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## Tb<sup>3+</sup>-doped *K*Pb<sub>2</sub>Br<sub>5</sub>: Low-energy phonon mid-infrared laser crystal

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## **Tb 3 + -doped K Pb 2 Br 5 : Low-energy phonon mid-infrared laser crystal**

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# Tb<sup>3+</sup>-doped KPb<sub>2</sub>Br<sub>5</sub>: 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<sup>3+</sup>-doped (nominal doping concentration was 5 mol % TbBr<sub>3</sub>) KPb<sub>2</sub>Br<sub>5</sub> were grown by the vertical Bridgman technique. X-ray diffraction measurements indicated that, at room temperature, the material was monoclinic with space group P2<sub>1</sub>/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<sup>3+</sup>-doped crystal showed different absorption bands of Tb<sup>3+</sup> at 4.5 μm, 3 μm, 2.3 μm, and 2 μm corresponding to <sup>7</sup>F<sub>6</sub>–<sup>7</sup>F<sub>α</sub> transitions, for α=2–5. The maximum phonon energy of undoped KPb<sub>2</sub>Br<sub>5</sub> at room temperature was determined to be 134 cm<sup>-1</sup> from Raman scattering spectrum.

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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<sub>2</sub>Cl<sub>5</sub> has recently emerged as a potential laser material operating at room temperature<sup>1–5</sup> with a low maximum phonon energy of 203 cm<sup>-1</sup>, while the conventional oxides and fluoride hosts usually show a maximum phonon energy in the range of ~500 cm<sup>-1</sup> and above.<sup>6</sup> Doping of rare-earth ions, such as Dy<sup>3+</sup>, Nd<sup>3+</sup>, Pr<sup>3+</sup>, Yb<sup>3+</sup>, Er<sup>3+</sup>, etc.<sup>1–10</sup> in KPb<sub>2</sub>Cl<sub>5</sub> 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.*<sup>11</sup> reported room-temperature laser operation at 7.2 μm with the low phonon (210 cm<sup>-1</sup>) LaCl<sub>3</sub> host doped with Pr<sup>3+</sup>, however, LaCl<sub>3</sub> is highly hygroscopic. In addition to being a low phonon energy material, KPb<sub>2</sub>Cl<sub>5</sub> 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<sub>2</sub>Br<sub>5</sub> which is expected to have smaller phonon vibrational frequency compared to KPb<sub>2</sub>Cl<sub>5</sub> due to the higher atomic mass of bromine. This will minimize the nonradiative decay due to multiphonon interactions. The melting point of KPb<sub>2</sub>Br<sub>5</sub> (382 °C) (Ref. 12) is less than that of KPb<sub>2</sub>Cl<sub>5</sub> (434 °C).<sup>13</sup> However, large good-quality KPb<sub>2</sub>Br<sub>5</sub> single crystals appear to be difficult to grow from melt due to the destructive phase transition which results in milk-white ingot.<sup>12</sup>

KPb<sub>2</sub>Br<sub>5</sub> can crystallize in two different crystal structures depending on the growth process. It was reported<sup>14,15</sup> to crystallize in tetragonal form when prepared from an aqueous solution. The structure of high-temperature synthesized KPb<sub>2</sub>Br<sub>5</sub> is controversial since it has been assigned as either orthorhombic<sup>14</sup> or monoclinic.<sup>15</sup> Beck *et al.*<sup>15</sup> in 1986 reported that KPb<sub>2</sub>Br<sub>5</sub> crystallizes in monoclinic form (space group P2<sub>1</sub>/c). The lattice parameters<sup>16</sup> 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 Tb<sup>3+</sup>-doped KPb<sub>2</sub>Br<sub>5</sub> crystals, on the phase transition and on the thermal stability of the compound. It is well known that PbCl<sub>2</sub> has a tendency to decompose during synthesis of KPb<sub>2</sub>Cl<sub>5</sub>.<sup>13</sup> In order to minimize the decomposition, KPb<sub>2</sub>Br<sub>5</sub> was synthesized in purified argon over pressure (4.5 psi over atmospheric pressure)

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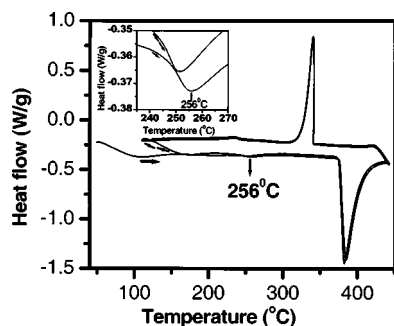


FIG. 1. DSC thermogram of undoped  $\text{KPb}_2\text{Br}_5$  crystal with successive heating and cooling cycles. The inset shows the enlarged version of the plot near phase transition.

from 5N purity  $\text{PbBr}_2$  and  $\text{KBr}$  (Alfa Aesar) starting material at  $450^\circ\text{C}$ . The synthesized material was purified by repeated zone refining. Undoped and  $\text{Tb}^{3+}$ -doped  $\text{KPb}_2\text{Br}_5$  crystals were grown by the vertical Bridgman method at a lowering rate of about 6 mm/day. The structural phase transition for undoped  $\text{KPb}_2\text{Br}_5$  was studied by powder x-ray diffraction (XRD) at different temperatures ranging from  $25$ – $300^\circ\text{C}$  under flowing  $\text{H}_2$  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  $\text{Tb}^{3+}$ -doped  $\text{KPb}_2\text{Br}_5$  crystals were carried out using a CARY500 spectrophotometer. Fourier-transform infrared (FTIR) absorption spectra were recorded using MIDAC spectrometer with a resolution of  $4\text{ cm}^{-1}$ . The phonon energy of the undoped  $\text{KPb}_2\text{Br}_5$  was determined by recording Raman spectra in right angle scattering geometry using double-grating spectrophotometer (SPEX Model 1403). The  $514.5\text{ nm}$  green line of argon-ion laser (Spectra Physics Model 164) of  $50\text{ mW}$  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  $\text{Mg } K_\alpha$  source ( $E=1253.6\text{ eV}$ ) with  $300\text{ W}$  power at  $15\text{ kV}$ . The work function of the spectrometer on the basis of the  $\text{Au } 4f_{3/2}$  peak energy of  $83.8\text{ eV}$  and the reported binding energies are referenced to  $\text{C } (1s)$  at  $284.6\text{ eV}$ .

Good-quality undoped and  $\text{Tb}^{3+}$ -doped (5 mol %  $\text{TbBr}_3$  doping concentration)  $\text{KPb}_2\text{Br}_5$  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 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  $\text{P}2_1/\text{c}$  consistent with the results of Beck *et al.*<sup>15</sup> The collected XRD patterns at elevated temperatures ( $100$ ,  $150$ ,  $200$ ,  $250$ , and  $300^\circ\text{C}$ ) with the heating rate of  $20^\circ\text{C}/\text{min}$ . revealed that the structure was monoclinic up to  $200^\circ\text{C}$ . Subtle changes in the diffraction pattern were observed at  $250^\circ\text{C}$ , but the phase was not fully transformed to a new phase until  $300^\circ\text{C}$ . At  $300^\circ\text{C}$ , the crystal structure transformed to a primitive orthorhombic unit cell with the calculated

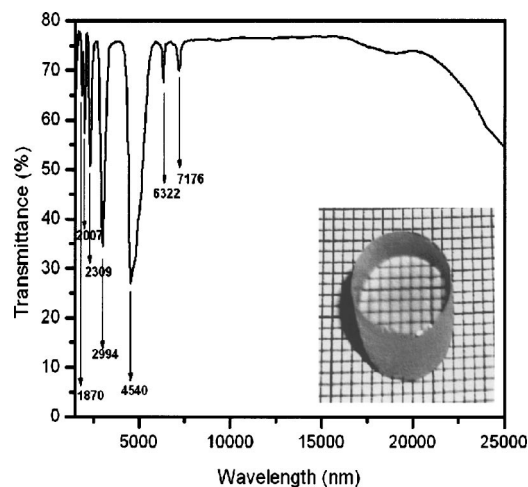


FIG. 2. Room-temperature optical transmission spectrum of  $\text{Tb}^{3+}:\text{KPb}_2\text{Br}_5$  crystal of thickness  $7.85\text{ mm}$ . The inset shows the photograph of  $\text{Tb}^{3+}:\text{KPb}_2\text{Br}_5$  crystal of  $10\text{ mm}$  diameter and  $7.85\text{ mm}$  thickness.

lattice parameters  $a=9.359(2)\text{ \AA}$ ,  $b=8.488(1)\text{ \AA}$ , and  $c=13.254(2)\text{ \AA}$ . However, the space group at  $300^\circ\text{C}$  could not be unambiguously determined because the diffraction pattern was matched with eleven possible space groups belonging to the  $\text{mm}2$  or  $\text{mmm}$  point groups. None of the possible space groups were supergroups of the monoclinic  $\text{P}2_1/\text{c}$  space group. The observed phase at  $300^\circ\text{C}$  was not isostructural to the tetragonal phase observed at high-temperature and high-pressure by Beck *et al.*<sup>15</sup> 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  $\text{KPb}_2\text{Br}_5$  for two successive heating and cooling cycles. The sample was heated to  $443^\circ\text{C}$  followed by cooling to  $110^\circ\text{C}$ , reheated to  $443^\circ\text{C}$  and subsequently cooled to  $124^\circ\text{C}$  at a constant rate of  $20^\circ\text{C}/\text{min}$ . 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  $375.6^\circ\text{C}$  and the heat of fusion was  $57.9\text{ J/g}$ . 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  $230^\circ\text{C}$  with a peak value at  $256^\circ\text{C}$ .  $\text{KPb}_2\text{Br}_5$  is reported to have a phase transition at  $242^\circ\text{C}$ .<sup>17</sup> The phase transition determined from the DSC measurement was consistent with the XRD data. In the XRD experiment, the subtle change began near  $250^\circ\text{C}$ , 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  $\text{KPb}_2\text{Br}_5$  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  $\text{Tb}^{3+}$ -doped samples in the spectral region  $0.3$ – $25\text{ }\mu\text{m}$ . The crystals were very transparent in the wavelength range from  $0.4\text{ }\mu\text{m}$  to  $25\text{ }\mu\text{m}$  (the measured range). The higher wavelength cutoff for  $\text{KPb}_2\text{Cl}_5$  is reported to be  $\sim 20\text{ }\mu\text{m}$ .<sup>5,8</sup> The transmission of the undoped  $\text{KPb}_2\text{Br}_5$  was



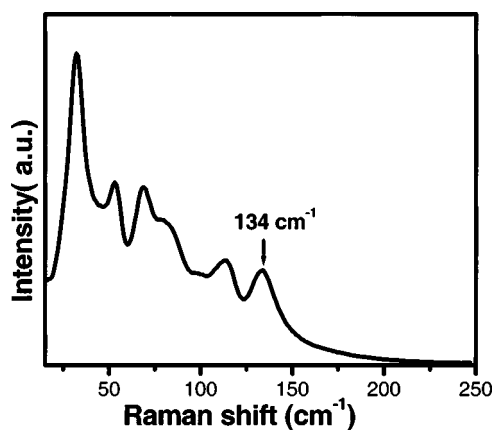


FIG. 3. Raman spectrum of undoped  $\text{KPb}_2\text{Br}_5$  crystal at room temperature.

found to be about 80% from  $1.5\ \mu\text{m}$  to  $25\ \mu\text{m}$ . The refractive index was measured to be  $n=2.1$  at  $1.5\ \mu\text{m}$ .<sup>16</sup> The refractive index was thus found to be very close to  $\text{KPb}_2\text{Cl}_5$  ( $n=2.016\pm0.005$ ). Similar to  $\text{KPb}_2\text{Cl}_5$ ,  $\text{KPb}_2\text{Br}_5$  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  $\text{Tb}^{3+}:\text{KPb}_2\text{Br}_5$  crystal of  $7.85\ \text{mm}$  thickness. A photograph of the polished  $\text{Tb}^{3+}:\text{KPb}_2\text{Br}_5$  crystal of  $10\ \text{mm}$  diameter size and  $7.85\ \text{mm}$  height is shown in the inset of Fig. 2. The absorption bands of  $\text{Tb}^{3+}$  corresponding to the transitions from  ${}^7F_6 \rightarrow {}^7F_\alpha$  ( $\alpha=2-5$ ) are prominent as shown in Fig. 2. The origin of the absorption bands near  $6.3\ \mu\text{m}$  and  $7.2\ \mu\text{m}$  however are not clear in the present investigation. The absorption band near  $7.2\ \mu\text{m}$  can be assigned to  $\text{NH}_4^+$  and was also found to be present in  $\text{KPb}_2\text{Cl}_5$  crystal.<sup>6</sup> In our present study, no appreciable absorption bands near  $6.3\ \mu\text{m}$  and  $7.2\ \mu\text{m}$  were observed in the zone refined undoped  $\text{KPb}_2\text{Br}_5$  crystals. Impurity from the dopant  $\text{TbBr}_3$  might be responsible for the two bands near  $6\ \mu\text{m}$  and  $7\ \mu\text{m}$ . The maximum phonon energy was determined from Raman scattering measurement of undoped  $\text{KPb}_2\text{Br}_5$  crystals at room temperature. Figure 3 shows the Raman scattering spectrum of undoped  $\text{KPb}_2\text{Br}_5$  crystal. The maximum phonon energy was found to be  $134\ \text{cm}^{-1}$ . The maximum phonon energy of  $\text{KPb}_2\text{Br}_5$  is considerably lower compared to the value for  $\text{KPb}_2\text{Cl}_5$ .

The XPS investigations of the  $\text{Tb}^{3+}:\text{KPb}_2\text{Br}_5$  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  $3\ \mu\text{m}$ ,  $5\ \mu\text{m}$ , and  $7.9\ \mu\text{m}$  were recorded at room temperature from the grown  $\text{Tb}^{3+}$ -doped  $\text{KPb}_2\text{Br}_5$  crystals and is reported elsewhere.<sup>16</sup> The emission was observed by pumping with a  $2\ \mu\text{m}$  source. The room-temperature emission lifetimes were found to vary between 3–22 ms for the  ${}^7F_5$  level ( $5\ \mu\text{m}$ ) and 0.2–0.4 ms for the  ${}^7F_4$  level ( $7.9\ \mu\text{m}$ )<sup>16</sup> for different samples. The quantum efficiencies for the  ${}^7F_5$  level for different  $\text{Tb}^{3+}$ -doped  $\text{KPb}_2\text{Br}_5$  crystals were also observed to be higher than  $\text{Tb}^{3+}$ -doped  $\text{KPb}_2\text{Cl}_5$  as described earlier.<sup>16</sup>

In summary, we have grown both undoped and  $\text{Tb}^{3+}$ -doped  $\text{KPb}_2\text{Br}_5$  crystals by the vertical Bridgman growth technique. A phase transition was observed around  $256\ ^\circ\text{C}$ , was completely reversible, and was not found to prevent the formation of good-quality large crystals. Compared to  $\text{KPb}_2\text{Cl}_5$ , 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  $\text{KPb}_2\text{Cl}_5$ ,  $\text{KPb}_2\text{Br}_5$  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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