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Tb$^{3+}$-doped KPb$_2$Br$_5$: Low-energy phonon mid-infrared laser crystal

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Crystals of potassium lead bromide (KPB), a moisture-insensitive low-energy phonon laser host, were synthesized and purified. High-quality undoped and Tb$^{3+}$-doped (nominal doping concentration was 5 mol % TbBr$_3$) KPb$_2$Br$_5$ were grown by the vertical Bridgman technique. X-ray diffraction measurements indicated that, at room temperature, the material was monoclinic with space group $P2_1/c$, 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 Tb$^{3+}$-doped crystal showed different absorption bands of Tb$^{3+}$ at 4.5 μm, 3 μm, 2.3 μm, and 2 μm corresponding to $^7F_6$ → $^7F_5$, $^7F_6$ → $^7F_4$, $^7F_6$ → $^7F_3$, and transitions, for $\alpha$=2–5. The maximum phonon energy of undoped KPb$_2$Br$_5$ at room temperature was determined to be 134 cm$^{-1}$ from Raman scattering spectrum.


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. KPb$_2$Cl$_5$ has recently emerged as a potential laser material operating at room temperature with the low phonon energy material, KPb$_2$Cl$_5$ 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 KPb$_2$Br$_5$ which is expected to have smaller phonon vibrational frequency compared to KPb$_2$Cl$_5$ due to the higher atomic mass of bromine. This will minimize the nonradiative decay due to multiphonon interactions. The melting point of KPb$_2$Br$_5$ (382 °C) (Ref. 12) is less than that of KPb$_2$Cl$_5$ (434 °C). However, large good-quality KPb$_2$Br$_5$ single crystals appear to be difficult to grow from melt due to the destructive phase transition which results in milk-white ingot. KPb$_2$Br$_5$ can crystallize in two different crystal structures depending on the growth process. It was reported$^{14,15}$ to crystallize in tetragonal form when prepared from an aqueous solution. The structure of high-temperature synthesized KPb$_2$Br$_5$ is controversial since it has been assigned as either orthorhombic$^{14}$ or monoclinic.$^{15}$ Beck et al.$^{15}$ in 1986 reported that KPb$_2$Br$_5$ crystallizes in monoclinic form (space group $P2_1/c$). The lattice parameters$^{16}$ were determined to be $a=9.256(2)$ Å, $b=8.365(2)$ Å, $c=13.025(3)$ Å, and $b=90.00(3)^{\circ}$.

In this letter, we report on the synthesis and growth of large good-quality undoped and Tb$^{3+}$-doped KPb$_2$Br$_5$ crystals, on the phase transition and on the thermal stability of the compound. It is well known that PbCl$_3$ has a tendency to decompose during synthesis of KPb$_2$Cl$_5$.$^{13}$ In order to minimize the decomposition, KPb$_2$Br$_5$ was synthesized in purified argon over pressure (4.5 psi over atmospheric pressure)
from 5N purity PbBr₂ and KBr (Alfa Aesar) starting material at 450 °C. The synthesized material was purified by repeated zone refining. Undoped and Tb³⁺-doped KPb₂Br₅ crystals were grown by the vertical Bridgman method at a lowering rate of about 6 mm/day. The structural phase transition for undoped KPb₂Br₅ was studied by powder x-ray diffraction (XRD) at different temperatures ranging from 25–300 °C under flowing H₂ atmosphere using a Scintag PAD X vertical goniometer equipped with a modified Buehler HDK-2 diffractometer. The simultaneous differential scanning calorimetry (DSC)/thermovimetric 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 Tb³⁺-doped KPb₂Br₅ 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 KPb₂Br₅ was determined by recording Raman spectra in right angle scattering geometry using double-grating spectrophotometer (SPIEX 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 Kα source (E=1253.6 eV) with 300 W power at 15 kV. The work function of the spectrometer on the basis of the C (1s) at 284.6 eV.

Good-quality undoped and Tb³⁺-doped (5 mol % TbBr₃ doping concentration) KPb₂Br₅ single crystals were grown by the vertical Bridgman technique. No reaction of the material with the quartz ampoule was observed and the crystals were very transparent in the wavelength range from 0.4 μm to 25 μm (the measured range). The crystals were free from any microinclusions, bubbles, and visible crystalline defects. However, a few cracks occurred during cooling.

The XRD results at room temperature showed monoclinic structure with the space group symmetry to be P2₁/c consistent with the results of Beck et al. 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 P2₁/c space group. The observed phase at 300 °C was not isosctructural to the tetragonal phase observed at high-temperature and high-pressure by Beck et al. 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 KPb₂Br₅ 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. KPb₂Br₅ is reported to have a phase transition at 242 °C. 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 KPb₂Br₅ 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 Tb³⁺-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 KPbCl₃ is reported to be ~20 μm. The transmission of the undoped KPb₂Br₅ was...
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found to be about 80% from 1.5 μm to 25 μm. The refractive index was measured to be n = 2.1 at 1.5 μm. The refractive index was thus found to be very close to KPb2Cl5 (n = 2.016±0.005). Similar to KPb2Cl5, KPb2Br5 also is colorless, hard, rugged, and very stable in normal atmosphere. No deterioration of the polished surface was observed for a couple of months by exposure to the normal laboratory environment. Figure 2 shows the unpolarized FTIR transmission spectrum at room temperature of Tb3+:KPb2Br5 crystal of 7.85 mm thickness. A photograph of the polished Tb3+:KPb2Br5 crystal of 10 mm diameter size and 7.85 mm height is shown in the inset of Fig. 2. The absorption bands of Tb3+ corresponding to the transitions from 7F6 → 7F2 (α=2–5) are prominent as shown in Fig. 2. The origin of the absorption bands near 6.3 μm and 7.2 μm however are not clear in the present investigation. The absorption band near 7.2 μm can be assigned to NH2 and was also found to be present in KPb2Cl5 crystal.8 In our present study, no appreciable absorption bands near 6.3 μm and 7.2 μm were observed in the zone refined undoped KPb2Br5 crystals. Impurity from the dopant TbBr3 might be responsible for the two bands near 6 μm and 7 μm. The maximum phonon energy was determined from Raman scattering measurement of undoped KPb2Br5 crystals at room temperature. Figure 3 shows the Raman scattering spectrum of undoped KPb2Br5 crystal. The maximum phonon energy was found to be 134 cm−1. The maximum phonon energy of KPb2Br5 is considerably lower compared to the value for KPb2Cl5.

The XPS investigations of the Tb3+:KPb2Br5 crystals were 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 μm, 5 μm, and 7.9 μm were recorded at room temperature from the grown Tb3+-doped KPb2Br5 crystals and is reported elsewhere.16 The emission was observed by pumping with a 2 μm source. The room-temperature emission lifetimes were found to vary between 3–22 ms for the 7F3 level (5 μm) and 0.2–0.4 ms for the 7F4 level (7.9 μm)16 for different samples. The quantum efficiencies for the 7F2, 7F4 level for different Tb3+-doped KPb2Br5 crystals were also observed to be higher than Tb3+-doped KPb2Cl5 as described earlier.16

In summary, we have grown both undoped and Tb3+-doped KPb2Br5 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 KPb2Cl5, 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 KPb2Cl5, KPb2Br5 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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