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Tb³⁺-doped KPb₂Br₅: Low-energy phonon mid-infrared laser crystal

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Crystals of potassium lead bromide (KPbBr₅), a moisture-insensitive low-energy phonon laser host, were synthesized and purified. High-quality undoped and Tb³⁺-doped (nominal doping concentration was 5 mol % TbBr₃) KPb₂Br₅ were grown by the vertical Bridgman technique. X-ray diffraction measurements indicated that, at room temperature, the material was monoclinic with space group P2₁/c, while at a high temperature the phase transformed to orthorhombic form. A reversible phase transition was observed around 256 °C upon the heating and cooling cycle from differential scanning calorimetric measurements. The material was found to be transparent in the broad range from ~0.4 μm to 25 μm and above. The transmission spectrum of a Tb³⁺-doped crystal showed different absorption bands of Tb³⁺ at 4.5 μm, 3 μm, 2.3 μm, and 2 μm corresponding to ⁷F₆→⁷F₄ transitions, for α=2−5. The maximum phonon energy of undoped KPb₂Br₅ at room temperature was determined to be 134 cm⁻¹ from Raman scattering spectrum. © 2005 American Institute of Physics. [DOI: 10.1063/1.1901815]

The continued search for solid-state laser crystal hosts for the longer side of mid-infrared (IR) wavelength (3–15 μm) suitable for use at room temperature and above, has been the subject of both research and technological interest for various applications including active remote detection of chemical and biological agents with characteristic absorbances in these regions. High power, portable, compact and easily deployed mid-IR solid-state lasers have several applications such as IR LIDAR remote sensing, free space communication, IR countermeasures, infrared imaging, and medical surgery. KPb₂Br₅ has recently emerged as a potential laser material operating at room temperature with a low maximum phonon energy of 203 cm⁻¹, while the conventional oxides and fluoride hosts usually show a maximum phonon energy in the range of 500 cm⁻¹ and above. Doping of rare-earth ions, such as Dy³⁺, Nd³⁺, Pr³⁺, Yb³⁺, Er³⁺, etc. in KPbCl₃ have been reported by various workers in the recent past. The quenching of luminescence beyond 4 μm is the limiting factor for room-temperature laser operation in the longer-wavelength region for the conventional hosts. Sulfides and chloride laser hosts however are low-energy phonon materials. Bowman et al. reported room-temperature laser operation at 7.2 μm with the low phonon (210 cm⁻¹) LaCl₃ host doped with Pr³⁺, however, LaCl₃ is highly hygroscopic. In addition to being a low phonon energy material, KPb₂Cl₃ has an added advantage that the material is moisture insensitive and is stable at room temperature in air.

As it is well known now that the key factor for long-wavelength room-temperature laser operation is the low phonon laser host to prevent the luminescence quenching, materials with higher atomic mass would be suitable for this purpose, which will enable them to emit efficiently in the longer-wavelength region. In this present study, we have chosen KPb₂Br₅ which is expected to have smaller phonon vibrational frequency compared to KPbCl₃ due to the higher atomic mass of bromine. This will minimize the nonradiative decay due to multiphonon interactions. The melting point of KPb₂Br₅ (382 °C) is less than that of KPbCl₃ (434 °C). However, large good-quality KPb₂Br₅ single crystals appear to be difficult to grow from melt due to the destructive phase transition which results in milk-white ingot.

KPb₂Br₅ can crystallize in two different crystal structures depending on the growth process. It was reported to crystallize in tetragonal form when prepared from an aqueous solution. The structure of high-temperature synthesized KPb₂Br₅ is controversial since it has been assigned as either orthorhombic or monoclinic. Beck et al. in 1986 reported that KPb₂Br₅ crystallizes in monoclinic form (space group P2₁/c). The lattice parameters were determined to be a=9.256(2) Å, b=8.365(2) Å, c=13.025(3) Å, and β=90.00(3)°.

In this letter, we report on the synthesis and growth of large good-quality undoped and Tb³⁺-doped KPb₂Br₅ crystals, on the phase transition and on the thermal stability of the compound. It is well known that PbCl₃ has a tendency to decompose during synthesis of KPbCl₃. In order to minimize the decomposition, KPb₂Br₅ was synthesized in purified argon over pressure (4.5 psi over atmospheric pressure)

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from 5N purity PbBr$_2$ and KBr (Alfa Aesar) starting material at 450 °C. The synthesized material was purified by repeated zone refining. Undoped and Tb$^{3+}$-doped KPb$_2$Br$_5$ crystals were grown by the vertical Bridgman method at a lowering rate of about 6 mm/day. The structural phase transition for undoped KPb$_2$Br$_5$ was studied by powder x-ray diffraction (XRD) at different temperatures ranging from 25–300 °C under flowing H$_2$ atmosphere using a Scintag PAD X vertical goniometer equipped with a modified Buehler HDK-2 diffraction furnace. The simultaneous differential scanning calorimetry (DSC)/thermogravimetric analysis were performed to study the phase transition temperature, melting point, and the thermal stability of the material using TA instruments model SDT 2960. Optical absorption in the ultraviolet-visible-near-infrared range of both undoped and Tb$^{3+}$-doped KPb$_2$Br$_5$ crystals were carried out using a Cary500 spectrophotometer. Fourier-transform infrared (FTIR) absorption spectra were recorded using MIDAC spectrometer with a resolution of 4 cm$^{-1}$. The phonon energy of the undoped KPb$_2$Br$_5$ was determined by recording Raman spectra in right angle scattering geometry using double-grating spectrophotometer (SPEX Model 1403). The 514.5 nm green line of argon-ion laser (Spectra Physics Model 164) of 50 mW of power was used as excitation source. X-ray photoelectron spectroscopy (XPS) investigations were carried out using a Vacuum Generator ESCALAB MKII equipped with an XPS/Auger spectrometer with a Mg $K_a$ source ($E=$1253.6 eV) with 300 W power at 15 kV. The work function of the spectrometer on the basis of the Au 4f$_{3/2}$ peakenergy of 83.8 eV and the reported binding energies are referenced to C (1s) at 284.6 eV.

Good-quality undoped and Tb$^{3+}$-doped (5 mol % TbBr$_3$ doping concentration) KPb$_2$Br$_5$ single crystals were grown by the vertical Bridgman technique. No reaction of the material with the quartz ampoule was observed and the crystals were taken out easily from the ampoule. The crystals were free from any microinclusions, bubbles, and visible crystal-line defects. However, a few cracks occurred during cooling.

The XRD results at room temperature showed monoclinic structure with the space group symmetry to be P2$_1$/c consistent with the results of Beck et al.$^{15}$ The collected XRD patterns at elevated temperatures (100, 150, 200, 250, and 300 °C) with the heating rate of 20 °C/min. revealed that the structure was monoclinic up to 200 °C. Subtle changes in the diffraction pattern were observed at 250 °C, but the phase was not fully transformed to a new phase until 300 °C. At 300 °C, the crystal structure transformed to a primitive orthorhombic unit cell with the calculated lattice parameters $a=9.359(2)$ Å, $b=8.488(1)$ Å, and $c=13.254(2)$ Å. However, the space group at 300 °C could not be unambiguously determined because the diffraction pattern was matched with eleven possible space groups belonging to the mm2 or mmm point groups. None of the possible space groups were supergroups of the monoclinic P2$_1$/c space group. The observed phase at 300 °C was not isosstructural to the tetragonal phase observed at high-temperature and high-pressure by Beck et al.$^{15}$ The phase change was completely reversible upon cooling to room temperature.

The phase transition, melting point, and the thermal stability of the material after the heating and cooling cycle were studied using DSC measurement under a dry nitrogen flow. Figure 1 shows the thermogram of undoped KPb$_2$Br$_5$ for two successive heating and cooling cycles. The sample was heated to 443 °C followed by cooling to 110 °C, reheated to 443 °C and subsequently cooled to 124 °C at a constant rate of 20 °C/min. The single arrow depicts the first heating cycle and the double arrow indicates the second heating cycle as shown in Fig. 1. The onset of the melting process was determined to be 375.6 °C and the heat of fusion was 57.9 J/g. The inset shows the enlarged version of the thermogram near the phase transition region As shown in the inset of Fig. 1, the phase transition was not sharp. The onset of the phase change occurred about 230 °C with a peak value at 256 °C. KPb$_2$Br$_5$ is reported to have a phase transition at 242 °C.$^{17}$ The phase transition determined from the DSC measurement was consistent with the XRD data. In the XRD experiment, the subtle change began near 250 °C, as discussed earlier. No appreciable weight loss change in the melting, solidification, and the phase transition temperature after repeated heating and cooling cycle manifested, indicating that KPb$_2$Br$_5$ is a stable compound and melts congruently. This observation also depicts the fact that the phase transition is completely reversible and agrees well with our XRD experiment.

Optical transmission experiments were carried out with both undoped and Tb$^{3+}$-doped samples in the spectral region 0.3–25 μm. The crystals were very transparent in the wavelength range from 0.4 μm to 25 μm (the measured range). The higher wavelength cutoff for KPbCl$_3$ is reported to be $\approx 20$ μm.$^{18}$ The transmission of the undoped KPb$_2$Br$_5$ was

![FIG. 1. DSC thermogram of undoped KPb$_2$Br$_5$ crystal with successive heating and cooling cycles. The inset shows the enlarged version of the plot near phase transition.](Image)

![FIG. 2. Room-temperature optical transmission spectrum of Tb$^{3+}$:KPb$_2$Br$_5$ crystal of thickness 7.85 mm. The inset shows the photograph of Tb$^{3+}$:KPb$_2$Br$_5$ crystal of 10 mm diameter and 7.85 mm thickness.](Image)
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The maximum phonon energy of KPb$_2$Br$_5$ is considerably increased after 15 min Ar etching. The presence of air was carried out to examine various impurity concentrations at the crystal surfaces as well as within its bulk. The presence of C and O on the crystal surface was observed, and decreased considerably after 15 min Ar etching.

Broadband emission with peak wavelengths of 3 $\mu$m, 5 $\mu$m, and 7.9 $\mu$m were recorded at room temperature from the grown Tb$^{3+}$ doped KPb$_2$Br$_5$ crystals and is reported elsewhere. The emission was observed by pumping with a 2 $\mu$m source. The room-temperature emission lifetimes were found to vary between 3–22 ms for the $^7F_3$ level (5 $\mu$m) and 0.2–0.4 ms for the $^7F_4$ level (7.9 $\mu$m) for different samples. The quantum efficiencies for the $^7F_4$ level for different Tb$^{3+}$ doped KPb$_2$Br$_5$ crystals were also observed to be higher than Tb$^{3+}$ doped KPb$_2$Cl$_5$ as described earlier.

In summary, we have grown both undoped and Tb$^{3+}$-doped KPb$_2$Br$_5$ crystals by the vertical Bridgman growth technique. A phase transition was observed around 256 °C, was completely reversible, and was not found to prevent the formation of good-quality large crystals. Compared to KPb$_2$Cl$_5$, the bromide version has a similar refractive index with the added advantage of a higher cutoff wavelength and lower melting point. Having a considerably lower maximum phonon energy compared to KPb$_2$Cl$_5$, KPb$_2$Br$_5$ appears to be a promising material for a room-temperature laser host in the longer-wavelength side of mid-IR region.

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