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The effect of the molar ratio of cations and citric acid on the synthesis of barium ferrite using a citrate process

WEN-JIUNG LEE, TSANG-TSE FANG
Department of Materials Science and Engineering, National Cheng Kung University, Tainan, 70101 Taiwan

A model is presented to evaluate the concentration of species in a citric solution for preparing barium ferrite powder. The evaluated concentration of species provides valuable information and help in selecting the optimal condition for preparation of the barium ferrite powder using the citrate process. The influence of the molar ratio of cations and citric acid on the formation of barium ferrite is studied. The formation temperature of barium ferrite decreases as the ratio increases. When the molar ratio of cations and citric acid is 13:20, the barium ferrite can completely form at 700 °C.

1. Introduction

Barium ferrite of magnetoplumbite structure is chemically stable and has excellent magnetic properties. Since its introduction by the Phillips laboratory in 1952, it has been used widely in industry. In recent years, barium ferrite particulate media have generated a lot of research interest for advanced magnetic recording applications, e.g. video recorder and flexible disk memories because of their high recording density and relatively low manufacturing cost [1]. The characteristics of the barium ferrite powder are of great importance because of their influence on the quality of the final product. The conventional method of preparation of the powder is to calcine the mixture of barium carbonate and iron oxide at a high temperature, which has disadvantages of large aggregates and inhomogeneous compositions. Several chemical methods [2, 3] were usually reported to be able to overcome these problems, but their control of the homogeneity of composition is overestimated, and aggregation of powders using these methods cannot be escaped.

The Pechini or citrate process [4] was usually considered to have the advantage of mixing ions on the atomic scale in the liquid state, so it is easy to control accurately the composition of the powder. However, there are many types of cation citrate complexes in the solution, so the concentration of citric acid could affect the formation of citrate complexes and further affect precipitation and segregation during gelling and charring, respectively. Moreover, Lessing [5] showed that the molar ratio of citric acid and ethylene glycol could affect the powder morphology. Messing [6] also reported that the pH value of solution has an influence on the powder morphology of $BaTiO_3$. Therefore, in this investigation [7–9], a model is presented to evaluate the influence of the cations and citric acid on the concentration of the cation citrate complexes in solution, which in turn would provide the citrate or Pechini process with effective control and predictable compositions in preparing the barium ferrite powder.

2. Experimental procedure

The Fe-solution was prepared by dissolving $Fe(NO_3)_3$ in distilled water, and the iron content in the solution was quantitatively determined. The Fe-solution and $BaCO_3$ dissolved in the variably concentrated citric acid solution were in the molar ratio 12:1. The concentrations of Ba, Fe and nitrate ions, 0.01, 0.12 and 0.36 M, respectively, were kept constant; but the concentration of the citric acid and the pH value were varied. Analytical grade NH_4OH solution was used to adjust the pH of the solution. A few per cent of ethylene glycol were added in order to produce long-chain organic molecules. The clear solution was slowly heated and evaporated until a highly viscous gel was formed.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were employed to investigate the thermal decomposition of gel at a heating rate of 10 °C min^{-1}. Gels of different citric acid concentrations had similar thermal behaviours according to DTA. Weight loss and exothermic heat were large below 400 °C, as shown in Fig. 1. In order to avoid deflagration, the gels were prefired at 400 °C to burn off the organic matter, referred to as the "precursor". The precursor was heated at different temperatures in the range 600–900 °C. X-ray diffraction (using CuK$_\alpha$ radiation) was used to examine the phases of the calcined powder.

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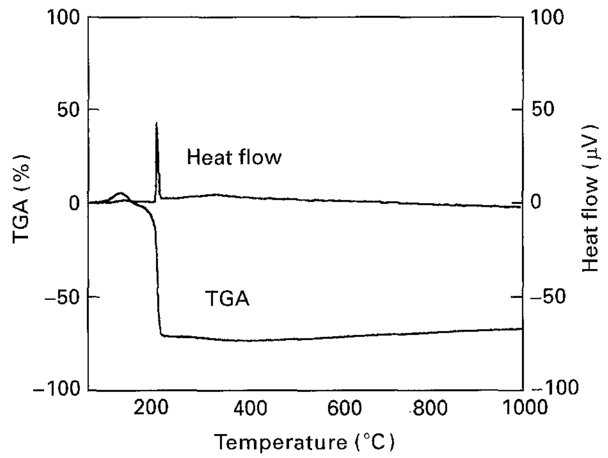

Figure 1 Thermal behaviour of the gel in which the molar ratio of cations and citric acid is 13:13.

3. A model for evaluating the concentration of iron and barium citrate complexes in a solution under different conditions

In this model, the concentration of citric acid, pH and temperature affecting the formation of iron and barium citrate complexes have been taken into consideration. Several assumptions involved were that

1. solutions were assumed to be ideal,
2. one citrate ion could form a chelate with only one cation, and
3. concentration of the complexes could not change as temperature increased.

The concentration at 25 °C was taken as the reference.

The dissociation of the citric acid involving three stages of ionization was written as follows

$$H_3Cit \Leftrightarrow H_2Cit^- + H^+$$

$$k_1 = \frac{[H_2Cit^-][H^+]}{[H_3Cit]} \quad (1)$$

$$H_2Cit^- \Leftrightarrow HCit^{2-} + H^+$$

$$k_2 = \frac{[HCit^{2-}][H^+]}{[H_2Cit^-]} \quad (2)$$

$$HCit^{2-} \Leftrightarrow Cit^{3-} + H^+$$

$$k_3 = \frac{[Cit^{3-}][H^+]}{[HCit^{2-}]} \quad (3)$$

H_3Cit represents citric acid and k_1, k_2, k_3 are the equilibrium constants of citric acid. Equations 1, 2 and 3 could be rewritten as

$$[H_3Cit] = \frac{[Cit^{3-}][H^+]^3}{k_1 k_2 k_3} \quad (4)$$

$$[H_2Cit^-] = \frac{[Cit^{3-}][H^+]^2}{k_2 k_3} \quad (5)$$

$$[HCit^{2-}] = \frac{[Cit^{3-}][H^+]}{k_3} \quad (6)$$

The total iron concentration is the sum of equilibrated citric complexes of iron

$$[Fe^{3+}]_T = [Fe^{3+}] + [Fe(HCit)^+] + [Fe(Cit)] + [Fe(OH)^{2+}] \quad (7)$$

where $[Fe^{3+}]_T$ is the total concentration of iron in the solution. The formation of $[Fe(HCit)^+]$ complex is

$$Fe^{3+} + HCit^{2-} \Leftrightarrow Fe(HCit)^+$$

$$k_4 = \frac{[Fe(HCit)^+]}{[Fe^{3+}][HCit^{2-}]} \quad (8)$$

Combining Equations 6 and 8, one obtains

$$[Fe(HCit)^+] = [Fe^{3+}][Cit^{3-}][H^+]k_4/k_3 \quad (9)$$

Similarly, one obtains

$$[Fe(Cit)^+] = [Fe^{3+}][Cit^{3-}]k_5 \quad (10)$$

$$[Fe(OH)^{2+}] = [Fe^{3+}][OH^-]k_6 \quad (11)$$

Substituting Equations 9–11 into Equation 7, one obtains

$$[Fe^{3+}]_T = [Fe^{3+}](1 + k_6[OH^-]) + [Fe^{3+}][Cit^{3-}](k_4[H^+]/k_3 + k_5) \quad (12)$$

The total barium concentration is expressed as follows

$$[Ba^{2+}]_T = [Ba^{2+}] + [Ba(H_2Cit)^+] + [Ba(HCit)] + [Ba(Cit)^-] + [Ba(NO_3)^+] \quad (13)$$

where $[Ba^{2+}]_T$ is the total concentration of barium in the solution. The formation of $[Ba(H_2Cit)^+]$ complex is

$$Ba^{2+} + H_2Cit^- \Leftrightarrow Ba(H_2Cit)^+$$

$$k_7 = \frac{[Ba(H_2Cit)^+]}{[Ba^{2+}][H_2Cit^-]} \quad (14)$$

Combining Equations 5 and 14, one obtains

$$[Ba(H_2Cit)^+] = [Ba^{2+}][Cit^{3-}][H^+]^2 k_7/(k_2 k_3) \quad (15)$$

Similarly, one obtains

$$[Ba(HCit)] = [Ba^{2+}][Cit^{3-}][H^+]k_8/k_3 \quad (16)$$

$$[Ba(Cit)^-] = [Ba^{2+}][Cit^{3-}]k_9 \quad (17)$$

$$[Ba(NO_3)] = [Ba^{2+}][NO_3^-]k_{10} \quad (18)$$

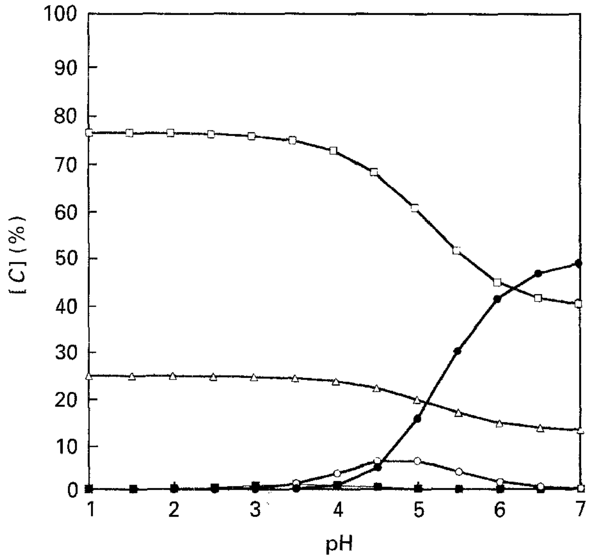

Figure 2 The evaluated concentration of barium species in the solution, in which the molar ratio of cations and citric acid is 13 : 13 : (Δ) Ba^{2+}, (□) $Ba(NO_3)^+$, (●) $Ba(Cit)^-$, (○) Ba(HCit), and (■) $Ba(H_2Cit)^+$.

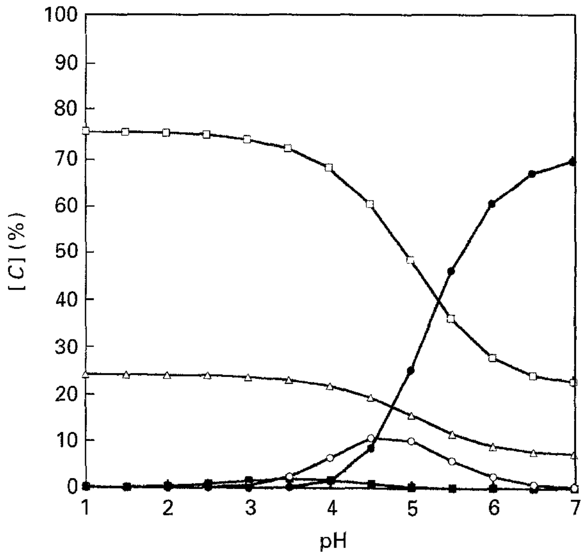

Figure 3 The evaluated concentration of barium species in the solution, in which the molar ratio of cations and citric acid is 13 : 14 : (Δ) Ba^{2+}, (□) $Ba(NO_3)^+$, (●) $Ba(Cit)^-$, (○) Ba(HCit), and (■) $Ba(H_2Cit)^+$.

Substituting Equations 15–18 into Equation 13, one obtains

$$[Ba^{2+}]_T = [Ba^{2+}](1 + k_{10}[NO_3^-]) + [Ba^{2+}][Cit^{3-}]([H^+]^2 k_7/k_2\, k_3) + [H^+]k_8/k_3 + k_9) \qquad (19)$$

Finally, the total citrate concentration could be expressed as the sum of all equilibrated citrate complexes of concentration as follows

$$[Citrate]_T = [H_3Cit] + [H_2Cit^-] + [HCit^{2-}] + [Cit^{3-}] + [Fe(HCit^+] + [Fe(Cit)] + [Ba(H_2Cit)^+] + [Ba(HCit)] + [Ba(Cit)^-] \qquad (20)$$

where [Citrate] $_T$ is the total concentration of citric acid in the solution.

Substituting Equations 4–6, 9,10, 15–17 into Equation 20, one obtains

$$[Citrate]_T = [Cit^{3-}]\,([H^+]^3/(k_1k_2k_3) + [H^+]^2/(k_2k_3) + [H^+]/k_3 + 1) + [Fe^{3+}][Cit^{3-}] \times ([H^+]k_4/k_3 + k_5) + [Ba^{2+}][Cit^{3-}] \times ([H^+]^2k_7/(k_2k_3) + [H^+]\, k_8/k_3 + k_9) \qquad (21)$$

It should be noted that the nitrate concentration should be considered in the solution because it also formed a complex with barium ion

$$[NO_3^-]_T = [NO_3^-] + [Ba(NO_3^-)^+] \qquad (22)$$

where $[NO_3^-]_T$ is the total concentration of nitrate ion in the solution.

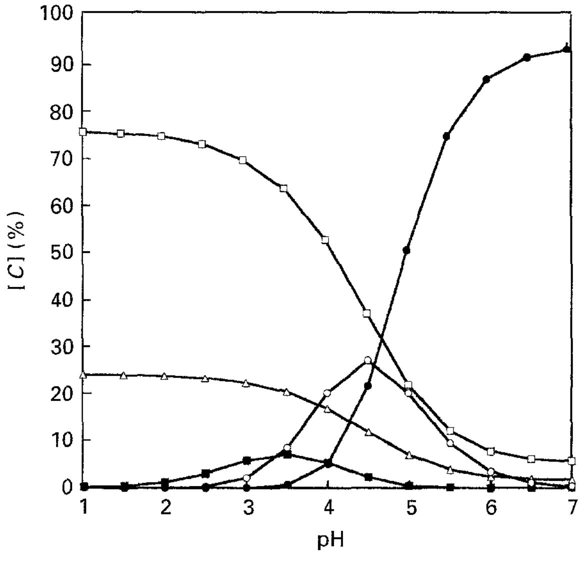

Figure 4 The evaluated concentration of barium species in the solution, in which the molar ratio of cations and citric acid is 13 : 20 : (Δ) Ba^{2+}, (□) $Ba(NO_3)^+$, (●) $Ba(Cit)^-$, (○) Ba(HCit), and (■) $Ba(H_2Cit)^+$.

Substituting Equation 18 into Equation 22, one obtains

$$[NO_3^-]_T = [NO_3^-] + [Ba^{2+}][NO_3^-]k_{10} \qquad (23)$$

For simplification, one rewrites these Equations 12, 19, 21 and 23 as

$$[Citrate]_T = A[Cit^{3-}] + B[Cit^{3-}][Fe^{3+}] + C[Cit^{3-}][Ba^{2+}]$$

$$[Fe^{3+}]_T = D[Fe^{3+}] + B[Cit^{3-}][Fe^{3+}]$$

$$[Ba^{2+}]_T = [\ Ba^{2+}] + E[Ba^{2+}][NO_3^-] + C[Cit^{3-}][Ba^{2+}]$$

$$[NO_3^-]_T = [NO_3^-] + E[Ba^{2+}][NO_3^-]$$

TABLE 1 Equilibrium constants for citric acid and cation complexes at 25 °C

Species	Equilibrium constant	Reference
H_3Cit	$k_1(1.17 \times 10^{-3})$	[10]
H_2Cit^-	$k_2(4.17 \times 10^{-5})$	[10]
$HCit^{2-}$	$k_3(1.82 \times 10^{-6})$	[10]
$Fe(HCit)^+$	$k_4(5 \times 10^6)$	[10]
$Fe(Cit)$	$k_5(1.58 \times 10^{11})$	[10]
$Fe(OH)^{2+}$	$k_6(1 \times 10^{11})$	[11]
$Ba(H_2Cit)^+$	$k_7(6.17)$	[12]
$Ba(HCit)$	$k_8(56.23)$	[12]
$Ba(Cit)^-$	$k_9(776.25)$	[12]
$Ba(NO3)^+$	$k_{10}(8.7)$	[13]

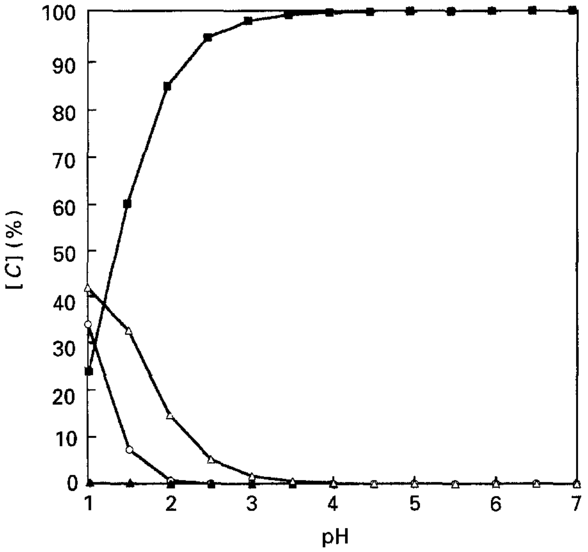

Figure 5 The evaluated concentration of iron species in the solution, in which the molar ratio of cations and citric acid is 13:13: (○) Fe^{3+}, (▲) $Fe(OH)^{2+}$, (△) $Fe(HCit)^+$, and (■) Fe(Cit).

where A, B, C, D and E are defined as follows

$$A = [H^+]^3/k_1k_2k_3) + [H^+]^2/(k_2k_3) + [H^+]/k_3 + 1$$

$$B = [H^+]k_4/k_3 + k_5$$

$$C = [H^+]^2k_7/(k_2k_3) + [H^+]k_8/k_3 + k_9$$

$$D = 1 + k_6[OH^-]$$

$$E = k_{10}$$

The total equilibrium constants are listed in Table I.

4. Results and discussion

Figs 2–4 show the theoretically calculated barium complex concentrations at different pH values and concentrations of citric acid. In these figures, the concentration of barium and barium nitrate ions decreases with increasing pH values; however, the concentration of the $Ba(Cit^{3-})$ complex increases at pH values > 4. The concentrations of the other two barium citrate complexes $[Ba(H_2Cit)^+$ and $Ba(HCit)]$ existing in a certain range of pH, initially increase and finally decrease with increasing pH values. As the concentration of citric acid increases, the concentration of the barium cation and barium nitrate ion reduce but the concentration of the $Ba(Cit^{3-})$ complex increases when pH > 4. The concentrations of $Ba(H_2Cit)^+$ and Ba(HCit) also increase as the concentration of citric acid increases.

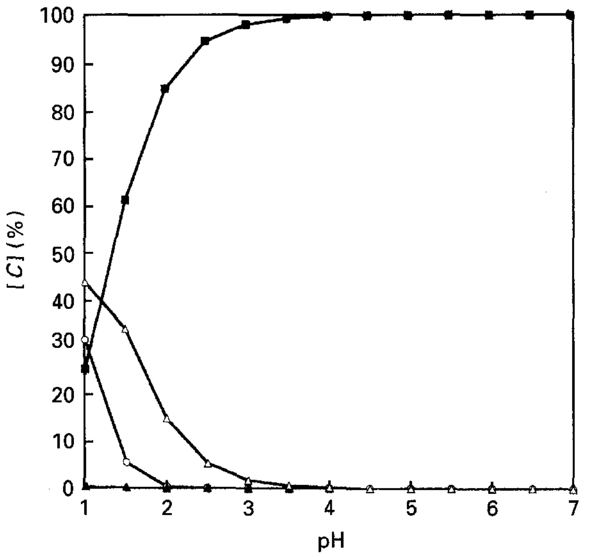

Figure 6 The evaluated concentration of iron species in the solution, in which the molar ratio of cations and citric acid is 13:14: (○) Fe^{3+}, (▲) $Fe(OH)^{2+}$, (△) $Fe(HCit)^+$, and (■) Fe(Cit).

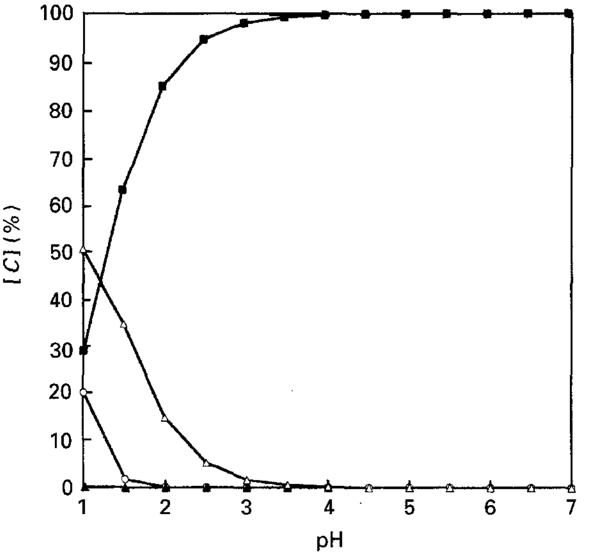

Figure 7 The evaluated concentration of iron species in the solution, in which the molar ratio of cations and citric acid is 13:20: (○) Fe^{3+}, (▲) $Fe(OH)^{2+}$, (△) $Fe(HCit)^+$, and (■) Fe(Cit).

Figs 5–7 show the theoretically calculated iron complex concentrations at different pH values and concentrations of the citric acid. The concentration of the iron complexes had the same trend in these three figures, i.e. the concentration of citric acid has little influence on those of the iron complexes, but as pH values increase only $Fe(Cit^{3-})$ increases, the rest of the complexes decreasing, and at pH > 3, all iron ions completely form iron citrate complex $Fe(Cit^{3-})$.

It was usually found that the $Ba(NO_3)_2$ compound is easy to precipitate during the evaporation process if the processing parameters are not properly controlled, which in turn would form $BaCO_3$ during decomposi-

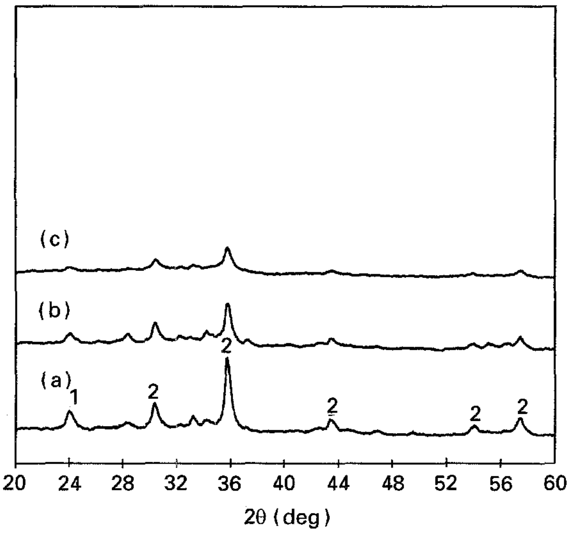

Figure 8 X-ray diffraction patterns of the gel with different (cations): (citric acid) molar ratio decomposed at 400 °C: (a) 13 : 13, (b) 13 : 14, and (c) 13 : 20. Where (1) $BaCO_3$, and (2) γ-Fe_2O_3.

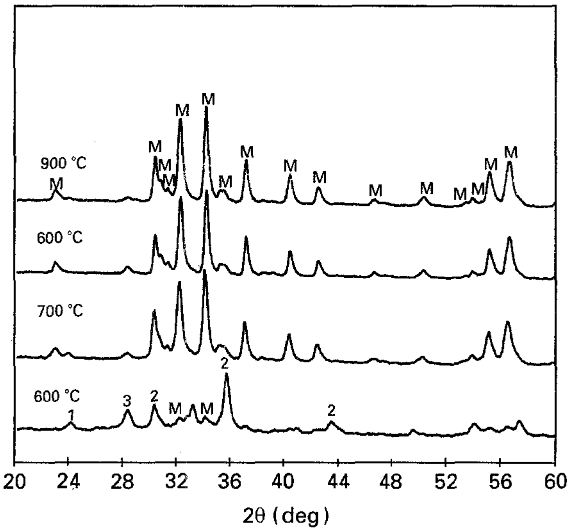

Figure 9 X-ray diffraction patterns of the precursor with a (cations): (citric acid) molar ratio 13 : 13, which was heated at different temperatures: (M) $BaFe_{12}O_{19}$, (1) $BaCO_3$, (2) γ-Fe_2O_3, and (3) $BaFe_2O_4$.

tion and increase the calcination temperature. Therefore, to reduce the concentrations of barium and barium nitrate ions would be very important in avoiding the precipitation of $Ba(NO_3)_2$. According to the theoretical model (Figs 2–4), at a given concentration of citric acid, the amount of the precipitation of $Ba(NO_3)_2$ will be reduced as pH increases to seven because of reduction of the barium nitrate ion, which is consistent with the observations, i.e. no precipitation occurred at pH > 5 in this investigation.

Moreover, as observed in Figs 2–4, the concentration of citric acid has a significant influence on those of the barium ion, barium nitrate ion and barium citrate complexes in the solution, which in turn would affect the precipitation of $Ba(NO_3)_2$ during the evaporation process. In order to further evaluate the theoretical model, the pH value of solution was fixed at seven and the concentration of citric acid varied. As inferred from the Figs 2–4, the precipitate of $Ba(NO_3)_2$ will decrease as the concentrations of barium ion and barium nitrate ion decrease; therefore, $BaCO_3$ will reduce during the decomposition process. As observed in Fig. 8, the amount of γ-Fe_2O_3 and $BaCO_3$ reduces as the cation and citric acid molar ratio increases, which further supports this model. Since $BaCO_3$ and γ-Fe_2O_3 reduce as the ratio increases, the intermediate phase of $BaFe_2O_4$ (Figs 9–11), which is usually observed in the solid state reaction, apparently reduces. Thus, M type ferrite could form completely at low temperature, 700 °C. Accordingly, the model proposed in this investigation to evaluate theoretically the concentration of species in a solution could provide valuable information in preparing ceramic powders using the citrate process.

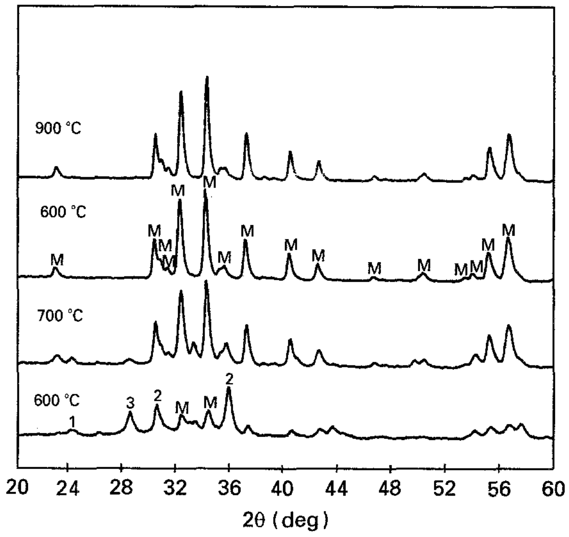

Figure 10 X-ray diffraction patterns of the precursor with a (cations): (citric acid) molar ratio of 13:14, which was heated at different temperatures: (M) $BaFe_{12}O_{19}$, (1) $BaCO_3$, (2) γ-Fe_2O_3, and (3) $BaFe_2O_4$.

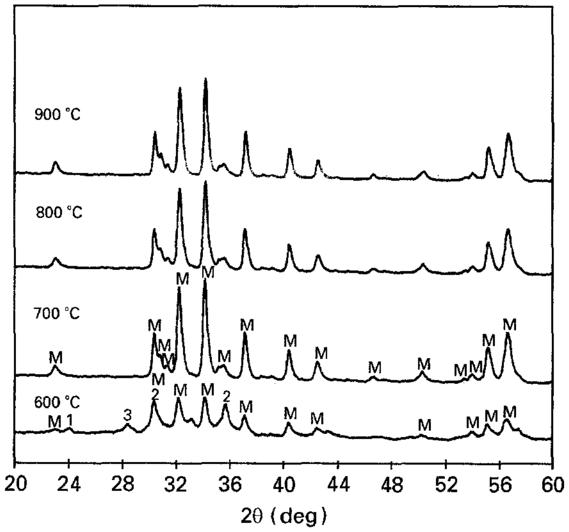

Figure 11 X-ray diffraction patterns of the precursor with a (cations): (citric acid) molar ratio of 13 : 20, which was heated at different temperatures: (M) $BaFe_{12}O_{19}$, (1) $BaCO_3$, (2) γ-Fe_2O_3, and (3) $BaFe_2O_4$.

5. Conclusions

The concentrations of barium and barium nitrate ions are the major factors affecting the precipitation of $Ba(NO_3)_2$ during the evaporation process and the formation of $BaCO_3$ during the decomposition process. Increasing the concentration of citric acid and pH values can reduce the amount of $BaCO_3$ and the formation temperature of barium ferrite. The barium ferrite can completely form at 700 °C as the ratio of cations and citric acid is 13 : 20 and the pH value of the solution is seven. The theoretical model could provide valuable information and help in preparing ceramic powders using the citrate process.

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