

Chapter 3

Results

In the work of Laongjit Chaiyapoom (M.S.Thesis, 2004), the products from $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ and $K_3[Al(C_2O_4)_3] \cdot 3H_2O$ were synthesized by mixing small amount of $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ with $K_3[Al(C_2O_4)_3] \cdot 3H_2O$ and NaCl at room temperature. Three types of crystals were obtained, two with dark red color almost black and the other was blue color. They are designated as RedCubic, RedHexagonal, and Blue. The three complexes were studied for their solubility and were characterized by other techniques such as, scanning electron microanalysis/energy dispersive x-ray fluorescence (SEM/EDX), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), single crystal X-ray diffraction, uv-visible absorption spectroscopy (UV-Vis), Fourier-transformed infrared spectrometry (FT-IR), X-ray powder diffraction (XRD), thermogravimetry analyzer(TGA), and differential scanning calorimeter(DSC).

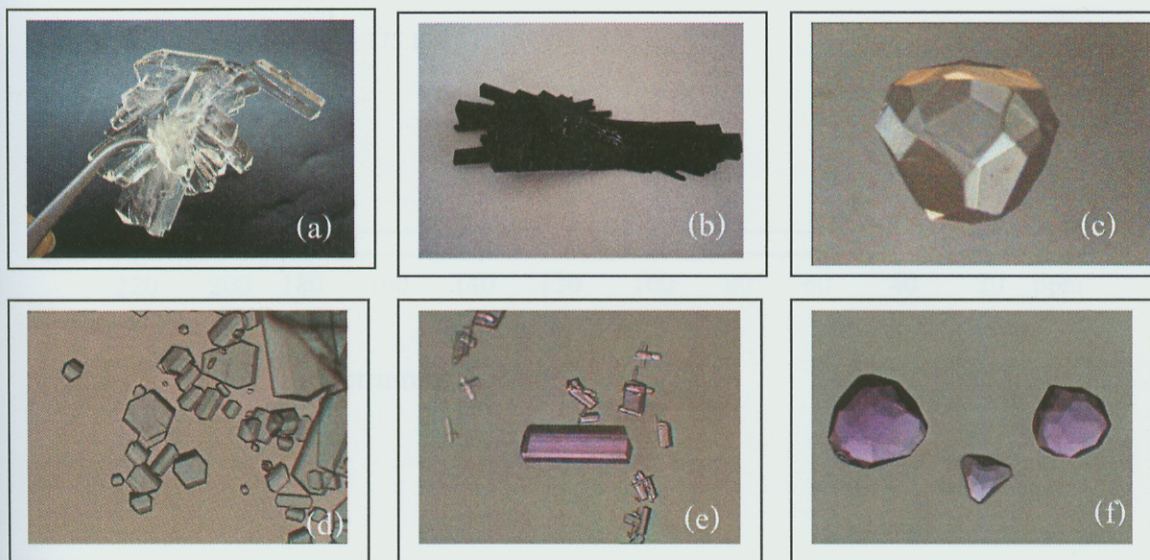


Figure 6 Pictures of (a) $K_3[Al(C_2O_4)_3] \cdot 3H_2O$, (b) $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$, (c) AlCubic in saturated solution, (d) Blue in saturated solution, (e) RedHexagonal in saturated solution, and (f) RedCubic in saturated solution

In this work, the products were further studied for their properties by UV-Vis, ^{13}C -NMR, EPMA/EDX; moreover, AlCubic was prepared and characterized by EPMA/EDX and XRD. The products from the same reaction as Laongjit's but with the variation of the amount of Cr were also prepared and characterized by ICP-AES and WDXRF.

3.1 Characterization of products by other techniques

3.1.1 ^{13}C -NMR

^{13}C -NMR spectra of compounds were acquired at the Scientific Equipment Center, Prince of Songkla University, Hat Yai, Songkla, using Fourier-Transformed NMR spectrometer 500MHz, Model UNITY INOVA, Varian, Germany. Samples were dissolved in D_2O . ^{13}C chemical shift was referred to the central peak of $\text{DMSO-}d_6$ ($\delta=39.7$). Their spectra are shown in Figures 7-12.

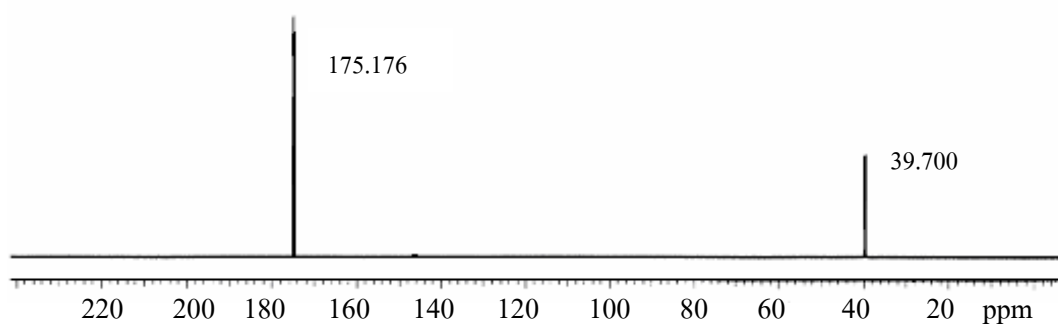


Figure 7 ^{13}C -NMR spectrum of $\text{K}_2\text{C}_2\text{O}_4$

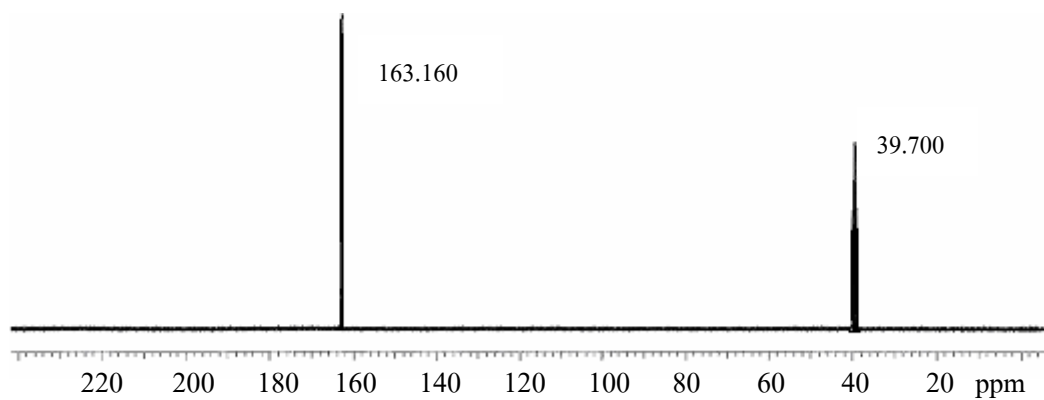


Figure 8 ^{13}C -NMR spectrum of $\text{H}_2\text{C}_2\text{O}_4$

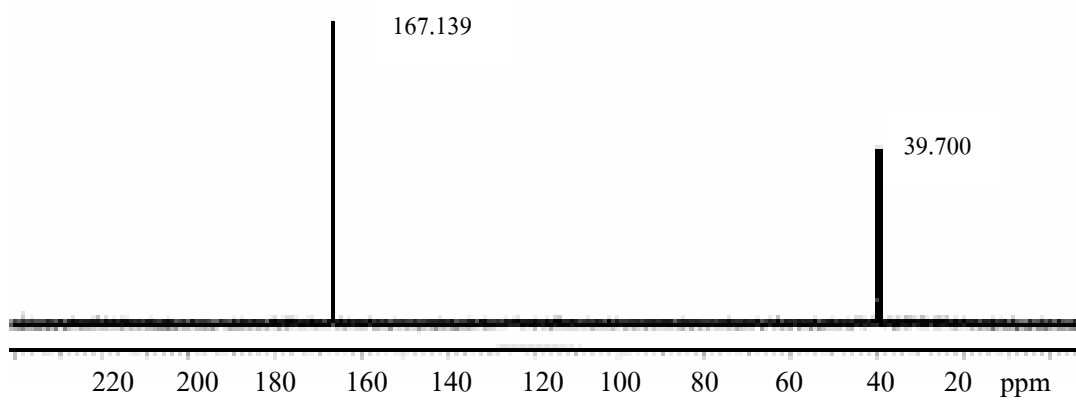


Figure 9 ^{13}C -NMR spectrum of $\text{K}_3\text{Al}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$

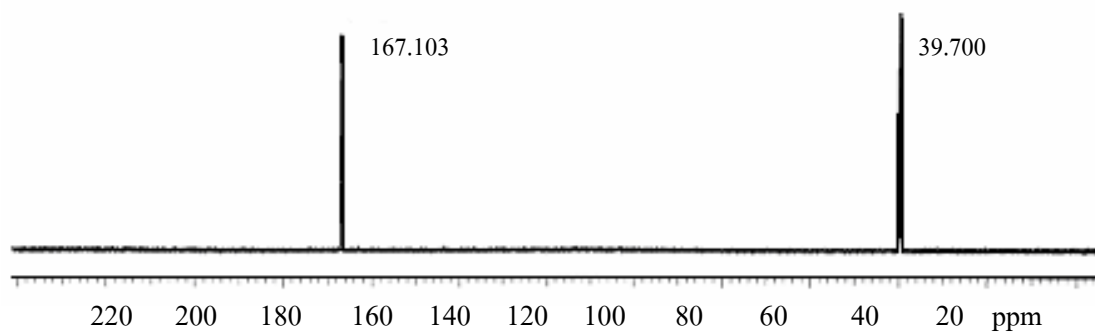


Figure 10 ^{13}C -NMR spectrum of RedHexagonal

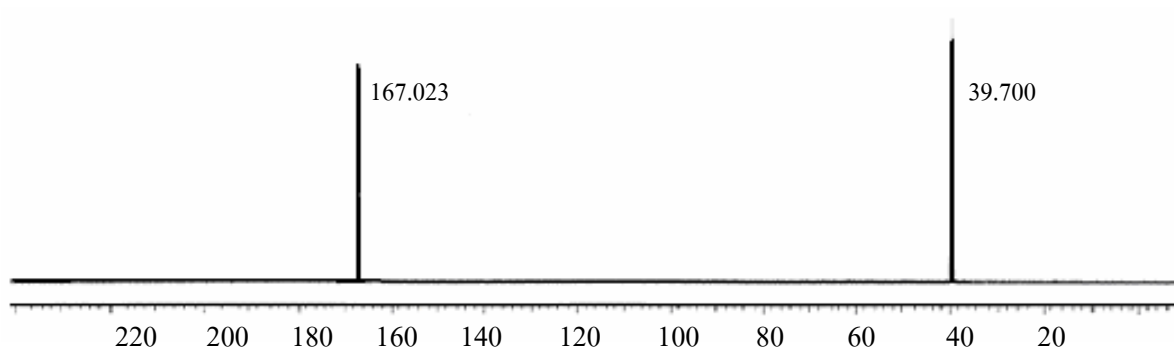


Figure 11 ^{13}C -NMR spectrum of RedCubic

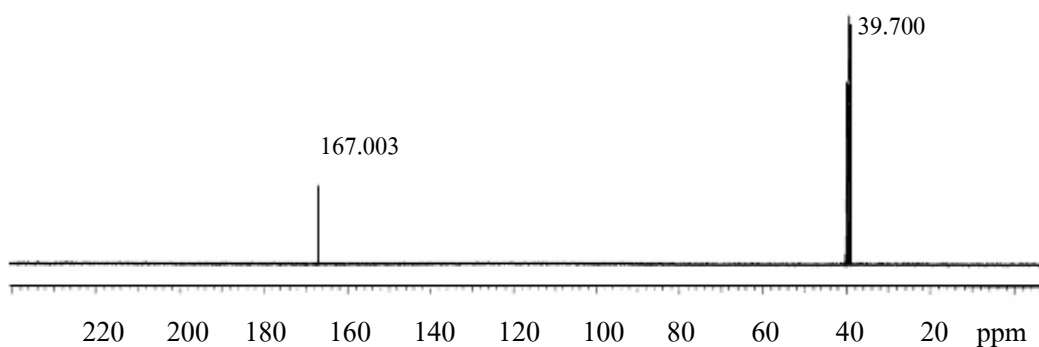


Figure 12 ^{13}C -NMR spectrum of Blue

3.1.1 EPMA/EDX

The EPMA/EDX spectra of compounds in crystal form were acquired at the Scientific Equipment Center, Prince of Songkla University, Hat Yai, Songkla, using Electron Probe Microanalyzer, JXA-8800R, JEOL, Japan, with energy dispersive X-ray spectrometer EDX, Oxford ISIS 300, UK. The spectra was is run in high vacuum mode, brass stub, and 20 KeV. Figures 13 -16 display EPMA/EDX spectra obtained for $\text{K}_3\text{Al}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$, Blue, AlCubic, and RedCubic, respectively.

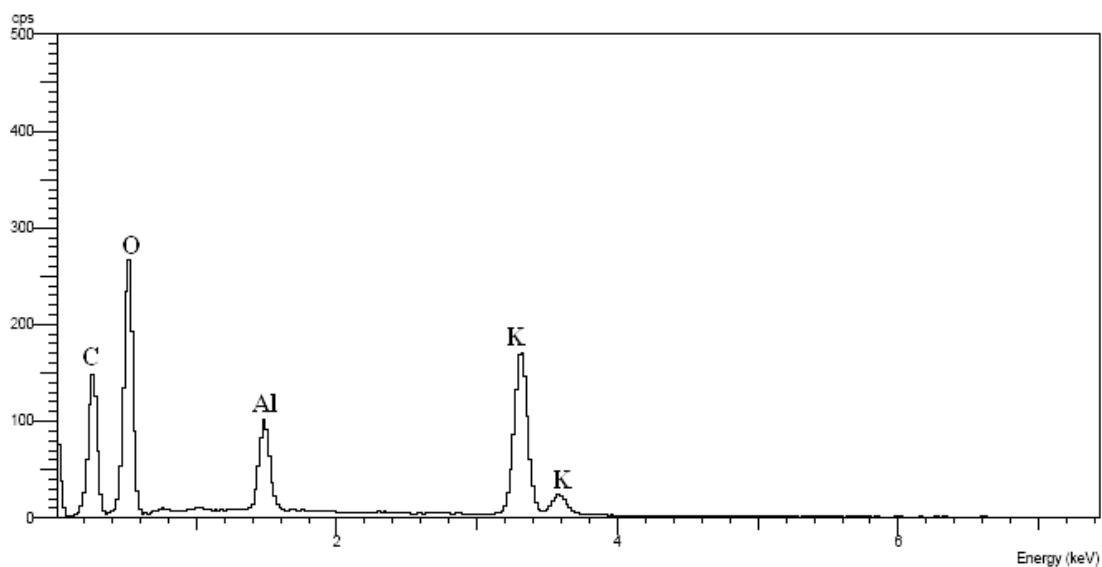


Figure 13 EPMA/EDX spectrum of $K_3Al(C_2O_4)_3 \cdot 3H_2O$ complex

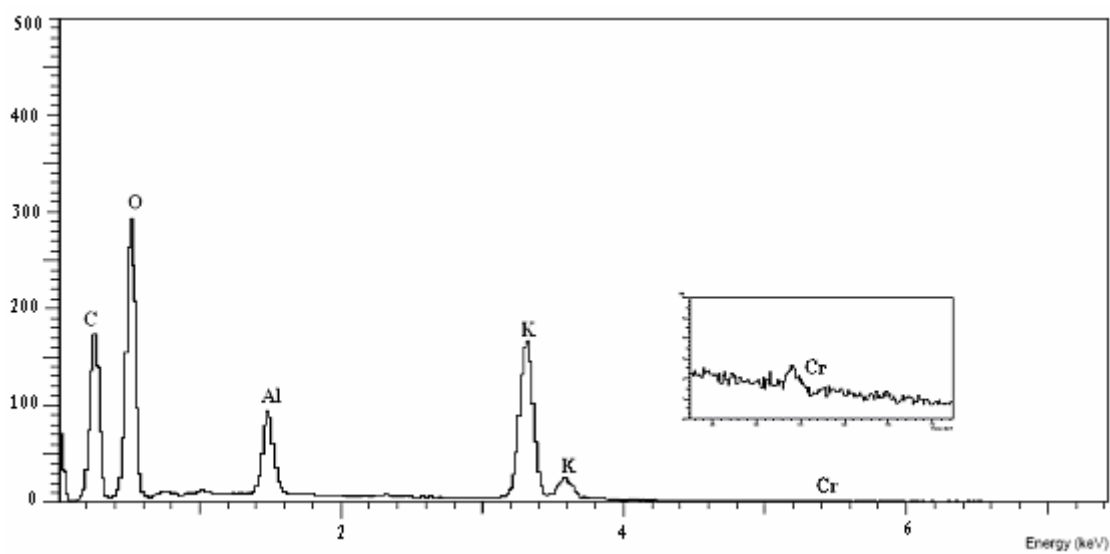


Figure 14 EPMA/EDX spectrum of Blue complex

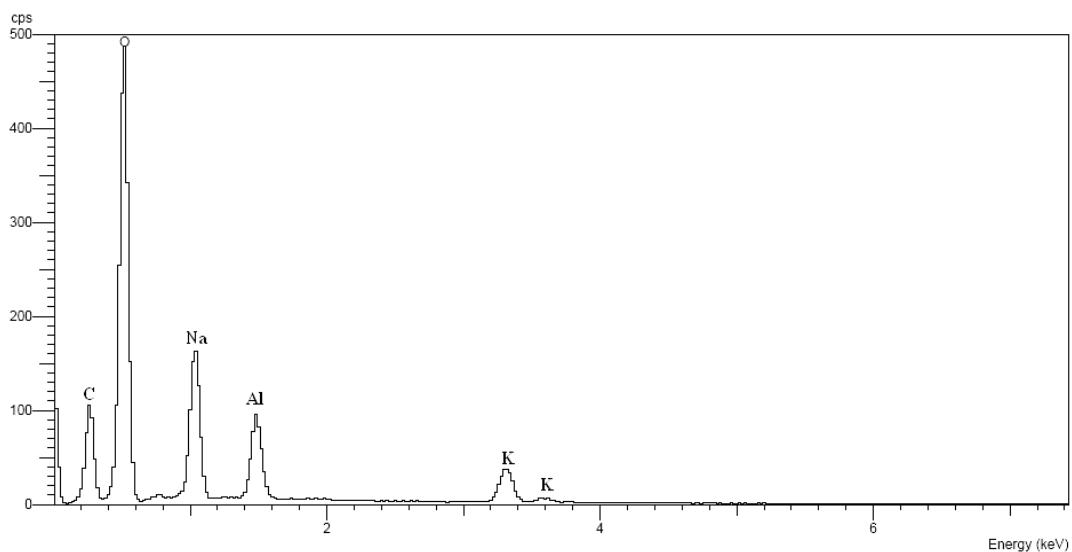


Figure 15 EPMA/EDX spectrum of AlCubic complex

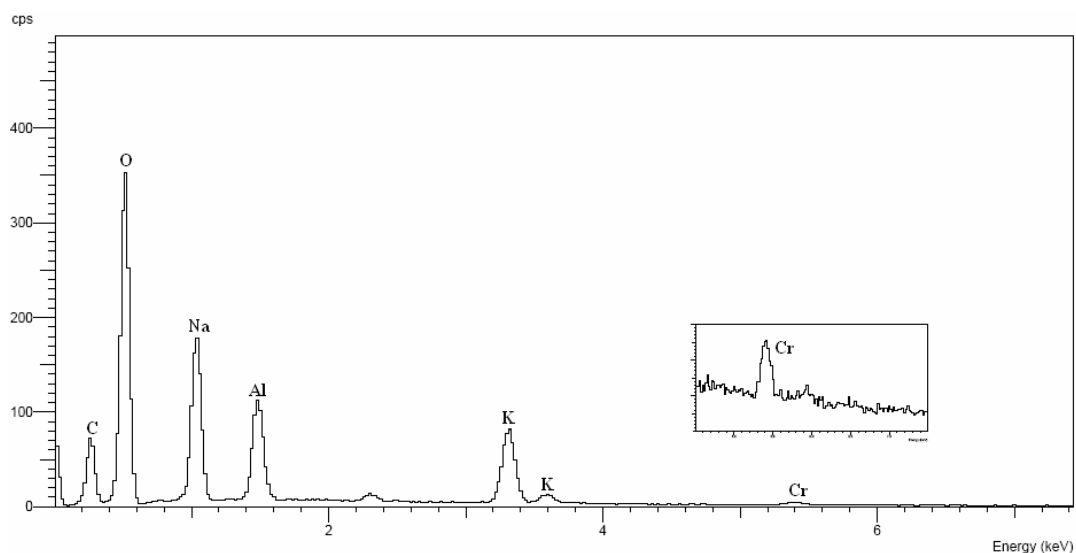


Figure 16 EPMA/EDX spectrum of RedCubic complex

3.1.3 XRD

The X-ray powder diffraction method is unique in that it is the only analytical method that is capable of providing qualitative and quantitative information about the compound present in a solid sample. The identification of a species from its powder diffraction pattern is based upon the position of the line (in terms of θ or 2θ) and their relative intensities. (Skoog and Leary, 1992) XRD patterns are shown for comparison between product and precursor in Figures 17-18.

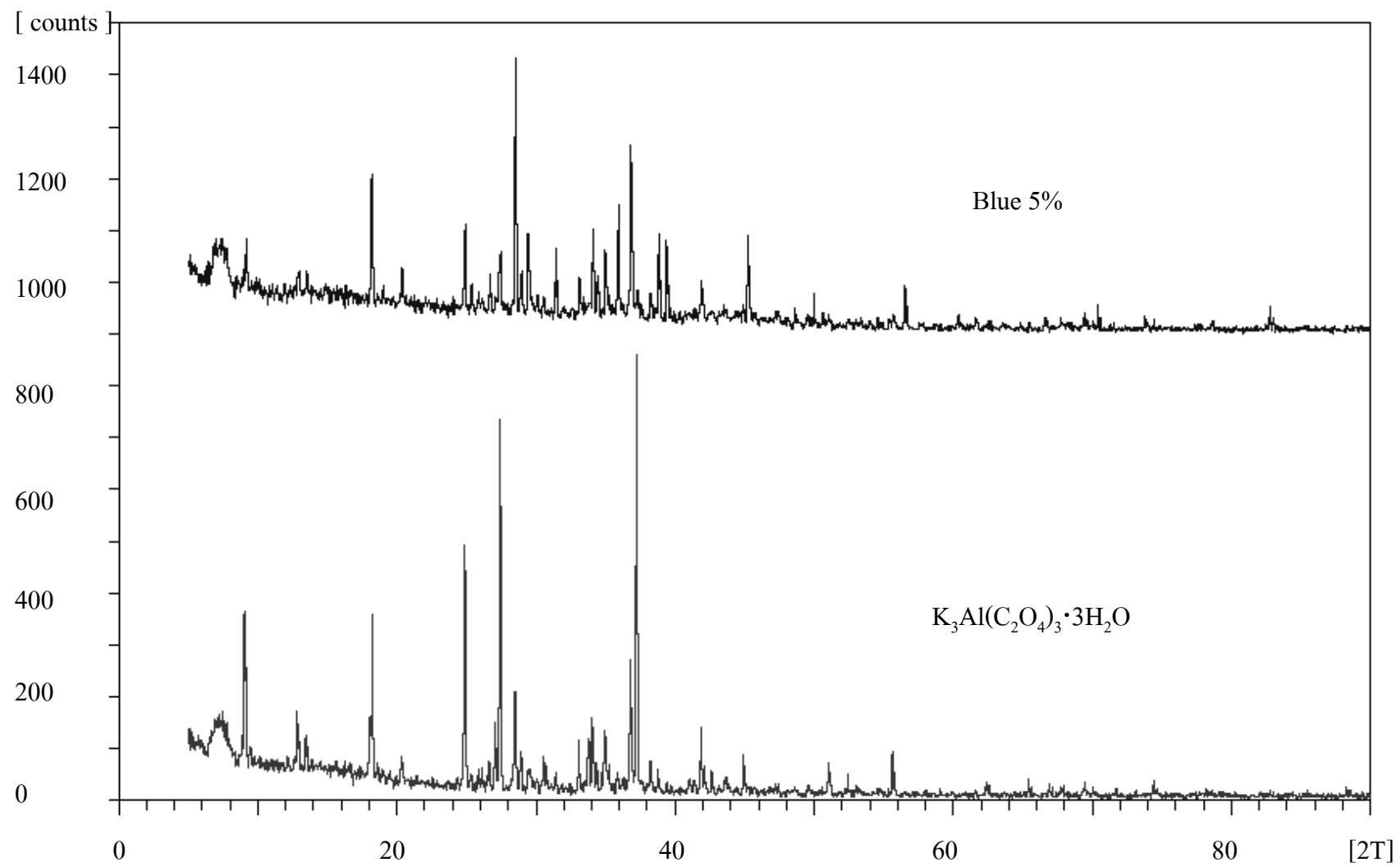


Figure 17 Powder X-ray diffraction patterns of Blue 5% and precursor $K_3Al(C_2O_4)_3 \cdot 3H_2O$

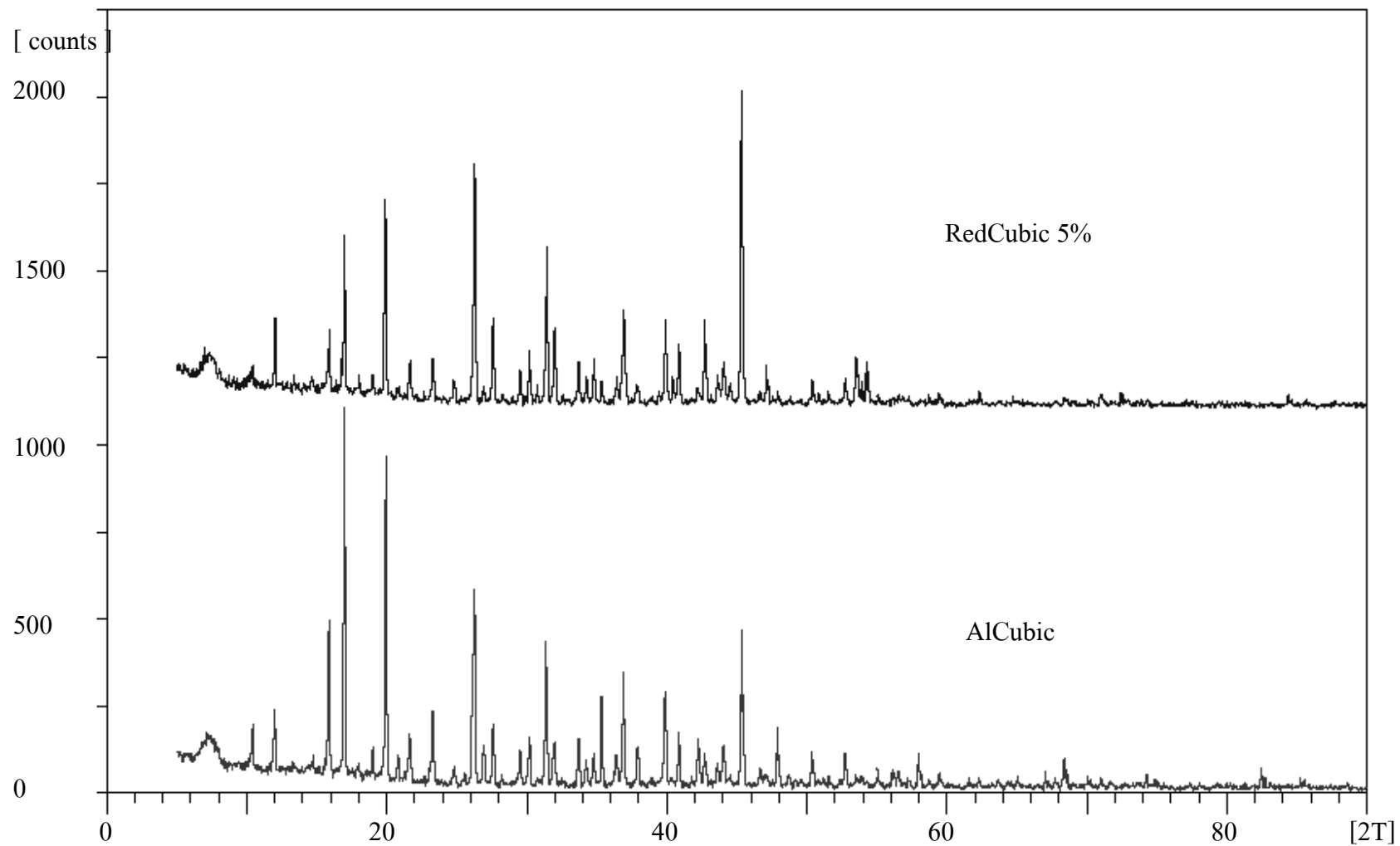


Figure 18 Powder X-ray diffraction patterns of RedCubic 5% and precursor AlCubic

3.1.4 Crystal density measurement

Density of complexes were determined by observing unknown solution that has the same density as that of the single crystal sample with pycnometer. Only density of RedCubic crystal at 25°C was measured and showed a value of 1.92 Mg/m³ because densities of Blue and RedHexagonal appeared to be higher than the solution available for this measurement.

3.1.5 General formula of products

General formula of products concluded from results by many techniques such as XRF, ICP-AES, TGA, and titration are shown in Table 3.

Table 3 General formula of products

Sample	General formula
Blue 5%	$K_3[(Al_{0.95}Cr_{0.05})(C_2O_4)_3] \cdot 3H_2O$
RedCubic 5%	$KNa_2[(Al_{0.95}Cr_{0.05})(C_2O_4)_3] \cdot 4H_2O$
AlCubic	$KNa_2[(Al)(C_2O_4)_3] \cdot 4H_2O$

3.1.6 Single crystal X-ray diffraction

Single crystal X-ray diffraction is the most common experimental method of obtaining the details of the molecular structures. Blue, RedCubic, and AlCubic were measured and attempted to elucidate their structures by single crystal X-ray diffraction. The unit cell parameters and intensity data were collected at 293 K on a 4k Bruker SMART APEX CCD area-detector diffractometer with graphite monochromated Mo K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) at Department of Chemistry, Faculty of Science, Prince of Songkla University. The results are shown in Table 4 but their structures could not be solved in this work.

Table 4 The unit cell parameters of Blue, RedCubic, and AlCubic

sample	Crystal system	Unit cell dimensions					
		a(Å)	b(Å)	c(Å)	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$
Blue5% ^a	monoclinic	7.6828	19.4309	10.2155	90	108.111	90
RedCubic5% ^a	Cubic	20.9992	20.9992	20.9992	90	90	90
AlCubic	Cubic	20.960	20.964	20.966	90	90	90

^a This percentage showed % $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ in the preparation

3.1.7 UV-Visible absorption spectroscopy

Oxalic acid, potassium oxalate, and potassium trisoxalatoaluminate complex were studied by UV-Visible spectroscopy. The absorption spectra of this compound in water and solid state were recorded in the range 200-800 nm and shown in Figures 22-24.

The products (RedCubic and Blue) and $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ were measured in aqueous solution, powder form (Figure 19) and crystalline forms at ambient temperature. Their spectra are shown in Figures 20-24, and the maximum bands are summarized in Table 5.

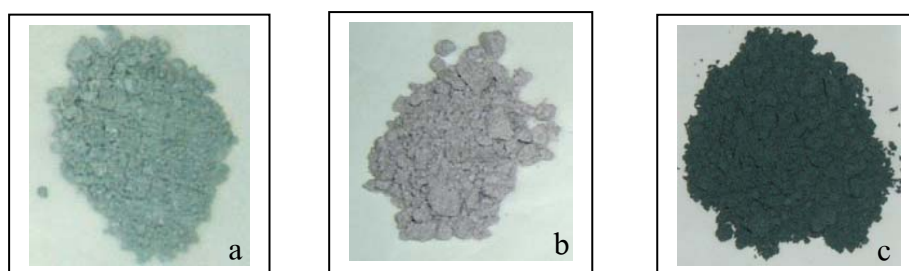


Figure 19 Pictures of (a) powder of Blue, (b) powder of Redcubic, and (c) powder of $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$

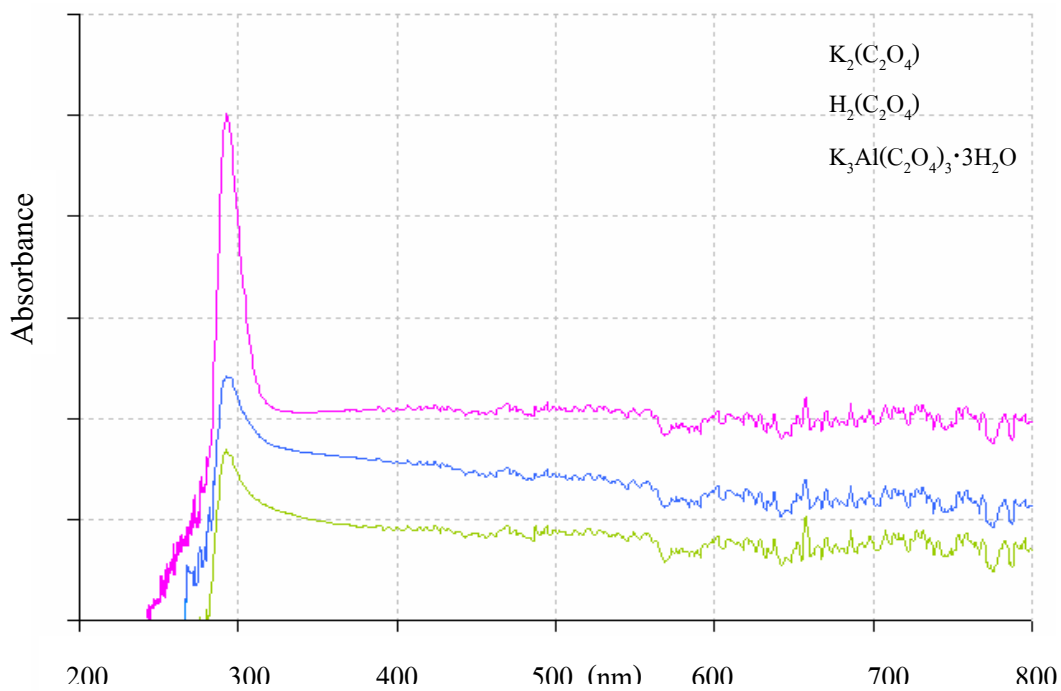


Figure 20 UV-Visible absorption spectra of $K_2(C_2O_4)$, $H_2(C_2O_4)$, and $K_3Al(C_2O_4)_3 \cdot 3H_2O$ in aqueous solution

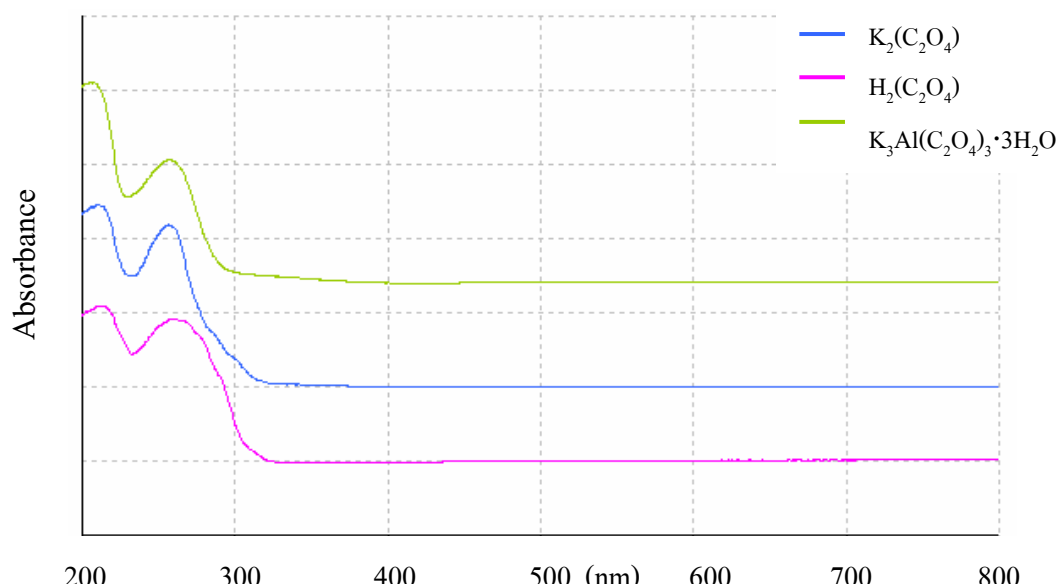


Figure 21 UV-Visible absorption spectra of $K_2(C_2O_4)$, $H_2(C_2O_4)$, and $K_3Al(C_2O_4)_3 \cdot 3H_2O$ in powder form by diffused reflectance method

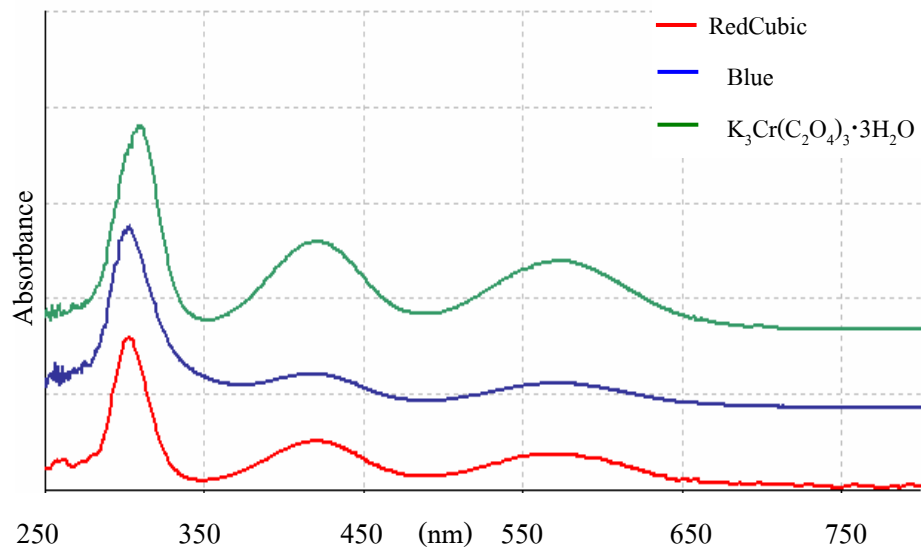


Figure 22 UV-Visible absorption spectra of RedCubic, Blue, and $K_3Cr(C_2O_4)_3 \cdot 3H_2O$ in aqueous solution

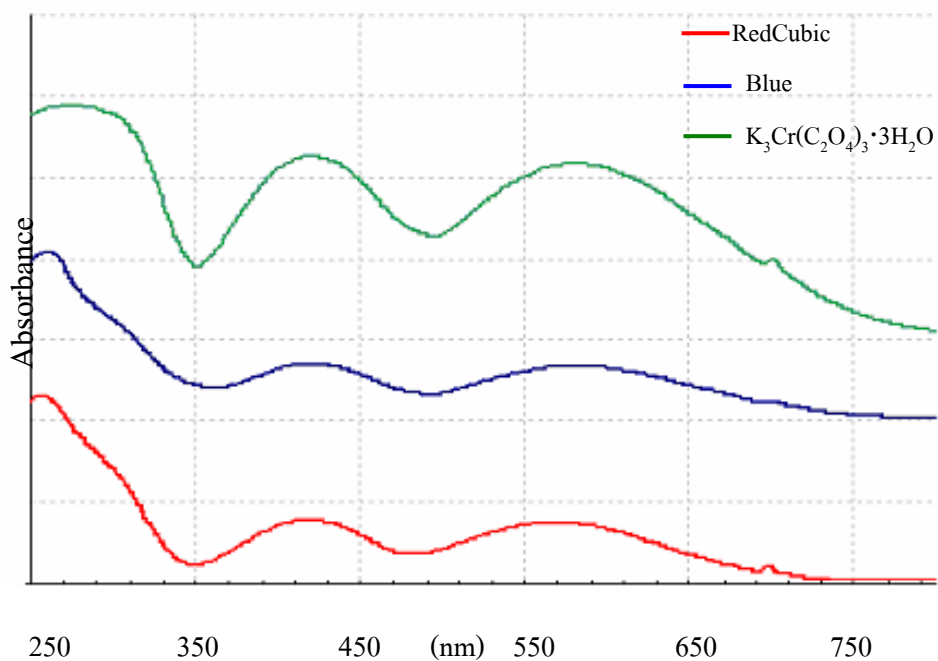


Figure 23 UV-Visible absorption spectra of RedCubic, Blue, and $K_3Cr(C_2O_4)_3 \cdot 3H_2O$ in powder form by diffused reflectance method

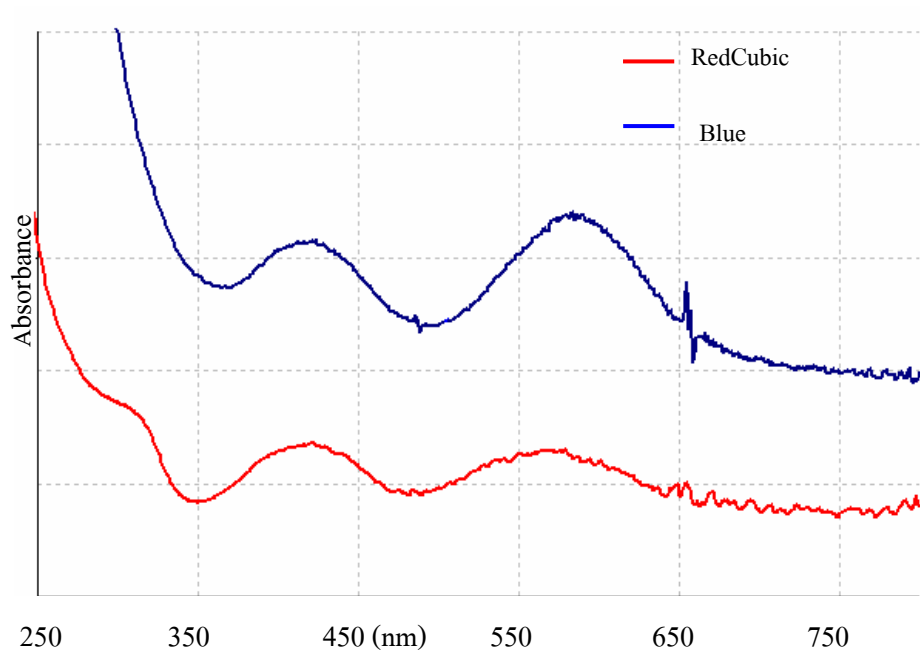


Figure 24 UV-Visible absorption spectra of RedCubic and Blue in crystalline form

Table 5 Absorption band of products and other oxalate compounds

Complex	Sample state	Absorption band (nm)		
		Oxalate anion	${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$	${}^4A_{2g} \rightarrow {}^4T_{2g}$
RedCubic	Solution	293	423	575
	Powder	256	419	571
	Crystalline	-	422	567
Blue	Solution	293	422	573
	Powder	260	420	580
	Crystalline	247	419	582
$K_3[Cr(C_2O_4)_3] \cdot 3H_2O$	Solution	308	422	574
	Powder	273	421	581
$K_3[Al(C_2O_4)_3] \cdot 3H_2O$	Solution	293	-	-
	Powder	253	-	-
$K_2(C_2O_4)$	Solution	293	-	-
	Powder	253	-	-
$H_2(C_2O_4)$	Solution	293	-	-
	Powder	253	-	-

3.2 Characterization of product obtained by varying %Cr

In this work, RedCubic and Blue were prepared with varying %Cr. Their color and elemental composition were changed and the elemental composition was studied by ICP-AES and XRF. The pictures of the resulting products are shown in Figure 25.

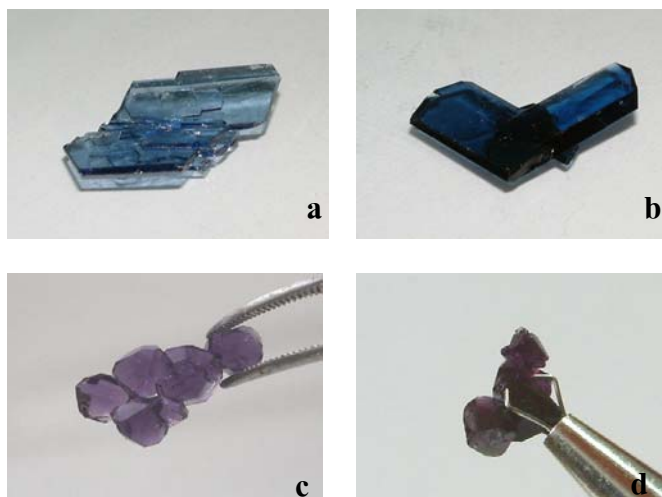


Figure 25 Pictures of product by varying %Cr (a) Blue1%,
(b) Blue5%, (c) RedCubic 1%, and (d) RedCubic 5%

3.2.1 Wavelength dispersive X-ray fluorescence spectrometry (WDXRF)

The pressed powder samples varying % Cr were measured for the intensities of elements by the wavelength dispersive X-ray fluorescence spectrometer at the Scientific Equipment Center, Prince of Songkla University, Hat Yai, Songkla. The calibration curve (Figure 26) was prepared to determine the quantity of the element. The resulting elemental composition of RedCubic and Blue, are shown in Figures 27-28, respectively.

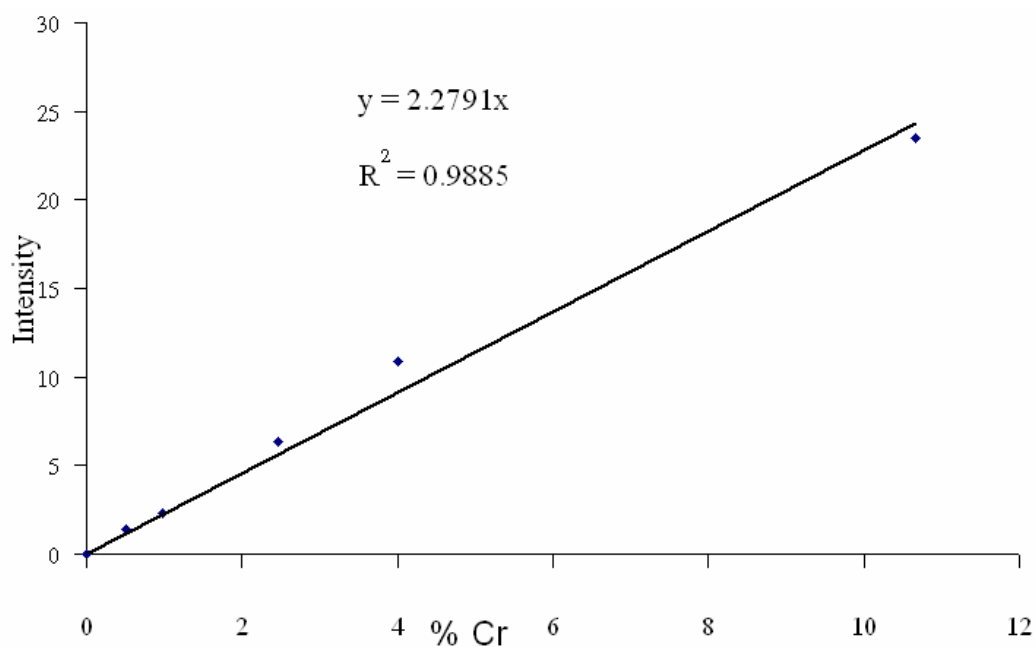


Figure 26 Calibration curve from the standards prepared by mixing $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ and $K_3[Al(C_2O_4)_3] \cdot 3H_2O$

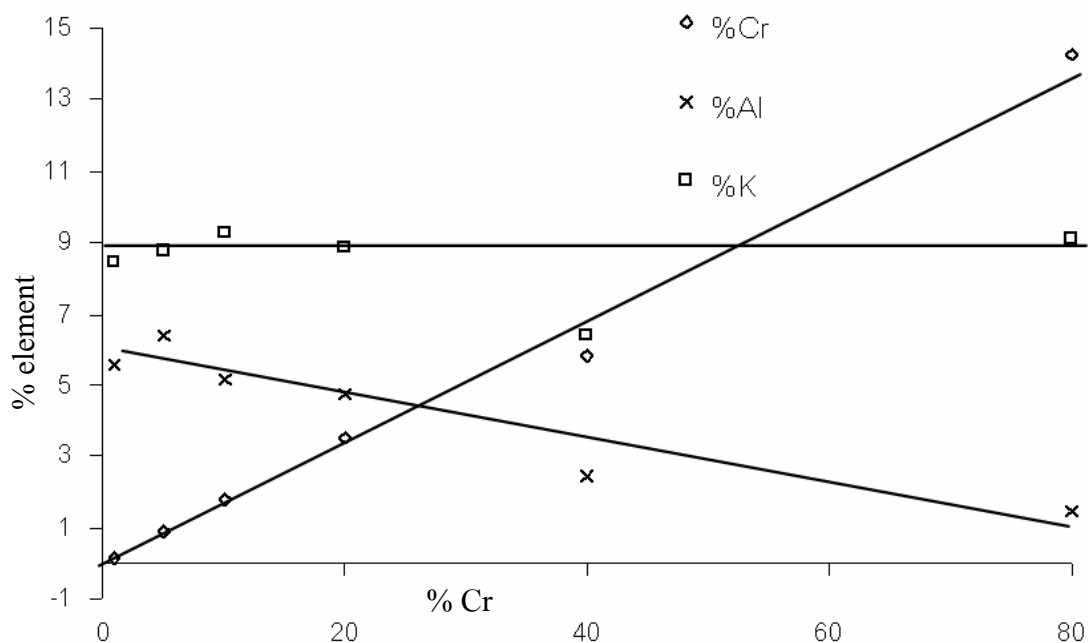


Figure 27 % element in Redcubic crystals prepared by varying the amount of Cr

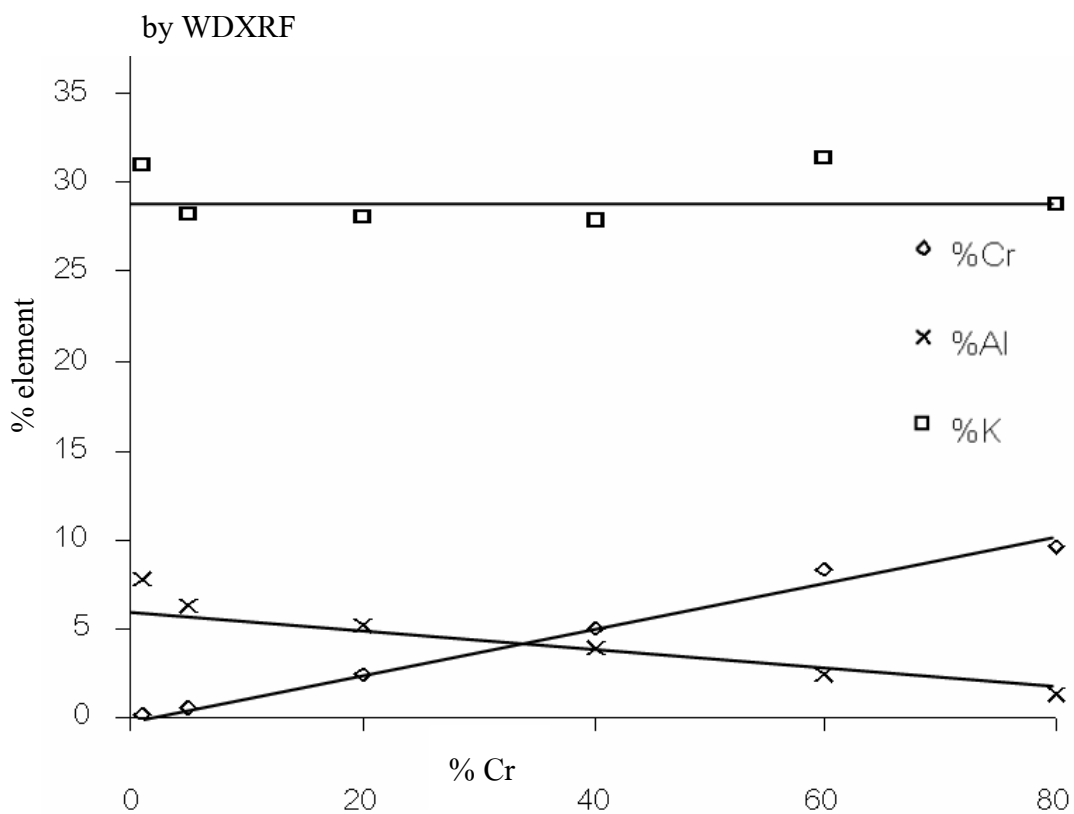


Figure 28 % element in Blue crystals prepared by varying the amount of Cr

by WDXRF

3.2.2 Inductively-coupled plasma/atomic emission spectroscopy (ICP-AES)

Samples of RedCubic and Blue with varying %Cr were dissolved in water and the elemental composition (K, Na, Cr, and Al) were determined with ICP-AES at the Central Equipment Unit, Faculty of Science, PSU. The results are shown in Figures 29 – 30.

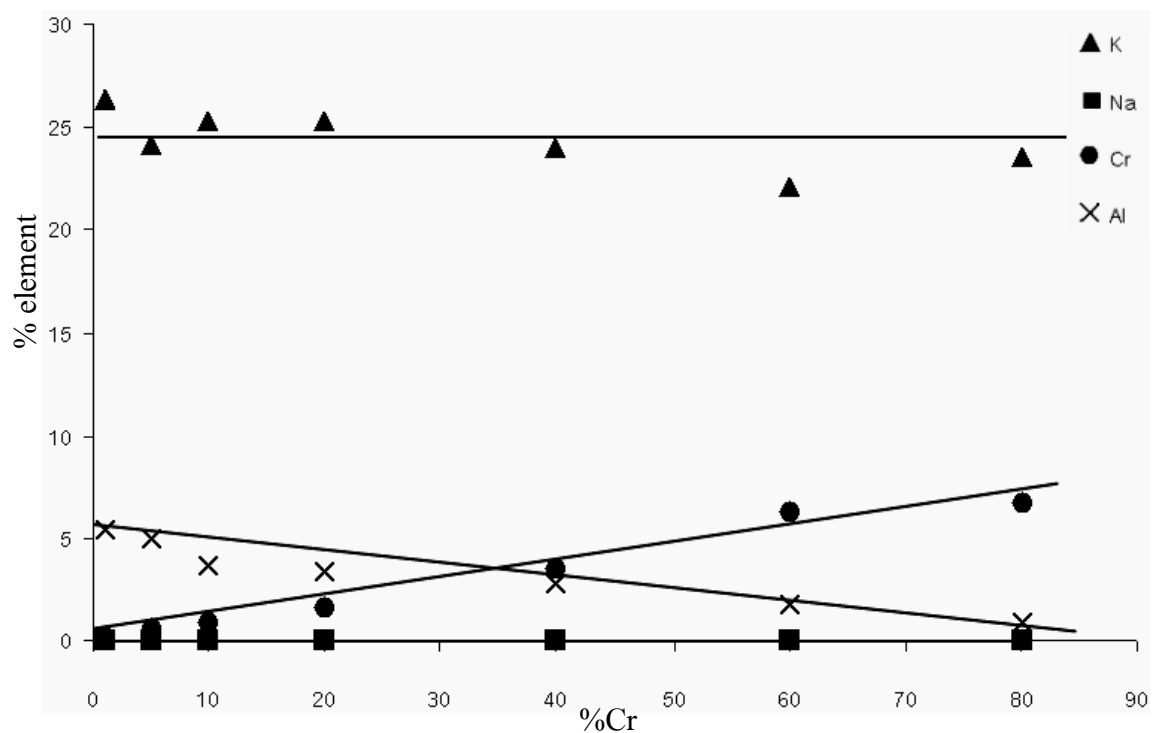


Figure 29 % element in Redcubic crystals prepared by varying the amount of Cr using ICP-AES.

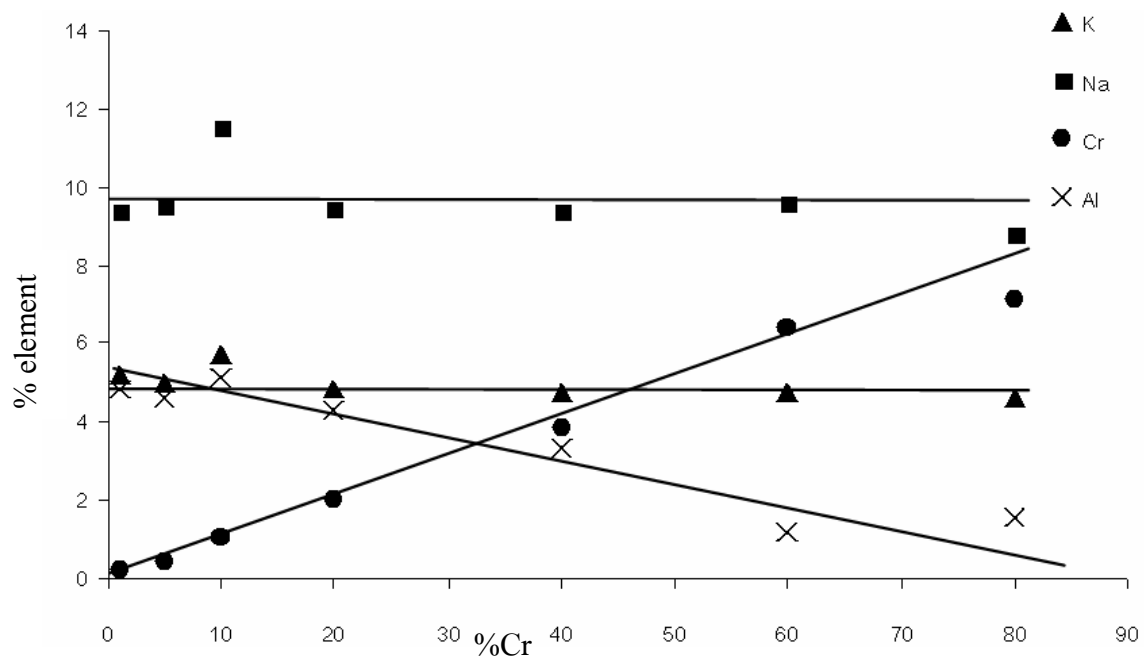


Figure 30 % element in Blue crystals prepared by varying the amount of Cr using ICP-AES.