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Electron microscopy and krypton adsorption characterization of high purity LiF powders

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In the present work, a comparative study of LiF powders has been undertaken Methods for the preparation of well-defined, high-purity LiF powders are reported Sample characterization is carried out by combining transmission electron microscopy (TEM) with krypton gas adsorption isotherms LiF crystallites obtained via precipitation in aqueous solutions are perfect regular cubes surrounded by {100} faces. However, fine particles produced by evaporation of LiF powders in an inert gas grow to more complicated polyhedra, surrounded by a predominant plane, which has been identified as a {111} plane

1. Introduction

One of the most significant developments in surface science during the last decade deals with 2D phase transitions. Phase transformations in the monolayer are responsible of stepwise adsorption isotherms, when they take place on an energetically uniform surface. In contrast to well defined single crystals, high surface area powders are generally of much lower quality in terms of surface uniformity and structure.

First, methods are described for the preparation of LiF powders of great uniformity and ultra-high purity. Second, these powder samples are characterized not only structurally by TEM, but from the viewpoint of surface uniformity on an atomic scale using krypton adsorption. TEM is an excellent tool to characterize powder morphology, and krypton adsorption is remarkably sensitive to surface uniformity.

2. Experimental

Two methods of preparation were used.

First, LiF "W" was prepared by mixing aqueous solutions of NaF (0.8M) and LiCl (2M) at room temperature with stirring. The liquid was decanted and the precipitate was washed with a large quantity of distilled water, since LiF has a very small solubility in water. Outgassing of H_2O was performed at about 10^{-5} Pa and up to 700°C and monitored by mass spectrometry.

Second, fine LiF "G" crystallites are produced by a gas evaporation method, i.e., the evaporation in an atmosphere of an inactive gas. The evaporation is carried out in a work chamber such as used for vacuum evaporation. Argon is introduced into the chamber, after it has been highly evacuated. The LiF vapour produced by heating at 1100°C is cooled and condensed in the gas atmosphere in the pressure range 30–300 Torr.

Specimens for electron microscopy were prepared by placing a droplet of LiF powder suspension in isopropanol onto a copper grid covered with a holey carbon film.

Krypton adsorption isotherms were determined at 77.3 K on a conventional volumetric apparatus with a 10 Torr capacitive monometer (datametrics type 699) to measure pressures with an accuracy of 10^{-3} Pa.

3. Results

Fig. 1 shows the micrographs and fig 2 the diffraction patterns respectively for gas-evaporat-

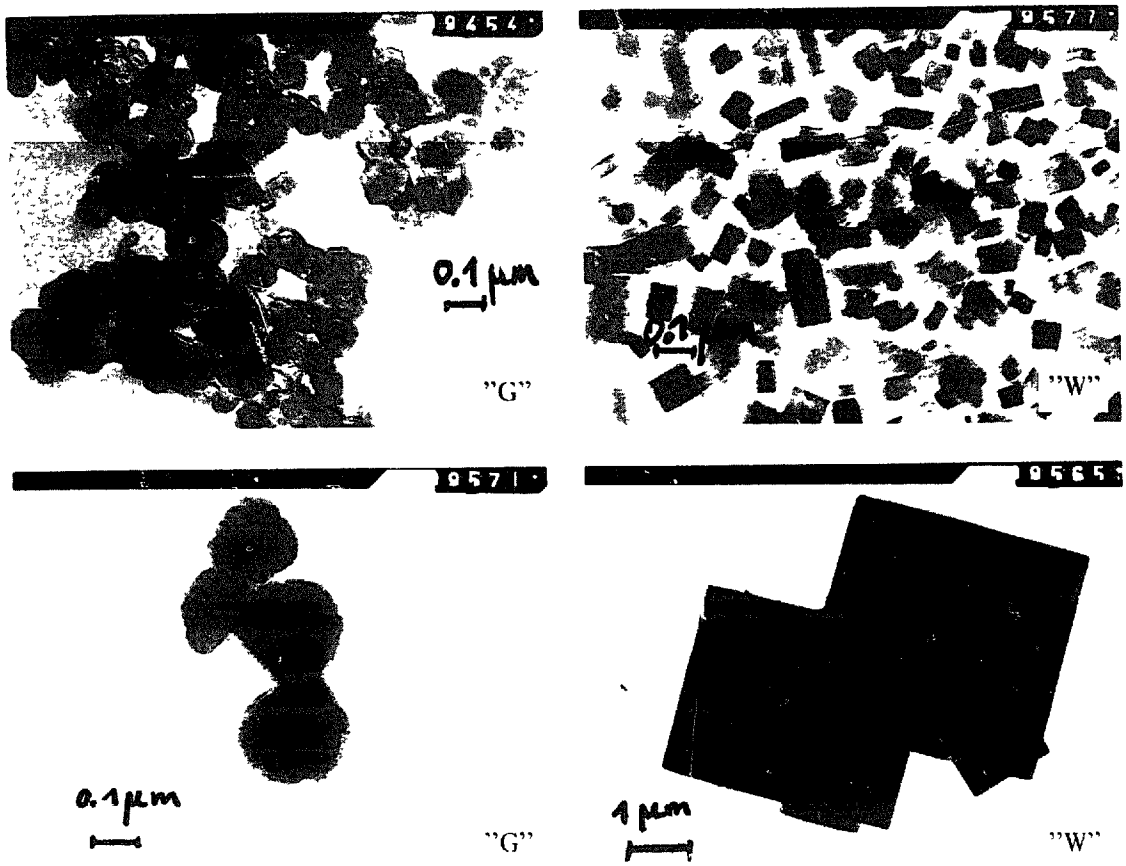

Fig. 1 TEM micrographs of LiF particles LiF "W" are obtained by precipitation in water, LiF "G" are produced by evaporation and condensation in Ar gas at a pressure of 100 Torr

ed LiF "G" and water-precipitated LiF "W". The LiF "W" crystallites are perfect regular cubes surrounded by {100} faces, and the LiF "G" fine particles are more complicated polyhedra, mainly octahedra surrounded by {111} faces.

Fig. 3 shows krypton adsorption isotherms at 77.3 K for the LiF "W" and "G". Stepwise isotherms are observed after room-temperature outgassing for LiF "G" and after vacuum outgassing at 400°C for LiF "W". Such steps occur

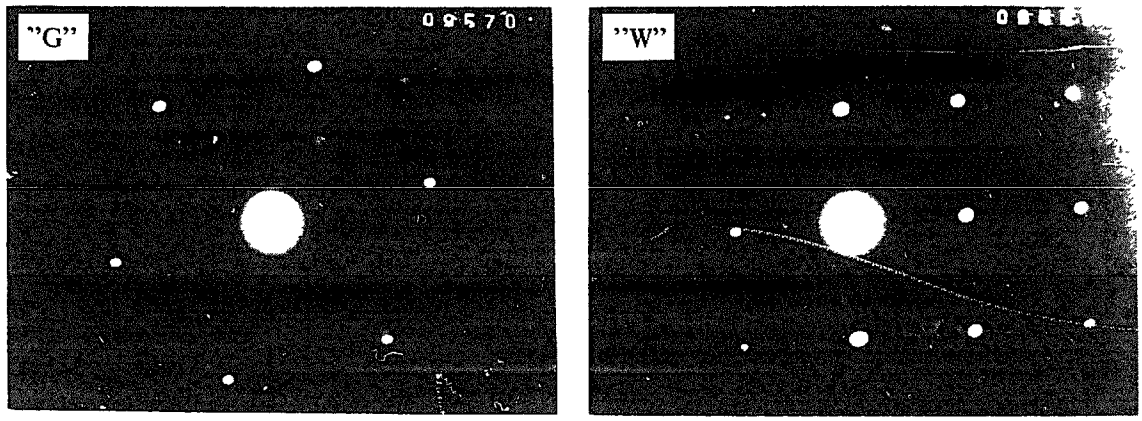

Fig. 2 Diffraction patterns of LiF particles LiF "W" 200, 220, 400, 420 spots, LiF "G" 220 spot

providing the temperature is below a certain critical value, i.e., the two-dimensional critical temperature, and providing the surface is uniform. Krypton adsorption isotherms on LiF "W" exhibit a single sharp step at a pressure of 1.2 Torr, in good agreement with previous experimental determinations [1,2]; relative pressure is 0.6. Such steps have been reported previously on many adsorbents, but they occur at much lower pressure, e.g. 5×10^{-4} Torr for krypton on graphite. Krypton adsorption isotherms on LiF "G" display a first step at a pressure of 0.6 Torr, and a smooth step at about 1.4 Torr, close to the saturation pressure, i.e., 1.73 Torr. Estimation of surface areas of the samples would give roughly 1 m^2/g for LiF "W" and 13 m^2/g for LiF "G".

4. Discussion

Adsorption isotherms prove the development of one regular crystallographic plane in each case. The crystallites are of very homogeneous character with respect to defects. It is well known that this material may be prepared in single-crystal form with a high degree of perfection, so that it has a low density of dislocations less than 5×10^4 cm^{-2} [3].

These planes have been identified by TEM as {100} for LiF "W" and {111} for LiF "G".

NaCl-type crystals of alkali halides can undergo a habit change from cube to octahedron when they grow in a polar solvent [4–6]. Octahedron faces {111} appear at high supersaturation while cubic faces {100} appear at low supersaturation. The habit change has been explained in terms of growth rates of the faces that depend differently on the supersaturation. In the inert-gas evaporation process LiF molecules effused from the source will rapidly lose their energy by collisions with gas atoms, i.e., macroscopically the element vapour is cooled in the gas. The collision mean free path is very short. This efficient cooling produces locally a high supersaturation of vapour.

The {100} surface is known to be a stable surface, whereas the {111} surface cannot retain its ideal structure. Mark [7] calculated the Madelung potential for various faces of several ionic compounds and found that for the alkali halides only the {100} surface is stable. Therefore, a {111} surface must be faceted into three sets of {100} planes inclined at 54.7° to the original surface normal. Henrich [8] demonstrated that a MgO {111} surface was constructed to give a complete faceting only by Ar^+ bombardment at room temperature and annealing at 1400 K. However, Henishi et al. [9] could not observe the complete faceting even by annealing at 1000 K.

Our experimental results show that the LiF {111} planes are not an arrangement of {100} planes because isotherms on LiF "G" should have displayed a step at the same value as observed on LiF "W". On the other hand, LiF {111}

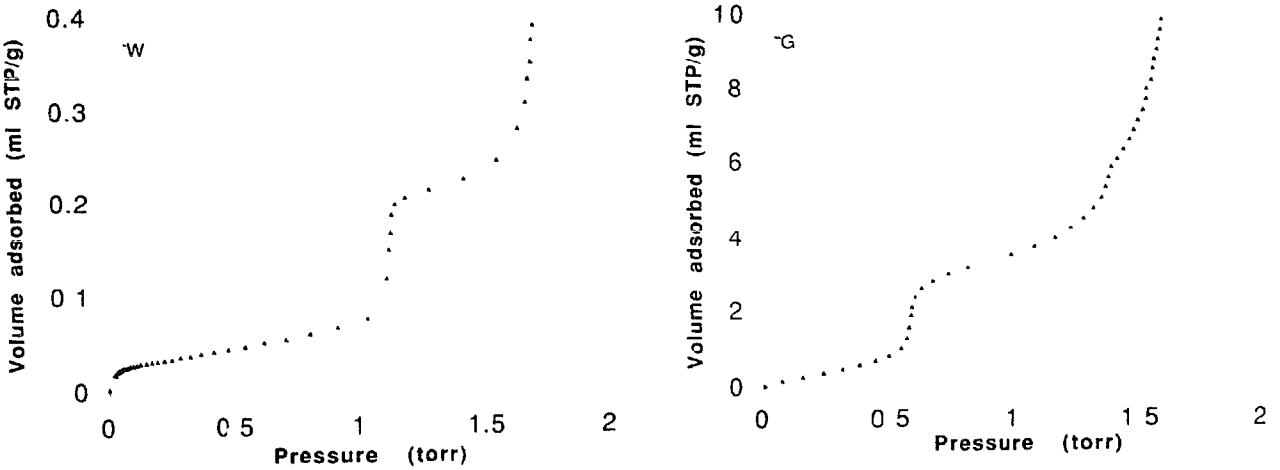

Fig 3 Adsorption isotherms for krypton on LiF powders at 77 3 K for LiF "W" and LiF "G", saturating pressure 1 73 Torr

surfaces are stable at temperatures at least up to 600°C, because no change in isotherms occurred during the annealing of LiF "G" samples up to 600°C This face is stable if it is considered as a K (kinked) face. The model of octupoles proposed previously by Bienfait et al. [5] seems to be an adequate model for the description of the LiF {111} face, which will be made up of regular microfacets with an edge dimension of about 4 Å.

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