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Short Communication

COEFFICIENTS OF THERMAL EXPANSION OF THE POTASSIUM AND RUBIDIUM HALOGENIDE PLUMBATES

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The temperature dependence of unit cell parameters for KPb_2Br_5, $RbPb_2Cl_5$ and $K_{0.5}Rb_{0.5}Pb_2Br_5$ crystals was studied in the range of 100 to 298 K. Linear and volume thermal expansion coefficients were determined. Analysis revealed the thermal expansion effect on formation of nets of twin boundaries in crystals.

Keywords: *anisotropy, single crystals, thermal expansion, twinning, X-ray diffraction*

Introduction

Crystals KPb_2Br_5, $RbPb_2Cl_5$ and $K_{0.5}Rb_{0.5}Pb_2Br_5$ attract attention as new low-phonon energy ($h\omega$<200 cm^{-1} for chlorides and $h\omega$<150 cm^{-1} for bromides) host materials for mid-IR applications. The MPb_2Hal_5 (M=K, Rb; Hal=Cl, Br) crystals show high chemical resistance, satisfactory mechanical properties and have low hygroscopicity, unlike the known simple tri-chloride crystals (Re:$LnCl_3$). Crystals are transparent in the wide spectral range from 0.3 to 30 microns [1, 2].

However, formation of the nets of twin boundaries makes it difficult to grow the crystals of high optical quality [3]. It was shown in literature that an anisotropy of thermal expansion along different crystallographic axes promotes strongly the twinning. The lead halogenides have a strongly pronounced cleavage plane and crystals crack along these planes. Since crystals are grown in the ampoules by the Bridgman technique, it is necessary to provide conditions when the growing crystal does not undergo stresses resulting from the anisotropy of the thermal expansion coefficients.

Moreover, the techniques of protecting/anti-reflecting coating of the polished faces of optical elements from these crystals also depend on the character of their thermal expansion.

Monoclinic KPb_2Br_5, $RbPb_2Cl_5$ and $K_{0.5}Rb_{0.5}Pb_2Br_5$ are isostructural with $NH_4Pb_2Cl_5$ [4, 5]. Two structure solutions in [4, 5] differ from one another, but become identical after transformation x'=1/2–x, y'=–y, z'=z, not belonging to the $P2_1/c$ symmetry group. Such a transformation is inconsistent with the monoclinic system. It is possible due the monoclinic angle, which is close to 90°. The two models found for $NH_4Pb_2Cl_5$ correspond to the two twin components of KPb_2Br_5, $RbPb_2Cl_5$ and $K_{0.5}Rb_{0.5}Pb_2Br_5$. The same structure and similar problems with twinning were found out for KPb_2Cl_5 [6]. The detail analysis of structure, cation polyhedrons and anionic net of KPb_2Cl_5 and KPb_2Br_5 was made in early our work [6].

The goal of present work was to determine the coefficients of linear thermal expansion (CLTE) of KPb_2Br_5, $RbPb_2Cl_5$ and $K_{0.5}Rb_{0.5}Pb_2Br_5$ monoclinic crystals. We believed that a comparison of CLTE for different crystals allows us to understand better the reasons of the twinning in the above-mentioned compounds and to improve techniques of polishing/coating of the optical elements.

Experimental

Crystals were synthesized from high quality chloride and bromide salts. The starting reagents $PbCl_5$, $PbBr_2$,

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KCl, KBr, RbCl and RbBr were additionally purified using the multiple recrystallization with the removing of the contaminated parts. 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 to 4 mm day^{-1}.

Crystals for the measurements were prismatic in shape, 0.04–0.1 mm along *x* and *y* axis and 0.1–0.2 mm along *z*.

To determine the unit cell parameters depending on temperature, the single crystal X-ray structural analysis was carried out using the Bruker Nonius X8 diffractometer with MoK_α radiation, adjusted with the CCD camera and a device for temperature variation, with the accuracy of ±0.1 K. The unit cell parameters were determined using the software APEX2 (Version 1.08) and SAINT (Version 7.03).

Results and discussion

The results of determination of the parameters of crystal unit cells at different temperatures are given in Table 1.

To calculate the CLTE from the UC values measured at different temperatures in a wide temperature range, one uses usually the ratio of differences $\alpha=(a_2-a_1)/a_1(T_2-T_1)$. For example, such results were given in the paper [7], where measurements have been carried out at temperatures 298 and 1073 K. In our case the temperature range is smaller but a number of temperature points is larger: thus, the detailed temperature dependence can be analyzed. We used the following equations:

$$\alpha = \frac{1}{l}\frac{\mathrm{d}\ln l}{\mathrm{d}T} \text{ and } \beta = \frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}T} = \frac{\mathrm{d}\ln V}{\mathrm{d}T} \qquad (1)$$

where *l* is one of the CUC parameters and *V* is the unit cell volume.

The logarithms of the UC parameters in the 100 to 298 K range were approximated by the least-squares method using the following linear dependences:

$$\ln l = \overline{\alpha}T + C_l \text{ and } \ln V = \overline{\beta}T + C_V \qquad (2)$$

where $\overline{\alpha}$ and $\overline{\beta}$ are the averaged coefficients of linear and volume thermal expansion coefficients; C_l and C_V are approximation coefficients.

The coefficients of linear and volume thermal expansion averaged upon the temperature range under examination are given in Table 2.

Comparison of the coefficients of volume thermal expansion (CVTE) and of the anisotropy of CLTE for monoclinic crystals inclined to twinning shows a direct correlation between these characteristics. The minimum CVTE value, obtained for mixed $K_{0.5}Rb_{0.5}Pb_2Br_5$ crystal corresponds to minimum inclination to microtwins formation. Anisotropy of CLTE values is also minimum for this crystal. The maximum CVTE value is typical of the KPb_2Br_5 crystal, which is inclined to twinning in the maximum degree. The same crystal demonstrates also

Table 1 Unit cell parameters (UC) for MPb_2X_5 at different temperatures

	Temperature/K				
	100	150	200	250	298
			$RbPb_2Cl_5$ ($P2_1/c$)		
a/Å	8.9462(14)	8.9553(14)	8.9685(12)	8.9819(12)	8.9900(17)
b/Å	7.9415(12)	7.9538(11)	7.9689(12)	7.9853(10)	7.9963(17)
c/Å	12.460(2)	12.482(2)	12.505(2)	12.5228(16)	12.541(2)
β/°	90.122(18)	90.145(16)	90.145(14)	90.159(13)	90.20(2)
V/Å^3	885.2(4)	889.1(4)	893.7(4)	898.2(5)	901.5(6)
			KPb_2Br_5 ($P2_1/c$)		
a/Å	9.192(2)	9.214(2)	9.231(2)	9.245(2)	9.269(4)
b/Å	8.303(2)	8.320(4)	8.335(1)	8.352(1)	8.362(3)
c/Å	12.944(4)	12.960(3)	12.981(3)	13.010(3)	13.008(6)
β/°	90.03(2)	90.05(2)	90.02(2)	90.01(2)	89.95(3)
V/Å^3	987.4(4)	993.4(5)	998.7(5)	1004.6(6)	1008.2(4)
			$K_{0.5}Rb_{0.5}Br_5$ ($P2_1/c$)		
a/Å	9.2659(18)	9.2758(14)	9.2899(19)	9.302(2)	9.314(2)
b/Å	8.356(2)	8.372(2)	8.384(3)	9.399(3)	8.412(3)
c/Å	12.976(3)	125.988(2)	13.014(2)	13.035(3)	13.053(3)
β/°	90.131(12)	90.107(10)	90.103(12)	90.109(13)	90.097(15)
V/Å^3	1004.7(3)	1008.7(4)	1013.6(4)	1018.3(4)	1022.7(5)

Table 2 The coefficients of linear and volume thermal expansion (in 10^{-6} K^{-1}) for the MPb_2X_5 crystals averaged upon the 100 to 298 K temperature range

	$RbPb_2Cl_5$	KPb_2Br_5	$K_{0.5}Rb_{0.5}Pb_2Br_5$
$\overline{\alpha}_a$	26	40	27
$\overline{\alpha}_b$	36	36	33
$\overline{\alpha}_c$	33	28	31
$\overline{\beta}$	94	107	91

maximum CLTE anisotropy. Results of the present work testify to the CLTE effect on formation of the twinning boundaries. A detailed investigation of this phenomenon requires a structural analysis at higher temperatures close to those of phase transitions and crystal melting.

Conclusions

The temperature dependence of the parameters of crystal unit cell was studied for KPb_2Br_5, $RbPb_2Cl_5$ and $K_{0.5}Rb_{0.5}Pb_2Br_5$ crystals in the 100 to 298 K range. Coefficients of linear and volume thermal expansion were determined. Analysis revealed the thermal expansion effect on formation of the nets of twin boundaries in these crystals. Obtained data can be used for option of the seed orientation when growing crystals as well as for optimization parameters of the protection/antireflection coating of the element faces.

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