



Growth and optical properties of RE-doped ternary rubidium lead chloride single crystals



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ABSTRACT

This paper reports on the growth of pure and Nd³⁺, Pr³⁺, Yb³⁺, and Dy³⁺ doped rubidium lead chloride (RbPb₂Cl₅) crystals by the atmosphere-controlled micro-pulling-down method. Structural and composition measurements are reported, further completed by the absorption, radio- and photoluminescence spectra and decay measurements on the prepared single crystals. Potential of these materials and preparation method for the application in the infrared solid state laser field are discussed.

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1. Introduction

Ternary alkali lead halide (TALH) single crystals with stoichiometric relation of MX:PbX₂ equal to 1:1, 2:1, 1:2 and 4:1, where M is K, Rb or Cs and X is Cl, Br or I, have been intensively studied for many years. Although the initial reason for this research activity was polymorphism in CsPbCl₃ (CPC) [1], higher importance was applied to the study of Pb²⁺ emission center in various hosts and their large concentration range achievable in TALH crystal structures: KPb₂Cl₅ (KPC) [2], RbPb₂Cl₅ (RPC) [3], CsPbCl₃ [4]. This fact made the above mentioned compounds together with Pb²⁺ doped alkali halide and M⁺ doped lead halides important model systems [5] for the study of their chemico-physical, optical, and luminescence properties. Nanophases formation of the CPC and CsPbBr₃ (CPB) in CsCl and CsBr matrixes has been also investigated [6,7].

Recently, there has been growing interest in congruently melting TALH with stoichiometric relation 1:2 such as KPb₂Cl₅, RbPb₂Cl₅, KPb₂Br₅ (KPB), and RbPb₂Br₅ (RPB) [8]. When doped with rare earth (RE) elements (Nd³⁺, Dy³⁺, Pr³⁺ and Er³⁺), they were found suitable as a host for solid state lasers at room temperature in the broad spectral range from mid-IR to vacuum ultraviolet [9–11].

Such materials must possess high mechanical strength, photo- and thermal stability, and chemical resistance. Most importantly, their absorption and emission spectra must contain strong,

homogeneously broadened, polarized lines, which are of importance for pumping with the diode lasers, whose radiation is polarized and is concentrated in a relatively narrow spectral range [12]. The search for new halide laser materials for mid infrared spectral region, which have high quantum yield and lowest possible nonradiative losses, is still of high interest [13–15].

Ternary potassium lead chloride KPb₂Cl₅ [16–20] seems to be the most studied ternary halide as a low phonon IR laser host, but the attention is also paid to other congruently melting ternary halides, such as RbPb₂Cl₅ [21,22] and RbPb₂Br₅ [8]. RbPb₂Cl₅ belongs to the structural homogeneous family of MPb₂X₅ and crystallizes in monoclinic structure with lattice parameters $a = 8.915 \text{ \AA}$, $b = 7.950 \text{ \AA}$, $c = 12.445 \text{ \AA}$, $\alpha = \gamma = 90 \text{ deg}$, $\beta = 90.14 \text{ deg}$, and space group P2₁/c [5]. Owing to low symmetry these crystals should show anisotropic optical properties depending on the polarization of incoming light [22].

Crystal growth of TALH still remains a challenge due to high affinity of lead halides to react with atmospheric moisture under formation of hydroxy-halides which convert to oxide-halides when heated. These impurities must be unconditionally removed from starting halides before the crystal growth and purified materials must be handled under protective oxygen-free atmosphere throughout all the manufacturing process. The TALH disposition for grain and mosaic blocks forming, cracks appearance during cooling to room temperature [12], and high segregation of doping elements [23,24] is also a practical obstacle. In Prague laboratory a very efficient purification method of halides was developed. It con-

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sists of a halogenation of molten halide by a mixture of gaseous halogenating agents and a subsequent zone refining [5,25]. The TALH and lead halide single crystals of high quality have been successfully grown from the melt by the unseeded vertical Bridgman method [5,25,26]. Recently, the micro-pulling-down (μ -PD) method [27] was successfully applied to grow pure and Pr^{3+} -doped lead chloride single crystals [24].

This contribution deals with preparation of high purity RbPb_2Cl_5 starting materials, their doping with RE elements such as Pr^{3+} , Dy^{3+} , Nd^{3+} and Yb^{3+} , and their crystal growth by the atmosphere-controlled μ -PD method. Fundamental optical and luminescence properties in visible and IR spectral regions are characterized. The potential of μ -PD method to prepare crystals of sufficient optical quality for IR laser applications is discussed. To the best of our knowledge, preparation and crystal growth of pure and RE-doped RbPb_2Cl_5 single crystals by the μ -PD method has not been published so far.

2. Experimental

2.1. Preparation and crystal growth

Starting rubidium lead chloride was prepared by direct synthesis from molten PbCl_2 and RbCl in stoichiometric relation 2:1. Preparation of high purity starting lead chloride (PbCl_2) was described in [5,25] as well as purification of commercially available rubidium chloride (RbCl) of p.a. purity. The oxy- and hydroxy-impurities were removed by the introduction of gaseous mixture of chlorination agents into the molten RbPb_2Cl_5 followed by zone refinement [5,25]. Travel rate of the molten zone was 25 mm/h and its width about 20 mm.

Two manufacturing routes for preparation of RE admixtures into RPC host were used: (i) preparation from commercially available RE carbonates by reaction with hydrochloric acid, and (ii) by direct reaction of RE metal element with hydrogen chloride.

Eleven samples of RbPb_2Cl_5 pure and doped with NdCl_3 , PrCl_3 , YbCl_3 , and DyCl_3 were prepared (see Table 1). Four of them were doped with NdCl_3 , PrCl_3 , YbCl_3 , and DyCl_3 prepared from their carbonates in nominal concentration 0.5 mol% and six of them were doped with DyCl_3 , YbCl_3 , and NdCl_3 prepared from their metals in nominal concentrations of 0.5 mol% and 5 mol% for each RE element. Samples with 5 mol% RECl_3 doping were additively loaded with 5 mol% of RbCl for charge compensation. All samples were sealed in eleven quartz ampoules under protective atmosphere for their secure transportation. All RbPb_2Cl_5 starting materials were prepared at the Institute of Physics AS CR, Prague, Czech Republic.

Single crystals of RbPb_2Cl_5 pure and doped with Nd^{3+} , Pr^{3+} , Dy^{3+} , and Yb^{3+} were grown by the atmosphere controlled μ -PD method at the Institute for Materials Research (IMR), Sendai, Japan. In

Fig. 1 the scheme of the μ -PD apparatus with removable chamber, high-frequency induction coil, CCD camera, and turbo molecular pump is shown [28]. The experiment was performed in the same manner as described in [24]. The additional removable chamber allowed setting the experiment (starting material, crucible, hot zone, etc.) in a glove box under continuously controlled protective oxygen free atmosphere. Charge of about 0.5 g of the starting RbPb_2Cl_5 (pure or doped) was loaded into a carbon crucible of outer diameter 17 mm with bottom conical part and with a hole of 2 mm in diameter. An alumina insulator and carbon afterheater were set around the carbon crucible and positioned in the removable chamber. A Pt-wire as a seed 0.5 mm in diameter and length of about 10 mm was attached into a pulling mechanism.

After setting the experiment in the glove box, the chamber was closed and transported to μ -PD apparatus, where it was adjusted and connected to high-frequency induction source, viewing system (CCD camera), and connected to the controlling PC with software control. The chamber was evacuated at high vacuum (10^{-4} Pa) and simultaneously heated (baked) for minimal power output (ca. 200–300 °C) to release adsorbed moisture or atmosphere from the surfaces of the crucible and the hot zone. After this baking process was finished, the chamber was filled with commercially available dry high purity argon (6N).

After evacuating and filling the chamber with high purity argon atmosphere, the crystal growth was started with a pulling rate of 0.03 mm/min. During the growth the pulling rate was increased up to 0.09 mm/min and kept at this speed until the end of the growth. Position of the crystal/melt interface was held at the edge of the crucible hole (see Fig. 2a).

Samples were cut for further study of their optical properties from the transparent middle part of grown crystals in dimensions $5 \times 2 \times 1 \text{ mm}^3$ in longitudinal direction and polished under protective nitrogen atmosphere. For luminescence measurements the perpendicular slices were also cut from the parent rod and polished.

2.2. Characterization

The powder XRD was measured using a Rigaku RINT2000 diffractometer with $\text{Cu K}\alpha$ lamp at room temperature in the 2θ range between 5 and 100 deg by a step of 0.02 deg. X-ray emission spectra (EPMA) were measured in three different points on polished samples cut from transparent middle part of grown crystals using an X-ray microanalyzer JXA-733 (14–17 kV, 100 nA) at room temperature. Concentrations of the doping RE ions were calculated as a mean value from received signals of L-alpha lines.

Absorption spectra of the samples were measured by a Shimadzu 3101PC spectrometer. In 200–750 nm spectra range, the radio-luminescence (RL) and photoluminescence (PL) spectra were measured under X-ray (40 kV, 10 mA) tube (Seifert GmbH) and D_2 -lamp (Heraeus, D200F) excitation, respectively, by the custom made 5000 M model spectrofluorometer Horiba Jobin Yvon equipped with photon-counting detector TBX-04 (IBH Scotland). Slow decays over the μs –ms time scale were measured under microsecond xenon flashlamp excitation and using the multichannel scaling method. A deconvolution procedure was applied to determine the true decay times using SpectraSolve software (Ames Photonics). All spectra were corrected for spectral distortions of the experimental setup. The surface of the samples was protected when measured by thin layer of the immersing, waterless, UV/VIS transparent silicon oil.

IR luminescence spectra of Nd-doped samples were measured under excitation by a AlGaAs laser diode emitting at 806 nm. The excitation pulse was 0.4 ms long and its excitation energy was 2.5 mJ. Luminescence was detected by two fiber spectrometers. The StellarNet Blue Wave NIR-50 with linear CCD chip was used

Table 1
Prepared high purity starting materials of RbPb_2Cl_5 pure and doped with RE elements.

No.	Compound	Doping RE elem.	Nominal RE conc. (mol%)	Source of RE doping	Add. charge of RbCl (mol%)
12	RbPb_2Cl_5	–	–	–	–
16	RbPb_2Cl_5	Yb^{3+}	0.5	Carbonate	–
17	RbPb_2Cl_5	Nd^{3+}	0.5	Carbonate	–
18	RbPb_2Cl_5	Pr^{3+}	0.5	Carbonate	–
19	RbPb_2Cl_5	Dy^{3+}	0.5	Carbonate	–
32	RbPb_2Cl_5	Nd^{3+}	0.5	Metal	–
38	RbPb_2Cl_5	Nd^{3+}	5	Metal	5
40	RbPb_2Cl_5	Yb^{3+}	5	Metal	5
43	RbPb_2Cl_5	Yb^{3+}	0.5	Metal	–
44	RbPb_2Cl_5	Dy^{3+}	0.5	Metal	–
45	RbPb_2Cl_5	Dy^{3+}	5	Metal	5

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