Mechanochemical Changes of Neodymium Phosphates by Grinding

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Synopsis. The effect of mechanochemical treatment on some neodymium phosphates was investigated. It is worth noting that on mechanochemical treatment $NdPO_4 \cdot 0.5H_2O$ (hexagonal) is gradually transformed into $NdPO_4$ (monoclinic) at room temperature, while thermal change of $NdPO_4 \cdot 0.5H_2O$ to $NdPO_4$ (monoclinic) happens at above 600 °C. Condensed phosphates, meta- and ultraphosphates, easily turned to X-ray amorphous structure by grinding.

Mechanochemical treatment influences structures, physical and chemical properties, and reactivity of solids. We have investigated the mechanochemical effect of various phosphates by grinding. In the present study, four neodymium phosphates ($NdPO_4$, $NdPO_4 \cdot 0.5H_2O$, $Nd(PO_3)_3$, and NdP_5O_{14}), were used. Rare earth phosphates were used for the laser materials, semiconductor, and ceramics, which have been studied for the last several years[1,2] The effecat of mechanochemical treatment on 1) X-ray diffraction patterns, 2) IR spectra, 3) DTA-TG diagrams, and 4 solubility of neodymium phosphates, was investigated.

Experimental

Neodymium phosphates used were prepared by the procedure described in a previous paper.[3] Grinding was performed with Ishikawa's grinding mill, AG-Z type, at a temperature range of 20—30 °C, humidity at 15—30%, in nitrogen atmosphere. The X-ray diffraction analysis was carried out with a Rigaku Denki Geigerflex diffractometer using nickel-filtered Cu $K\alpha$ radiation. Thermal analysis (DTA-TG) was carried out by a Rigaku 8002 SD thermal analyzer. The IR spectra were taken by means of a KBr tablet.

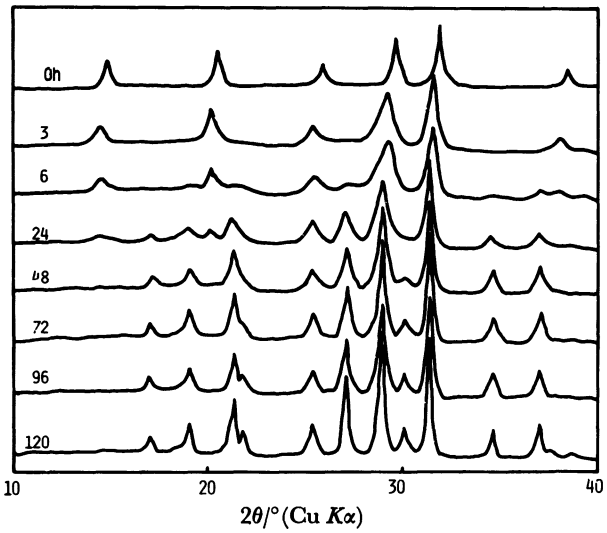

Fig. 1. X-Ray diffraction patterns of ground $NdPO_4 \cdot 0.5H_2O$.

Results and Discussion

Mechanochemical Changes of Orthophosphates. Figure 1 shows the X-ray diffraction patterns of $NdPO_4 \cdot 0.5H_2O$ at various stages of grinding. With grinding over 24 h, some new diffraction peaks, at 2θ= 17.5, 19.5, 22, 27.5, 30.5, 35, and 37.5°, appeared. These peaks coincided in position with those of $NdPO_4$ (monoclinic), and their intensities increased with further grinding. It is clear from this fact that $NdPO_4 \cdot 0.5H_2O$ turned to anhydrate ($NdPO_4$) by grinding. On the other hand, as for $NdPO_4$ (monoclinic), a remarkable change of X-ray diffraction patterns was not observed.

Figure 2 shows the IR spectra of $NdPO_4 \cdot 0.5H_2O$ by grinding. With grinding, the intensity of each absorption peak gradually decreased. Also, characteristic absorptions due to the O–H bond of water of crystallization in the region of 3400—3500 and 1600 cm^{-1} became weak, while those attributable to the P–O bond were gradually increased at about 960 and 560—580 cm^{-1}, and IR spectrum after 24 h's grinding coincided with that of anhydrate, that is, the water of crystallization was released and turned to the anhydrate ($NdPO_4$).

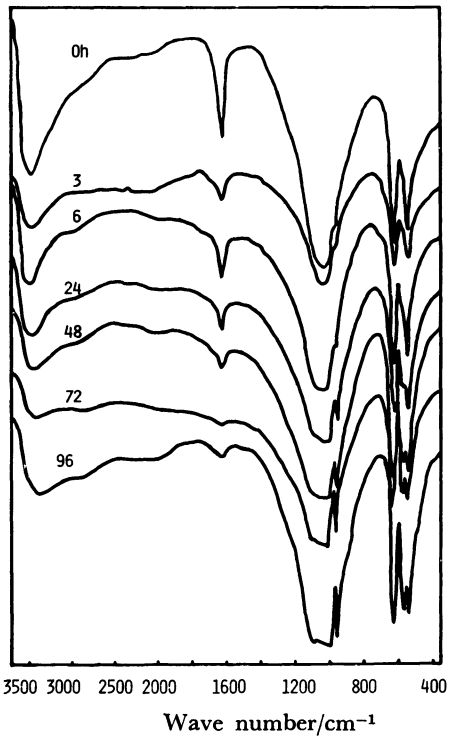

Fig. 2. IR spectra of ground $NdPO_4 \cdot 0.5H_2O$.

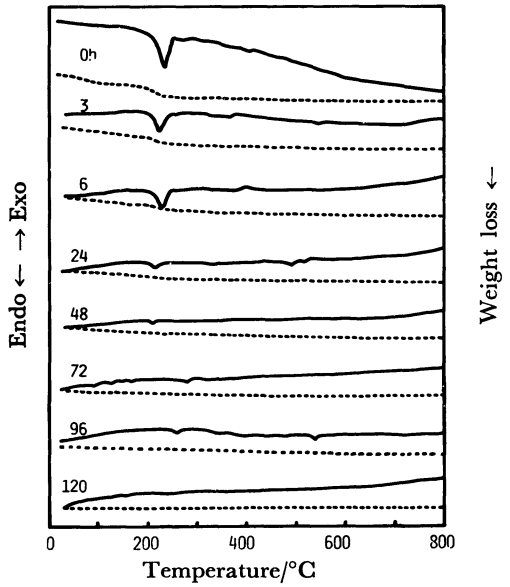

Fig. 3. DTA-TG curves of ground $NdPO_4 \cdot 0.5H_2O$. Solid line: DTA, dotted line: TG.

Figure 3 shows the DTA-TG curves of $NdPO_4 \cdot 0.5H_2O$ by grinding. An endothermic peak in the 210—220 °C region with a weight loss, being due to the dehydration of water of crystallization, decreased gradually with increasing the grinding time and almost disappeared in the samples ground for more than 24 h. When $NdPO_4$ (monoclinic) was ground, a remarkable change of DTA-TG curves was not observed. On heating, the thermal changes of $NdPO_4 \cdot 0.5H_2O$ were shown as follows:[3]

$$NdPO_4 \cdot 0.5H_2O(\text{hexagonal}) \underset{\text{standing in air}}{\overset{210\text{—}220\,^\circ C}{\rightleftarrows}}$$

$$NdPO_4(\text{hexagonal}) \begin{cases} \xrightarrow[\text{long time}]{600\,^\circ C} NdPO_4(\text{monoclinic}) \\ \xrightarrow[\text{short time}]{800\,^\circ C} NdPO_4(\text{monoclinic}) \end{cases}$$

On the other hand, in the case of mechanochemical treatment, the conversion of $NdPO_4 \cdot 0.5H_2O$ (hexagonal) to $NdPO_4$ (monoclinic) proceeds at room temperature for above 24 h. This finding is very interesting in view of the fact that the mechanochemical treatment had the same effect as heat energy on the transition of $NdPO_4 \cdot 0.5H_2O$ (hexagonal) to $NdPO_4$ (monoclinic), and this transition took place without X-ray amorphous structure.

Mechanochemical Changes of Condensed Phosphates. In order to compare the difference in mechanochemical changes of the structure of phosphates, two condensed phosphates, neodymium metaphosphate ($Nd(PO_3)_3$) and ultraphosphate (NdP_5O_{14}), were examined. Because an ultraphosphate is generally very unstable, crystalline substances are almost unknown.[4] Neodymium ultraphosphate is one of the stable, crystalline ones and their mechanochemical investigation have not been reported. The X-ray diffraction intensities of $Nd(PO_3)_3$ and NdP_5O_{14} decreased with increasing the grinding time, the line-width broadened, and their diffraction peaks disappeared at last. From their IR spectra, with grinding, the intensities of their absorption peaks decreased and the peak-width broadened because of X-ray amorphous structure. From the results of DTA-TG, the ground $Nd(PO_3)_3$ has an endothermic peak at about 100 °C with a weight loss by the dehydration of adsorbed water, and an exothermic one at about 650 °C, being due to the restoring of the lattice distortion produced by grinding. The exothermic peak increased gradually with grinding time. This shows that its crystal structure was distorted by grinding, and finally transformed to the X-ray amorphous structure; metaphosphate showed the structure change similar to alkaline metaphosphates,[5] that is, the increasing of amorphous substance with grinding time and the yielding of shorter-chain phosphate molecules as a result of random cleavage of the P-O-P linkage upon grinding. When NdP_5O_{14} was ground for more than 3 h, large weight loss at about 100 and 300—400 °C was observed. It is suggested from the results of X-ray diffraction patterns, IR spectra, and DTA that the crystal structure of neodymium ultraphosphate was very unstable for grinding.

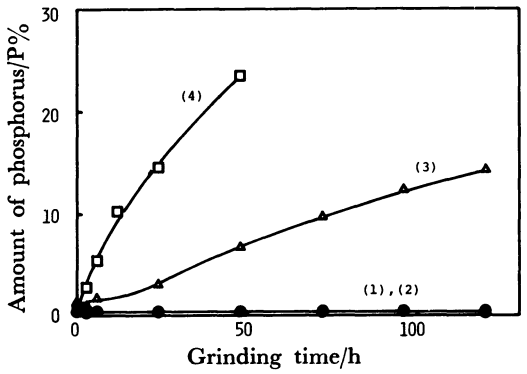

Fig. 4. Changes in the solubility of ground samples in water. (1): $NdPO_4$, (2): $NdPO_4 \cdot 0.5H_2O$, (3): $Nd(PO_3)_3$, (4): NdP_5O_{14}.

Solubility of Ground Samples in Water. Figure 4 shows the changes in the solubilities of various ground phosphates in water. Species dissolved was almost orthophosphate, seldom, pyrophosphate. The amounts of dissolved phosphates were 23.5% for ultraphosphate ground for 48h, and 14.3% for metaphosphate ground for 120h. But the ground samples of orthophosphates ($NdPO_4$ and $NdPO_4 \cdot 0.5H_2O$) were not entirely dissolved, showing that the crystal structure of condensed phosphates was rather unstable than those of orthophosphates on grinding.

References

1) B. C. Tofield, H. P. Weber, T. C. Damen, and G. A. Pasteur, *Appl. Phys.*, **9**, 435 (1974).
2) E. Snitzer, *Appl. Optics*, **51**, 1487 (1966).
3) M. Tsuhako, S. Ikeuchi, T. Matsuo, I. Motooka, and M. Kobayashi, *Nippon Kagaku Kaishi*, **1978**, 676.
4) C. Barthou, B. Blanzat, and J. M. Letoffe, *J. Appl. Phys.*, **52**, 6847 (1981).
5) I. Motooka, G. Hashizume, and M. Kobayashi, *Nippon Kagaku Kaishi*, **87**, 255, 953 (1966).