PREPARATION OF LEAD IODIDE AS INPUT MATERIAL FOR X-RAY DETECTORS

M. MATUCHOVÁ[1], O. PROCHÁZKOVÁ[1], K ŽĎÁNSKÝ[1], J. ZAVADIL [1], J . MAIXNER[2],
[1]*Institute of Radio Eneineeruing and Electronics. Czech Academy of Science, Chaberská 57, 182 51 Praha 8*
[2]*Institute of Chemical Technology, Technická 5, 160 28 Prague, Czech Republik*
E-mail:Marie.Matuchova@tiscali.cz

1. Introduction

Lead iodide (PbI_2) belongs to one of promising materials for high efficiency uncool solid state detectors (in the range of 1kev-1MeV) operating at room temperatures. It can be applied over a wide temperature range from 200°C up to 130°C in detectors in devices used within and outside the laboratory, for example, for ecological measurements (poluted waste water, sewage, etc.), and for improved diagnostic methods in biology and medicine (radiography and tomography). Lead iodide is often compared with mercuric iodide. Especially two important physical properties make PbI_2 a more interesting material for detector applications than HgI_2. These are its lower vapour pressure, and its higher chemical stability. No degradation was observed in the PbI_2 detectors under laboratory ambient in 6 month. The polytypism of PbI_2 seems to be also one significant property of this material. PbI_2 has not a structure modification change.

The chemical analysis and stoichiometry has been determined by X-Ray spectrometer ARL 9400XP. The specific resistance and photoluminescence measurement has been also measured.

2. Aims

The aim of this work is to study the new method of direct synthesis of lead and iodine as the input material of PbI_2. This method has not been studied for this material till now, and seems to be one of the new methods for preparation of the input material. The photoluminescence measurement and measurement of specific resistivity has been done and compared with the measurements done by precipitation and zone purification.

3. Methods

Basic data of PbI_2

Crystallographic system hexagonal type of CdI_2 (Fig.1)
Space group P3m1
Space parameters a = 0.4557 nm
c = 0.6979 nm
PbI_2 forms polytypes: the crystals can have different c parameter
32 polytypes known, basic polytype 2H

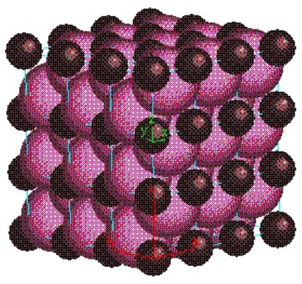

Fig.1 PbI_2 crystal structure

Possible sources of PbI_2 material

commercial material of PbI_2: the commercial material can not be used for the disturbed stoichiometry

material prepared by precipitation of $Pb(NO_3)_2$ and KI : Using the precipitation method the stoichiometry can be experimentally adjusted to the theoretical. The precipitated material must be purified by zone melting further.

direct synthesis of PbI_2 using elements Pb and I_2 Direct synthesis is experimentally more demanding than the preparation of the input material by precipitation. However, it is possible to restrict or even dispense with the zone-melting purification step (Fig. 2).

Method of direct synthesis

The method of direct synthesis is based on the direct synthesis of the elements Pb and I_2 by the appropriate technological parameters. The reaction is feasible and sufficiently fast. The temperature is kept by the temperature controller The apparatus consists from the following main parts: regulator, quartz glass resistance furnace

A special constructed ampoule for synthesis with technological parameters in both sections is in Fig. 3. The ampoules are evacuated to 10^{-6} mbar.

Experiments

The small inside ampoule with iodine is broken before starting experiment. The glass ampoule is heated to 200 C in iodine section and to 700 C in lead section. PbI_2 is formed in lead section. The duration of synthesis is approximately one week. The temperature is controlled by EUROTHERM controller. The synthesized material is demonstrated in Fig. 4. Comparison with the material after precipitation and zone melting. is in Fig.5.

Characterization of PbI_2

Molecular Weight 461.00894
Melting point of Pb 327 C
Melting point of PbI_2 408 C
Boiling point of PbI_2 954 C
G of PbI_2 starts to be negative at 500 C,
the chemical reaction is possible from
this temperature

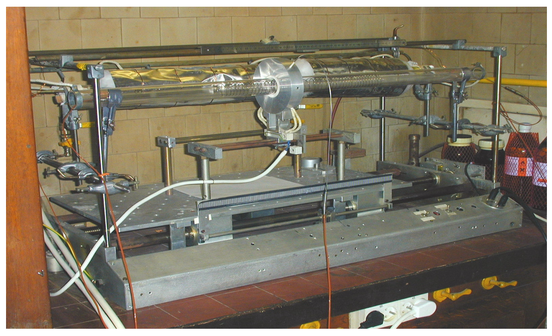

Fig. 2 Apparatus for direct synthesis (back part) and zone melting

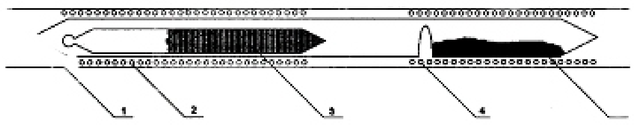

Fig.3 Direct synthesis of PbI_2, quartz glass ampule

Fig. 4 PbI_2 material after synthesis

Fig. 5 PbI_2 prepared by precipitation and purification by zone melting

4. Results and discussions

Microscopic measurements

The microscopic measurements present the layered structure of material (Fig.6a, 6b, 7) Equipment: microscope VEGA TS 5136MM, LVSTD (Low Vacuum Secondary Tescan Detector) has been used for microscopic measurements. It enables the detection of secondary electrons by the condition of low vacuum in the microscope chamber and the detector BSE for back reflected electrons for the contrast observation. Till now we could not go to atomic structure because of the lack of appropriate detector. The analytical analysis has been done as well, but not with the success. The recelebration of the analyser must be done. Several pictures are presented. The height of steps has been calculated.

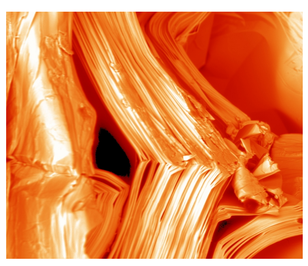

Fig. 6a Layered structure of PbI_2

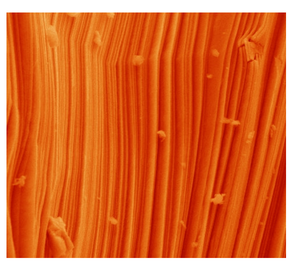

Fig. 6b Layered structure of PbI_2

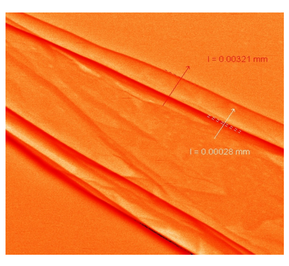

Fig. 7 Steps and kinks on the structure

Electrical measurements

Maestro software for Windows has been used. The electrical characteristic current versus voltage has been measured by the room temperature using the unit source-meter of the Keithly firm "236 source Measure Unit" in the range from 0 to 100 V with the positive and negative polarity as is shown in the Fig. 6. The resulted resistivity is estimated from the linear parts of the characteristics, which are in the region of the higher voltage. The value of the specific resistivity by both polarities is the same 1.0 x 10/ 10 ohm cm. Two measurements are compared: the sample after direct synthesis (Fig. 8.1.) with the sample (Fig. 6.2.) prepared by precipitation and purified by zone melting (10 passes and the movement of the zone 30mm/h). The resistivity for the sample from one melting is about 2 times higher. It means that purity is higher than by direct synthesis. However, the differences are not so essential and direct synthesis is comparable with precipitation. It is supposed even to purify the samples after direct synthesis by zone melting. Otherwise the number of passes though the zone can be sufficiently lowered. The arrangement of the contact and the plate is in Fig..9

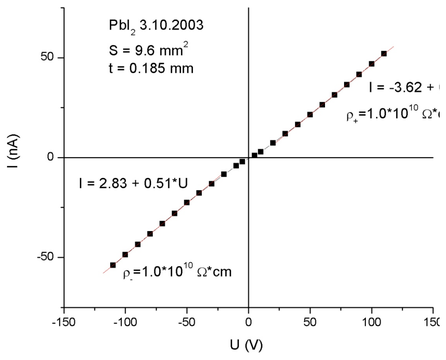

Fig. 8.1 Specific resistance estimation Electrical characteristics current-voltage

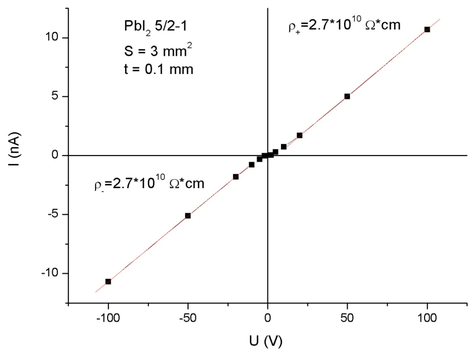

Fig. 8.2 Electrical characteristics of current versus voltage. Evaluation of resistance

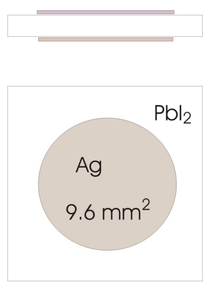

Fig. 9 Arrangement of the contact and the plate

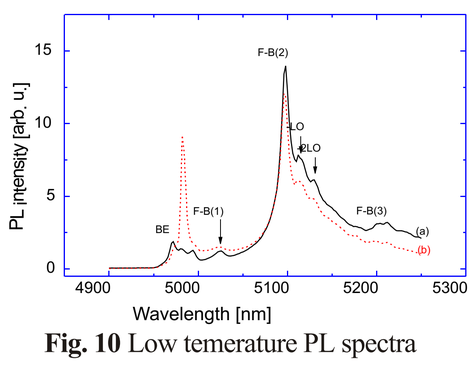

Fig. 10 Low temerature PL spectra

Low temperature photoluminiscence measurements

Low temperature PL spectra of typical PbI_2 crystals prepared by precipitation followed by zone melting (8.1.) and by direct synthesis (8.2.) are shown in Figs. 8. Application of zonal melting leads to the narrowing of spectral bands and appearance of fine spectral features, characteristic of pure material, low in defects.

Categories: band-edge (BE) transitions at about 2.49 eV and free to shallow donor levels (F-B) related transitions at 2.46, 2.43 or 2.38 eV. The high energy band (BE) in Fig. 8 exhibits superlinear behaviour with increasing excitation power and results from the decay of excitons. Phonon assisted transitions associated with exciton recombination as well as with shallow defect level (2), and involving 5-8 meV LO phonons, could also be seen in Fig. 10.

5. Discussion

The method of direct synthesis has been compared with the method preparing material by precipitation and subsequent purification. The first measurements of electrical resistivity and photoluminescence confirm high quality material after direct synthesis. If the zone purification would be needed, not many passes through the zone would be necessary, and the time of experiments can be shortened.

The next development of our research:

the study of the influence of lanthanides on the properties of material
the study oft the purification by zone melting after direct synthesis
the construction 2 or 3 zones by zone apparatus
the study of the mutual relations of the purity of material and photoelectrical and electrical properties
growing of bulk crystals by Bridgman-Stockbarger method

CONCLUSION

The method of the direct synthesis of lead iodide has been successfully implemented. The technology has been worked out, the analysis, and the characterization has been introduced to measure the quality of this material.

This work is supported by the Grant Agency of the Czech Republic, Projects No.102/01/1338, No.102/03/0379 and by Academy of Sciences of the Czech Republic, Project KSK 1010104