ELSEVIER

Journal of Alloys and Compounds 224 (1995) L1–L3

Journal of ALLOYS AND COMPOUNDS

Letter

Preparation of rhabdophane-type $RPO_4 \cdot nH_2O$ (R = Y or Er, n = 0.7–0.8) by pot-milling churchite-type $RPO_4 \cdot 2H_2O$ at 20–25 °C in air

Yasuo Hikichi, Kishin Yogi and Toshitaka Ota

Ceramic Research Laboratory, Nagoya Institute of Technology, 10-6-29, Asahigaoka, Tajimi-city 507, Japan

Received 7 October 1994; in final form 28 January 1995

Abstract

Rhabdophane-type (r-) $RPO_4 \cdot nH_2O$ (R = Y or Er, n = 0.7–0.8) was prepared by pot-milling churchite-type $RPO_4 \cdot 2H_2O$ (starting sample) at 20–25 °C in air. The duration of pot-milling the 30 g sample causes the structural distortion and eventual disintegration that accompanies the formation of r-$RPO_4 \cdot nH_2O$, after 5 days (for R = Y, or 13 days for R = Er), through the intermediate stage of an amorphous phosphate. For conversion of churchite into rhabdophane by a mechanical method, it is necessary to keep the H_2O/RPO_4 (H/R) mole ratio around 1, such as 1.1–1.3 (amorphous phosphate) with a pot-mill (impact), or 0.8–1.0 (rhabdophane coexisting with churchite) with a mortar (shearing), before the formation of a single phase rhabdophane. When the 5 g sample was pot-milled, r-$RPO_4 \cdot nH_2O$ (n = 0.5–0.6) was obtained within 10 h, then changed to an amorphous phosphate after 1 day because the H/R ratio decreased abruptly to below 0.4.

Keywords: Pot-milling; Rhabdophane; Churchite; Mechanical conversion; Rare earth phosphate

1. Introduction

Mooney [1], Hezel and Ross [2] and Hikichi et al. [3] prepared rhabdophane-type (r-) $RPO_4 \cdot nH_2O$ (R = La–Dy, n = 0.5–1) by precipitation from aqueous solutions. There is no other documented study on the preparation of r-$RPO_4 \cdot nH_2O$ (R = Y, Er–Lu) because churchite-type (c-) $RPO_4 \cdot 2H_2O$ precipitates preferentially from aqueous solutions [3]. However, Hikichi et al. [4,5] were able to prepare the new r-$RPO_4 \cdot nH_2O$ (R = Y or Er) by grinding c-$RPO_4 \cdot 2H_2O$ at 20–25 °C in air using a mortar and pestle.

In this study, it is demonstrated that r-$RPO_4 \cdot nH_2O$ (R = Y or Er) can also be prepared by pot-milling c-$RPO_4 \cdot 2H_2O$ at 20–25 °C in air. The main purposes of this paper are to show the experimental results of the formation of r-$RPO_4 \cdot nH_2O$ (R = Y or Er) by pot-milling c-$RPO_4 \cdot 2H_2O$ (5 g or 30 g), and to compare the mechanical reactions when this process is carried out with a pot-mill, and with a mortar.

2. Experimental details

A starting sample of c-$RPO_4 \cdot 2H_2O$ (R = Y or Er) was prepared by precipitation from a mixture of aqueous solutions of RCl_3 and H_3PO_4 [4]. X-ray diffraction (XRD) patterns of the starting sample showed that churchite is the only crystalline phase in the material. The R_2O_3 wt.% was determined on the basis of the Japanese Industrial Standard (JIS) M8404 method and the P_2O_5 wt.% was determined by the gravimetric method using ammonium phosphate-molybdate. The quantity of H_2O was determined by measuring the difference in weight between samples heated to 120 °C and to 400 °C for 2 h in air. The chemical formulae of the samples as calculated from the chemical compositions were almost the same as the theoretical $RPO_4 \cdot 2H_2O$. The initial particle size of the starting sample, based on examination by scanning electron microscopy, is 0.3 μm (for R = Y, or 0.5 μm for R = Er) on average.

Samples of 5 g and 30 g, derived from the starting material, were ground without the addition of water at 20–25 °C for 21 days in air, using an alumina pot-mill (150 mm inside diameter, 190 mm in depth) and alumina balls (21–33 mm in diameter, number of balls = 50) at a rate of 70 rev per minute. In order to compare the mechanical reactions resulting from grind-

0925-8388/95/$09.50 © 1995 Elsevier Science S.A. All rights reserved
SSDI 0925-8388(95)01568-X

ing with a pot-mill with those resulting from use of a mortar, a 30 g sample, derived from the same starting material, was ground using an alumina mortar (220 mm inside diameter, 110 mm in depth). The temperature of the samples, as measured by a thermometer, was in the range of 20–25 °C. There were no phase differences observed in the ground samples between 20 °C and 25 °C.

XRD analysis was conducted with a diffractometer (Ni-filtered CuKα radiation).

3. Results and discussion

A 30 g sample derived from the starting material, was milled with a pot-mill. Fig. 1 shows the XRD patterns of the milled sample. XRD peak intensities of the sample became weak within 1 day, with the XRD patterns then becoming indicative of an amorphous phosphate for days 1–4 (for R = Y, or days 1–12 for R = Er). Upon continued milling, on day 5 (for R = Y, or day 13 for R = Er) new diffraction peaks appeared in the XRD patterns. These peaks coincided in position with those of rhabdophane and their intensities increased with increased milling time. Fig. 2 shows the relation between the H_2O/RPO_4 (H/R, R = Y or Er) mole ratio of the milled sample and milling time. The H/R ratio quickly decreased to about 1.1 (for R = Y) or 1.3 (for R = Er) within 1 day, then stayed at about 1.1 (for R = Y) for days 2–4, or 1.1–1.3 (for E = Er) for days 2–12. Finally, the H/R ratio dropped to 0.7–0.8 in the case of R = Y for days 5–21 and, in the case of R = Er, in the same range for days 13–21. When the milled sample had an H/R ratio in the range of 0.7–0.8, it showed an XRD pattern typical of rhabdophane.

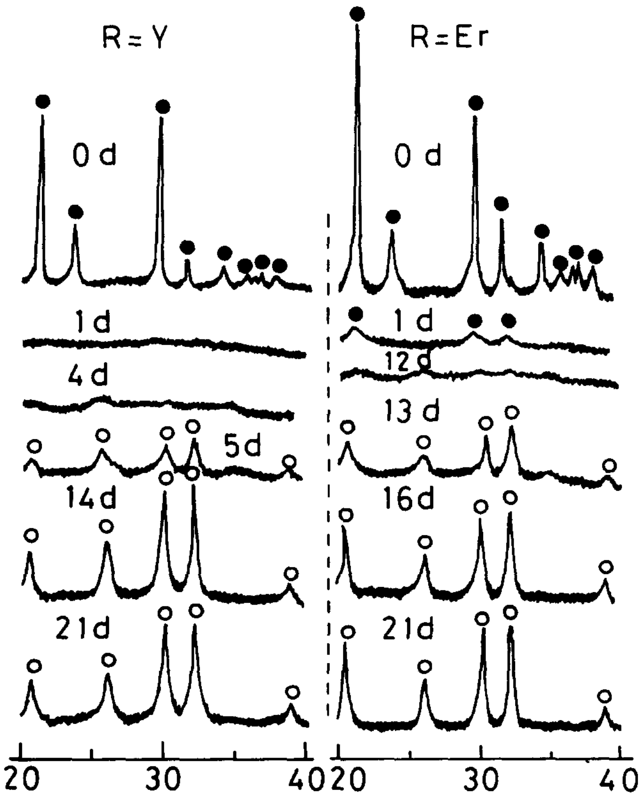

Fig. 1. XRD patterns of the sample obtained by pot-milling a 30 g sample of churchite-type $RPO_4 \cdot 2H_2O$ (R = Y or Er) for days 0–21 at 20–25 °C: ●, churchite-type $RPO_4 \cdot 2H_2O$; ○, rhabdophane-type $RPO_4 \cdot nH_2O$.

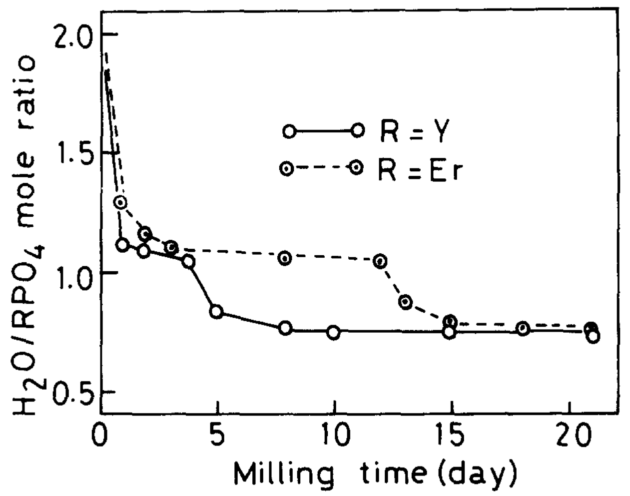

Fig. 2. Relation between H_2O/RPO_4 mole ratio and milling time (day) for the sample obtained by pot-milling a 30 g sample of churchite-type $RPO_4 \cdot 2H_2O$ (R = Y or Er) for days 0–21 at 20–25 °C: ○, R = Y; ⊙, R = Er.

When a 5 g sample was pot-milled, XRD peak intensities of the sample became weak within 10 h, after which the XRD patterns indicated low-crystalline r-$RPO_4 \cdot nH_2O$ (R = Y or Er, n = 0.5–0.6). Upon continued milling, the XRD patterns of the milled sample indicated only an amorphous phosphate for days 1–21. The H/R ratio of the milled sample decreased abruptly to below 0.4 within 1 day, and remained at nearly 0 up to day 21. The reason for the rapid reduction of water content in the 5 g sample is considered to be related to the total energy given by grinding as compared with the small amount of sample. This is the typical difference between the amorphous phosphate (H/R ratio below 0.4) developed by milling the 5 g sample and the amorphous phosphate (H/R ratio of 1.1–1.3) which was obtained by milling the 30 g sample.

A 30 g sample was then ground with a mortar. XRD peak intensities of the sample gradually weakened within 1 day (H/R ratio of 1.6–1.7). On day 3 (for R = Y, or day 4 for R = Er) new diffraction peaks were observed. These peaks coincided in position with those of rhabdophane, and their intensities gradually increased with further grinding, while peaks corresponding to churchite gradually decreased up to day 8 (for R = Y, or day 10 for R = Er); the H/R ratio decreased to 0.8–1.0 (rhabdophane coexisting with churchite). After 8 days (for R = Y, or 10 days for R = Er), the XRD patterns showed only r-$RPO_4 \cdot nH_2O$ (R = Y or Er, n = 0.8–0.9).

Mooney [1] and Hikichi et al. [3,4,6] reported that the presence of zeolitic water corresponding to nH_2O (0.5–1) must be essential to the rhabdophane structure. For conversion of churchite into rhabdophane by a mechanical method, it is necessary to keep the H/R ratio around 1, such as 1.1–1.3 (amorphous phosphate) with a pot-mill, or 0.8–1.0 (rhabdophane coexisting with churchite) with a mortar, before the formation of a single phase rhabdophane.

It is said in general that, in grinding with a mill the dominant process is impact, whereas with a mortar the dominant process is shearing. Distortion and disintegration of the churchite structure when processed by impact seems to be stronger than that with shearing. Therefore, the duration of pot-milling the 30 g sample encourages the structural distortion and eventual disintegration that accompanies the formation of rhabdophane through the intermediate stage of an amorphous phosphate. This intermediate stage of an amorphous phosphate is not observed when ground with a mortar.

Natural rhabdophane is usually described as a hydrated cerium phosphate with cerium as the predominant rare earth element. However, Bowles and Morgan [7] note that genesis appears to be more important than the crystal structure in determining the composition of rhabdophane and the mineral rhabdophane should not be categorized as cerium selective. For this reason, our present results might be useful for the study of the rare earth phosphate minerals.

Acknowledgments

The present work was supported by a Grant-in-Aid for Scientific Research on Priority Areas "New Development of Rare Earth Complexes" No. 06241235 from The Ministry of Education, Science and Culture.

References

[1] R.C.L. Mooney, *Acta Crystallogr., 3* (1950) 337.
[2] A. Hezel and S.D. Ross, *J. Inorg. Nucl. Chem., 29* (1967) 2085.
[3] Y. Hikichi, K. Hukuo and J. Shiokawa, *Bull. Chem. Soc. Japan, 51* (1978) 3645.
[4] Y. Hikichi, T. Sasaki, K. Murayama, T. Nomura and M. Miyamoto, *J. Am. Ceram. Soc., 72* (1989) 1073.
[5] Y. Hikichi, C.F. Yu, M. Miyamoto and S. Okada, *J. Alloys Comp., 192* (1993) 102.
[6] Y. Hikichi, T. Sasaki, S. Suzuki, K. Murayama and M. Miyamoto, *J. Am. Ceram. Soc., 71* (1988) c354.
[7] J.F.W. Bowles and D.J. Morgan, *Mineral. Mag., 48* (1984) 146.