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MICROWAVE DEHYDRATION MODELLING OF TINCALCONITE

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ABSTRACT

Boron is known element due to wide range of application areas. Microwave dehydration has more advantages than conventional dehydraion. Differ dehydraion mechanism, higher dehydraion rate and higher level of safety are some of this advantages. Furthermore, most of minerals give better result in microwave for temperature increase. Particle size, microwave power and sample mass are parameters which effect to dehydration directly. Structure of tincalconite is suitable for the investigation of dehydration behavior by microwave because of their five moles of crystal water. Tincalconite is a type of sodium borate mineral which has a white color, trigonal system and molecule formula of Na2B4O7•5H2O. Tincalconite contains 48.8% of boron oxide(B2O3) and 29.47% of structural water. In this study, dehydration behavior of tincalconite was studied with using microwave irradiation with the power level of 180 and 360 W. The kinetic parameters of reaction were determined by using the dehydration kinetic models of Lewis, Henderson and Pabis and Wang and Singh. Tincalconite and dehydrated tincalconite characterized by the techniques of X-ray diffraction (XRD) and Raman spectroscopy. According to the results obtained tincalconite was dehydrated successfully at the microwave power level of 360 W at 14 min, on the contrary at 180 W, only the 68% of the structural water was dehydrated. Among the models, which are applied only at 360 W, Wang and Singh model best fits the data with the coefficient of regression (R2) value of 0.9965.

Keywords: *Tincalconite, Microwave, Dehydration, Modelling, XRD, Raman*

INTRODUCTION

Boron minerals have many using areas because of their properties. The main features of different borates are heat resistance, corrosion resistance and having high elasticity coefficient [1, 2].

Tincalconite ($Na_2B_4O_7•5H_2O$) occurs dehydration of borax or other sodium borates. Tincalconite mineral has the appearance of white and its hardness is 2. Tincalconite is closely related to borax [3, 4].

The dehydration of sodium borate minerals has been investigated for a long time. This has generally been based on slow dehydration and thermogravimetric methods. The thermal behaviour of mineral generally is determined by Thermal Gravimetric Analysis (TGA), Differential Thermal Gravimetric Analysis (DTG) and Differential Thermal Analysis (DTA) techniques. Dehydration of boron minerals could be explained by two steps. First step is removed in the crystal water from the structure. The second step is called dehydroxylation which is removal hydroxyl groups on a compound as water molecules. Dehydration and dehydroxylation are the reactions of thermal dissociation involving the removal of water combined in the structure of minerals and inorganic compounds in the form of H_2O molecules and OH groups [5].

Microwave technology has been successfully used in many applications including communication, cooking food, tempering and thawing, mineral synthesis and curing of wood. Microwave is a type of electromagnetic wave, with frequency between 3×10^8 Hz and 3×10^{11} Hz, making bigger penetration depth in dielectrics. Microwave heating is realized by increasing molecular thermal motion and collisions; as a result, direct heating of materials through the energy exchange and high efficiency are reached without temperature gradient heating. The properties of the microwave heating define the advantages of microwave drying, for example reduction of processing costs, shortening operation time, reduction of equipment area, better production quality and reduction of released pollutants [6,7].

Previous microwave studies published in literature about especially minerals were examined [8-19]. Microwave dehydration behavior on different types of minerals such as goethite, boric acid, ilmenite, inderite,

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colemanite and ulexite was studied in the literature [8-19]. Thamsebi et al. studied different microwave output power levels were used to analyze drying kinetic of coal in this experiment [8]. Saito et al. researched the dehydration behavior of goethite mineral blended with graphite at different mole ratios [9]. Ozdogan et al. researched the microwave dehydration behavior of the mineral inderite [10]. Eskibalci et al. examined the effect of microwave treatment on the electrostatic separation of boron minerals, namely colemanite and ulexite [12]. Erdogan et al. In this study, some boron mineral samples which are howlite, ulexite and tunellite have analysed by DTA and TG methods [15]. Li et al. studied the effects of power level and sample mass on the microwave drying characteristics of ilmenite [16]. Roussy et al. determined the dehydration kinetic model of 13X zeolite as first order [17]. Eymir and Okur showed that ulexite mineral could be dried using microwave energy [18]. Kocakusak et al. studied the microwave dehydration of boric acid in the range of 100–700 W [19]. From the studies in the literature it is seen that the microwave dehydration of tincalconite was not studied. So in this study, it is aimed to study the dehydration behaviour of tincalconite mineral using the microwave energy. Products were identified with X-ray diffraction (XRD) and Raman spectroscopy. Also, the kinetic parameters of reaction were determined by using the dehydration kinetic models.

MATERIALS AND METHODS

Tincalconite was obtained from Bandırma Boron Works (Eti Maden, Balıkesir, Turkey) with the purity of 99%. The experiment was conducted with 0.1 gram tincalconite sample. To characterize the mineral and the dried compounds X-ray diffraction (XRD) and Raman spectroscopy were used and for XRD analysis PANalytical X-ray diffraction instrument (Figure 1) was used.

Figure 1. PANalytical X-ray diffractometer

Perkin Elmer Raman instrument (Figure 2) was used for Raman analysis.

Figure 2. Perkin Elmer Raman instrument

In Figure 3, a programmable domestic microwave oven (BOSCH-HMT 72G 420, Turkey) with maximum output of 800 W was used for the drying experiments**.**

Figure 3. Bosch-HMT 72G 420 model domestic microwave oven

In experiments, power levels were determined as 360 and 180 W. A determined amount of tincalconite were exposed to microwave radiation and the mineral was weighted at 60 seconds and 120 seconds intervals till to get a constant weight at 360 and 180 W, respectively.

Structural water content (SWC) (kg structural water / kg dehydrated mineral), dehydration rate (DR) (kg structural water / kg dehydrated mineral × minute), structural water ratio (SWR) (dimensionless) of tincalconite were calculated using the Equations. of (1), (2) and (3):

$$SWC = \frac{w_{sw}}{w_d} \tag{1}$$

$$DR = \frac{SW_{t+dt} - SW_t}{dt} \tag{2}$$

$$SWR = \frac{SW_t - SW_e}{SW_i - SW_e} \tag{3}$$

where w_{sw} is the structural water amount (g), w_d is the dehydrated mineral amount (g), SW_{t+dt} is the structural water amount at $t + dt$ (kg structural water / kg dehydrated mineral), t is the dehydration time (min), SW_t, SW_e and SW_i are the structural water content at selected time, at equilibrium and the initial value.

Statistica 8.0 (StatSoft Inc., Tulsa, USA) was used for the estimation of model parameters. The calculated data using the three different models evaluated by using the coefficient of determination (R^2), reduced chi-square (χ^2) and root mean square error (RMSE). χ^2 and RMSE equations are given in Equation 4 and 5 respectively:

$$\chi^2 = \frac{\sum_{i=1}^{N} \left(SWR_{exp,i} - SWR_{calc,i}\right)^2}{N - z} \tag{4}$$

$$\text{RMSE} = \left(\frac{1}{N} \times \sum_{i=1}^{N} \left(SWR_{pre,i} - SWR_{calc,i}\right)^2\right)^{1/2} \tag{5}$$

where SWR_{exp} and SWR_{calc} represent experimental and calculated values of structural water content ratios, respectively. N is the total number of experiments, and z is the number of constants in the model.

The dehydration curves obtained from 360 W microwave power level was fitted to three different models, which are given in Table 1.

Table 1. Models used for fitting the experimental data

Model	Equation	Reference
Lewis	SWR=exp(-k×t)	22
Henderson and Pabis	SWR= a×exp(-k×t)	21
Wang and Singh	SWR=1+a×t+b×t^2	20

k is the structural water loss rate constant or coefficient (min^{-1}) and a and b are the constants (dimensionless).

RESULTS AND DISCUSSION

X-ray diffraction (XRD) pattern of pure tincalconite and dehydrated mineral at 360 W can be seen in Figure 4.

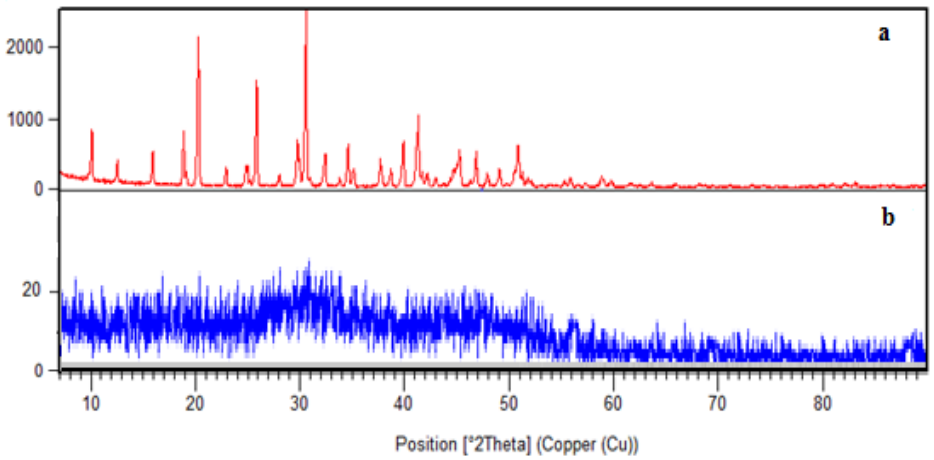

Figure 4. XRD patterns of tincalconite minerals a. Raw tincalconite mineral, b. Microwave dehydrated mineral at 360 W

According to Figure 4, it can be seen that microwave dehydrated mineral at 360 W has an amorphous structure.

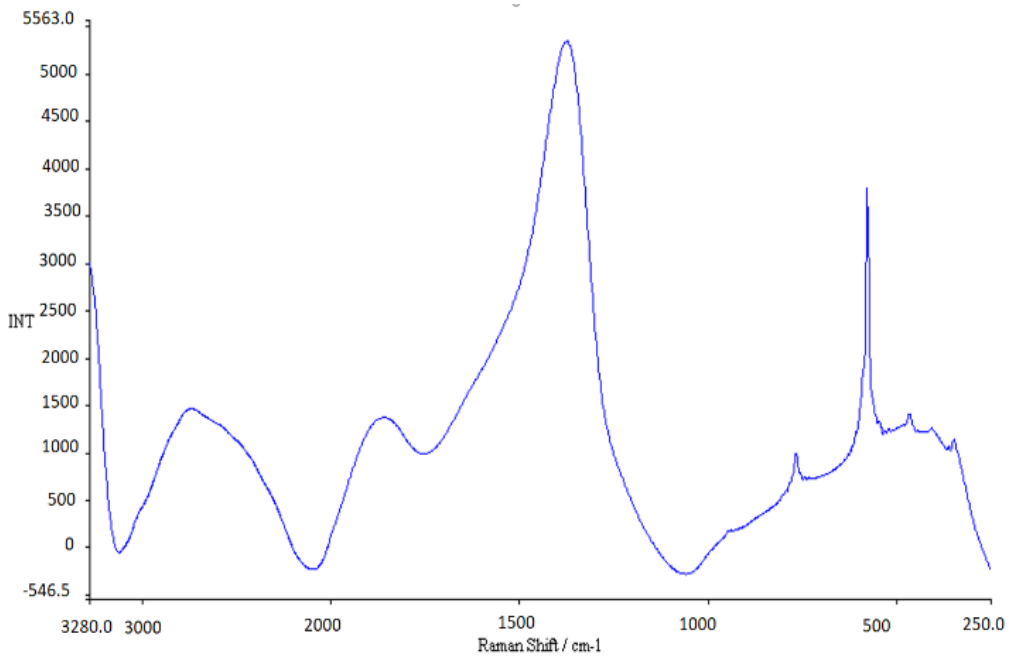

Figure 5. Raman spectrum at 180 W

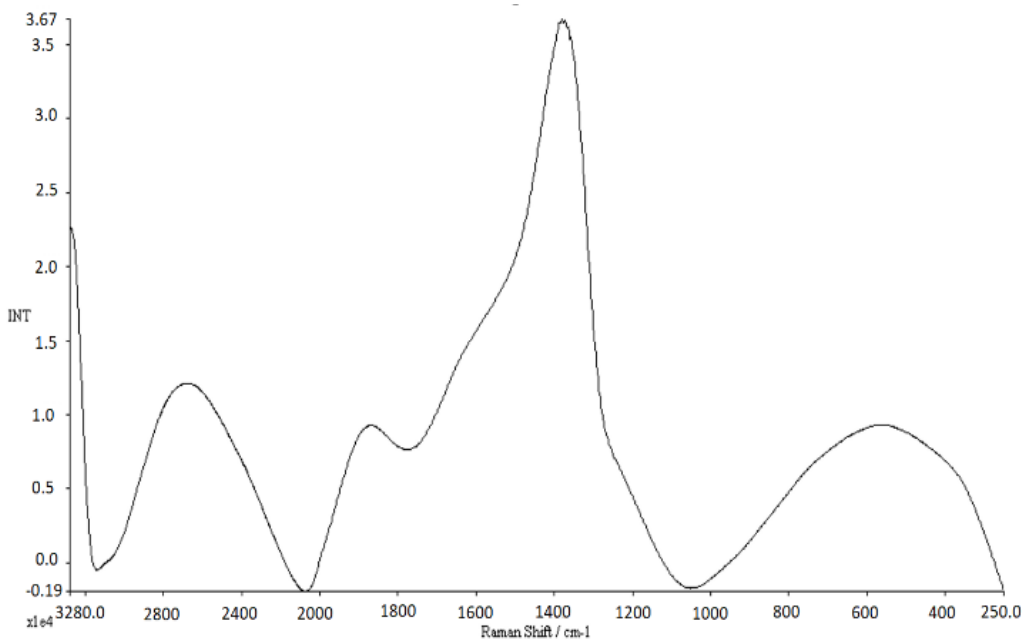

Figure 6. Raman spectrum at 360 W

As can be seen from the Raman analysis spectrum (Figure 5 and Figure 6), there is no peak value for tincalconite mineral. The results show that the samples were not suitable for Raman analysis.

Tincalconite has a theoretical amount of 29.47% of crystal water. As can be shown from Table 2, structural water was decreased over time.

Table 2. Microwave dehydration at 360 W

Time (min)	SWC	DR	SWR	ln(SWR)
0	0.4178	0	1.0000	-
1	0.3498	0.06803	0.8372	-0.1777
2	0.2917	0.05811	0.6981	-0.3594
3	0.2411	0.05057	0.5771	-0.5498
4	0.1962	0.04488	0.4697	-0.7557
5	0.1612	0.03504	0.3858	-0.9524
6	0.1318	0.02946	0.3153	-1.1542
7	0.1051	0.02666	0.2515	-1.3803
8	0.0805	0.02454	0.1928	-1.6462
9	0.0595	0.02102	0.1425	-1.9486
10	0.0413	0.01826	0.0988	-2.3150
11	0.0279	0.01332	0.0669	-2.7048
12	0.0167	0.01121	0.0401	-3.2176
13	0.0104	0.00631	0.0249	-3.6911
14	0.0041	0.00630	0.0099	-4.6178

If the results of experiments were compared, it can be said that dehydration time is longer at 180 W power level. When dehydration time is 14 minute at 360 W power level, this time is 24 minute at 180 W power level. If the results of experiments were compared, it can be said that dehydration time is longer at 360 W power level. We can said that if microwave power increased, dehydration time is longer.

In Table 2 and 3, it can be seen that drying rate (DR) and moisture rate (MR) were decreased proportionally.

Table 3. Microwave dehydration at 180 W

Time (min)	SWC	DR	SWR	ln(SWR)
0	0.4228	0	1.0118	
2	0.3638	0.02948	0.8707	-0.1385
4	0.3078	0.02802	0.7365	-0.3058
6	0.2685	0.01962	0.6426	-0.4422
8	0.2412	0.01368	0.5772	-0.5496
10	0.2229	0.00911	0.5336	-0.6281
12	0.2188	0.00209	0.5236	-0.6471
14	0.2019	0.00843	0.4832	-0.7273
16	0.1942	0.00385	0.4648	-0.7661
18	0.1802	0.00702	0.4312	-0.8411
20	0.1711	0.00456	0.4094	-0.8931
22	0.1417	0.01470	0.3390	-1.0817
24	0.1382	0.00174	0.3307	-1.1066

When the first step of the changes in structure water content were examined at 180 and 360 watts, it appears that these values were decreasing suddenly. The changes in the later steps are less than the decrease in the first step.

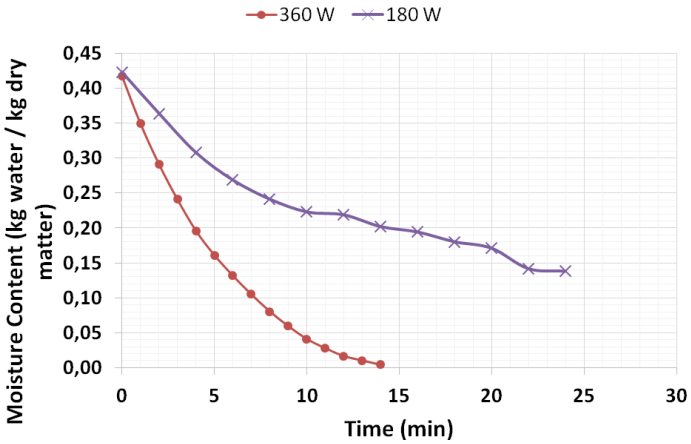

Figure 7. Moisture contents of tincalconite with changing in dehydration time

When t equals zero, the moisture content is 42% (kg water/kg dry matter) at all 180 and 360 W power level. After one minute, it was taken sample from microwave oven, the biggest drop has at 360 W power level. When the graph (Figure 7) was examined, a rapid decline was observed in the first measurement at 360 W power level. Then, it continued to decrease step by step. At 12, 13 and 14 min, it was seen that the change was very little.

In Figure 8, x-axis and y-axis represent the drying rate and moisture content at 180 and 360 W. According to the graph, before the sample begins to dehydration in the microwave oven, the dehydration rate is zero. In the first measurement, the dehydration rate was the maximum point at which the rate could be reached.

Dehydration processes of hydrate structures include the rising rate, constant and falling periods [6]. At 180 and 360 W, rising rate period was observed at the SW values between 0.42 and 0.36 kg structural water / kg dehydrated mineral and 0.42 and 0.35 kg structural water / kg dehydrated mineral, respectively. Likewise, the falling rate period was observed at the SW values between 0.36 and 0.14 kg structural water / kg dehydrated mineral, 0.35 and 0.00 kg structural water / kg dehydrated mineral for the 180 and 360 W, respectively.

In Figure 7 and Figure 8 show that the structural water of tincalconite did not decompose completely at 180 W power level. For this reason, microwave power may not be unsufficient in dehydration process or the sample may take moisture due to its longer time at 180 W power level.

The kinetic parameters of dehydration was determined by using the drying kinetic models of Lewis, Henderson and Pabis and Wang and Singh.

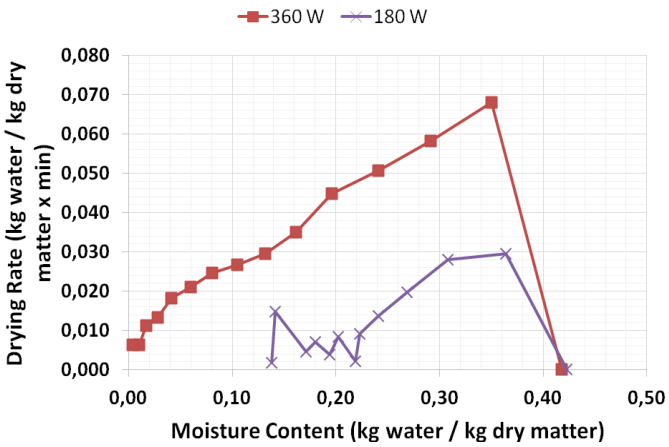

Figure 8. Drying rate of tincalconite by changing moisture content

Table 4. Results of dehydration models

Model	Parameter	360 W
Lewis	k	0.203107
	R^2	0.989870
	χ^2	0.001003
	RMSE	0.030596
Henderson and Pabis	a	1.034404
	k	0.209893
	R^2	0.991410
	χ^2	0.000916
	RMSE	0.028176
Wang and Singh	a	-0.148675
	b	0.005698
	R^2	0.996555
	χ^2	0.000367
	RMSE	0.017841

According to Table 4, Wang and Singh model best fits the data with the coefficient of regression (R^2) value of 0.9965.

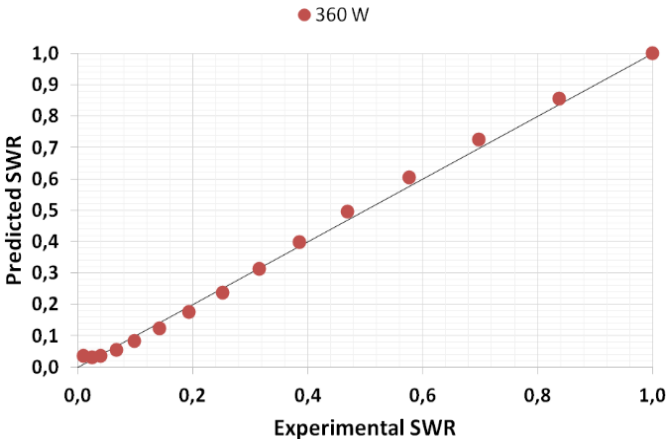

Figure 9. Wang and Singh Model

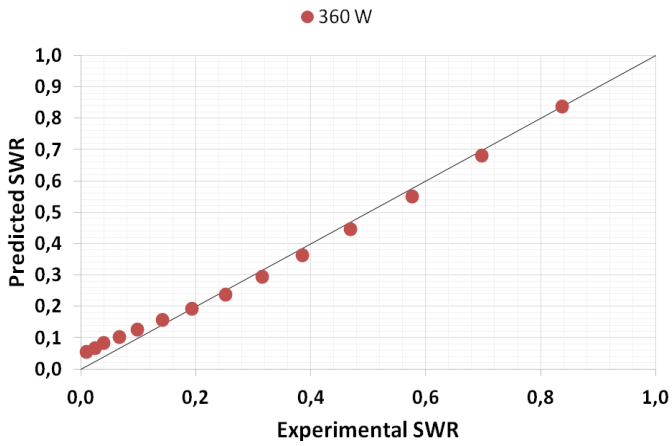

Figure 10. Henderson and Pabis Model

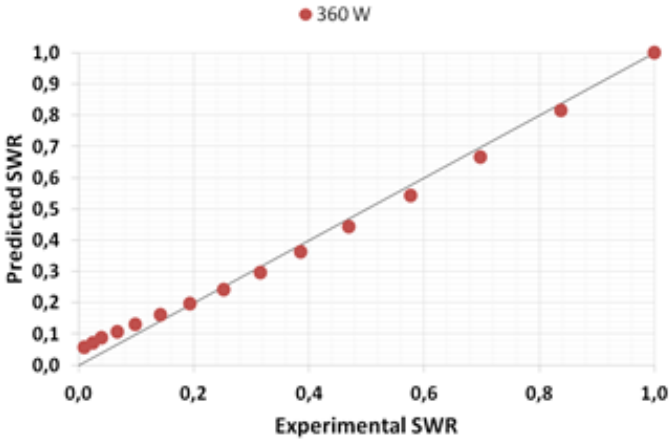

Figure 11. Lewis Model

The matching of the experiment and the dehydration models was determined by the coefficient of regression, root mean squared error and χ^2. If R^2 value is close to 1 and RMSE and χ^2 is close to 0, the experimet matches with the model.

In Figure 9, Figure 10 and Figure 11, experimental and predicted SWR values are around x equals to y line. This was showed suitability of the matching of the drying models. Deviations which around x equals to y line will increase errors in the drying models.

CONCLUSION

In this study, thermal dehydration behavior of tincalconite mineral is experimented by different microwave energy. The results showed that microwave power was the most important variable in the experiment. Microwave power levels were determined as 180 and 360 W. Dehydration processes of hydrate structures include the rising rate, constant and falling periods.

If microwave powers are compare, it can be concluded 360 W has better yield than 180 W for the dehydration process. At the end of the dehydration time in microwave of 14 mins and 360 W microwave power, all of structural water is removed from the mineral. Furthermore, Lewis model, Henderson and Pabis model and Wang and Singh model are applied for the experiment results. According to R^2, RMSE and χ^2 values, it was determined that Wang and Singh model was suitable for tincalconite. For tincalconite mineral, the highest R^2 and the lowest χ^2 and RMSE values are obtained as 0.9965, 0.000367 and 0.017841, respectively.

As a result of the XRD analysis, the dehydrated sample can not be determined by XRD due to the lack of characteristic peak observation, which indicates the amorphous structure formation. Additionally, the dehydrated samples did not observe any peak for Raman analysis.

In conclusion, tincalconite is a suitable mineral for the investigation of thermal dehydration kinetics using microwave energy. Under suitable conditions, the structural water of tincalconite mineral can be dehydrated using microwave energy.

NOMENCLATURE

DTG	Differential thermal gravimetric analysis
TGA	Thermal gravimetric analysis
DTA	Differential thermal analysis
XRD	X-ray diffraction
SWC	Structural water content
DR	Drying rate
SWR	Structural water ratio
MR	Moisture rate
DM	Drying matter
R^2	Coefficient of regression
RMSE	Root mean squared error

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