JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 10, No. 9, September 2008, p. 2360 – 2362

Melt growth of pure and Mn^{2+} -doped KPb_2Cl_5 single crystals

C. NEAMTU*, AL. DARABONT
National Institute for R&D of Isotopic and Molecular Technologies, 65-103 Donath Street, POB 700, 400293 Cluj-Napoca, Romania

Single crystals of KPb_2Cl_5 were grown by vertical Bridgman method, in sealed quartz ampoules, starting from KCl and $PbCl_2$ previously purified and synthesized in single crystalline form. KCl single crystals were obtained using the Czochralski technique. $PbCl_2$ single crystals were grown by the Bridgman method, in sealed ampoules, under chlorinating atmosphere. The resulted KPb_2Cl_5 single crystals, up to 3 cm long and 1.5 cm in diameter, were of good optical quality. For the Mn^{2+} -doped crystals, EPR measurements indicate the presence of the paramagnetic ions in the crystalline host in one of the Pb^{2+} two distinct sites, namely the one with the lower crystalline symmetry.

(Received February 25, 2008; accepted August 14, 2008)

Keywords: Lead halides, Crystal growth, Paramagnetic ions, Mn^{2+} in KPb_2Cl_5

1. Introduction

A relatively new family of materials, the ternary alkali lead halides, MPb_2X_5 (where M = Na, K, Cs, Rb and X = Cl, Br), have caused a strong interest over the past few years, due to their set of remarkable physicochemical properties and application potential.

The presence of divalent lead emission centers in the crystal structure, with high concentration of lead (the MX - PbX_2 ratio is 1:2) make from these compounds an attractive subject for luminescence mechanism studies. Due to their low phonon energy, the rare-earth doped crystals have been identified as promising active media for solid-state lasers operating in the mid-IR range.

These compounds have a high chemical stability, melt at low temperatures, are only slightly or not hygroscopic and have a broad transparency window in the IR range.

A representative of the MPb_2X_5 family is potassium lead chloride, KPb_2Cl_5 (KPC). At room temperature, KPC is monoclinic (space group $P2_1/c$) with four molecules in the unit cell and lattice parameters $a = 0.8831$ nm, $b = 0.7886$ nm, $c = 1.243$ nm and $\beta = 90.14^\circ$. The Pb^{2+} ions occupy two crystallographic non-equivalent positions. The first one, Pb(1), has a distorted octahedral environment. The second one, Pb(2), assumes the same coordination as Pb^{2+} in $PbCl_2$ [1]. The loose packing of large-radius ions in the lattice gives the possibility of varying the composition and properties of these crystals, and therefore expanding the range of potential applications.

Studies regarding the crystal structure [1,2], the luminescence mechanism of divalent lead emission centres [3], absorption and emission properties [1, 4] are available. Recently, KPC crystals doped with rare-earth trivalent ions were synthesized, making good candidates as laser host materials [5-9].

KPC can be grown from aqueous solution, from the melt or by sublimation, but single crystals of high quality have been grown from the melt by the Bridgman method. Despite the relatively large amount of work dedicated to the investigation of this compound, there are still difficulties in obtaining the dimensions and quality required by its various potential applications. It is well known that the purity of the starting materials (prone to hydrolysis, formation of unwanted compounds and even decomposition), represents a significant limitation in the growth of high-quality KPC [1]. Chlorination of the melt and subsequent zone refining were successfully applied as a solution to this problem [7-9]. Additional aspects regarding the growth process, such as the structural phase transitions that occur during cooling [1, 8-10], may affect the final product, the accumulated strain making the crystals prone to cracking.

Previously we reported on the growth of pure and Mn doped $PbWO_4$ crystals [11].

The present publication reports on the synthesis of undoped and Mn^{2+} -doped KPb_2Cl_5 single crystals. Special attention is paid to the purification of the starting materials, which were synthesized as single crystals previously to the preparation of the final compound. The experimental conditions and steps for the growing process are described. The resulting crystals were identified by X-ray diffraction measurements. For the doped KPC, preliminary EPR measurements confirm the presence of the Mn^{2+} paramagnetic ions in the crystalline host.

2. Experimental

2.1. Starting materials – purification and crystal growth

The starting materials were anhydrous KCl 99.8% ("Reactivul" Bucharest) and $PbCl_2$ $\geq 98\%$ (Merck). Purification of these reagents was achieved by synthesis in single crystalline phase. Successive growth processes resulted in ultra pure single crystalline material.

Single crystals of KCl were obtained by pulling from the melt (Czochralski method). The initial powder was melted in a 40 cm^3 platinum crucible, using an electric furnace with kanthal A wire heating element that generates up to 1200 W of electric power. High-quality seed crystals were selected and used to initiate each growth process. During growth, the crystals were pulled from the melt at 4-5 mm/h and rotated at 5-8 rpm. After removing the lower (last to freeze) part of the resulted crystal, in which the remaining impurities have been separated, the growth was repeated up to 3-5 times, to obtain ultrapure single crystalline KCl. The resulted crystals (up to 2.5 cm in diameter and 10 cm long) were of very good quality, cloudless and transparent.

The purification and crystal growth of $PbCl_2$ are described in extenso in [12]. $PbCl_2$ powder was melted under controlled Cl_2 atmosphere. The chlorine gas was bubbled directly through the melt (using a quartz tube immersed along the recipient until it almost reached its bottom). After the melt turned clear, it was slowly cooled down too room temperature. Further purification was achieved by repeated horizontal zone refining, under continuous flow of chlorine gas. After each run, only the clearest parts were selected from the bulk material. Up to nine passes were needed to obtain colourless and transparent ingots, yielding single-domain crystals over a length of several centimeters.

From the previously purified material, $PbCl_2$ single crystals were obtained by the vertical Bridgman technique. The sharp-tipped glass ampoule, sealed under chlorinating atmosphere, was lowered through a vertical gradient ($5^oC/cm$) electrical furnace at 6 mm/h. The resulted single crystals, with maximum 1.5 cm in diameter and 5 cm long, were clear and crack-free.

2.2. KPb_2Cl_5 – crystal growth

Potassium lead chloride, KPb_2Cl_5, was synthesized by the Bridgman technique from ultra pure single crystals of potassium chloride, KCl, and lead (II) chloride, $PbCl_2$, in stoichiometric amounts.

The single crystals of KCl and $PbCl_2$ were cleaved and splited, respectively, into smaller crystalline pieces and loaded in a quartz ampoule. This was heated to 300-350^oC in dynamic vacuum for 1 h (to remove any residual moisture from the crystalline surfaces exposed to air during transfer), slowly cooled to room temperature and then sealed at ~10^{-3} Torr. It was placed inside a vertical Bridgman furnace with a temperature gradient (measured in the empty furnace) of $5^oC/cm$.

The crystalline charge was slowly heated at a temperature slightly above the melting temperature of one of its components ($PbCl_2$) and maintained at this temperature for 2 hours, to ensure the homogenization of the melt and to eliminate any potential gas bubbles from it. When the yellow melt has become clear and bubble-free, the ampoule was lowered at a rate of 6-2 mm/h. Quartz ampoules with a pointed end were used to act as seed selector and promote single crystal growth. A complete run took approximately 25 to 80 hours (at 6 or 2 mm/h, respectively). After all the length of the charge has passed through the gradient zone and complete solidification of the crystal was achieved, the temperature of the furnace was gradually lowered down to room temperature in 8 hours. At least two passes were needed in order to obtain good quality crystals.

The KPb_2Cl_5 crystals doped with paramagnetic Mn^{2+} ions were obtained by adding 0.1% (mass) of polycrystalline manganese chloride (produced by "Reactivul" Bucharest) to the starting materials. The $MnCl_2 \times 4\ H_2O$ powder was previously desiccated at about 200^oC for 1 hour.

3. Results and discussion

Growth of ternary alkali halides like KPb_2Cl_5 is drastically influenced by the purity of the starting materials. KCl is relatively stable to the influence of atmospheric oxygen and only slightly hygroscopic, but $PbCl_2$ is very sensitive to both oxygen and moisture. Moreover, $PbCl_2$ has a tendency to decompose at higher temperatures and has high vapour pressure. In the molten state, the presence of O_2 and H_2O facilitates the formation of lead hydroxy- and oxide chlorides. The chlorination of the melt proved to be a necessary step in the purification of $PbCl_2$, eliminating the unwanted impurities and preventing the decomposition and formation of metallic lead (observed as a black precipitate).

In addition, it has to be pointed out that the synthesis of the starting materials in single crystalline state not only represents a further purification process, but also reduces the contact between the purified material and the air (containing oxygen and water).

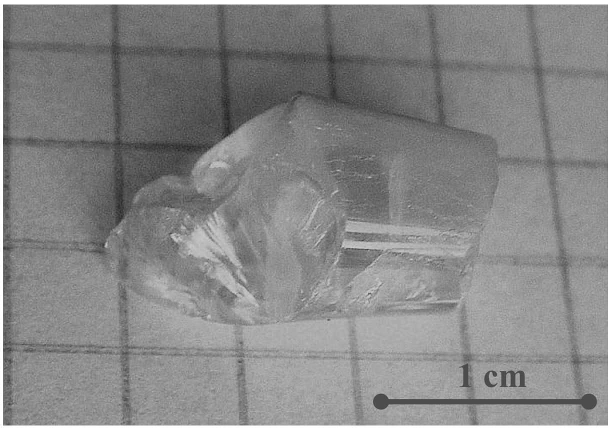

Fig. 1. KPb_2Cl_5 crystal obtained by the vertical Bridgman method (still sealed in its growth ampoule).

The obtained single crystals of KCl and $PbCl_2$ were of high quality, free of defects, and transparent. The KCl crystals were all colourless. In some of the $PbCl_2$ crystals, a slight yellow coloration occurred, due to a surplus of chlorine gas included during the growth process.

Several crystals of KPb_2Cl_5 have been grown by the method described above.

X-ray diffraction measurements proved the formation of the KPC compound and confirmed the structural data given by Nitsch et al. [1].

Fig. 1 shows a crystal as grown in the ampoule. Cracking and cloudiness are evident in some regions, but transparent zones are also easy to perceive (in spite of the thin semi opaque layer deposited on the inner glass wall).

At least two consecutive passes were needed to obtain crystals of better optical quality. Crack-free pieces, up to 1.5 cm in length (see Fig. 2), were harvested from these ingots. To the unaided eye, they appear colourless and highly transmissive.

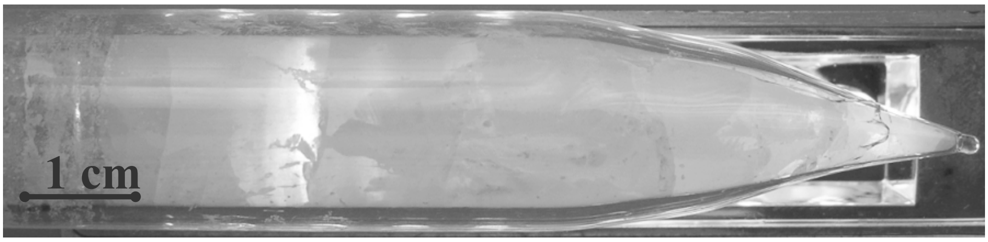

Fig. 2. Single crystalline KPb_2Cl_5 harvested from a larger crystal (no cleavage facets are visible).

According to literature data [5, 9], the material has a high thermal expansion coefficient, which can lead to the formation of cracks during the cooling process. A slower rate of transit through the thermal gradient zone, combined with a longer cooling time, can improve the quality of the resulted crystals.

Due to the fact that $PbCl_2$ has a relatively high vapour pressure, special attention has to be paid to ensure a uniform and constant temperature along the entire ampoule during the homogenization of the melt. Consequently, unwanted evaporation and variations in the stoichiometry of the final compound will be avoided.

Another factor that has a positive influence on the quality of the obtained crystal is the presence (in the sealed ampoule) of gaseous Cl_2 in excess. This was achieved either by using $PbCl_2$ crystals with surplus of Cl_2 included during the growth, or by sealing the ampoule under gaseous chlorine.

The presence of the paramagnetic ions in the crystalline KPC was evidenced by EPR measurements. The initial studies have shown that the Mn^{2+} ions substitute the Pb(2)-type lead ions, which have the lower crystalline symmetry from the two allowed non-equivalent positions.

4. Conclusions

Good quality undoped and Mn^{2+}-doped KPb_2Cl_5 crystals, up to 1.5 cm in diameter and 3 cm in length, were grown by the vertical Bridgman technique. X-ray diffraction measurements confirmed the monoclinic crystalline structure with the Pb^{2+} ions occupying two crystallographic non-equivalent positions.

The use of thoroughly purified starting materials and the synthesis in single crystalline state of both KCl and $PbCl_2$ proved very effective for the elimination of unwanted compounds. Additionally, the handling operations of starting materials were greatly facilitated.

Preliminary EPR studies on the Mn^{2+}-doped crystals suggest that the paramagnetic divalent ions are located in the crystalline host at the Pb^{2+} site with the same coordination as Pb^{2+} in $PbCl_2$, that is to say the site with the lower crystalline symmetry.

Further EPR and luminescence studies are in progress for the synthesized pure and doped crystals.

Acknowledgements

This study was supported by the Ministry of Education and Research, National Agency for Scientific Research, CEEX Program (project no. 2-Cex-06-11-38/ /25.07.2006).

References

[1] K. Nitsch, M. Dušek, M. Nikl, K. Polák, M. Rodová, Prog. Crystal Growth Charact. **30**, 1 (1995).
[2] P. W. J. Jansen, Rec. Trav. Chim. **87**, 1021 (1968).
[3] M. Nikl, K. Nitsch, I. Velická, J. Hybler, K. Polák, T. Fabian, Phys. Stat. Sol. (b) **168**, K37 (1991).
[4] V. A. Pustvarov, I. N. Ogorodnikov, N.S. Bastrikova, A.A. Smirnov, L.I. Isaenko, A.P. Eliseev, Optics and Spectroscopy **101**(2), 234 (2006)
[5] U.N. Roy, Y. Cui, M. Guo, M. Groza, A. Burger, G. J. Wagner, T.J. Carrig, S.A. Payne, J. Cryst. Growth **258**, 331 (2003)
[6] R. Balda, J. Fernández, A. Mendioroz, M. Voda, M. Al-Saleh, Optical. Mat. **24**, 91 (2003)
[7] M. Voda, M. Al-Saleh, G. Lobera, R. Balda, J. Fernández, Optical Mat. **26**, 359 (2004)
[8] M. Velásquez, A. Ferrier, J.P. Chaminade, B. Menaert, R. Moncorgé, J. Cryst. Growth **286**, 324 (2006).
[9] N.J. Condon, S. O'Connor, S.R. Bowman, J. Cryst. Growth, **291**, 472 (2006)
[10] T. N. Sumarokova, T. P. Modestova, Zh. Neorg. Chim. **5**, 2477 (1960)
[11] Al. Darabont, C. Neamtu, J. Optoelectron. Adv. Mater. 9(5), 1254 (2007).
[12] C. Neamtu, Al. Darabont, J. Optoelectron. Adv. Mat. **9**(5), 1257 (2007)

---

*Corresponding author: cneamtu@gmail.com