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Journal of Fluorine Chemistry 107 (2001) 137–139

JOURNAL OF FLUORINE CHEMISTRY

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On the interactions of potassium bromide with alkali fluorides

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Received 26 April 2000; accepted 2 October 2000

Abstract

The interactions of alkali fluorides (LiF, NaF, KF, CsF) with potassium bromide (KBr) by milling and by crystallization from water solutions have been studied by X-ray diffraction and IR techniques. KBr reacts with CsF according to $CsF + KBr \rightarrow KF + CsBr$. With LiF and NaF, KBr does not react. With KF, KBr forms a very hygroscopic solid in which KF partially dissolves in the water of hydration and also forms the crystalline phase $KF \cdot 2H_2O$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Alkali fluorides; Mechanochemistry; KBr interactions

1. Introduction

Mechanochemical reactions of KBr with a large number of inorganic and organic compounds have been widely studied due to the generalized use of the KBr disk technique for obtaining IR spectra of solid compounds [1–13]. The milling of KBr with crystalline analytes can lead to a variety of reactions such as polymorphic transformations, ionic exchange, solid solution, oxidation–reduction processes, and complex formation [13].

The reactions of KBr with alkali halides are rather simple, and have been reported by Yariv and Shoval [4,5]. They have also noticed the formation of mixed salts when milling alkali halides among themselves. Lithium halides incorporate water when milled with other halides. The small Li cation incorporates one H_2O molecule when substituting a large cation such as Cs and Rb [2,3]. Sodium halides also introduce water, forming solid solutions or salts of definite stoichiometry such as $Cs(Na \cdot H_2O)_2Cl_3$ [1,2,4–8].

Potassium halides form solid solutions with other alkali halides without hydration [1,2,9–12]. However, KCl does not form stable solid solutions with NaCl except at high temperatures [1].

In spite of this wide research effort on mixed alkali halide systems, we are not aware of any reports on the interactions of KBr with alkali fluorides. In this paper, we present a study of mechanochemical reactions in these systems, using IR and XRD to monitor the processes. Crystallization from aqueous solution is also studied.

2. Experimental

All reagents used were analytical grade commercial products from Sigma, Merck, and J.T. Baker. The reagents were mixed in different molar ratios of KBr to fluorides, which run from 4:1 to 1:4, and then milled together in an agate mortar. Some of these compositions were also dissolved in water and then recrystallized by evaporation. Others were prepared by milling the components in a mortar under a dry Ar atmosphere and then were covered with nujol. Samples with compositions KBr:LiF and KBr:NaF were additionally milled for 1 h in a Spex-8000 ball mill and then annealed at 500°C for 1 h. The hygroscopic samples were dried at 100°C before recording their XRD and IR spectra.

IR spectra were run in a Bruker Equinox FTIR spectrometer. XRD data were obtained in a Siemens D-5000 diffractometer using Cu Kα radiation.

Quantitative analysis of the obtained phases by the external standard method was performed for non-reacting systems.

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PII: S0022-1139(00)00387-0

3. Results and discussion

3.1. Mechanochemistry of LiF and NaF with KBr

The milling of LiF with KBr did not produce any mechanochemical transformation even under high impact milling. No change in the reaction mixture was detected in the IR spectra or in the XRD powder patterns with respect to the initial reagents. NaF presents a similar behavior to LiF. The inert behavior of Li and Na fluorides with respect to KBr must result from the highly cohesive binding in their crystalline structures, which is due to the small sizes of the cations and the F^- anion. Also the lack of solid solution formation might be due to the large difference in ionic radii of the F^- and Br^- anions [4].

Experiments with water solutions of NaF and KBr lead to mixtures of the pure crystals of the components. LiF is insoluble in water and could not be handled in this way.

Quantitative analysis of the phase ratio in the mixtures agreed with those of the sample preparation.

3.2. Interactions of KF with KBr

Mechanical grinding of KF with KBr in a mortar leads to a rapid transformation of the solid mixture, which turns pasty due to the absorption of water vapor. With mole ratios of KF to KBr below 0.3, the XRD powder patterns showed the disappearance of the KF phase (see Fig. 1).

Crystallization from water solutions leads to a solid, which showed only the KBr lines in the diffraction pattern when the molar ratio of KF:KBr is below 1:2. The loss of the KF peaks suggests the formation of solid solutions in the range $KF_{0–0.3}KBr_{1–0.7}$. If the KF concentration is greater, the KF and $KF{\cdot}2H_2O$ signals appear.

Precise measurements of the diffractograms showed that the cell parameters determined for the supposed solid solutions were identical with those of KBr reported in PDF card no. 36-1471 [14], and measured from the XRD powder pattern of the KBr used in the mixtures. As the formation of solid solutions with ions of very different radii (F^-, Br^-) would necessarily bring a change in the cell parameters, we proceeded to study further this system.

The samples of milled KF–KBr were studied by IR spectroscopy in KBr pressed disks and in nujol mulls. Strong absorption from atmospheric water dominates the spectra. A strong broad band at 3316 cm^{-1}, the ν_{OH} antisymmetric stretch, is due to weakly bound associated water molecules. In very hygroscopic samples, as those that have been milled for many minutes, the band broadens extending from 3700 to 3000 cm^{-1}. A medium intensity peak at 2220 cm^{-1} is attributed to strongly bound water as in $KF{\cdot}2H_2O$. The bending mode of water is observed as an intense band at 1657 cm^{-1}, and around 700 cm^{-1} appears an intense and broad absorption band due to rocking and wagging motion of bound water [2]. The KF–KBr system contains, therefore, at least two types of water, one weakly bound and another strongly bound to KF.

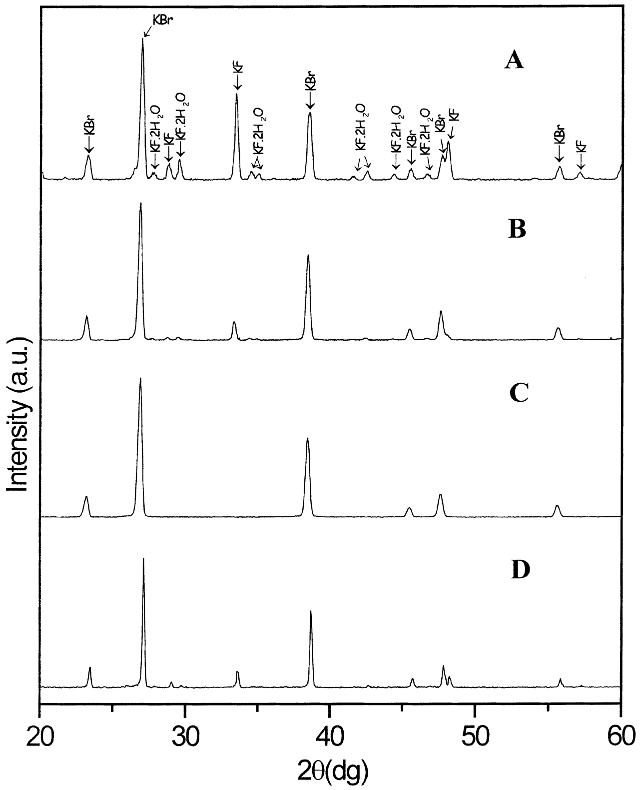

Fig. 1. XRD powder patterns of KBr + KF milled samples: (A) KBr + 2KF; (B) 2KBr + KF; (C) 3KBr + KF; (D) 3KBr + KF dried at 400°C. Observe that in pattern (C), there are no peaks either from KF or from $KF{\cdot}2H_2O$. In pattern (D), after the annealing, the KF peaks reappear and became narrow.

The disappearance of the KF lines in the XRD powder pattern of the KF–KBr system could be associated to the dissolution of the KF phase in the water of the strongly hygroscopic system.

The milled samples of KF and KBr with mole ratios of 1:2 and 1:4, which did not show the presence of the KF phase, were heated to 400°C for 6 h in an oven. The dried samples were run immediately in the X-ray diffractometer. All diffractograms showed the presence of the KF phase. These samples when exposed to the atmosphere regained water, and the XRD patterns showed the continual diminishing of the KF signals (see Fig. 1).

Also, the KF:3KBr sample was prepared by milling in a mortar the components under an Ar atmosphere in a glove box. Part of the obtained mixture was submerged in nujol and measured immediately in the X ray diffractometer. The obtained pattern showed the presence on the KF phase. The rest of the sample was exposed to air for 12 h, and then the XRD pattern was recorded. The KF phase could not be seen.

The phenomena, therefore, is not the formation of a KF–KBr solid solution but the dissolution of the KF minority component in the water of the crystalline system.

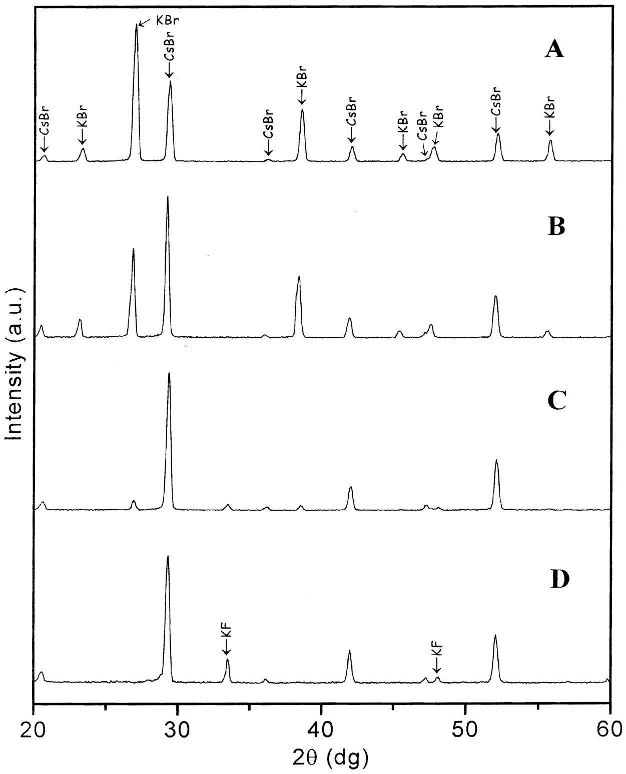

Fig. 2. XRD powder patterns of KBr–CsF system milled samples: (A) 2KBr + CsF; (B) KBr + CsF; (C) KBr + 2CsF, and (D) KBr + 3CsF.

3.3. Mechanochemical reaction of CsF with KBr

CsF is a hygroscopic solid that reacts immediately with KBr on milling in a mortar. The mixture is also hygroscopic, and when KBr was mixed with CsF in any proportion the powdered sample turned pasty. Special care was taken for drying the samples and putting them immediately in the X-ray diffractometer. By the end of the measurement, all the samples were again humid.

The XRD powder patterns of milled samples with molar ratio of KBr to CsF of 2:1, 1:1, 1:2, and 1:3 are shown in Fig. 2. It can be seen that in all cases the following reaction takes place:

$$\mathrm{KBr} + \mathrm{CsF} \rightarrow \mathrm{CsBr} + \mathrm{KF}$$

If excess of KBr is used, the KF lines are not observed due to the dissolution of KF in the water of the system, as discussed earlier.

The driving force for the reaction resides in the favorable enthalpy of the process, as discussed by Milne for mechanochemical reactions [15].

The phase CsF was not present in any of the diffraction patterns, not even in cases when the KBr was still present, indicating that the chemical reaction was not complete. This can be associated with the high hygroscopicity of CsF: the cesium fluoride was forming an aqueous solution at the time of the XRD measurements, similarly to KF.

4. Conclusions

KBr milled with KF forms a very hygroscopic system in which the KF phase dissolves in the absorbed water. When the samples are milled under a dry Ar atmosphere and protected in a nujol mull, the KF peaks can be observed in the XRD powder pattern. At higher KF concentration, the KF and $KF \cdot 2H_2O$ phases can be detected.

KBr reacts immediately with CsF on milling in a mortar according to the following reaction:

$$\mathrm{KBr} + \mathrm{CsF} \rightarrow \mathrm{CsBr} + \mathrm{KF}$$

The system is strongly hygroscopic, the KF phase dissolving in the absorbed water. KBr does not react with LiF or NaF even under strong mechanical impact.

Acknowledgements

We wish to express our appreciation to Dr. Hernani Yee Madeira for the use of reagents and equipment of the Mössbauer Laboratory.

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