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Coefficients of thermal expansion of KPb_2Cl_5 and $RbPb_2Br_5$ crystals

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Abstract The temperature dependence of unit cell parameters for monoclinic KPb_2Cl_5 and tetragonal $RbPb_2Br_5$ crystals was studied in the range of 100–298 K. Linear and volume thermal expansion coefficients were determined.

Keywords Single crystals · Thermal expansion · X-ray diffraction · Halogenide plumbates

Introduction

Usage of diode lasers for selective pumping of active media based on the rare earth-doped crystals stimulates the search for new crystalline matrices with absorption lines which agree with laser emission wavelength. The rare earth-doped crystals of the MPb_2X_5 family with M = K or Rb, X = Cl or Br are related to such matrices [1, 2]. These crystals are characterized with a low energy phonon spectrum (below 200 cm^{-1}) and laser action beyond the 4 μm is possible [1, 2]. The other features of these crystals are low thermal losses and a high quantum yield. Crystals under investigation are considered to be promising as active media for visible and mid-IR lasers, telecom amplifiers, and optical communication lines. Unfortunately, there is a problem of twin formation in some parts of the boule [3]. The coefficient of linear thermal expansion (CLTE) is one of the most important parameters, which affects the twin formation when cooling crystal. It is important to determine CLTE in order to optimize the seed orientation and to produce crystals of high quality.

The data on low temperature thermal expansion for crystals of the MPb_2X_5 (M = K or Rb, X = Cl or Br) family in particular $RbPb_2Cl_5$, KPb_2Br_5 and $K_{0.5}Rb_{0.5}Pb_2Br_5$ were given in article [4]. In the present article, we continue the study of thermal expansion versus composition for monoclinic KPb_2Cl_5 and tetragonal $RbPb_2Br_5$ crystals.

Experimental

Single crystals were grown using the Bridgman technique with a linear temperature gradient of about 20 °C cm^{-1} in the growth zone. The rate of the ampoule motion was 1–4 mm day^{-1}. Details are given in [4].

To determine the unit cell parameters depending on temperature, the single crystal X-ray structural analysis was carried out using a Stoe STADI-4 four-circle diffractometer (MoK_α radiation, graphite monochromator). The temperature was controlled with a 600 Series Cryostream Cooler (Oxford Cryosystem) with a gas temperature stability of 0.1 K. 25 strong reflections in the 2θ range between 20° and 30° were used for cell refinement. To increase the precision, each reflection was measured at both sides of the primary beam. An ω-scan was carried out at + and -2θ and ω, the center of gravity of reflections was determined for both scans, and the observed 2θ was given by the difference of two ω centers, eliminating zero point errors.

Thermal dependence of lattice parameters for KPb_2Cl_5 and $RbPb_2Br_5$ was plotted using the technique of least squares.

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Table 1 Unit cell parameters of the MPb_2X_5 crystals at different temperatures

	100/K	150/K	200/K	250/K	298/K
KPb_2Cl_5 ($P2_1/c$)					
a/Å	8.810(7)	8.822(7)	8.834(6)	8.849(6)	8.863(5)
b/Å	7.880(4)	7.890(4)	7.904(4)	7.920(3)	7.931(3)
c/Å	12.416(7)	12.431(6)	12.454(5)	12.476(5)	12.494(4)
β/°	90.06(5)	90.07(4)	90.09(4)	90.09(4)	90.11(3)
V/Å^3	861.9(6)	865.3(6)	869.6(5)	874.4(5)	878.2(4)
$RbPb_2Br_5$ ($I4/mcm$)					
a/Å	8.3837(11)	8.3976(8)	8.4120(7)	8.4279(5)	8.4428(7)
c/Å	14.431(4)	14.467(3)	14.5066(22)	14.5535(18)	14.5903(24)
V/Å^3	1014.3(3)	1020.25(21)	1026.50(18)	1033.73(14)	1040.01(19)

Table 2 Coefficients of linear and volume thermal expansion for crystals of the MPb_2X_5 family, 10^6 (K^{-1})

	KPb_2Cl_5	$RbPb_2Br_5$
α_a	32	36
α_b	34	36
α_c	33	58
V	99	130

Results and discussion

The results of measuring the unit cell parameters at different temperatures are given in Table 1.

The coefficients of linear (α) and volume thermal expansion (β) were calculated from the unit cell parameters in Table 1 data using the following equations:

$$\alpha = \frac{1}{l}\frac{\mathrm{d}l}{\mathrm{d}T} = \frac{\mathrm{d}\ln l}{\mathrm{d}T} \quad \text{and} \quad \beta = \frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}T} = \frac{\mathrm{d}\ln V}{\mathrm{d}T},$$

where l is a cell parameter and V is the unit cell volume.

The logarithms of the unit cell parameters for KPb_2Cl_5 and $RbPb_2Br_5$ were approximated by linear dependences $\ln l = \alpha T + C_l$ and $\ln V = \overline{\beta} T + C_v$ using the least squares method. Here $\overline{\alpha}$ and $\overline{\beta}$ are average coefficients of linear and volume thermal expansion, respectively, and C_l and C_v-are approximation coefficients, which have no physical meaning. Coefficients of linear and volume thermal expansion are shown in Table 2.

Investigations of thermal expansion coefficients at low temperatures (100–298 K) for KPb_2Cl_5 showed that a, b, c parameters and unit cell volume increase uniformly (Table 1). The coefficients of linear expansion values are identical for all three cell parameters within the observation accuracy range (Table 2), therefore, the crystal expands isotropically.

For tetragonal $RbPb_2Br_5$ a, c parameters and unit cell volume also increase as temperature grows (Table 1). In contrast to monoclinic KPb_2Cl_5, coefficients of linear expansion along the a, c axis are quite different from each other, and we can make a conclusion about anisotropic expansion of RbPb2Br5.

Conclusions

The temperature dependence of the parameters of crystal unit cell was studied for monoclinic KPb_2Cl_5, and tetragonal $RbPb_2Br_5$ crystals in the range of 100–298 K. Coefficients of linear and volume thermal expansion were determined.

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