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Effect of ultrasonic irradiation on precipitation of lead oxalate from aqueous solution

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A precipitation reaction between a lead-nitrate solution and oxalic acid was carried out with and without ultrasound, and the effect of ultrasonic irradiation in solution was investigated. The oxalate precipitates were a mixture of Pb oxalate and an X-phase, which seems to be a lead salt containing $C_2O_4^{2-}$, NO_3^-, and OH^-. It was found that irradiation with ultrasound during the precipitation reaction accelerated the formation of the X-phase.

1. Introduction

Irradiation of a solution with ultrasonic waves during a precipitation reaction may accelerate the reaction [1], and it may be possible to control the crystallization of the precipitates [2, 3, 4]. Also, a reaction which does not take place under normal conditions is expected to proceed via the ultrasonic energy [5]. For the improvement of the homogeneity in the precipitates, ceramic powders are often prepared by coprecipitation processing which is generally conducted by introducing a stream of a solution containing cationic ions into an excess-precipitant solution. Even in this method, it is still difficult to precipitate all of the cations simultaneously, because local compositional fluctuation is inevitable [6] owing to the different reactivities of each cation with the precipitant. When ultrasonic energy activates the reactants, it is expected that all the cations are coprecipitated at similar reaction rates different from those of the normal reaction, and that the local compositional fluctuation would disappear. We applied ultrasound during the hydrolysis of metal alkoxides to facilitate the preparation of a mullite-composition powder [7] and, by this ultrasonic irradiation, the hydrolysis rate of Si alkoxide was increased to the same degree as that of Al alkoxide so that compositional segregation was avoided. There are few possible applications of ultrasound for the preparation of a ceramic raw powder, however. One of the authors has also been investigating with co-workers the effect of ultrasonic irradiation on the precipitation of Pb–Zr–Ti oxalate from aqueous solution [8].

In this work, to gain a better understanding of the effect in the ternary system, ultrasonic irradiation was applied to the lead-oxalate-precipitate reaction alone.

2. Experimental procedure

High-purity $Pb(NO_3)_2$ (> 99%) was used as the source of Pb and > 99% pure $H_2C_2O_4$ was used as the precipitant. As is shown in the flow diagram of the preparation sequence in Fig. 1 lead nitrate was dissolved in distilled water to prepare the aqueous solution of 0.028 mol l^{-1}. The lead-nitrate aqueous solution was added at various temperatures into a 0.028 mol l^{-1} solution of oxalic acid dissolved in ethanol under mechanical stirring (MS). Stage A in Fig. 1 was performed for 3 min. An ethanol solution was used because metal oxalates have very low solubilities in ethanol [9]. At the same time a small amount of ammonia solution, at various concentrations, was added in order to stabilize the oxalates [10]; it took 2 min to perform stage B. The precipitate was filtered, washed twice by ethanol and dried for 1.5 days in air at room temperature. Ultrasonic waves were applied to the solution during the precipitating treatment. Four kinds of ultrasonic frequencies/input-powers were employed, namely 200 kHz/120 W, 500 kHz/30 W, 1740 kHz/13 W, and 4000 kHz/14 W. The temperature of the reaction chamber was kept constant using a water bath, as is shown in Fig. 2, to exclude the influence of a temperature rise caused by the ultrasound. The precipitates were evaluated by

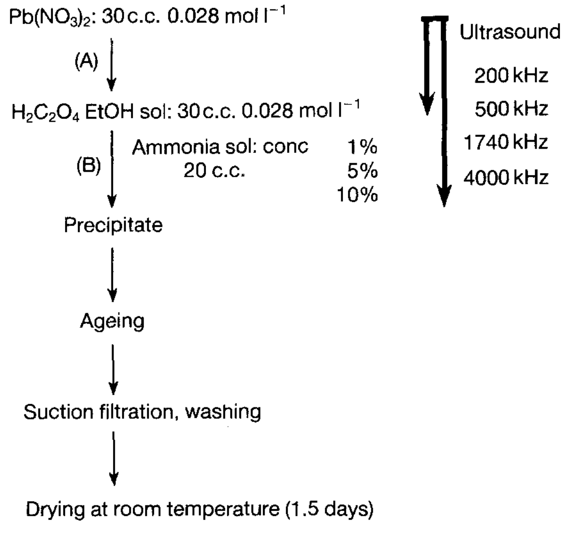


Figure 1 Flow chart of the experiment.

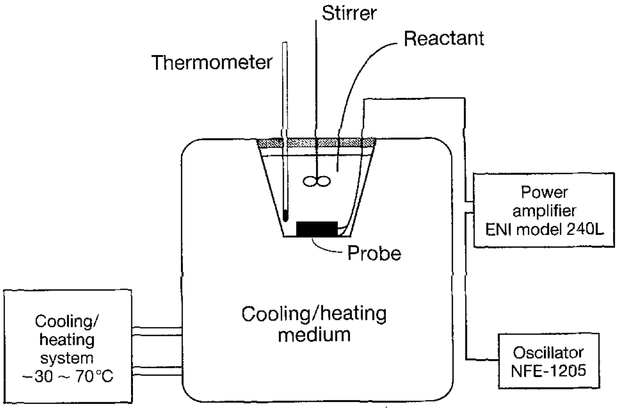


Figure 2 A schematic illustration of the apparatus.

X-ray diffraction (XRD), thermogravimetric/differential thermal analysis (TGA/DTA), scanning electron microscopy (SEM), and Fourier-transform infrared spectroscopy (FT-IR).

3. Results and discussion

3.1. Identification of the X-phase

XRD analysis revealed that most of the precipitates were a mixture of lead-oxalate anhydrate (PbC_2O_4) and the X-phase. The latter is an unknown phase at present. The precipitates, XRD patterns are shown in Fig. 3. The main peak intensity ratio of lead oxalate (0 1 1), (CuK_α $2\theta \fallingdotseq 26.3°$) to the X-phase ($2\theta \fallingdotseq 17.3°$) was calculated to roughly evaluate their relative amounts ($= PbC_2O_4/(PbC_2O_4 + \text{X-phase})$). By this evaluation, for example, the relative amount of PbC_2O_4 in Fig. 3b is about 5%. Under some conditions, a single phase of either PbC_2O_4 or the X-phase can be obtained. In the following, the characteristic differences in the two phases will be shown.

Fig. 4 shows scanning electron micrographs of these two phases. Their morphologies are different; that is, the PbC_2O_4 particles have a blocky shape and the X-phase is composed of plate crystals. Fig. 5 shows XRD patterns of the X-phase quenched at various temperatures. Lead nitrate and lead oxalate were observed at 240 °C and $Pb(NO_3)_2 \cdot 5PbO$ [11] was observed at 420 °C. Their DTA/TGA data are illustrated in Fig. 6. Lead oxalate, Fig. 6a, simply shows one exothermic peak at 360 °C on DTA, while the X-phase, Fig. 6b, shows three endothermic peaks at 180, 320 and 490 °C, and one exothermic peak at 350 °C. On the TGA curves, lead oxalate, Fig. 6a, has

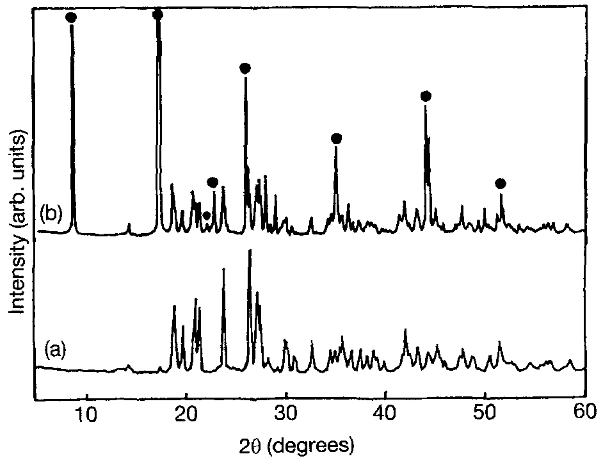


Figure 3 XRD patterns (CuK_α) of the precipitates for two ratios of PbC_2O_4 to the X-phase: (a) 100%, and (b) 5%. (●) X-phase.

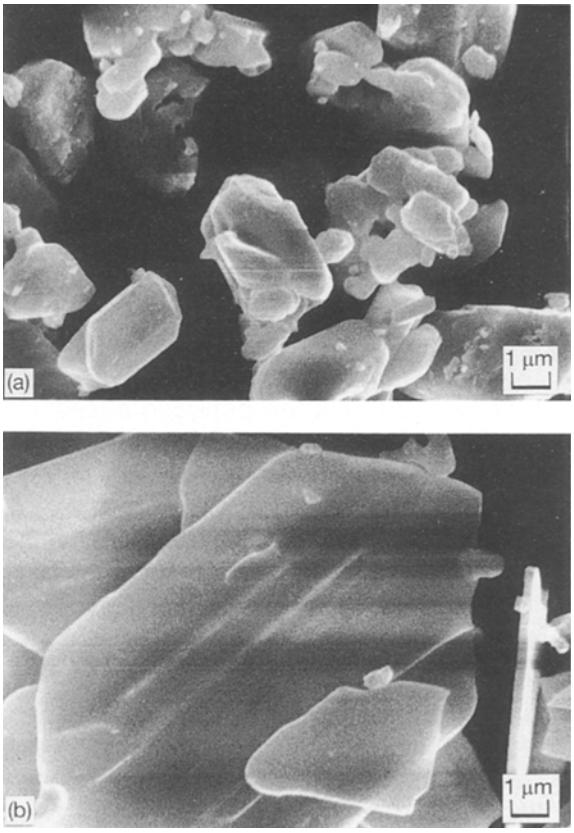


Figure 4 Scanning electron micrographs of the precipitates: (a) PbC_2O_4, and (b) X-phase.

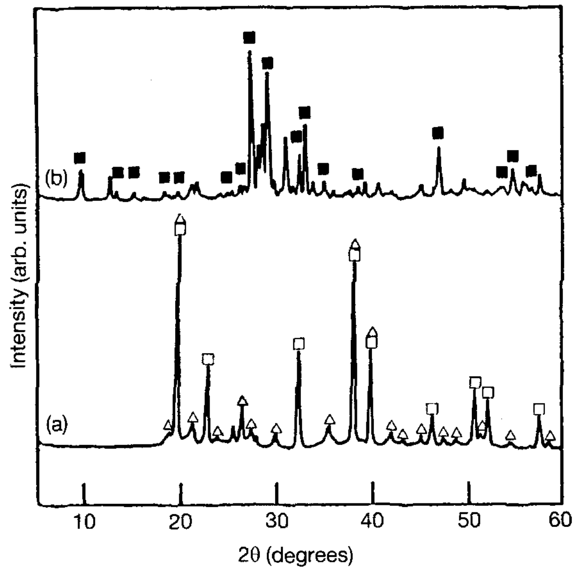


Figure 5 XRD patterns (CuK_α) of the X-phase at the following temperatures: (a) 240 °C, (□) $Pb(NO_3)_2$ and (△) PbC_2O_4; and (b) 410 °C, (■) $Pb(NO_3)_2 \cdot 5PbO$.

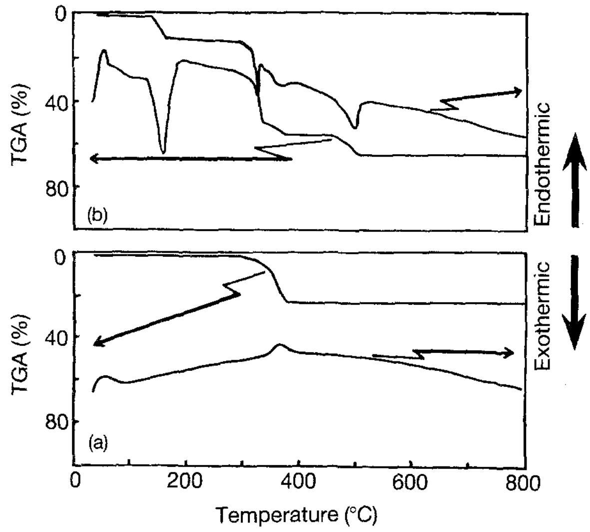


Figure 6 TGA and DTA curves of the precipitates: (a) PbC_2O_4, and (b) the X-phase.

a large weight loss at 300 ~ 360 °C, while the X-phase, Fig. 6b, reveals its first weight loss at about 180 °C, its second weight loss between 300 and 400 °C (due to the decomposition of oxalate [12]) and its third weight loss is by the decomposition of nitrate radical, as will be clarified later by FT-IR analysis. These results show that the X-phase seems to be a lead salt containing $C_2O_4^{2-}$, NO_3^- and OH^-. The exothermic reactions of lead oxalate at about 350 °C can be related to the combustion of CO which was generated from the decomposition of the oxalate. Fig. 7 is an FT-IR spectra of the powder of the X-phase at various temperatures. The band in the 1670–1640 cm^{-1} region is ascribed to $C_2O_4^{2-}$ [13]. With increasing treatment temperatures, this band became weaker. At the higher treatment temperature, 410 °C, the bands disappeared. This implies that the $C_2O_4^{2-}$ decomposed between 240 and 410 °C. The strong absorption band in the 1410–1340 cm^{-1} region and the weak peak in the 860–800 cm^{-1} region were due to NO_3^- [13]. The strong band exists up to 410 °C. It is confirmed from the FT-IR result that NO_3^- exists in the X-phase and that it does not decompose at 410 °C. Fig. 8 shows the XRD patterns of the precipitates heated at 10 °C min^{-1} up to 550 °C and then rapidly cooled to room temperature, where the volatile components in the precipitates are completely removed. The products were a mixture of massicot (high-temperature form, PbO) and litharge (low-temperature form, PbO). The pattern from lead oxalate showed mostly litharge, whereas the pattern from the X-phase showed predominantly massicot. It can be inferred that litharge resulted from the lower decomposition temperature of PbC_2O_4 and that the massicot resulted from the higher decomposition temperature of $Pb(NO_3)_2 \cdot 5PbO$, which is formed from the X-phase.

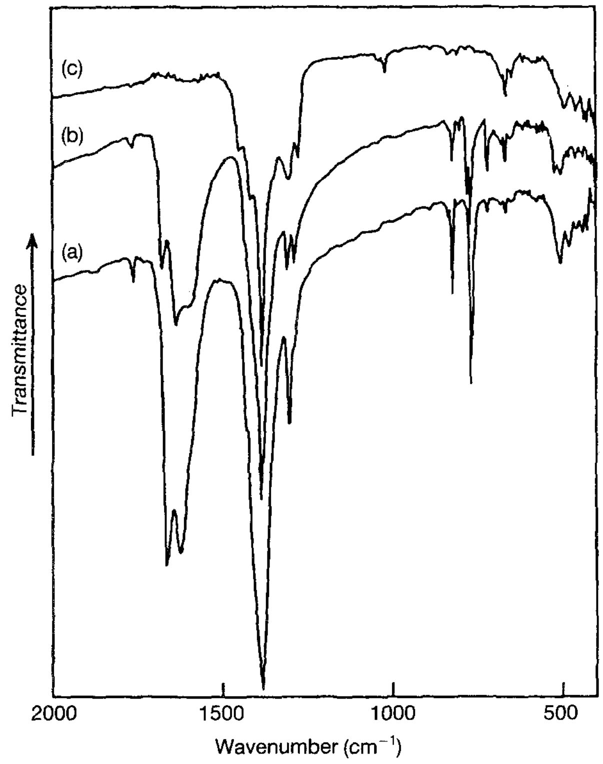


Figure 7 The FT-IR spectra of the X-phase quenched at various temperatures: (a) room temperature, (b) 240 °C, and (c) 410 °C.

3.2. Effect of ultrasonic irradiation

Fig. 9 shows the relative amounts of the X-phase and PbC_2O_4 in products at various temperatures and various ammonia concentrations with and without ultrasonic irradiation. Apparently, the relative amount of the X-phase in the precipitates increased with ultrasonic irradiation, (compared with the case with mechanical stirring) and with decreasing temperature and ammonia concentration. The amount of the X-phase also increased with the duration of stirring, as is shown in Fig. 10. Since the amount of the X-phase increased with the reaction time, it could be considered that the X-phase is stable, that lead oxalate is a metastable phase in this condition, and that the precipitate reaction is accelerated by the irradiation by ultrasound. The use of ultrasound to enhance chemical reactivity is becoming common [14]. The effects of

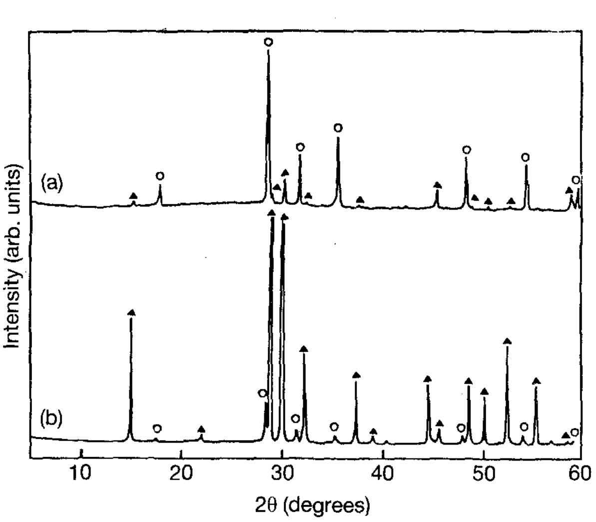
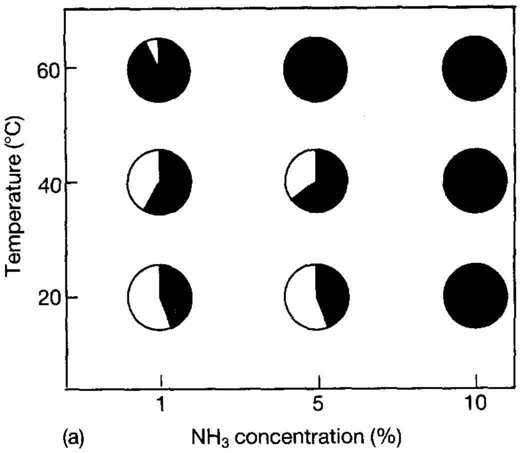


Figure 8 XRD patterns (CuK_α) of the precipitates at 550 °C: (a) PbC_2O_4, (▲) PbO (massicot) and (○) PbO litharge; and (b) 95% X-phase + 5% PbC_2O_4.



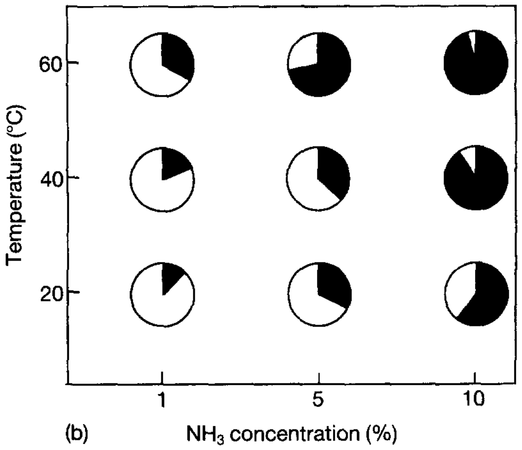


Figure 9 The ratio of PbC_2O_4 (0 1 1) and the X-phase was calculated by the XRD peak intensity. The relative amounts are denoted by black and white corresponding to PbC_2O_4 and the X-phase, respectively: (a) with mechanical stirring, and (b) with ultrasound (200 kHz–120 W).

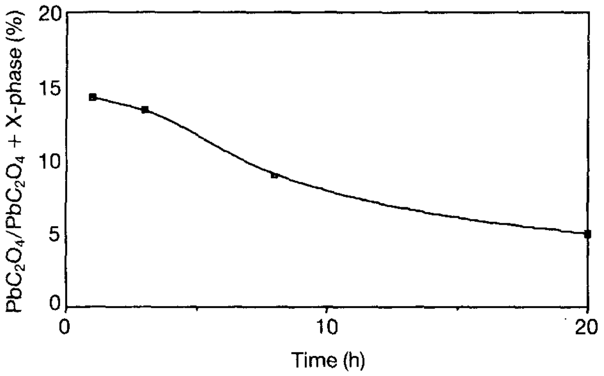


Figure 10 The ratio of PbC_2O_4 (0 1 1) and the X-phase calculated by the XRD peak intensity according to the reaction time at mechanical stirring 1% NH_4OH.

ultrasound applied to a solution can be attributed to three phenomena [15].

(i) rapid movement of fluids, caused by variation of sonic pressure which subjects the solvent to compression and rarefaction;

(ii) the formation and collapse of microbubbles (cavitation); and

(iii) microstreaming, which occurs when a large amount of vibrational energy is put into a small volume with little heating.

In general, a chemical reaction accelerates with increasing temperature. But in this reaction a different tendency was observed; that is, ultrasound accelerates the reaction, which enhances the reaction with decreasing reaction temperature. This phenomenon is very interesting. Further work will be necessary to explain the mechanism of the ultrasonic effect on the precipitate reaction in this lead-oxalate system.

4. Conclusion

The effect of ultrasonic irradiation on the precipitation of lead oxalate from a nitrate solution, and from an ethanol solution of oxalic acid, was investigated. The products were a mixture of lead oxalate and an X-phase. The relative amount of the X-phase increased with decreases in temperature and pH, and with increases in the reaction time. Irradiation with ultrasonic waves during the precipitation reaction accelerated the formation of the X-phase. The X-phase seems to be a lead salt containing $C_2O_4^{2-}$, NO_3^- and OH^-.

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