Synthesis and Characterization of Lead(II) Iodide Grown in Space

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Crystals of lead(II) iodide were grown on earth and in space on the Discovery space shuttle mission of September 1988. A reaction apparatus was designed that allowed solutions of lead(II) acetate and potassium iodide to diffuse toward a natural cellulose membrane. In space, crystals formed on all regions of the membrane, whereas on earth, crystals formed only on the lower half of the membrane. On earth, crystals nucleated either on the membrane or at sites on or near other crystals. Similar crystal growth occurred in space; however, crystals also formed freely in solution. Characterization of the surface and bulk compositions, morphologies, structural phases, and X-ray luminescence of both earth- and space-grown crystals were carried out. Results of these studies suggest that on earth more PbI(OH) impurity forms with respect to crystallization occurring in space. Even though more nucleation sites and crystals were formed in space, the size of the crystals (up to 2 mm in diameter) was comparable to earth-grown crystals.

Introduction

Crystallization in space[1-7] has been done by several methods including floating zone processes,[4] melt techniques,[8-11] vapor diffusion, and dialysis.[12,13] Preparation of lead(II) iodide crystals[8,11] on earth[14,15] has primarily been done in silica gels.

Experiments of lead(II) iodide grown in space reported here are the first space experiments we are aware of that involve nucleation at a membrane.[16] Solutions of lead(II) acetate [$Pb(Ac)_2$] and potassium iodide (KI) diffused toward each other from opposite sides of a cellulose membrane. Similar control experiments were done on earth.

Videotaping and still shots of the nucleation process were collected on earth and in space. Characterization of both sets of crystals was done to determine differences in bulk concentrations, surface homogeneity, morphology, purity, structure, size, and emissive properties.

Experimental Section

Synthesis. (1) Apparatus. A four-chamber 36-cm-long Plexiglas acrylic container made of solid acrylic endplates, bulkheads, and valves were used. Ethylene propylene O-rings and Delrin screws were used to seal bulkheads and endplates. A natural cellulose Spectropore membrane, Fisher Scientific Co., Rochester, NY, was used to separate the two solutions.

(2) Solutions. The four chambers were filled respectively through the fill plugs with 0.0624 M lead(II) acetate, deionized water, and a solution of potassium iodide. Solid salts were purchased from Alfa Ventron, Danvers, MA. The KI concentrations for the three space experiments (based on earlier experiments on earth) were 0.090, 0.180, and 0.0360 M.

(3) Synthetic Procedures. Experiments were initiated when the valves were opened. In the space experiments, three separate apparatus were used having the different KI concentrations. Similar experiments were done on earth. The sample apparatus were loaded on the flight deck of the September 1988 Discovery space shuttle mission, and experiments were initiated by an astronaut opening the exterior valves of the apparatus after about 2 days into this mission. Crystals were isolated 10 days later.

Characterization. (1) Scanning Electron Microscopy and Energy-Dispersive X-ray Analysis. Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) experiments were done on a LICO scanning electron microscope Model 1820/AMRAY 9100/60 instrument.[17]

(2) Scanning Auger Microscopy. Samples for Auger electron spectroscopy (AES) experiments were prepared by pressing crystals into indium foil. A PHI Model 610 scanning Auger microscope was used for all experiments. Further details of AES experimental conditions can be found elsewhere.[18]

(3) X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) experiments were done on a Leybold Heraeus Model 3000 spectrometer equipped with an EA-10 hemispherical energy analyzer. Procedures used for the analysis can be found elsewhere.[18]

(4) X-ray Diffraction. X-ray powder diffraction experiments were done with a Rigaku RU-300 diffractometer. A diffracted beam flat graphite monochromator, Cu K α radiation, and a scintillation detector were used. Continuous scans were collected at 2° 2θ/min.

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Figure 1. Photograph of nucleation of lead(II) iodide crystals in space and apparatus.

(5) X-ray Fluorescence. A Kevex energy-dispersive X-ray fluorescence (EDXRF) spectrometer with a Rh X-ray tube and secondary target excitation capabilities was used for all experiments. Net intensity ratios were measured for Pb Lα and Kα lines by using Gd secondary target excitation with a Gd filter at 60 kV, 0.70 mA in a vacuum atmosphere.

(6) X-ray Induced Prompt Emission Spectra. X-ray induced prompt emission spectra were done with unfiltered radiation from a tungsten target, beryllium window X-ray tube operated at 70 kV and 30 mA. The tube was about 1 ft from the sample, and a 12-min irradiation time was used.

Results

Synthesis. Seconds after opening of the valves, yellow crystals were observed in both the space and earth experiments. Crystals grown in space were observed to grow primarily as platelets on the membrane, attached to crystals on the membrane and in solution away from the membrane and other crystals. A photograph showing nucleation in solution for the space-grown crystals is given in Figure 1. Crystals grew evenly across the whole surface of the membrane in all three space experiments.

Crystals grown on earth formed only on the lower half of the vertical membrane. In addition, secondary nucleation sites formed either on crystals that were already formed on the membrane or close to these crystals. No nucleation was observed in free solution. About 10 min after opening the valves, a shelf of crystals was observed to form in the region about halfway up the membrane. Eventually, after about 40 min, crystals from this shelf fell off the shelf to the bottom of the apparatus. There did not appear to be any differences with respect to the above observations for the three different concentration levels of KI for either the space- or earth-grown crystals although the number of crystals was considerably different for these different levels.

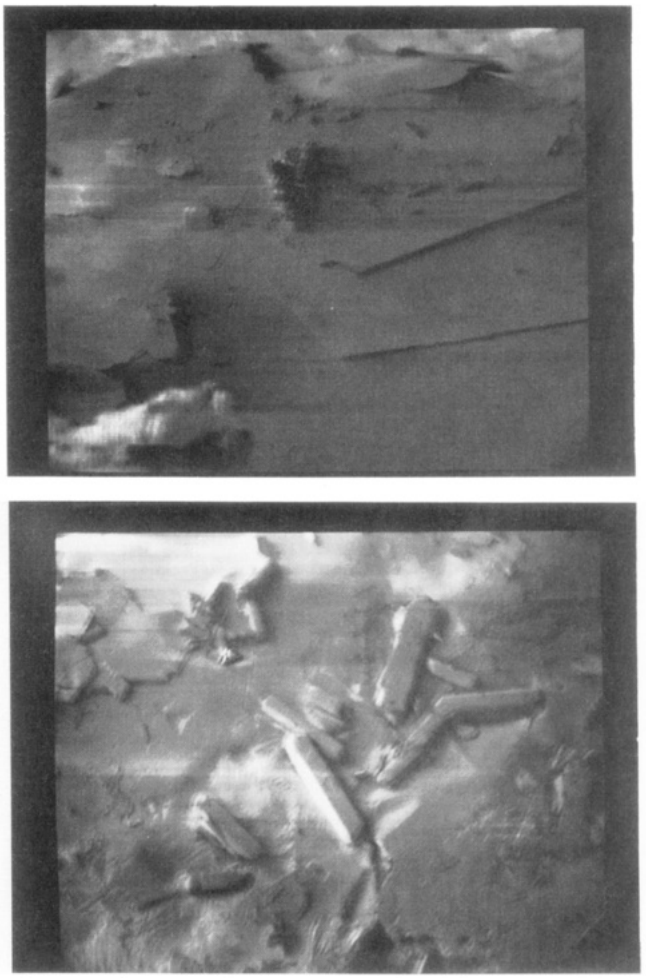

Figure 2. Scanning electron micrographs of the surface of (top) space-grown crystals and (bottom) earth-grown crystals; magnification = 100×.

The amount of crystals for the 0.360 M KI batch was considerably larger than for the other two batches that had lower iodide concentrations. In addition, the 0.360 M KI concentration experiment for crystals grown in space gave about 3 times the number of crystals that were grown on earth.

Characterization. (1) Scanning Electron Microscopy. Scanning electron micrographs of space-grown crystals and earth-grown crystals are given in Figure 2. The space grown crystals shown in Figure 2, top, are relatively flat, and some show a hexagonal symmetry. In addition, there are some smaller needle crystallites on the surface. The earth grown crystals shown in Figure 2, bottom, show flat platelets as was seen in the space-grown crystals, although earth-grown materials have considerably more (3 times) needles. Energy dispersive X-ray analyses for both the earth- and space-grown crystals show peaks for carbon, iodine, oxygen, and lead.

(2) X-ray Photoelectron Spectroscopy (XPS). XPS data for the I($3d_{3/2}$) and I($3d_{5/2}$) transitions for space-grown and earth-grown crystals are given in Figure 3. Two types of iodine species are readily apparent on the surface of the space-grown crystals. A similar trend is observed for the Pb($4f_{5/2}$) and the Pb($4f_{7/2}$) transitions for space-grown crystals and earth-grown crystals. The I/Pb ratio at the surface of the space crystals is about 1.3, while the I/Pb ratio at the surface of the earth grown crystals is about 1.1.

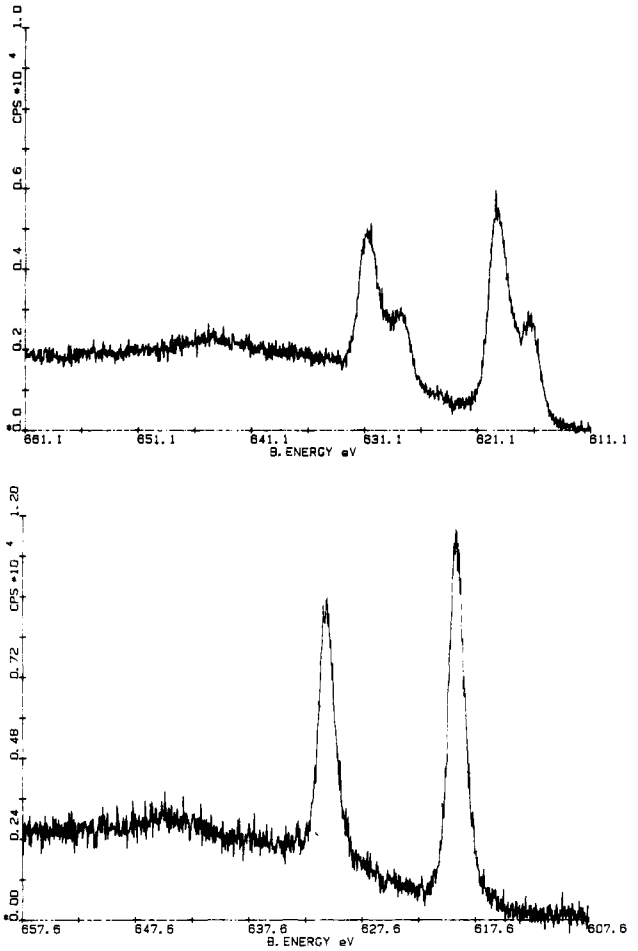

Figure 3. X-ray photoelectron spectroscopy data for $I(3d_{3/2})$ and $I(3d_{5/2})$ transitions for (top) space-grown crystals and (bottom) earth-grown crystals.

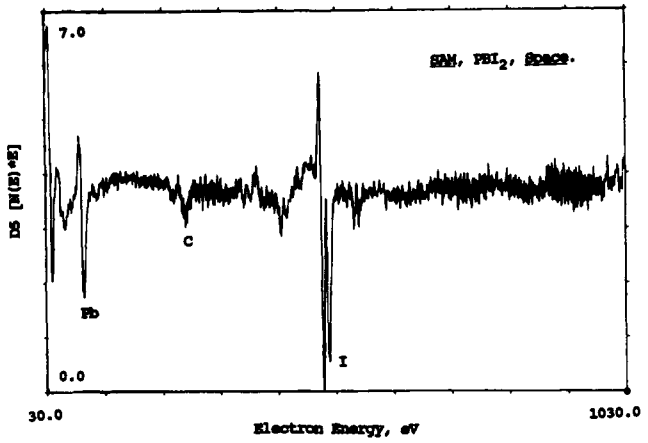

Figure 4. Scanning Auger electron spectrum of space-grown crystals.

(3) Auger Electron Spectroscopy (AES). AES data for the space grown crystals are given in Figure 4. Peaks for Pb, C, and I are observed. The C peak is considerably smaller (about 5 times) than that of the earth-grown crystals initially at the surface. A depth profile for the space-grown crystals shows that the relative concentrations of I, Pb, and C do not appreciably change as sputtering time is increased. A similar trend was found for the earth-grown crystals.

(4) X-ray Powder Diffraction (XRD). XRD patterns for space-grown and earth-grown crystals are given in Figure 5. Two separate phases are identified in both

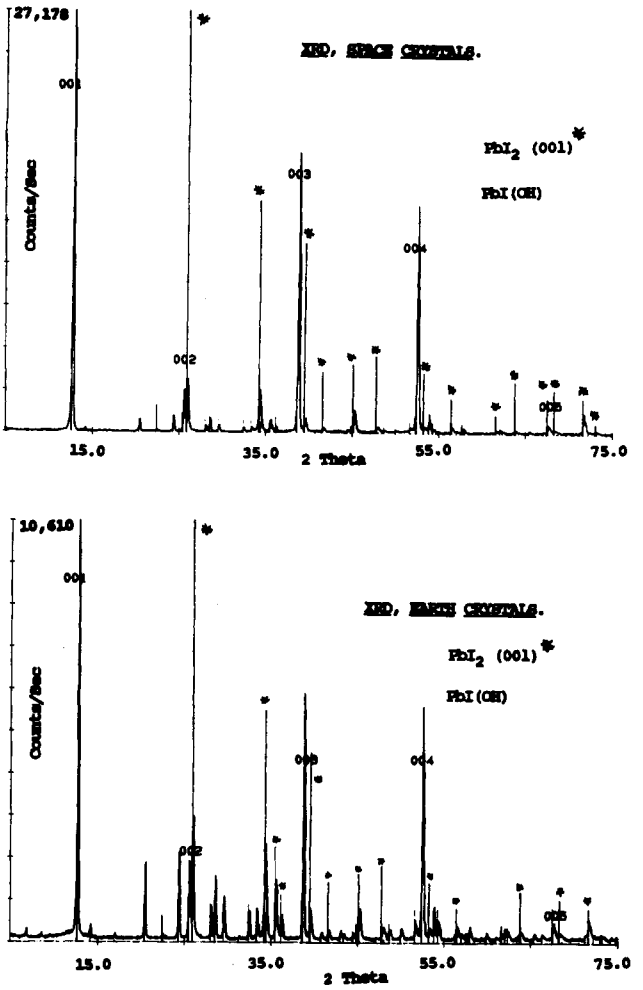

Figure 5. X-ray powder diffraction data for (top) space-grown crystals and (bottom) earth-grown crystals.

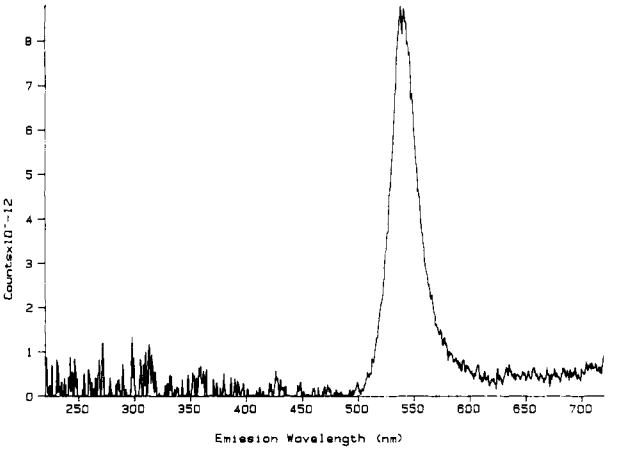

Figure 6. X-ray induced prompt emission spectrum of space-grown crystals.

patterns, one of which is PbI_2, the other PbI(OH). There is a strong (001) orientation for the PbI_2 phase for both ground and unground samples. There are no significant differences in line broadening or line position between the space- and earth-grown crystals.

(5) X-ray Fluorescence (XRF). Net intensity ratios for the space-grown crystals for Pb/I were found to be 1:0.09. Net intensity ratios for the earth-grown crystals were found to be 1:6.85.

(6) X-ray Induced Prompt Emission Spectra (XIPES). The intensities of both space- and earth-grown

crystals in (XIPES) are weak. Spectra for the space- and earth-grown crystals are similar. XIPES data for the space grown crystals are given in Figure 6. There is a broad emission band centered around 545 nm. The resolution of the wavelength scale is better than 2 nm full width at half-maximum, and the ordinate is proportional to W(nm cm^2).

Discussion

Phases and Morphologies. It is clear from XRD data of Figure 5 that two phases are present in all crystals. The major phase in both cases in PbI_2 with a strong (001) orientation and a minor phase of PbI(OH). There is more PbI(OH) in the earth-grown sample. Due to preferred orientation of the PbI_2 crystals of both earth- and space-grown materials, quantification of each phase with this method is not possible, and other methods (vide infra) will be used for this purpose.

Since there is no difference in line broadening or position of the diffraction lines, there is no detectable difference in crystallite size, defect concentration, or lattice constants for the space- and earth-grown material.

The morphology of the PbI_2 crystals is that of a hexagonal plate as shown in Figure 2. Scanning Auger micrographs and scanning electron micrographs as well as image analyses show that the size of the PbI_2 crystals is about the same for both the space-grown and earth-grown crystals. This is consistent with the above-mentioned XRD data; however, this is surprising since there were about 3 times more crystals and there were more nucleation sites (whole membrane vs half) in space.

The needles shown in Figure 2, bottom, for the earth-grown crystals are the PbI(OH) phase. Image analyses show that about 5 times more PbI(OH) forms in the earth crystals than in the space crystals, in agreement with the XRD data.

The XPS data of Figure 3 show that there are clearly two types of lead and iodide species for the space-grown crystals. The absence of two distinct types of lead and iodide species for the earth-grown crystals may be due to poor resolution since the amounts of the two species are closer to each other than in the space-grown crystals.

Surface and Bulk Concentrations. EDX and AES data show there are carbon and oxygen contaminants. AES depth profiles show that carbon is present throughout the material. The ratio of I/Pb determined by XPS, AES, and XRF for the space-grown crystals is closer to that of pure PbI_2 than the earth-grown crystals, suggesting again that the PbI(OH) contaminant phase is significantly greater in the earth-grown material. The external carbon concentration of the space-grown material as observed in Figure 4 is lower than the earth-grown crystals, although bulk levels are similar.

C. Synthesis and Mechanism. The data of Figures 1–6 and the XRF data suggest that there are marked differences between the space- and earth-grown crystals. Most importantly, there is more of the impurity phase PbI(OH) in the earth-grown crystals. The specific growth mechanism of the space and earth crystals is quite different since crystals form in free solution in space but not on earth. The formation of a shelf in the earth-grown crystals suggests that density gradient effects are important in the earth experiments. The absence of the shelf and the uniformity of the crystallization at the membrane of the space-grown crystals is due to the microgravity environment. More efficient mixing of the lead acetate and potassium iodide solutions must be occurring in space.

The mechanism of formation of PbI(OH) on earth has been studied.[14,15] PbI(OH) is a secondary nucleation phase in PbI_2 systems. On earth, PbI_2 crystals are first formed from lead acetate and potassium iodide. The byproduct potassium acetate is alkaline. As the reaction proceeds the alkalinity increases, which leads to a dissolution of some of the crystallized PbI_2 with concomitant formation of PbI(OH).[14] Assuming that similar equilibria occur in space, then the reason there is less PbI(OH) formed in space has to do with the greater number of nucleation sites, which depletes the lead concentration in solution and could lead to higher alkalinity. This also suggests that the pH of the space solution may be more alkaline.

Conclusions

We have shown here that the primary difference between the space-grown and earth-grown crystals is the increased amount of impurity phase PbI(OH) in the earth crystals. The number of nucleation sites and overall yield of space-grown crystals (for the most concentrated solutions) are greater than those for earth-grown materials, and similar size crystals are formed in both locations. The enhanced yield (3-fold) without sacrifice in crystal size may be due to the slower rate of nucleation in space, which is apparent from videotapes of these experiments. XIPES experiments show that the lead(II) iodide crystals are luminescent and potential applications of these materials may result. Such results may be applicable to future studies[19] such as the growth of zeolites in space, which is believed to be influenced by gravitational effects.[20]

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