Mechanochemical Syntheses of Perovskite KM\textsuperscript{II}F\textsubscript{3} with Cubic Structure (M\textsuperscript{II} = Mg, Ca, Mn, Fe, Co, Ni, and Zn)

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An equi-molar mixture of potassium fluoride (KF) and one of alkaline-earth or transition metal fluoride M\textsuperscript{II}F\textsubscript{2} (M\textsuperscript{II} = Mg, Ca, Mn, Fe, Co, Ni, and Zn) was ground in air by using a planetary ball mill to investigate mechanochemical (MC) synthesis of fluoroperovskites KM\textsuperscript{II}F\textsubscript{3}. Rietveld refinement for the ground mixtures was conducted on the basis of XRD data to inquire into structural properties of the KM\textsuperscript{II}F\textsubscript{3} synthesized mechanochemically. The synthesis reactions proceed with grinding time, and ultimately a single phase of cubic structural KM\textsuperscript{II}F\textsubscript{3} (Pnma, Z = 1) was obtained after grinding for 21.6 ks. The values of unit cell parameter, a, of KM\textsuperscript{II}F\textsubscript{3} synthesized by MC reaction, are slightly larger than those by solid-state reaction at high temperature, and this may be attributed to structural distortions caused by intensive grinding.

(Received February 6, 2003; Accepted May 20, 2003)

Keywords: mechanochemical synthesis; fluoroperovskite (KM\textsuperscript{II}F\textsubscript{3}); Rietveld refinement; structural distortion

1. Introduction

Complex fluorides have unique characteristics in electrical, optical, and luminescent properties and also show various interesting structures.\textsuperscript{1,2} Among them, especially ternary fluorides with perovskite structure, KM\textsuperscript{II}F\textsubscript{3}, have been in the limelight in these days and have been actively researched due to their high-temperature super-ionic behavior and physical properties, such as piezoelectric characteristics, ferromagnetic, nonmagnetic insulator behavior and so on.\textsuperscript{3–7}

The physical and structural properties of KM\textsuperscript{II}F\textsubscript{3} depend on its production process, so much attention has been paid on their synthesis methods. Several methods have been employed to synthesize them.\textsuperscript{8–14} However, there are some serious drawbacks. For example, very rigorous equipments are necessary in the solid-state reaction at high temperature, the purity of product is relatively low in precipitation method, and the reduced temperature and pressure is desired in hydrothermal method. Therefore, it has been required strongly the alternative KM\textsuperscript{II}F\textsubscript{3}-synthesis process which is much simpler.

The authors have reported an alternative method for synthesizing functional materials such as rare-earth oxylides (R-OX, R = rare-earth, X = halogen element) including lanthanum oxyfluoride (LaOF), chloride (LaOCI), bromide (LaOBr), with nano-structure from their constituent mixture, rare-earth oxide (R\textsubscript{2}O\textsubscript{3}) and halide (RX\textsubscript{y}), without heating.\textsuperscript{15–19} This method uses only an intensive grinding machine such as a planetary mill, so that it is a non-expensive and environmental-safety method. Generally the impurity in materials synthesized by MC method would be higher than that by solid-state reaction at high temperature. Wearing of pot and balls due to intensive grinding causes the impurities. Therefore, the authors used a zirconia pot and balls whose abrasion resistance was very good.

The purpose of this paper is to provide information on the synthesis of KM\textsuperscript{II}F\textsubscript{3} by the mechanochemical treatment of KF–M\textsuperscript{II}F\textsubscript{2} systems (M\textsuperscript{II}F\textsubscript{2}, M\textsuperscript{II} = Mg, Ca, Mn, Fe, Co, Ni, and Zn), and on their structural characteristics.

2. Experiments

2.1 Sample

Potassium fluoride (KF) and seven kinds of M\textsuperscript{II}F\textsubscript{2} (M\textsuperscript{II} = Mg, Ca, Mn, Fe, Co, Ni, and Zn) were used in this research as the starting materials. KF was supplied from Wako Pure Chemical Industries, Ltd. Japan, and M\textsuperscript{II}F\textsubscript{2} were supplied from Kojundo Chemical Laboratory Co., Ltd. Japan. They were analytical grade reagents with purity over 99.0 mass%. KF was mixed with each of M\textsuperscript{II}F\textsubscript{2} at equimolar ratio, and the seven kinds of mixtures were preserved in a gas-tight desiccator as the starting mixtures.

2.2 Methods

A planetary ball mill (Pulverisette-7, Fritsch GmbH) was used to grind the starting mixtures, KF–M\textsuperscript{II}F\textsubscript{2}. Two grams of each mixture was put in the pot (45 cm\textsuperscript{3} inner volume) with seven balls of 15 mm diameter, and was subjected to grinding in ambient conditions at 700 min\textsuperscript{−1} speed for various grinding time. The milling was stopped every 0.9 ks in order to prevent from the temperature increase of the pot and overload of machine. The ground mixtures were characterized using X-ray diffraction (XRD, RAD-B, Rigaku, Japan) with Cu–K\textsubscript{α} radiation (\(\lambda = 0.15418\) nm) to identify the phases formed in the ground products. The XRD data from 5° to 90° in scattering angle (2θ) was analyzed with the aid of the Rietveld profile method using LCR2 program.\textsuperscript{20} Morphology of the ground mixtures was observed using a scanning electron microscope (SEM, Hitachi 4100L, Japan). An X-ray photoelectron spectroscopy (XPS, PHI 5600, Ulvac-Phi., Japan) was measured to obtain information on the chemical bonds in the ground product.

3. Results and Discussion

3.1 Synthesis of KMgF\textsubscript{3}

Figure 1 shows the XRD patterns of the KF and MgF\textsubscript{2} mixture ground for various periods of time. By only one-hour grinding in this research, no peaks of KF are detected in the XRD pattern although some peaks of MgF\textsubscript{2} can be observed.
This indicates that KF tends to change into more activated state than MgF$_2$. Peak intensity of MgF$_2$ in the mixtures gradually decreases with grinding time, and ultimately no peaks of MgF$_2$ are observed in the mixture ground for 10.8 ks or more. In company with this change, new peaks appeared in the initial stage of grinding (within 3.6 ks). In other words, KF and MgF$_2$ directly formed into a new crystalline structure. Their intensities increase with grinding time. They are consistent with the peaks of KMgF$_3$ (Cubic, JCPDS 21, File Card No. 18-1033), and only peaks of KMgF$_3$ are observed in the mixtures ground for 10.8 ks or more. And also there are no noticeable differences in the XRD patterns of the mixture ground for 10.8 ks or more. This implies that KMgF$_3$ can be synthesized by MC method, and its structure can be sustained against intensive prolonged grinding.

To certify whether KMgF$_3$ in the mixture ground for 21.6 ks exists in single phase or not, the ground mixture was annealed at 673 K for 7.2 ks. As shown in Fig. 2, peaks of KMgF$_3$ in the mixture were sharpened and their intensities increase dramatically, but no peak except for KMgF$_3$'s can be observed. These results imply that the single phase of KMgF$_3$ can be synthesized mechanochemically by the grinding of the mixture of KF–MgF$_2$ powder. The synthesis reaction is followed as

$$\text{KF} + \text{MgF}_2 \rightarrow \text{KMgF}_3$$

(1)

Figure 3 shows the SEM observations for the KF–MgF$_2$ mixture ground for 21.6 ks. In micrograph (A), the product consists of agglomerates, whose size is distributed from several tens to submicrometer. However, these agglomerates consist of fine particles having about 200 nm as shown in micrograph (B).
3.2 Syntheses of other KM\textsuperscript{II}F\textsubscript{3} with cubic structure (M\textsuperscript{II} = Ca, Mn, Fe, Co, Ni, and Zn)

There are six fluoroperovskites KM\textsuperscript{II}F\textsubscript{3} (M\textsuperscript{II} = Ca, Mn, Fe, Co, Ni, and Zn), which have the same space group as KMgF\textsubscript{3} (Pm\textsubscript{3}m (221)). The mixture of powder, KF and M\textsuperscript{II}F\textsubscript{2}, was ground for 21.6 ks at the same condition of the synthesis of KMgF\textsubscript{3}. Figure 4 shows XRD patterns of the mixtures ground for 21.6 ks. In all cases, their XRD peaks are individually fitted to the new patterns of KCaF\textsubscript{3} (3-567), KMnF\textsubscript{3} (17-116), KFeF\textsubscript{3} (20-895), KCoF\textsubscript{3} (18-1006), KNiF\textsubscript{3} (21-1002), KZnF\textsubscript{3} (6-439). The XRD patterns show that M\textsuperscript{II}F\textsubscript{2} (M\textsuperscript{II} = Ca, Mn, Fe, Co, Ni, and Zn) react with KF to form single phase of KM\textsuperscript{II}F\textsubscript{3} with cubic structure, respectively, by grinding as the following six reactions:

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\begin{align*}
\text{KF} + \text{CaF}_2 & \rightarrow \text{KCaF}_3 \\
\text{KF} + \text{MnF}_2 & \rightarrow \text{KMnF}_3 \\
\text{KF} + \text{FeF}_2 & \rightarrow \text{KFeF}_3 \\
\text{KF} + \text{CoF}_2 & \rightarrow \text{KCoF}_3 \\
\text{KF} + \text{NiF}_2 & \rightarrow \text{KNiF}_3 \\
\text{KF} + \text{ZnF}_2 & \rightarrow \text{KZnF}_3
\end{align*}
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When fluorides were synthesized by solid-state reaction, the surface of them may be easily oxidized and hydroxidized. X-ray photoelectron spectroscopic (XPS) analysis confirmed the binding energies of KMgF\textsubscript{3}, KCaF\textsubscript{3}, KMnF\textsubscript{3}, KFeF\textsubscript{3}, KCoF\textsubscript{3}, KNiF\textsubscript{3}, and KZnF\textsubscript{3} synthesized mechanochemically by grinding for 21.6 ks, without forming bonds between metals and oxygen, K–O and M\textsuperscript{II}–O, in each sample. This results suggest that seven kinds of KM\textsuperscript{II}F\textsubscript{3} synthesized in this research were not easily oxidized or hydroxidized during reaction process.

We calculated the lattice parameters using the Rietveld method on the basis of XRD data. Figure 5 shows unit cell parameter, $a$, in KM\textsuperscript{II}F\textsubscript{3} synthesized by MC method to in them synthesized by solid-state reaction at high temperature.

4. Conclusions

KMgF\textsubscript{3} can be synthesized by the solid-state reaction between KF and MgF\textsubscript{2} mixture by grinding. The reaction proceeds as the grinding time and ultimately single phase of KMgF\textsubscript{3} is achieved within 21.6 ks. The synthesized KMgF\textsubscript{3} seems to be agglomerates of fine particles having diameter of about 200 nanometers. This MC reaction is also applicable to the synthesis of KM\textsuperscript{II}F\textsubscript{3} (M\textsuperscript{II} = Ca, Mn, Fe, Co, Ni, and Zn). By the effect of grinding, unit parameter, $a$, of the KM\textsuperscript{II}F\textsubscript{3} powder by the MC method is slightly larger than that of powders synthesized by solid-state reaction at high temperature.
REFERENCES

21) Joint Committee for Powder Diffraction Standards, Swarthmore, PA (now International Centre for Diffraction Data (ICDD), Newtown Square, PA).