$) synthesized from the 
solid-state method of homogenized $(\text{NH}_4)_2\text{HPO}_4$, CuO, and CaO.
state. They also described that an electron in an atom experiences the full charge of the positive nucleus. In contrast, in the case of many electrons, the electrons in an outer layer are simultaneously repelled by the negatively charged electrons and attracted to the positive nucleus. The lower the oxidation state of metals is, the less positive the overall charge of the atom. Consequently, to excite an electron from an orbital, more energy is required. In summary, when the metal has a more positive charge, the $E_0$ values (XANES spectra) shift to a higher energy.  

According to Table 2, in the Cu K-edge, the $E_0$ values of the synthesized $\text{Ca}_{2-x}\text{Cu}_x\text{P}_2\text{O}_7$ samples ($x = 0.50–2.00$) were similar to the $E_0$ values of $\text{Cu}^{2+}\text{O}$, indicating that $\text{Cu}^{2+}$ was monoclinic. In addition, the XANES spectra of
samples in the Ca K-edge showed \( E_0 \) values similar to \( \text{Ca}^{2+} \), indicating that there was \( \text{Ca}^{2+} \) in the crystal structure of the \( \text{Cu}_2\text{P}_2\text{O}_7 \) host, resulting in the formation of \( \text{Ca}^{2+} \text{Cu}^{x} \text{P}_2\text{O}_7 \). Figure 4 presents the local environment of Ca atoms when they entered the \( \text{Cu}_2\text{P}_2\text{O}_7 \) structure. The spectra of Ca and Cu in the \( \text{CuCaP}_2\text{O}_7 \) compound were different. These results demonstrated that the coordinated environments of the divalent Ca in \( \text{CuCaP}_2\text{O}_7 \) are significantly different.

The coordinated complexes with different properties have different colors, such as blue for \( \text{Cu} (\text{NH}_3)_4\text{H}_2\text{O})^2^{2+} \), red for \( \text{Co} (\text{NH}_3)_5\text{H}_2\text{O})^3^+ \), and green for \( \text{CoF}_6^{3−} \). This different color phenomenon was well explained by the crystal field theory (CFT) described by El Jazouli et al. and Chen et al.\cite{36,37} The optical properties and the corresponding CIE chromatic coordinates\cite{36,38,39} of \( \text{Ca}^{2−} \text{Cu}^{x} \text{P}_2\text{O}_7 \) samples (\( x = 0.00−2.00 \)) are shown in Fig. 5. All Ca/Cu ratio compounds, except the composition with \( x = 0.00 \) (\( \text{Ca}_2\text{P}_2\text{O}_7 \)), showed a greenish color, in which \( \text{Ca}_2\text{P}_2\text{O}_7 \) exhibited a colorless powder. The colors of the samples were dictated by the elongation or compression of the \( \text{z} \) ligand bonds of the \( \text{Cu}^{2+} \) ion. The result of the composition with \( x = 2.00 \) (\( \text{Cu}_2\text{P}_2\text{O}_7 \)) illustrated a yellowish-green color, while the binary metal compounds (\( x = 0.50−1.50 \)) presented color tones that changed from blue-green to bluish-green.

The mean static atomic dielectric constants (\( \varepsilon_r \)) of the synthesized \( \text{Ca}^{2−} \text{Cu}^{x} \text{P}_2\text{O}_7 \) compounds were estimated using the well-known Clausius-Mossotti relation\cite{40} as the following equation (Eq. (3)):

### Table 2. X-ray absorption edge energies (\( E_0 \)) of the synthesized \( \text{Ca}^{2−} \text{Cu}^{x} \text{P}_2\text{O}_7 \) compounds when \( x = 0.00−2.00 \). ND is not detected.

| \( x \) values | Compounds          | \( \text{X-ray absorption edge energies (} E_0 \text{)} / \text{electron Volt,eV} \) |
|----------------|-------------------|-----------------------------------------------|
|                | \( \text{Ca}^0 \) | \( \text{Cu}^0 \) ND 8978.45                   |
|                | \( \text{Cu}^{1+} \) | \( \text{Cu}_2\text{O} \) ND 8979.52          |
|                | \( \text{Cu}^{2+} \) | \( \text{CuO} \) ND 8987.72                   |
| 2.00           | \( \text{Cu}_2\text{P}_2\text{O}_7 \) | ND 8987.88                                   |
| 1.50           | \( \text{Ca}_x\text{Cu}_{3−x}\text{P}_2\text{O}_7 \) | 4033.14 8987.08                             |
| 1.00           | \( \text{Ca}_{1.0}\text{Cu}_{1.0}\text{P}_2\text{O}_7 \) | 4033.42 8987.09                             |
| 0.50           | \( \text{Ca}_{1.5}\text{Cu}_{0.5}\text{P}_2\text{O}_7 \) | 4033.42 8987.13                             |
| 0.00           | \( \text{Ca}_2\text{P}_2\text{O}_7 \) | ND ND                                       |

Figure 4. Local environment of Ca atoms when they entered the \( \text{Cu}_2\text{P}_2\text{O}_7 \) structure, resulting in the formation of \( \text{Ca}^{2−} \text{Cu}^{x} \text{P}_2\text{O}_7 \).
where $\alpha_D$ is the sum of the dielectric polarizabilities of individual ions and $V_m$ is the molar volume.

The effect of porosity on the permittivity was eliminated by applying Bosman and Havinga’s correction\(^\text{41}\) as shown in Eq. (4), which can be used for some materials, i.e., dense ceramics, having porosities lower than 5%:

$$\varepsilon_{\text{r,corrected}} = \varepsilon_{\text{r,measured}} (1 + 1.5P) \tag{4}$$

where $\varepsilon_{\text{r,measured}}$ and $\varepsilon_{\text{r,corrected}}$ are the measured and corrected relative permittivity, respectively, and $P$ is the fractional porosity.

After applying the Clausius-Mossotti relation (Eq. (3)), the dielectric constant ($\varepsilon_r$) values as a function of the composition $x$ of the synthesized Ca$_{2-x}$Cu$_x$P$_2$O$_7$ ($x = 0.00−2.00$) are presented in Fig. 6, which shows the combination values between the calculated data (atomic polarization part, red bars) and measured results (atomic polarization part + ionic polarization part, red and purple bars). The single metal pyrophosphates (Ca$_2$P$_2$O$_7$ and Cu$_2$P$_2$O$_7$) showed $\varepsilon_r$ values of 15.6 and 10.5, respectively, which were higher than the $\varepsilon_r$ value of binary metal pyrophosphates (i.e., CaCuP$_2$O$_7$, $\varepsilon_r = 9.8$). The $\varepsilon_r$ values of the mixing phases of binary metal pyrophosphates (Ca$_{1.50}$Cu$_{0.50}$P$_2$O$_7$ and 1.50 (Ca$_{0.50}$Cu$_{1.50}$P$_2$O$_7$) have not been estimated because of the unknown amount of exact phase composition. The Clausius-Mossotti equation focused on only the dielectric constant from atomic polarization (electron cloud bias in electric fields). Indeed, the samples were measured at a frequency of 1 MHz for the decreasing extrinsic factor, and the polarization caused the movement of both cations (Cu$^{2+}$, Ca$^{2+}$, and P$^{5+}$) and anions (O$^{2-}$) in the crystal Ca$_{2-x}$Cu$_x$P$_2$O$_7$ structure. The movement of the ions in the electric field was caused...
by an increasing dielectric constant compared to the calculated data using the Clausius-Mossotti equation. The equation used in this study considered the dielectric constant, using the bond angle, bond length, and volume of the $\text{MO}_6$ octahedra.

The extended X-ray absorption fine structure (EXAFS) spectra of the synthesized $\text{Ca}_{2-x}\text{Cu}_x\text{P}_2\text{O}_7$ samples are shown in Fig. 7. The environment around Cu atoms was investigated. The primitive EXAFS model was taken from parameters obtained from the Rietveld refinement of each sample.

Details of the EXAFS spectroscopic fitting of the $\text{Ca}_{2-x}\text{Cu}_x\text{P}_2\text{O}_7$ samples are summarized in Table 3, which shows the distortion of the $\text{CuO}_6$ octahedra. The spectra of $x = 0.00$ were undetectable because of the limitation of the instrument in beamline 8 of the National Synchrotron Research Center (Thailand). As presented in Table 3, the samples, when $x = 1.00$ and 2.00, showed three main shells. The first shell of the spectrum from the model consisted of four equatorial oxygen atoms, $\text{Cu}−\text{O}_{eq1}$, $\text{Cu}−\text{O}_{eq2}$, $\text{Cu}−\text{O}_{eq3}$, and $\text{Cu}−\text{O}_{eq4}$ of the $\text{CuO}_6$ octahedra. Then, the second shell detected only one axial oxygen atom, $\text{Cu}−\text{O}_{ax1}$. The last axial oxygen atom, $\text{Cu}−\text{O}_{ax2}$, was observed in the third shell. The Cu atoms of Cu–O6 were also combined with the phosphorus atom Cu–P.

Different radial distances ($R$/Å) between the Rietveld refinement and EXAFS fitting may be the cause of the measurement type of each technique. X-ray diffraction (Rietveld refinement) was used to investigate the global structure, while X-ray absorption (EXAFS fitting) was used to probe the details of the Cu/Ca local structure.

The fitting statistic factor ($R$-factor) of $x = 1.00$ was worse than that of $x = 2.00$ because of two important factors. First, the crystal structure of $\alpha$-$\text{CaCuP}_2\text{O}_7$ ($x = 1.00$) was less symmetric than that of another sample ($\text{Cu}_2\text{P}_2\text{O}_7$ ($x = 1.00$)). Second, $\alpha$-$\text{CaCuP}_2\text{O}_7$ ($x = 1.00$) exhibited four different types of atomic positions in the unit cell.

Vibrational spectroscopy. FTIR and Raman spectroscopies are good methods for identifying the chemical bonding of rotational, vibration, and other low-frequency modes in the phosphate group. After applying the Spectrum GX FTIR spectrometer, the FTIR spectra of the synthesized $\text{Ca}_{3-x}\text{Cu}_x\text{P}_2\text{O}_7$ samples are presented in Fig. 8, whereas the corresponding assignments are tabulated in Table 4. The FTIR spectra observed in this research are similar to the spectral results reported in the literature. They successfully synthesized and investigated the vibrational spectroscopy of various single, double, and triple metal pyrophosphates, i.e., $\text{Mg}_2\text{P}_2\text{O}_7$, $\text{Mn}_{1.5}\text{Co}_{0.5}\text{P}_2\text{O}_7$, $\text{Mn}_{1.5}\text{Cu}_{0.5}\text{Mg}_{0.5}\text{P}_2\text{O}_7$, $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Mn}_{0.5}\text{P}_2\text{O}_7$, and $\text{CoFeP}_2\text{O}_7$.

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**Figure 7.** Extended X-ray absorption fine structure (EXAFS) spectra of Cu$^0$, Cu$^{1+}$, Cu$^{2+}$, Ca$^{2+}$, and Ca$_{3-x}$Cu$_x$P$_2$O$_7$; $x = 0.00$–1.50.

**Table 3.** Bond length from EXAFS fitting for Ca$_{2-x}$Cu$_x$P$_2$O$_7$ samples; $x = 1.00$ and 2.00. Where eq and ax subscripts are equatorial and axial (or apical) positions, respectively. CN is the coordination number, $R$ is the radial distance, $\sigma^2$ is the mean squared displacement, and the $R$-factor is the fitting statistic factor.
The vibrational characteristics of the synthesized Ca$_{2-x}$Cu$_x$P$_2$O$_7$ are described in detail. The strong vibrational bands at approximately 1190 and 1060 cm$^{-1}$ were attributed to an asymmetric ($\nu_a$ PO$_3$) vibrational mode of the PO$_3$ unit of the pyrophosphate (O$_3$P−O−PO$_3^{4-}$ or P$_2$O$_7^{4-}$) ions, whereas a vibrational band at approximately 1100 cm$^{-1}$ was attributed to the symmetric stretching ($\nu_s$ PO$_3$) of the PO$_3$ unit. The asymmetric ($\delta_a$ PO$_3$) and symmetric ($\delta_s$ PO$_3$) bending modes are observed at the vibrational positions at approximately 580 and 540 cm$^{-1}$, respectively. The asymmetric ($\nu_a$ P−O−P) and symmetric stretching ($\nu_s$ P−O−P) modes of the P−O−P bridge of the O$_3$P−O−PO$_3^{4-}$ group were observed at vibrational positions of approximately 960 and 740 cm$^{-1}$, respectively. However, in the case of the Ca$_{2-x}$Cu$_x$P$_2$O$_7$ samples with $x = 0.50$ (Ca$_{1.5}$Cu$_{0.5}$P$_2$O$_7$) and $x = 1.5$ (Ca$_{0.5}$Cu$_{1.5}$P$_2$O$_7$), the P−O−P symmetric stretching mode appeared as two peaks in the range of 776−693 cm$^{-1}$, which corresponded to the vibrational characteristics (symmetric stretching) of the P−O−P bridge. These detected peaks may be due to the mixing phases of the metal pyrophosphate compounds, i.e., Ca$_2$P$_2$O$_7$ and CuCaP$_2$O$_7$. In addition, the rocking mode of the P−O−P deformations and the torsional and external modes were found in the 450−410 cm$^{-1}$ regions.

The Raman spectroscopic technique was additionally applied to investigate and support the FTIR results, especially the vibrational spectroscopy of the metal oxide (M−O) bond as well as the lattice vibration by observation in the low frequency range (650−100 cm$^{-1}$). Furthermore, the phase characteristics ($\alpha$-, $\beta$-phases) of the

### Table 4. Vibrational positions (wavenumber / cm$^{-1}$) and vibrational assignments (modes) of the synthesized Ca$_{2-x}$Cu$_x$P$_2$O$_7$ samples obtained from the FTIR and Raman techniques. NO is not observed.

| Compounds | Wavenumber/cm$^{-1}$ | FTIR     | Raman | Assignments                     |
|-----------|----------------------|----------|-------|---------------------------------|
| NO        | NO                   | No      | Weak  | $\alpha$-phase characteristics  |
| Ca$_{2-x}$Cu$_x$P$_2$O$_7$; $x = 0.00−2.00$ | 1250−1200 NO | Very strong | Weak | $\nu_a$ PO$_3$                 |
|           | 1200−1100 Very strong | Very strong | $\nu_a$ PO$_3$ |
|           | 1100−1050 Very strong | Very strong | $\nu_s$ PO$_3$ |
|           | 1050−1000 Very strong | Very strong | $\nu_s$ PO$_3$ |
|           | 980−950 Strong        | Very weak | $\nu_P$ P−O−P |
|           | 760−730 Medium        | Weak     | $\delta_{SO}$ |
|           | 650−280 Strong        | Strong   | $\delta$ OPO + $\nu_M$ O−M |
|           | 260−160 NO            | Weak     | $\nu_M$ M−O |
|           | 200−100 NO            | Medium   | Lattice vibration |
metal pyrophosphate compounds can be observed from this spectroscopic technique. After applying the DXR Raman microscope, the Raman spectra of the samples are shown in Fig. 9, and the corresponding vibrational assignments are listed in Table 4. It was observed that the result corresponded well to the FTIR result. The Raman results showed the specific phase, which formed at high temperature in pyrophosphate with $x = 1.00$ (CaCuP$_2$O$_7$), as described in the literature through an undetectably weak peak at approximately 1210 cm$^{-1}$. The three distinct peaks of Ca$_2_x$Cu$_x$P$_2$O$_7$, where $x = 0.00, 0.50, 1.50, 2.00$, which originated from the $\nu_{as}$ PO$_3$ vibrational characteristics, were observed and found to be at approximately 1210, 1140 and 1080 cm$^{-1}$. The Raman spectra clearly showed that the studied metal pyrophosphates displayed sharpness and splitting, especially in the investigated frequency region (1300–100 cm$^{-1}$). The vibrational analysis of the P$_2$O$_7^{4-}$ ion, which contained the O−P−O radi- cal (PO$_2^{−}$ of O$_2$P−OPO$_3^{−}$) and the P−O−P bridge (of O$_3$P−O−PO$_3^{−}$), was exhibited in the Raman spectra. Moreover, M−O stretching and phase characteristics were also observed. The Raman spectra observed in this research were similar to the spectra reported by Sronsri et al. and Boonchom et al. The strong vibrational band at approximately 1100 cm$^{-1}$ was attributed to the stretching of the PO$_3$ unit of O$_3$P−O−PO$_3^{−}$. The asymmetric ($\nu_{as}$ POP) and symmetric ($\nu_{sym}$ POP) stretching types of the P−O−P bridge of O$_3$P−O−PO$_3^{−}$ were detected at approximately 960 and 730 cm$^{-1}$, respectively. The asymmetric ($\delta_{as}$ PO$_3$) and symmetric ($\delta_{sym}$ PO$_3$) vibrational bending modes of O$_3$P−O−PO$_3^{−}$ were observed at approximately 600 and 520 cm$^{-1}$, respectively.

Dielectric and optical properties. Structural-dielectric relation. The bond angle and bond length were successfully investigated by using the Rietveld refinement technique, as shown in Table 1. The obtained refinement results were then used to describe the phenomena of the dielectric properties of the samples. In general, the dielectric properties of the metal pyrophosphate (M$_2$P$_2$O$_7$) group occurred from two important effects, which consisted of O-atom shifting in the collinear P−O−P bridge and M$^{2+}$-ion movement in the MO$_6$ octahedral. According to previous works, due to the shifting of the O atom in the collinear P−O−P bridge, the P−O−P bond angles of Ca$_2$P$_2$O$_7$ and Cu$_2$P$_2$O$_7$ of 130° and 157° were reported, respectively. In this section, only three synthesized Ca$_2_x$Cu$_x$P$_2$O$_7$ samples, when $x = 0.00, 1.00, 2.00$, were considered. The sample, when $x = 0.00$ (Ca$_2$P$_2$O$_7$), showed two different P−O−P bond angles. First, a bond angle of 116.52° appeared for 4 clusters per unit cell with asymmetric P−O bond lengths of 1.765 Å and 1.887 Å. Second, a P−O−P bond angle of 140.96° appeared for 4 clusters per unit cell with symmetric P−O bond lengths of 1.758 Å and 1.827 Å. The sample, when $x = 2.00$ (Cu$_2$P$_2$O$_7$), had a P−O−P bond angle of 154.6° and 4 clusters per unit cell with a symmetric P−O bond length of 1.574 Å. Pogorzelec-Glasier et al. reported that at high temperature, the binary metal pyrophosphate (CuM$^{2+}$P$_2$O$_7$) compounds crystallized in a monoclinic crystal system with the space group of C2/m, and the P−O−P angle was linear (180°). The sample, when $x = 1.00$ (CaCuP$_2$O$_7$), exhibited the space group of P2$_1$/n.
atom.

P4 1

angle. In addition, the long P−O bond length of the sample of $x = 0.00$ (Ca$_2$P$_2$O$_7$), resulting in weak bonding, as shown in Fig. 6. This was a very high polarization; it therefore caused and made the narrow P−O−P bond and the mixing solid phases for the obtained Ca$_{1.5}$Cu$_{0.5}$P$_2$O$_7$ and Ca$_{0.5}$Cu$_{1.5}$P$_2$O$_7$ samples. The tetragonal crys-

blue-green to bluish-green. The colorless compound, when

of the octahedral unit, as reflected in the dielectric constant of the compounds.

Table 5. Average bond length, octahedral volume, and distortion index of Ca$_{2-x}$Cu$_x$P$_2$O$_7$ samples ($x = 0.00$, $1.00$, and $2.00$).

| x values | Compounds     | Average bond lengths/Å | Octahedral volumes/Å$^3$ | Distortion index |
|----------|---------------|-------------------------|--------------------------|-----------------|
| 2.00     | Ca$_2$P$_2$O$_7$ | 2.1794                  | 12.6198                  | 0.1400          |
| 1.00     | CaCuP$_2$O$_7$  | 2.4032                  | 15.0050                  | 0.0886          |
| 0.00     | Ca$_{2-x}$P$_2$O$_7$ | 2.4479                  | 18.6696                  | 0.0655          |
Figure 10. Octahedral splitting diagram of the synthesized Ca$_{2-x}$Cu$_x$P$_2$O$_7$ samples; $x = 0.50-2.00.$

| $x$ values | Compounds       | Wavelengths/nm | $\Delta_0$/kJ·mol$^{-1}$ | Cu–O$_{ax}$ bond lengths/A |
|------------|-----------------|----------------|--------------------------|---------------------------|
|            |                 | Observed | Absorbed |                           | XRD | EXAFS |                 |
| 2.00       | Ca$_2$P$_2$O$_7$ | 561      | 403      | 297                       | 2.92 | 2.91 |
| 1.50       | Ca$_{1.5}$Cu$_{0.5}$P$_2$O$_7$ | 488 | 642 | 186 | ND | ND |
| 1.00       | Ca$_1$Cu$_1$P$_2$O$_7$ | 489 | 644 | 185 | 2.81 | 2.89 |
| 0.50       | Ca$_{1.5}$Cu$_{0.5}$P$_2$O$_7$ | 492 | 648 | 184 | ND | ND |
| 0.00       | Ca$_2$P$_2$O$_7$ | ND      | ND       | ND                        | ND | ND |

Table 6. Approximate wavelength of the energy absorption. ND is not detected.

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Author contributions

R.B. carried out the experiments and analysis, C.S. and S.T. contributed to the characterization and analysis, and K.C. and S.T. contributed to the experiments and analysis and approved the main manuscript text. N.M. approved the main manuscript text. B.B. designed the study, contributed to the experiments and analysis and wrote the

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**Competing interests**
The authors declare no competing interests.

**Additional information**
**Correspondence** and requests for materials should be addressed to S.T. or B.B.

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