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Effect of Growth Conditions on the Morphology and Structural Perfection of Vapor-Grown PbI_2 Crystals

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Abstract—Data are presented on the morphology and structural perfection of PbI_2 crystals grown from the vapor phase in a closed system. By varying growth conditions, platelike, ribbon, needle, twinned, and dendritic crystals were prepared, as well as combinations and intergrowths of these habits.

INTRODUCTION

The crystal habit is known to be governed by the thermal conditions of growth, partial pressures of the constituent components (stoichiometry of the growing crystal), and contamination level [1]. Depending on the relative importance of these factors, crystal may take a wide variety of habits, from ribbons oriented along a certain crystallographic direction to dendrites containing precipitates and polycrystalline inclusions.

In a number of cases, the growth habit is governed by the crystal structure, but typically a key role in determining the morphology of crystals is played by the growth conditions—temperature, impurities, supersaturation, and deviations from stoichiometry.

The purpose of this work was to assess the effect of growth conditions on the crystal habit of PbI_2 grown from the vapor phase in the presence of excess iodine.

EXPERIMENTAL

The growth conditions of PbI_2 crystals were optimized using thermodynamic analysis of the equilibrium vapor-phase composition in the Pb–I_2 system and theoretical and experimental studies of mass transport:

source temperature, 750–800 K;

deposition temperature, 630–660 K;

iodine overpressure, 4–10 kPa;

growth time, 2–4 h.

Crystals were grown in a two-zone furnace. The growth charge synthesized from a high-purity elemental mixture was sealed in a silica tube under vacuum. After holding for 2–4 h at different combinations of source and deposition temperatures, the tube was cooled to room temperature, and the crystals were withdrawn.

The structural perfection of the crystals was examined by optical and scanning electron microscopy (SEM) techniques and x-ray diffraction (Laue photographs).

RESULTS AND DISCUSSION

In most cases, under the optimal growth conditions, we obtained platelike or ribbon crystals. The growth habit was responsive to the thermal conditions, which determine the stoichiometry of the growing crystal. Typically, the platelets and ribbons had the same orientation. It is believed that, in vapor growth, platelike morphology is due to the lateral growth of needle crystals, acting as growth leaders. Platelike crystals may result not only from the vapor–liquid–solid mechanism but also from layer-by-layer growth by the vapor–solid mechanism.

The introduction of excess iodine with p_{I_2} = 2.2 kPa (PbI_2 flow of 15.4×10^{-5} mol/(m^2 s)) favors platelike morphology. At p_{I_2} = 4.0 kPa (PbI_2 flow of 9.93×10^{-5} mol/(m^2 s)), we observe growth of ribbons 10 mm in length and 1–2 mm in width. The source temperature in those runs was 770 K, and the deposition temperature was 650 K. Perfect ribbon crystals were also obtained at p_{I_2} = 8.5 kPa (PbI_2 flow of 4.54×10^{-5} mol/(m^2 s)) and the above source and deposition temperatures. The presence of impurities leads to a wide variety of growth habits, from isometric to acicular. At T_{source} = 820 K and p_{I_2} = 8.5 kPa (PbI_2 flow of 18.45×10^{-5} mol/(m^2 s)), we obtained imperfect crystals and polycrystalline material.

Figure 1 illustrates the morphology of PbI_2 crystals grown from the vapor phase in the form of ribbons, needles, and their intergrowths. The following types of morphology can be distinguished: long ribbons and their intergrowths (often twins), elongated crystals with sharp terminations, bent ribbons, complex habits based on ribbons and their intergrowths, and misshapen platelets (Fig. 1b). At high supersaturations, we observe dendritic morphology (Fig. 1c). Figure 1d shows a misshapen crystal with a twin band (dark area).

On the surface of regular ribbon crystals, we sometimes observe striations tilted to the crystal axis

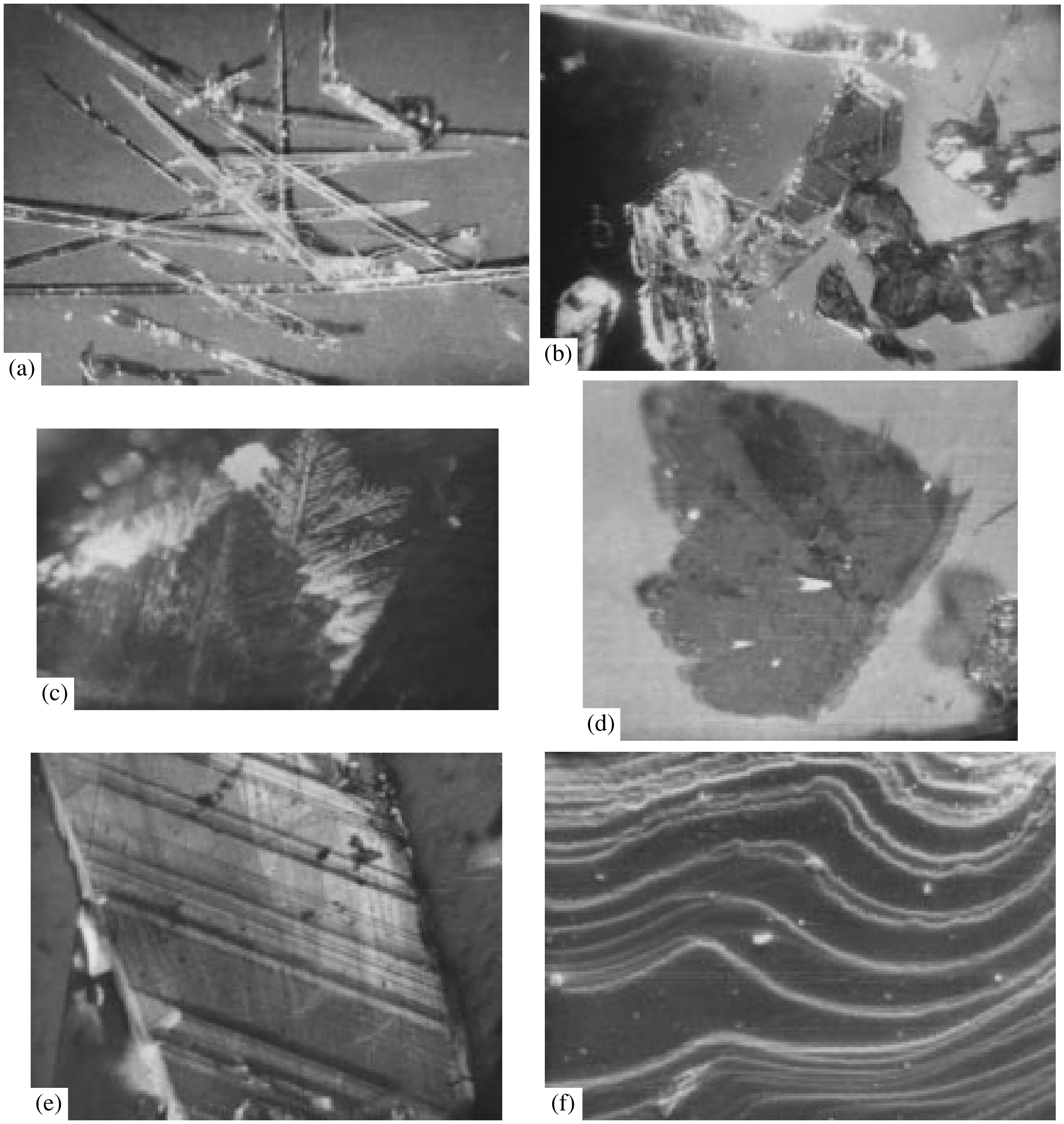

Fig. 1. (a–e, g) Optical and (f, h–j) SEM micrographs illustrating the morphology of PbI_2 crystals; magnifications: (a–e, g) ×50–200, (f, h) ×2000, (i, j) ×1000.

(Fig. 1e). Such striations can also be met on misshapen crystals.

The surface of most regular crystals is perfect; striations are discernible only in SEM micrographs taken at large magnifications. Other morphological features are illustrated in Figs. 1f–1j. Figure 1f shows an accumulation of growth spirals, which lead to the formation of so-called kinematic density waves at growth steps [2]. The appearance of such waves is commonly attributed to the particular character of the diffusion field near step sources and kinematic wave fronts. On the surface of less perfect crystals, we observe growth patterns and vicinal developments in the form of regular or irregular triangles and hexagons (Figs. 1g–1j). Figure 1i shows vicinal hillocks with a stepped structure. In Fig. 1j, one can see details of a hexagonal pattern formed by a set of parallel steps. On sufficiently perfect surfaces, we observe triangular patterns corresponding to stacking faults.

The peripheral parts of crystals grown at different temperatures are characterized by vicinal developments in the form of terraces, some with striations. We observed intergrowth of three terraces into a single aggregate. At long growth times, such terraces disappear and, as a result of the tapering of other platelets, a monolithic structure is formed. The elongation of cer-

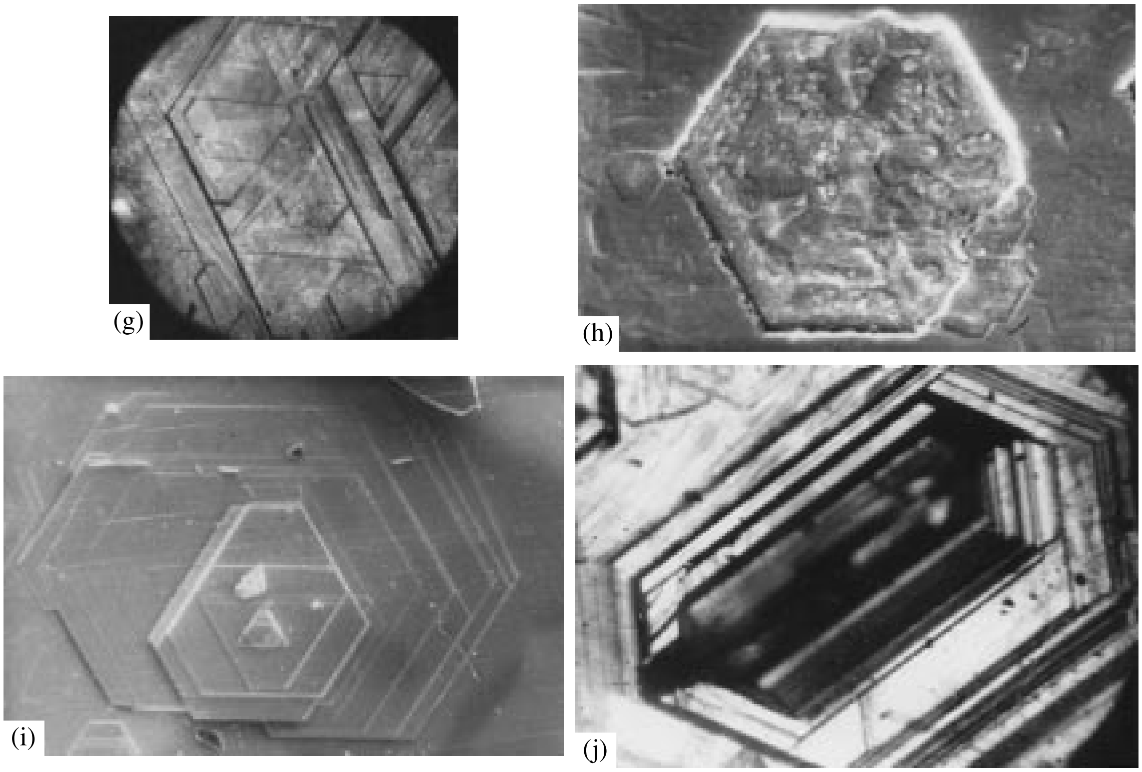

Fig. 1. (Contd.)

tain faces indicates that the growth rate is anisotropic, which is due to the anisotropy in the effective surface energy. The direction normal to the plane of Fig. 1 corresponds to the highest surface energy, while the in-plane directions correspond to the lowest surface energy, as evidenced by the higher rate of lateral growth, especially in the direction of the long axis.

On inhomogeneous surfaces, we observe bundles of slip bands characteristic of plastically deformed crystals. The slip bands run along the easy slip directions and correspond to the outcrops of slip planes. Occasionally, such slip bands alternate with twin boundaries. The latter can be distinguished by the characteristic tapering at the end of the twin boundary. The development of slip bands is related to the steep temperature gradient during growth.

The observed twinning may be due to the significant supersaturation during growth, thermal stress, and second-phase inclusions. In the last case, high mechanical stresses may arise because of the lattice and elastic modulus mismatches between the crystal and inclusion. Such stresses may give rise to twinning, as observed in some of the crystals. Analogous twins around inclusions were revealed in II–VI compounds, in particular, in CdTe [3], which is characterized by a low energy of stacking faults. The components of the elastic stress tensor around a Te inclusion, calculated in the Mott–Nabarro model [4], are close to the theoretical strength of CdTe; that is, inclusions are capable of generating deformation twins.

Twinning is also favored by sharp changes in growth conditions, which may cause a polymorphic transformation. On the surface of the crystals rapidly cooled after growth, we observe twinned structures. To avoid twinning, slow growth rates (low thermal gradients) and high purity of the starting materials are required.

The amount of twinning was found to rise with increasing PbI_2 vapor pressure. Crystallization at high supersaturations gives rise to the formation of cyclic twins. Note that some of the twins extend throughout the crystal and are easy to reveal by the brightness contrast under an optical microscope. The highest supersaturations result in dendritic structures (Fig. 1c).

It is of interest to note that, in the range of a steep temperature gradient, we observe the formation of both single crystals and polycrystalline material uniform in grain size. By varying the thermal conditions, we are able to control, to a certain extent, the grain size of polycrystals. This finding is of technological interest in preparing materials with controlled properties.

Thus, our results demonstrate that, depending on the supersaturation during growth, needle and platelike crystals, twinned platelets, and dendritic twins may be obtained.

The high structural perfection of the crystals selected for physical measurements is evidenced by the high intensity and small width of excitonic emissions. The presence of excess iodine in the growth system ensures a low intensity, if any, of the defect-related photoluminescence (PL) bands at 620 and 700 nm, which are commonly assigned to Pb and I vacancies, respectively [5].

Low-temperature PL studies of PbI_2 crystals grown under different conditions showed that, in the PL spectra of some crystals, the lowest-energy exciton state has a complex structure, which is commonly attributed to polytypism, inherent in layered crystals. Some of the crystals grown under nonoptimal conditions were found to consist of 2*H*- and 4*H*-polytypes (mixed-polytype crystals [6, 7]).

CONCLUSION

The habit, surface morphology, and structural perfection of PbI_2 crystals were studied as a function of growth conditions.

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