Mechanochemical Synthesis of Ternary Fluorides with Perovskite Structures

Jaeryeong Lee, Qiwu Zhang,* and Fumio Saito
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577

(Recdeived April 12, 2001; CL-010327)

Mechanochemical synthesis of ternary zinc fluorides, $AZnF_3$ (A = K, Na and NH_4) with perovskite structures was attempted by grinding equimolar mixtures of zinc fluoride (ZnF_2) and one of fluorides, i.e., potassium fluoride (KF), sodium fluoride (NaF) and ammonium fluoride (NH_4F), respectively, in air using a planetary ball mill. The grinding enables us to synthesize these compounds, and the crystallinity of them is improved as the grinding progresses. The synthesized materials formed in the ground mixtures seem to be agglomerates of fine particles having diameters of about several tens nanometer.

Much attention has been paid on $AM^{II}X_3$-type (A = alkali such as K, Na and ammonium, NH_4, M = metal, X = halide ions such as F, Cl and Br) with perovskite structures, due to their unique properties. Particularly, $AZnF_3$ is attractive material because it exhibits luminescent property besides radiation detection and laser medium.[1–3] $AZnF_3$ has been normally synthesized by two processes through a high-temperature solid-state reaction[4] and hydrothermal reactions.[5–7] However, the former process needs strict temperature and pressure control with a rigorous equipment, and the latter requires temperature over 160 °C for long time, and it is complicated procedure, respectively. These elaborate demands in synthesis of the fluoride compounds have resulted in high production cost and restriction of their applications although these processes would be improved. This is a motivation to provide availability of other economical processes for synthesizing such materials. In the meantime, we have proposed a novel process for synthesizing rare earth oxyfluorides (ROF, R = rare earth elements) through a mechanochemical (MC) reaction,[8] which would be possible to synthesize ternary fluoride compounds. The main purpose of this work is to introduce an alternative synthesis method for the $AZnF_3$ by the MC method.

Chemical reagents used in this experiment were zinc fluoride (ZnF_2) and two kinds of alkali-fluoride and ammonium fluoride (AF, A = K, Na and NH_4), supplied from Wako Chemical Co., Ltd. (Osaka, Japan). Their purities are guarantied at 99% or more. ZnF_2 was mixed with one of AF at equimolar ratio of Zn to A. The mixtures were subjected to grinding in air using a planetary mill (Pulverisette-7, Germany), as follows: 4 g of the mixture was put in the zirconia pot (45 cm^3 inner volume) with seven zirconia balls of 15 mm diameter. Rotational speed of the mill was set at 700 rpm and the mill was started running for various periods of time. These reaction products were evaluated by X-ray powder diffractometry (RAD-B, Rigaku, Japan) using Cu Kα radiation to identify the phases formed in the product. Morphology of ground samples was observed by transmission electron microscope (TEM, JEM-1200EXII, Japan).

Figure 1 shows XRD patterns of the ZnF_2 and KF mixture ground for 120 to 360 min. KF in the mixture tends to easily change into amorphous state easily, and no peaks of KF are observed in the pattern of the 120 min ground mixture, as shown in the figure (A). Peak intensity of ZnF_2 in the patterns decreases gradually with an increase in grinding time, while peaks of $KZnF_3$ appear in the patterns of the mixtures ground for 120 min or more, as the grinding processes increase. No other peaks can be observed in the patterns of the 360 min ground product. This indicates that $KZnF_3$ monophase is formed mechanochemically by the grinding.

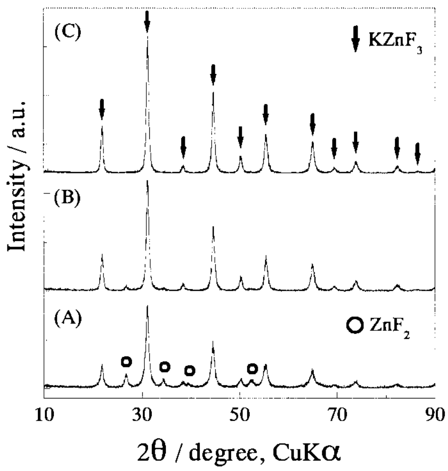

Figure 1. XRD patterns of the ZnF_2 and KF mixture ground for different times ((A) 120 min, (B) 240 min, (C) 360 min).

Figure 2 shows a TEM photograph of the 360 min ground mixture, in which $KZnF_3$ monophase is formed. The synthe-

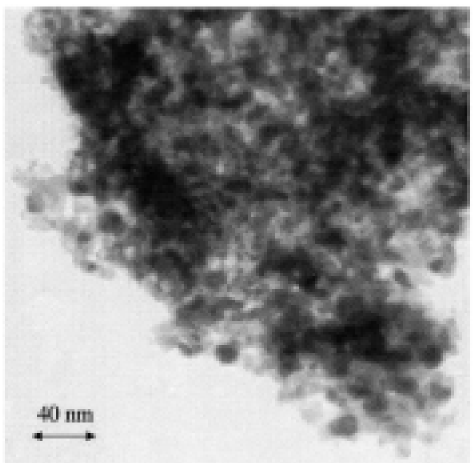

Figure 2. TEM photograph of the KF and ZnF_2 mixture ground for 360 min.

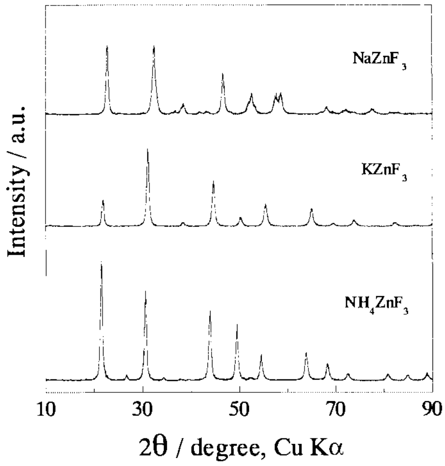

Figure 3. XRD patterns of the ZnF_2 and AF (A = Na, K and NH_4) mixtures ground for 360 min.

sized $KZnF_3$ in the mixture seems to be agglomerates of fine particles having diameter of about several tens nanometer.

Figure 3 shows XRD patterns of the 360 min ground samples obtained from the three kinds of mixtures of AF (A = Na, K and NH_4) and ZnF_2. Similarly, single phases of $NaZnF_3$ and NH_4ZnF_3 were formed mechanochemically by the grinding only for 360 min, respectively. Crystal structure of the former compound is orthorhombic and that of the latter is cubic, depending on the radii of A ions. According to the results of Figures 1 and 3, the reaction can be described as follows.

$$NaF + ZnF_2 \rightarrow NaZnF_3 \quad (1)$$
$$KF + ZnF_2 \rightarrow KZnF_3 \quad (2)$$
$$NH_4F + ZnF_2 \rightarrow NH_4ZnF_3 \quad (3)$$

In air, generally, the oxyfluoride compounds may be formed by solid-state reaction and the fluoride may be easily hydroxidized. X-ray photoelectron spectroscopic (XPS) analysis confirmed the binding energies of $NaZnF_3$, $KZnF_3$ and NH_4ZnF_3 in the three kinds of mixtures ground for 360 min, without forming bonds between metals and oxygen in each sample.

References

1 N. Knitel, P. Dorenbos, and I. Haas, the International Conference SCINT'95, Delft, Netherlands, August 28, 1995, Abstr., 81.
2 A. Gektin, I. Krasovitskaya, and N. Shiran, *J. Lumin.*, **72–74**, 664 (1997).
3 M. Mortier, I. Gesland, M. Rousseau, *Solid State Commun.*, **89**, 369 (1994).
4 S. Somiya, S. Hirano, M. Yoshimura, and K. Yanagisawa, *J. Mater. Sci.*, **16**, 813 (1981).
5 H. Li, Z. Jia, and C. Shi, *Chem. Lett.*, **2000**, 1106.
6 C. Zhao, S. Feng, R. Xu, C. Shi, and J. Ni, *Chem. Commun.*, **1997**, 945.
7 C. Zhao, S. Feng, Z. Chao, C. Shi, R. Xu, and J. Ni, *Chem. Commun.*, **1996**, 1641.
8 J. Lee, Q. Zhang, and F. Saito, *J. Am. Ceram. Soc.*, **84(4)**, 863 (2001).