Microwave Metathesis Synthesis and Characterization of *TM*PO_4 (*TM* = Cr, Mn, Fe, Co, Ni, Cu)

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The transition metal phosphates (*TM*PO_4, *M* = Cr, Mn, Fe, Co, Ni, Cu) are synthesized via microwave metathesis synthesis (MMS) with by-product sodium chloride which drives the MMS reaction to forward direction by dint of high lattice energy. The synthesis procedure is achieved at 850 W powers in a domestic microwave oven for a short time as 10 minutes. The structural, morphological and thermal properties of $CrPO_4$, $MnPO_4$, $FePO_4$, $CoPO_4$, $NiPO_4$ and $CuPO_4$ powders are dissolved by powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy/energy dispersive X-ray (EDS) analysis and thermogravimetric analysis (TGA). The unit cell parameters and crystal systems of the products are determined by Rietveld refinement method via powder X-ray diffraction data. All the samples with orthorhombic crystal system have same homogeneity of distorted circular micron size particles and relatively higher thermal stability than the other metal phosphates.

Keywords: microwave metathesis synthesis, transition metal phosphate, lattice energy, Rietveld refinement method, powder X-ray diffraction.

1. INTRODUCTION

The phosphor is one of the most abundant elements in earth crusts. The phosphates are strictly formed by various combinations of phosphor atom and one, two, or three oxygen atoms resulting basic monophosphate or polyphosphates. Monophosphate is demonstrated an anionic $(PO_4)^{3-}$ group which has a regular tetrahedral structure formed by phosphor and four oxygen atoms. Monophosphates have been commonly entitled as orthophosphates for a long time, and go on. Monophosphates are a broad family of phosphates because of well-known structure and thermal stability. The complex phosphates can be formed by infinite chains of monophosphates resulting $(P_nO_{3n+1})^{-(n+2)}$, $(P_nO_{3n})^{-(n)}$ and $(P_{(2m+n)}O_{(5m-3n)})^{-(n)}$ compounds [1]. Especially in the last ten years, importance of various types of phosphates has been increased in the wide usage area such as molecular elimination, ionic exchange and catalyst in inorganic and organic processes [2, 3].

The ABX_4 type compounds are crystallized either in zircon with space group I41/amd, Z ¼ 4 or scheelite structure with space group I41/a, Z ¼ 4 [4] at ambient conditions. Phosphates [5], zircon [6], orthovanadates [7, 8], chromates [9], fluorides [10], orthotungstates [11, 12], and molybdates [13] are the most widely investigated ones which are applicable as solid state scintillator materials, laser host materials, opto-electronic devices, etc. These types of compounds have been synthesized by high temperature solid state reaction [14], precipitation [15, 16], hydrothermal [17, 18], mechanochemical [19, 20], and micro-emulsion methods [18, 21], etc. in the literature. The previously applied syntheses methods have some disadvantages. Firstly, conventional solid state reactions process brings about oxygen deficiency and large grain sized materials. Secondly, pH regulation must be under proper control to overcome the formation of undesirable phases in precipitation method. Last of all, the wet processes take long reaction time, use expensive equipment, possess complicated stages and produce poor yield [22]. There is a method except all of them called microwave metathesis synthesis (MMS) driven by high lattice energy by-product such as NaCl by microwave energy emerging as an alternative method of synthesis of inorganic solids such as vanadates, phosphates, borates [23, 24], oxides [25], etc. [26, 27]. In the microwave heating purposes, the electromagnetic radiation with frequency range of 0.3 – 300 GHz is used as narrow frequency window, and at least one of the reactants must been interacted to microwave field [32]. In general, microwave ovens are preferred to use in laboratory scale, but large industrial types of microwave furnaces can be applicable to obtain large quantities of production in industry [28 – 31]. There are rising advantages of microwave heating; for instance, improved product uniformity, higher yield, energy saving, shorter processing time, and controlled microstructure resulting obtaining of fresh materials with unique properties [32 – 36]. The most fateful property of a metathetic reaction is the formation of NaCl by-product with high lattice energy ensured a local energy source which acts as the fundamental driving force for the reaction in a short amount of time [29]. When we consider all these aspects, microwave metathesis reactions become compulsory.

The remarkable side of this scientific research is microwave metathesis synthesis of transition metal phosphates (*TM*PO_4, *M* = Cr, Mn, Fe, Co, Ni, Cu) and calculation of unit cell parameters by Rietveld refinement method for the first time as far as we know. The

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morphological nature and vibrations of interatomic bonds of $CrPO_4$, $MnPO_4$, $FePO_4$, $CoPO_4$, $NiPO_4$ and $CuPO_4$ powders are controlled to show that performs of MMS.

2. EXPERIMENTAL SECTION

All chemical was supplied as analytical-grade by Sigma and Merck. Heavy metal chloride (hydrate or anhydrous) and aqueous sodium phosphate were used as starting materials to obtain the defined compounds. As an example, the preparation of chromium monophosphate was carried out by grinding chromium chloride and Na_3PO_4 in a molar ratio 1:1 in an agate mortar followed by microwave treatment in a domestic oven (2.45 GHz, 850 W powers) for 10 min. The final products were washed with distilled hot water and recrystallized at 400 °C to get rid of by-product NaCl. The X-ray powder diffraction analyses were realized two times; without washing and after washing. All transition metal phosphates were obtained in a same metathesis synthesis pathway.

The powder X-ray diffraction (XRD) measurements were carried out by Panalytical X'Pert Pro Diffractometer and CuK_α radiation (λ = 1.54056 Å, 40 mA, 50 kV) with a scan rate of 1 °/min with step size 0.02°. The Rietveld analysis of the samples was done by using the High Score Plus (HS+) Program (License number: 92000029). A Siemens V12 domestic microwave oven was used to synthesis of related compounds. Fourier transform infrared spectrum (FTIR) was recorded on a Perkin Elmer Spectrum 100 FTIR Spectrometer from 4000 to 650 cm^{-1}. Scanning electron microscopy/energy dispersive X-ray analysis was achieved in SEM JEOL 6390-LV/EDS. Recrystallization process was achieved in a Protherm conventional furnace. Perkin Elmer thermogravimetric analyzer (TGA) was used to determine thermal properties.

3. RESULTS AND DISCUSSION

The powder diffraction patterns of amorphous $CrPO_4$ (P1), $FePO_4$ (P2), $CoPO_4$ (P3), $NiPO_4$ (P4), $CuPO_4$ (P5), and $MnVO_4$ (P6) are shown in Fig. 1, without washing (Fig. 1 a) and after washing (Fig. 1 b). The by-product NaCl (ICSD = 98-005-3815) is marked with asterisks in Fig. 1 a. The formation of by-product NaCl with high lattice energy drives the reaction to forward direction. Therefore, previously described metathetic pathway was achieved successfully to complete progress of the reactions [37 – 39]. Therefore, transition metal monophosphates, $TMPO_4$ (M = Cr, Fe, Co, Ni, Cu, Mn), are synthesized by driving force of NaCl. According to example given in "synthesis procedure" section, the reaction equation of $CrPO_4$ formation is indicated as follows:

$$CrCl_3 + Na_3PO_4 \rightarrow CrPO_4 + 3NaCl \quad (1)$$

The reaction equations for the other compounds can be adapted by considering of the above equation. Therefore, targets compounds are obtained by microwave metathesis synthesis (MMS) reaction. The removal processes of the by-product is started with washing hot distilled water three times and continue with drying at 80 °C to remove the water. All the amorphous products are subjected to heat treatment at 800 °C to get best crystallization. The powder X-ray diffraction data of the recrystallized compounds are displayed in Table 1. The unit cell parameters of the recrystallized compounds are calculated with Rietveld refinement method by using powder diffraction data (Table 2).

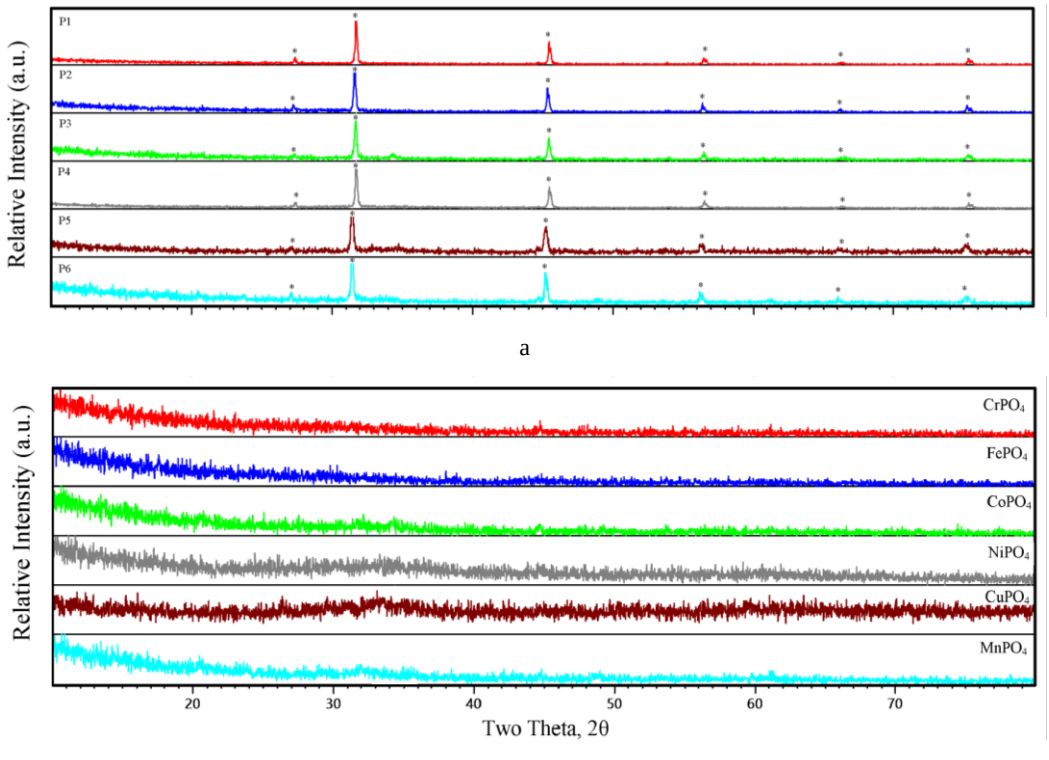

Fig. 1. Powder X-ray diffraction patterns of the samples: a – without washing; b – after washing

Table 1. Powder X-ray diffraction data of the recrystallized compounds

$CrPO_4$		$MnPO_4$		$FePO_4$		$CoPO_4$		$NiPO_4$		$CuPO_4$	
$d_{obs.}$, Å	$d_{calc.}$, Å	$d_{obs.}$, Å	$d_{calc.}$, Å	$d_{obs.}$, Å	$d_{calc.}$, Å	$d_{obs.}$, Å	$d_{calc.}$, Å	$d_{obs.}$, Å	$d_{calc.}$, Å	$d_{obs.}$, Å	$d_{calc.}$, Å
3.9848	3.9117	4.3251	4.3794	2.3231	2.4091	2.7843	2.6537	3.1733	3.3980	4.8752	4.4035
3.8651	3.6794	3.7384	3.6841	2.1230	2.1878	2.6214	2.6166	2.6825	2.6869	3.8479	3.9195
2.7043	2.6823	3.0635	2.0962	2.0421	2.0301	2.3428	2.3164	2.5958	2.5697	3.3799	3.3760
2.6861	2.6428	2.6320	2.6892	1.9263	1.9572	2.0602	2.0734	2.1887	2.1943	2.7146	2.6806
2.4348	2.3392	2.5259	2.5791	1.8213	1.8461	2.0263	2.0027	2.1357	2.0882	2.5697	2.5592
2.0418	2.0852	2.5039	2.3426	1.7815	1.7556	1.7075	1.7181	2.0315	2.0134	1.9460	1.9533
2.0250	2.0100	2.1552	2.1915	1.6453	1.6420	1.6561	1.6665	1.9328	1.9310	1.8677	1.8839
1.6604	1.6665	2.0270	2.0166	1.5024	1.5175	1.6368	1.6252	1.7034	1.7001	1.8145	1.8462
1.6286	1.6263	1.8790	1.8838	1.4321	1.4330	1.4879	1.4890	1.6887	1.6687	1.7554	1.6966
1.5889	1.5823	1.8601	1.8433	1.4142	1.4195	1.3165	1.3054	1.6139	1.6300	1.5504	1.5518
1.5698	1.5568	1.7161	1.7196	1.4109	1.3999	1.2127	1.2143	–	–	1.4827	1.4796
1.3314	1.3415	1.6732	1.6674	1.3790	1.3723	–	–	–	–	1.3437	1.3480
1.3101	1.3045	1.5467	1.5343	1.3685	1.3618	–	–	–	–	1.2730	1.2781
1.2567	1.2522	1.4722	1.4684	1.3101	1.3125	–	–	–	–	1.2433	1.2407

Table 2. Crystal system and unit cell parameters of $TMPO_4$ (*TM*=Cr, Fe, Co, Ni, Cu, Mn) calculated by Rietveld refinement method using X-ray powder diffraction data

Reactants		Product	Crystal system	Unit cell parameters		
				a, Å	b, Å	c, Å
$CrCl_3$	Na_3PO_4	$CrPO_4$	orthorhombic	4.8671	7.4341	5.8300
$MnCl_2$	Na_3PO_4	$MnPO_4$	orthorhombic	5.1085	7.4184	6.2125
$FeCl_3$	Na_3PO_4	$FePO_4$	orthorhombic	5.3593	7.3558	5.8566
$CoCl_2$	Na_3PO_4	$CoPO_4$	orthorhombic	5.3710	8.0487	5.8238
$NiCl_2$	Na_3PO_4	$NiPO_4$	orthorhombic	5.1799	7.7399	6.1157
$CuCl_2$	Na_3PO_4	$CuPO_4$	orthorhombic	5.6153	7.3667	5.7212

In Fig. 2 the FTIR spectrum of the samples are exhibited. The vibrations of $\upsilon_1(PO_4)$ [40, 41] and $\upsilon_{as}(POP)$ [42] groups which are an evidence of formation of phosphate groups are listed in Table 3.

Table 3. Crystal frequency data of sub-vibrations of monophosphate group at FTIR spectrum

Assignment	Frequency, cm^{-1}
$\upsilon_1(PO_4)$ [43, 44]	989 – 948
$\upsilon_{as}(POP)$ [45]	1026 – 916

In Fig. 3 and Fig. 4, scanning electron microscopy and energy dispersive X-ray graphics of the compounds are given which determine surface morphology and crystal composition of the samples, respectively. The SEM photographs of the samples show the homogeneity of distorted circular particles which is composed of large numbers of small grains with 1 – 5 μm size, except $NiPO_4$ and $CuPO_4$ with 15 – 20 μm size. The weight percentages (Table 4) of the compounds in a good accordance with chemical composition determined by powder X-ray diffraction pattern via Rietveld refinement method.

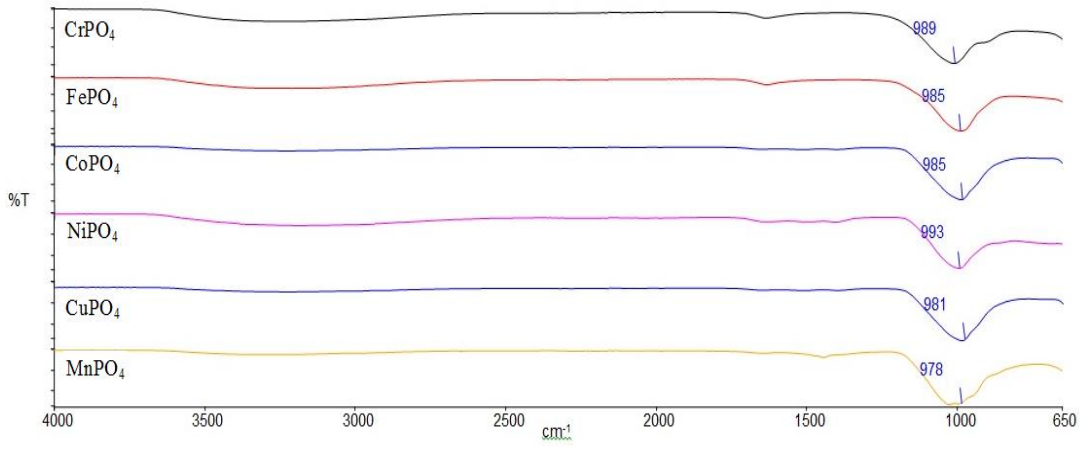

Fig. 2. The FTIR spectra of $CrPO_4$, $FePO_4$, $CoPO_4$, $NiPO_4$, $CuPO_4$, and $MnPO_4$

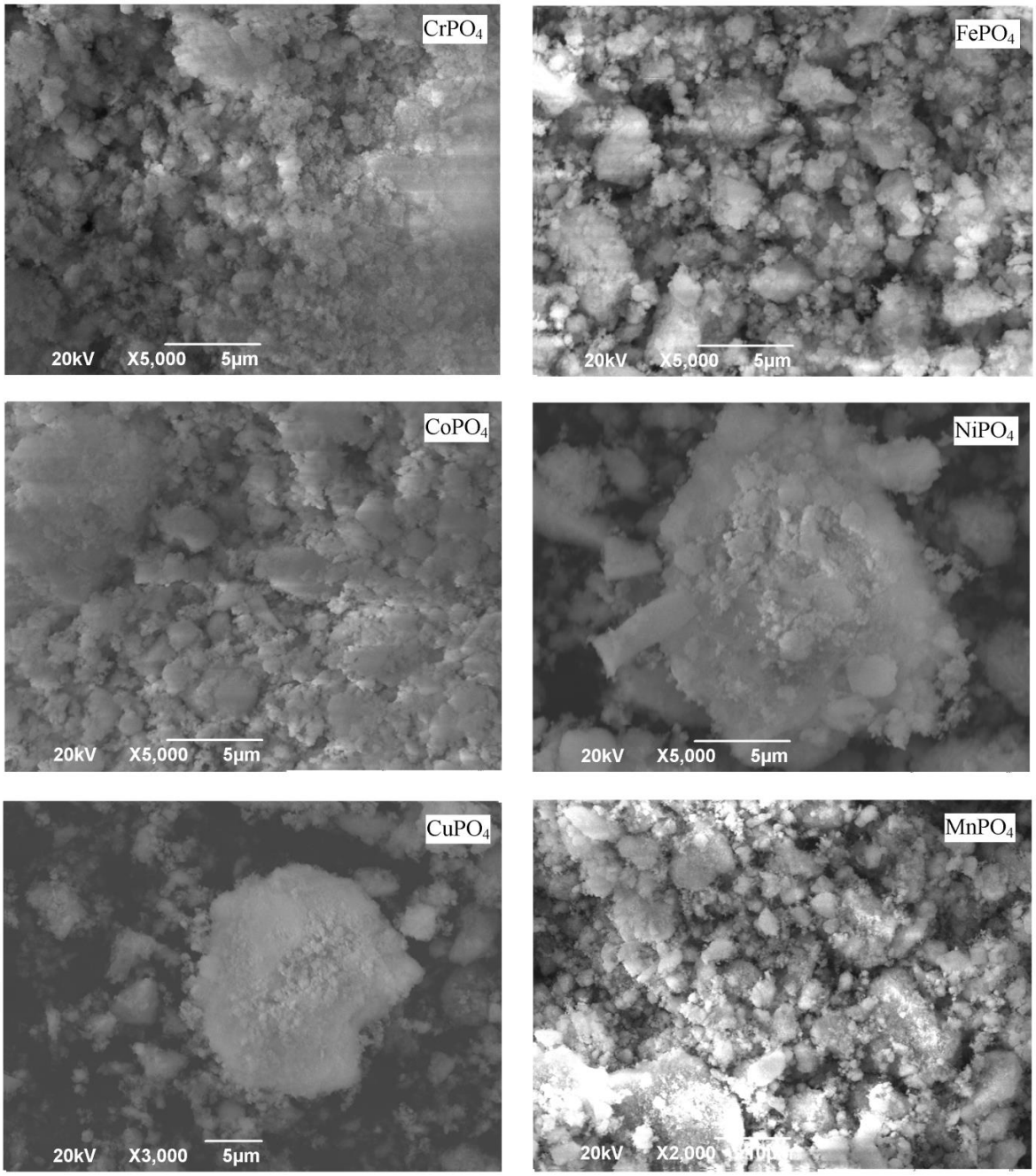

Fig. 3. Scanning electron micrographs of $CrPO_4$, $FePO_4$, $CoPO_4$, $NiPO_4$, $CuPO_4$, and $MnPO_4$

Table 4. Weight percentages of the compounds resulting by EDS

Compound	Composition	Percentages, %
$CrPO_4$	Cr-P-O	25-22-53
$FePO_4$	Fe-P-O	29-21-50
$CoPO_4$	Co-P-O	28-20-52
$NiPO_4$	Ni-P-O	27-21-52
$CuPO_4$	Cu-P-O	24-23-53
$MnPO_4$	Mn-P-O	26-22-52

Thermal analysis results of $CrPO_4$, $FePO_4$, $CoPO_4$, $NiPO_4$, $CuPO_4$, and $MnPO_4$ is displayed Fig. 5. Thermograms were measured in the range of 30 – 1200 °C. When we compared the mass losses of all compounds, quite similarities were appearing that describe very low mass decrease. In this case, the stabilities of $CrPO_4$, $FePO_4$, $CoPO_4$, $NiPO_4$, $CuPO_4$, and $MnPO_4$ compounds to thermal treatment were higher than the other members of the metal phosphate group [5].

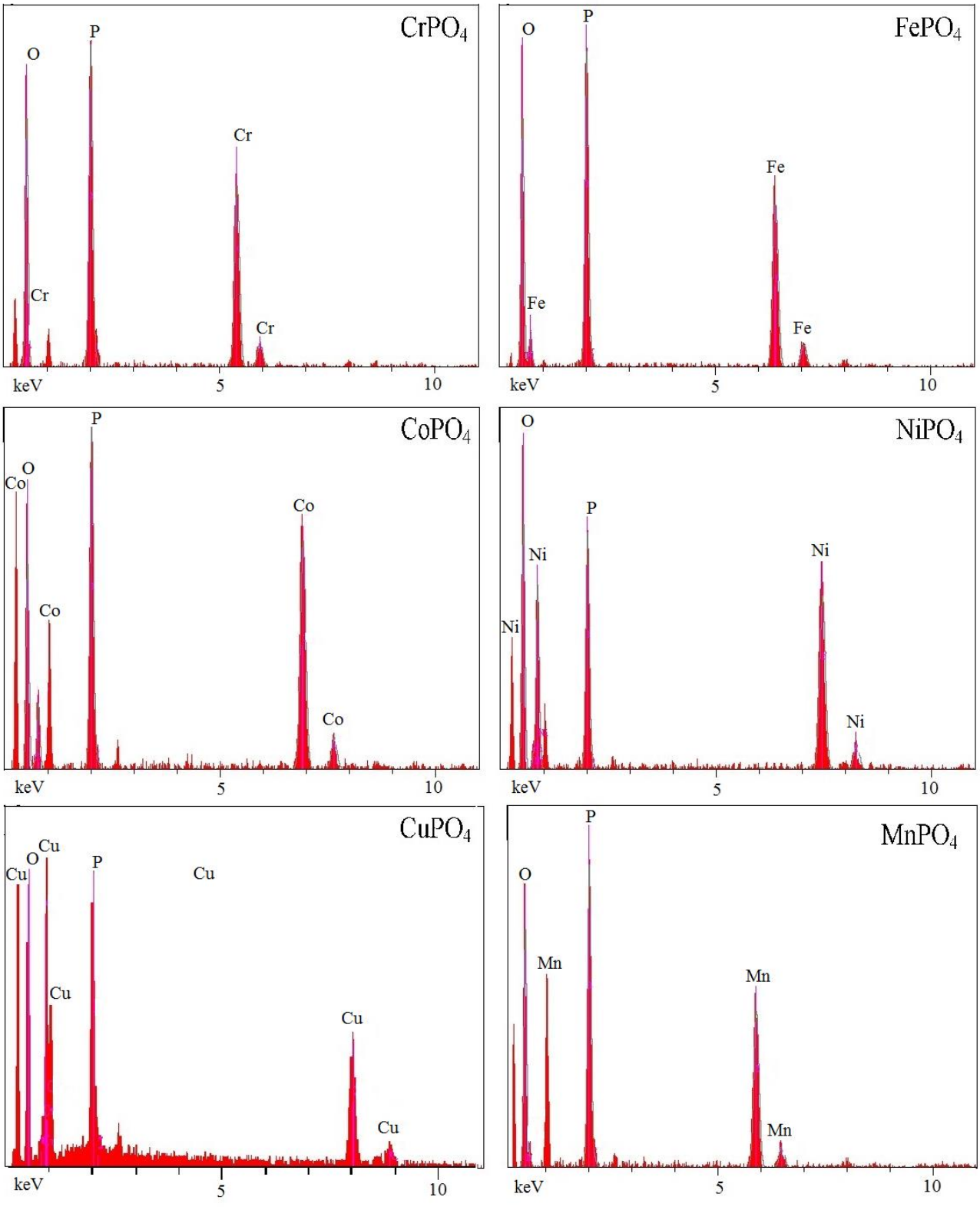

Fig. 4. EDS graphs of $CrPO_4$, $FePO_4$, $CoPO_4$, $NiPO_4$, $CuPO_4$, and $MnPO_4$.

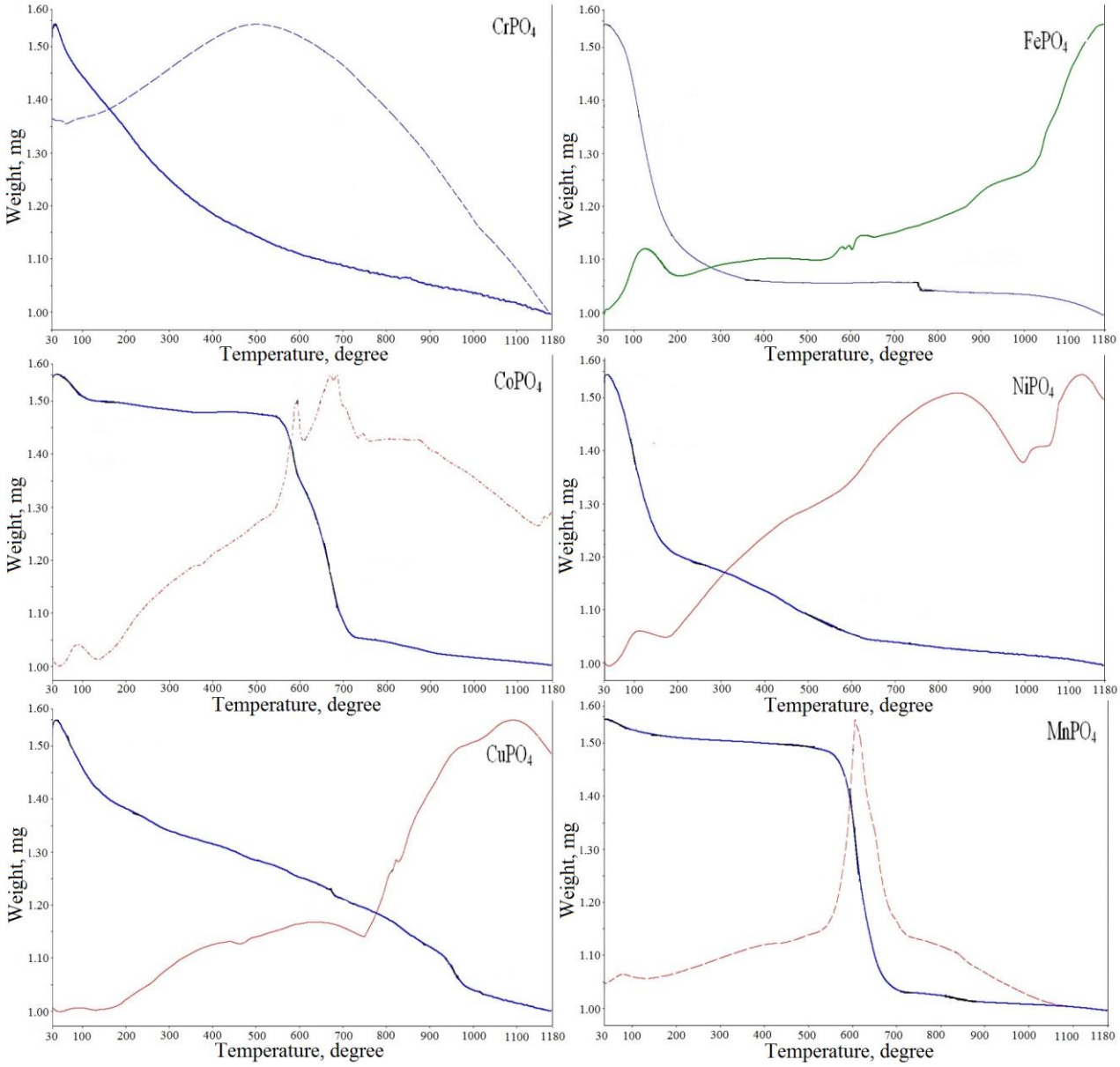

Fig. 5. TGA measurements of $CrPO_4$, $FePO_4$, $CoPO_4$, $NiPO_4$, $CuPO_4$, and $MnPO_4$.

4. CONCLUSIONS

The transition metal monophosphates, $TMPO_4$ (M = Cr, Fe, Co, Ni, Cu, Mn) are synthesized by microwave metathesis synthesis for the first time owing to driving force of by-product NaCl with high lattice energy. The synthesis process is achieved at 850 W powers for 10 minutes in a domestic oven with starting materials sodium monophosphate and transition metal chloride. Microwaves in synthesis methods decrease processing time and provide material with improved properties because the volumetric heating ability which allows for more rapid and uniform heating. The unit cell parameters are calculated by Rietveld Refinement Method using powder XRD data. The invention of vibrations of P-O bonds in FTIR spectrum, homogeny morphology and thermal stability of the samples are also support the formation of these transition metal monophosphates.

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