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Mechanochemical reactions in alkali halide pressed disks

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Abstract

Mechanochemical reactions that take place when milling and pressing analytes with KBr to form a disk suitable for IR spectral work are reviewed. The topic is extended to other alkali halides matrices. The literature from 1952 is surveyed from an analytical point of view. Several reactions are discussed at length with emphasis on the nature of the products. The mechanism and the factors affecting the mechanochemical changes are discussed in detail for copper sulphate, alkaline and transition metal ferricyanides, and Ag, Hg and Pb salts.

Keywords: Mechanochemistry; Infrared spectra; Exchange reactions; Oxidation–reduction reactions; Solid solutions

1. Introduction

IR spectra of solids are normally run in pressed KBr disks [1–5]. Also used are KCl, CsBr and CsI. During the grinding and pressing processes the analyte can undergo mechanochemical changes such as polymorphic transitions [6–16], mixed solutions [5,17–20], ion exchange [4,5,16,21–24], complex formation [25–29] and oxidation–reduction reactions [30,31]. The chemists are not always aware of these transformations and many pitfalls have been reported in the literature concerning IR spectra solids [32–36].

In the first part of this article we review the literature on analyte transformations in alkali halide pressed disks [1–17,23–31] which is of interest to all chemist users of IR spectra. In the second part we consider in detail important reactions of alkali halides with copper sulfate [37], alkaline and transition metal ferricyanides [38–41] and with Ag, Hg and Pb salts [42,43], with emphasis on the nature of products and intermediate compounds, the reaction mechanism and the factors affecting the mechanochemical transformation, which are of interest to solid state chemists.

2. Historical overview

The KBr pressed disk technique was developed simultaneously by Stimson and O'Donnell [1] and Schiedt, and Reinwein [2] in 1952. The method was generally adopted for the IR analysis of solids since the spectra were sharper than in mulls and did not have interfering bands from the supporting media. Unfortunately the sample can undergo mechanochemical transformations during the milling and pressing with KBr as was noted from the beginning [3].

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