Mechanochemical Synthesis of Nano-sized Complex Fluorides from Pair of Different Constituent Fluoride Compounds

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Complex fluorides ARF_4 (A = Li, Na, K, R = rare earthes) are synthesized by the mechanochemical solid reactions of AF and RF_3 powders at room temperature using a planetary ball mill. The reactions proceed with the increase of grinding time and have been completed at 4 h. Transmission electron microscope observation shows that the produced ARF_4 powders consist of agglomerates of nano-sized primary particles, which exhibit moderate water solubility. When the ground sample is calcined, the particle size is increased and the water solubility is depressed.

Complex fluorides ARF_4 have been investigated as host lattices for lasers and up-conversion materials when doped with rare earth ions. The $NaRF_4$: Yb^{3+}, Er^{3+} (R=Y, La, Gd), for example, are the efficient green-emitting phosphor with infrared excitation.[1] Among these fluorides, much attention has been concentrated on AYF_4, because Yb^{3+}, Er^{3+} doped ones emit visible light at least a factor of 2 more intense than of monophase YF_3: Yb, Er under narrow-band excitation at the optimum frequency.[2] In addition, AYF_4 doped with Tb^{3+} shows high luminescence effciency.[3,4] Moreover the $LiRF_4$ compounds present a strong magnetoelasticity and ferromagnetism at low temperatures.[5,6] Recently it was found that the fluorite type compounds (AYF_4) doped with activators have a potential application as solid electrolytes owing to their high ionic conductivity.[7,8]

These fluorides, for example $NaRF_4$, have normally been prepared by heating the mixture of NaF and RF_3 at a temperature of around 650 °C for a long period of time such as 6 h under HF gas.[9] Another synthesis route is a hydrothermal method,[10] that requires complicated apparatus and severe operational conditions. It is understood that these severe restrictions in synthesis, to some degree, have limited the development of functional fluoride materials, compared with the oxides. Recently we have synthesized a series of perovskite-type compounds by a mechanochemical treatment, a nonthermal synthesis method using high-energy ball mill.[11–14] An application of such a simple method to the synthesis of complex fluorides is expected to contribute to the understanding of fluorides, of which the synthesis and characterization of ARF_4 by means of mechanochemical solid reaction are reported.

Three grams mixtures of alkali metal fluorides AF and rare-earth fluorides RF_3 at equimolar ratios were put into a zirconia pot with seven zirconia balls 15 mm in diameter and ground at a speed of 700 rpm for various periods of time in air, using a planetary ball mill. It has been found that grinding in air does not bring the oxygen into the ground products.[12] The ground products were characterized by X-ray diffraction (XRD) analysis and transmission electron microscope (TEM) observation. The concentration of F^- was determined by an ion-chromatography instrument (IC).

Figure 1 shows the XRD patterns of NaF and YF_3 mixture ground for various periods of time and that of the 4 h ground products of LiF-YF_3 and KF-YF_3, respectively. Peak intensity of the starting fluoride YF_3 decreases gradually with an increase in grinding time and the peaks are unobservable from the pattern of 4 h ground sample. On the other hand, some new peaks are detected in the pattern of the 2 h ground sample and are identified as that of $NaYF_4$. Only the peaks of $NaYF_4$ can be observed in the 4 h ground sample. The XRD patterns of 4 h ground products of LiF-YF_3 and KF-YF_3 are identified as those of $LiYF_4$ and KYF_4, respectively, confirming that the following solid reactions occur by grinding.

$$AF + YF_3 = AYF_4$$

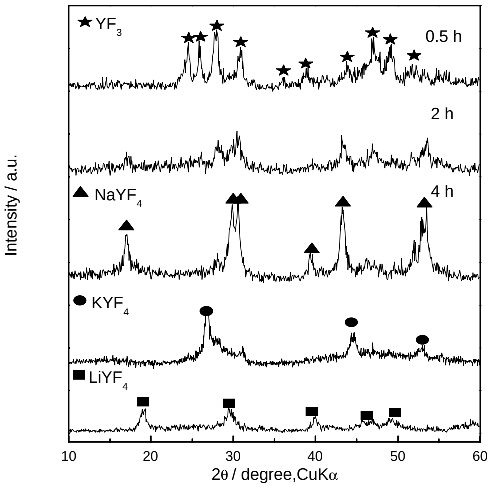

Figure 1. XRD patterns of the ground mixtures of AF and YF_3.

In order to assess whether the reactions proceed completely, the ground samples were dispersed in water to leach the soluble NaF out and the concentration of the soluble F was measured. It was found that as the grinding time increased, the yield of soluble F decreased rapidly in the early stage of grinding, from 12.43% at 0.5 h to 1.89% at 2 h. However, 0.86% of soluble F was still remaining in the sample ground for 4 h, and the yield did not approach to zero (actually 1.25%) even the grinding over 6 h was performed. In order to understand why the soluble F remains, the ground sample was calcined and then was ground again. The yield of soluble F in the 4 h ground mixture was reduced to 0 when heated at 300 °C. However, 1.19% of the soluble F was obtained again when the heated sample was ground for 6 h subsequently. This implies that the soluble F from the ground product comes from the prepared $NaYF_4$, rather than from the original NaF.

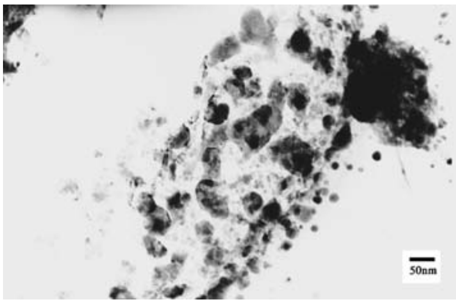

Figure 2. TEM photograph of $NaYF_4$ ground for 4 h.

In fact, the broadened peaks shown in Figure 1 indicate the very small crystallite size of the synthesized samples. The crystallite size was calculated from the Scherrer's equation based on the diffraction plane (101) in the XRD pattern. The size of the sample ground for 4 h is as small as 13.0 nm. This was confirmed by the TEM observation of the sample, shown in Figure 2. It is observed that the synthesized $NaYF_4$ powder contains the large agglomerates of particles, which consists of the nano-sized primary particles per average aggregate. The state of such small particles with crystalline disorder is considered to be the main reason for the soluble F detected. When heating the sample at 300 °C, the peak intensity of XRD pattern (not shown here) increases because of the particle growth and the crystalline size is calculated to increase to 34.5 nm. Together with the recovery of the disorder of crystalline during the calcination, the F solubility is depressed correspondingly.

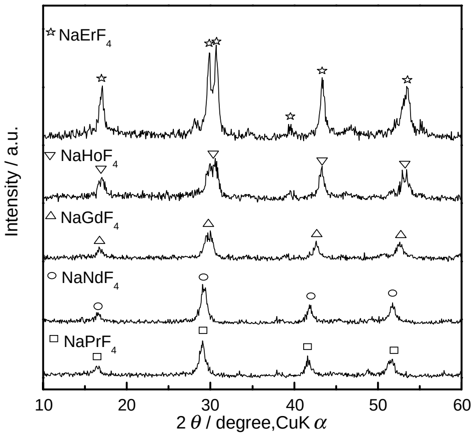

Figure 3. XRD patterns of $NaRF_4$ ground for 4 h.

Figure 3 shows the XRD patterns of $NaRF_4$ (R = Pr, Nd, Gd, Ho, Er) ground for 4 h. Similar to $NaYF_4$, single-phase $NaPrF_4$, $NaNdF_4$, $NaGdF_4$, $NaHoF_4$, $NaErF_4$ could be synthesized by grinding the constituent fluorides, respectively. Thoma[15] had summarized the correlation of the occurrence of AF-RF_3 complex compounds and their cation radius ratios. It is found that the binary mixtures of AF–RF_3 would form ARF_4 compounds when A^+/R^{3+} ratio lies in the range of 0.77 and 1.40. When the ratio is greater than 1.43, the mixture would form A_3RF_6 compounds. The experimental results indicate that the mechanochemical method allows the synthesis of ARF_4 when the radius ratio (A^+/R^{3+}) lies between 0.77 and 1.40. Furthermore, although not shown here, the synthesis of A_3RF_6 can be also carried out mechanochemically when the starting mixture with the radius ratio over 1.43 is used.

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