Inorganic Materials, Vol. 41, No. 9, 2005, pp. 901–905. Translated from Neorganicheskie Materialy, Vol. 41, No. 9, 2005, pp. 1031–1036.

Crystal Growth and Electrical Properties of β-CdP_2 Single Crystals

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Received March 22, 2005

Abstract—Optically homogeneous single crystals of tetragonal cadmium diphosphide (β-CdP_2) are prepared by vapor-phase growth, and their electrical conductivity, dielectric permittivity, and loss tangent are measured during slow heating from 78 to 400 K in the [001] and [100] directions at frequencies of 10^2, 10^3, 10^4, and 10^6 Hz. The permittivity of the crystals increases with temperature. The electrical properties of β-CdP_2 are shown to be anisotropic.

INTRODUCTION

CdP_2, a II–V semiconductor, crystallizes in tetragonal symmetry (sp. gr. $P4_12_12 = D_4^4$, $Z = 8$) [1] with lattice parameters $a = 5.2768(7)$ Å and $c = 19.753(3)$ Å. The band gap of CdP_2 is $E_g = 2.03$ eV [2]. Cadmium diphosphide crystals offer a large thermooptical coefficient, large Verdet constant which is a linear function of magnetic induction, and high optical activity which varies linearly with temperature [3]. Cadmium diphosphide is used in the fabrication of optical and thermal sensors, pulse stretchers and intensity stabilizers for solid-state lasers, and input polarizing prisms for thin-film waveguides [4, 5].

The above properties and applications of β-CdP_2 crystals have been the subject of many studies, whereas their dielectric properties have not yet been investigated in sufficient detail, and available data are often contradictory.

In this paper, we report the growth of optically homogeneous β-CdP_2 crystals and their conductivity and dielectric properties as functions of frequency in the range 78–400 K in the [001] and [100] directions.

EXPERIMENTAL

β-CdP_2 was synthesized from V5 phosphorus and KD-000 cadmium additionally purified by zone melting. A stoichiometric mixture of Cd and P was loaded into a silica ampule precleaned in several steps. First, the ampule was etched in a 1 : 20 mixture of HF and H_2O, rinsed in bidistilled water, dried, and fire-polished. Next, the ampule was etched in a mixture of HF and HNO_3 for 5 min and in concentrated HNO_3 for 10–16 h, followed by rinsing in bidistilled water and drying.

The mixture was sealed in the ampule under vacuum, and the ampule was introduced into a horizontal two-zone resistance furnace. The temperature was maintained by an RIF-101 temperature controller. The thermal conditions suitable for β-CdP_2 synthesis are summarized in the table.

Fig. 1. Single crystals of tetragonal cadmium diphosphide.

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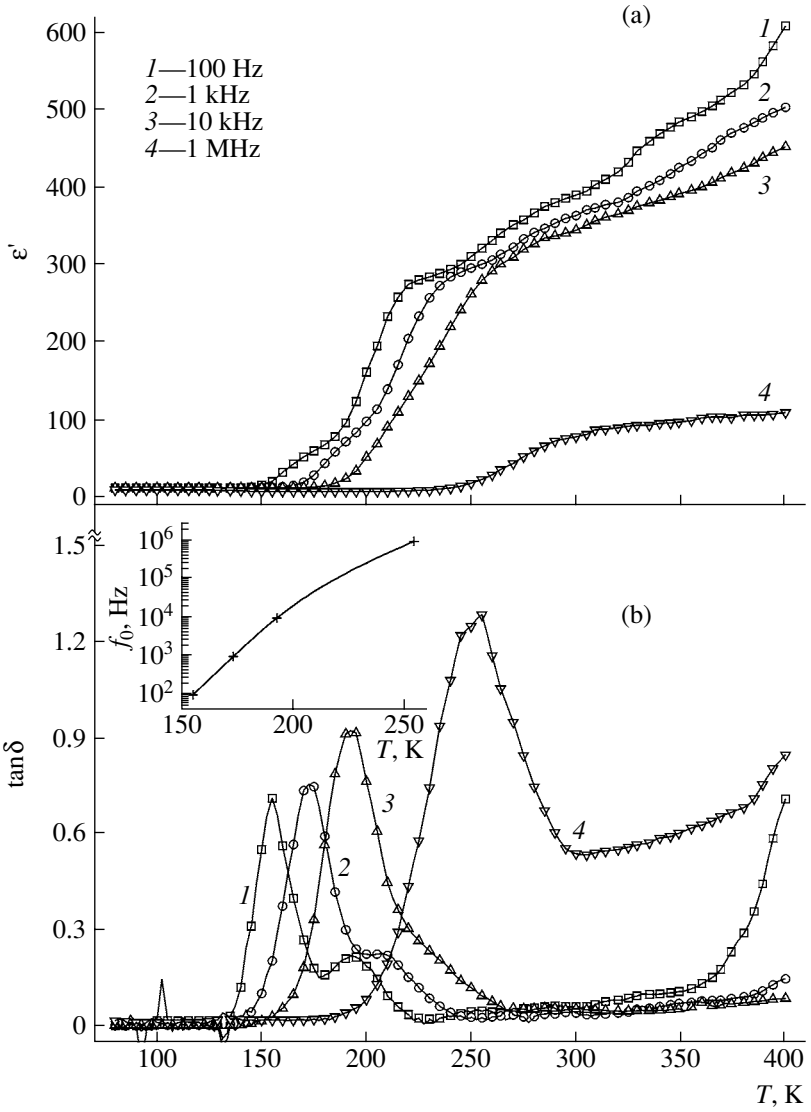

Fig. 2. Temperature dependences of (a) dielectric permittivity and (b) loss tangent in the [001] direction for β-CdP_2 single crystals at different frequencies.

The temperature of the evaporation zone in the first and second steps of synthesis ensured active reaction between the cadmium melt and phosphorus vapor. Increasing the temperature of the evaporation zone to above the limits indicated in the table might cause explosion because of the rapid heat release in the first step (exothermic reaction) and the high phosphorus vapor pressure in the second step. The temperature of the crystallization zone in the first two steps of CdP_2 synthesis ensured annealing of nucleation centers. In the third step, the reaction product was transported to the crystallization zone. The synthesized material was used as the charge for vapor-phase growth of β-CdP_2.

CdP_2 synthesis conditions

Step	$T_{\text{evaporation zone}}$, K	$T_{\text{crystallization zone}}$, K	τ, h
I	635–690	1070–1100	2–3
II	735–790	1070–1100	2–3
III	940–1020	900–990	80–120

To grow β-CdP_2 single crystals, one must ensure critical supercooling in the conical part of the ampule and a sufficient rate of CdP_2 transport from the evaporation zone to the crystallization one.

Critical supercooling for CdP_2 nucleation was found to be 3–8 K. The temperature of the crystallization zone was 980–1010 K. To control the nucleation process and restrict the growth duration to a reasonable level, we produced low supersaturation in large-diameter (18–20 mm) ampules. The growth rate then remained rather high. The ampule was translated toward the crys-

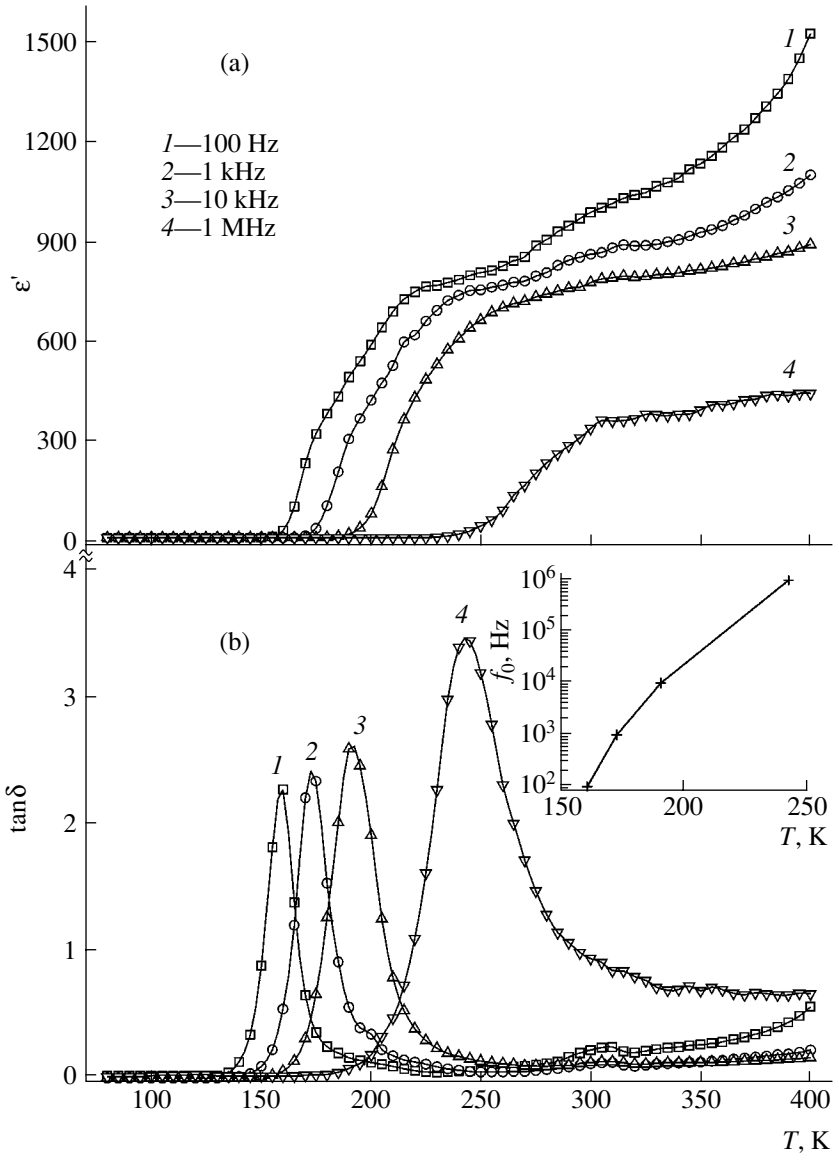

Fig. 3. Temperature dependences of (a) dielectric permittivity and (b) loss tangent in the [100] direction for β-CdP_2 single crystals at different frequencies.

tallization zone (steeper temperature gradient) at a rate of 0.6–0.8 mm/h, approximately equal to the growth rate, which ensured a constant temperature in the evaporation zone and stable growth conditions throughout the growth run.

Thus, we found an optimal combination of the growth temperature, critical supercooling, and ampule translation rate, which ensured stable growth of β-CdP_2 single crystals.

As a result, we obtained bulk single-crystal boules up to 20 mm in diameter at the back end and 40–50 mm in length (Fig. 1).

X-ray diffraction characterization (DRON-3 powder diffractometer, CuK_α radiation) showed that the crystals were single-phase and homogeneous.

In electrical measurements, we used 0.9- to 1.1-mm-thick single-crystal plates, which were oriented on the DRON-3 with an accuracy of ±0.5°. Dielectric permittivity ε', loss tangent $\tan\delta$, and electrical conductivity σ were measured along and across the *c* axis at frequencies of 10^2, 10^3, 10^4, and 10^6 Hz by a digital LCR meter during heating from 78 to 400 K at a constant rate of 1–2 K/min. Ohmic contacts to the sample faces were made with Aquadag (≈0.1-mm layer) after lapping. The sample was sandwiched between polished brass electrodes and introduced into a liquid-nitrogen cryostat. The accuracy in dielectric measurements was 0.1% or better. The temperature was controlled with an accuracy of 0.1–0.2 K.

RESULTS AND DISCUSSION

Figure 2a shows the temperature dependences of dielectric permittivity in the [001] direction for β-CdP_2 single crystals. The permittivity of β-CdP_2 increases with increasing temperature and decreases with increasing frequency. The low-temperature permittivity is 10 to 12 (depending on the sample), which is comparable to the values extracted from optical measurements [6]. At a frequency of 100 Hz, ε' varies little in the range 78–140 K and rises steeply to about 10^2 at higher temperatures. At higher frequencies, the rise in ε' begins at higher temperatures. The temperature dependences of [100] permittivity for β-CdP_2 single crystals are displayed in Fig. 3a. With increasing temperature, the permittivity along [100] rises more rapidly than that along [001], which means that β-CdP_2 has an anisotropic temperature coefficient of permittivity. The ε' along [100] exceeds that along [001] by a factor of 1.3 in the range 78–150 K and by a factor of 2.5 at higher temperatures.

Figures 2b and 3b show the temperature dependences of $\tan\delta$ for β-CdP_2 single crystals. The curves show a maximum in $\tan\delta$ in the temperature range of the steep rise in permittivity. The 0.1- and 1-kHz curves show a second peak at 190–210 K (Fig. 2b), suggesting that several polarization mechanisms may be operative.

Figure 4 displays the Arrhenius plots of conductivity in the [100] and [001] directions for single-crystal cadmium diphosphide. The conductivity of β-CdP_2 varies widely, from 10^{-9} to 10^{-2} S/cm, in accordance with earlier results [6]. The curves show a well-defined transition from low-temperature, impurity conduction to high-temperature, intrinsic conduction. In the temperature range of impurity depletion, the concentration of majority carriers is essentially constant, and the variation in conductivity is dominated by that in carrier mobility. The conductivity of β-CdP_2 depends significantly on frequency, which may be interpreted as evi-

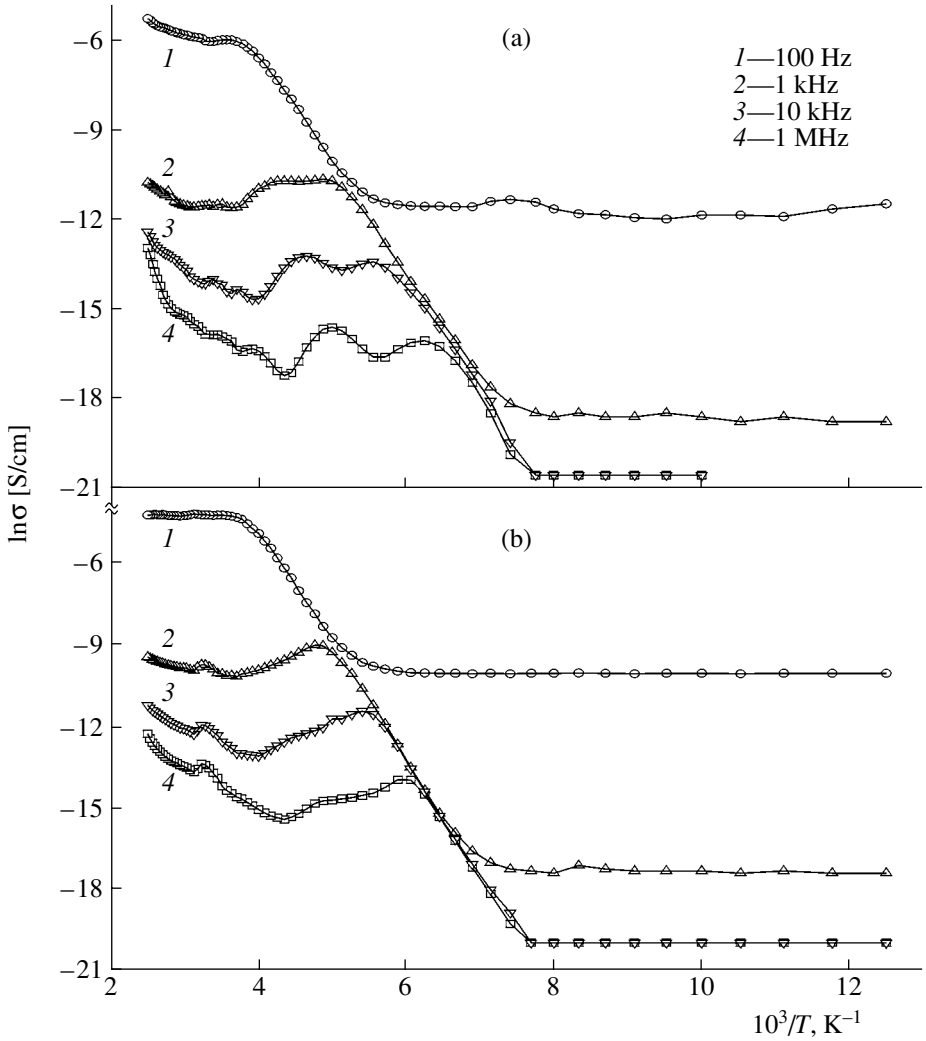

Fig. 4. Arrhenius plots of conductivity along (a) [001] and (b) [100] for β-CdP_2 single crystals at different frequencies.

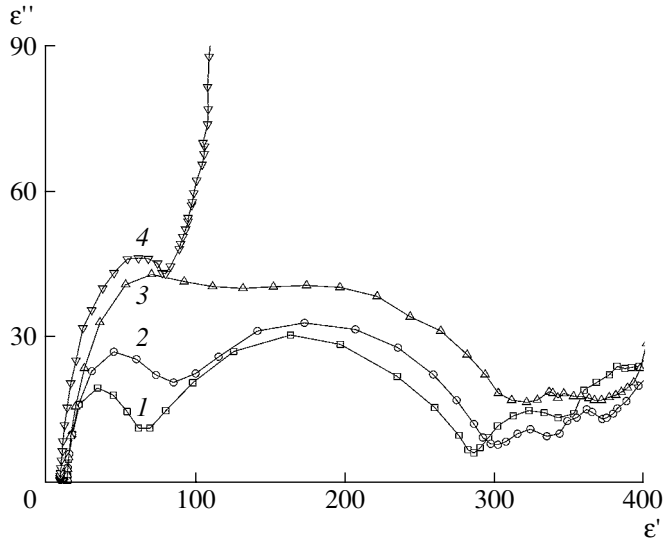

Fig. 5. Davidson–Cole diagrams for single-crystal β-CdP_2 in the [001] direction at frequencies of (*1*) 100 Hz, (*2*) 1 kHz, (*3*) 10 kHz, and (*4*) 1 MHz.

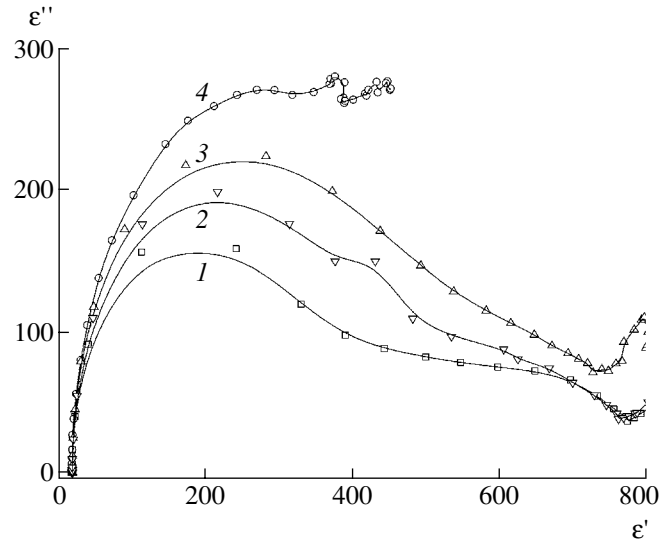

Fig. 6. Davidson–Cole diagrams for single-crystal β-CdP_2 in the [100] direction at frequencies of (*1*) 100 Hz, (*2*) 1 kHz, (*3*) 10 kHz, and (*4*) 1 MHz.

dence of hopping conduction between structural defects.

Figures 5 and 6 show the Davidson–Cole diagrams (ε" versus ε' at varying temperature and constant frequency) for the [100] and [001] directions, respectively. The semicircles in Fig. 5 suggest that dielectric relaxation is due to two species, differing in relaxation time.

Our temperature-dependent permittivity data suggest that several mechanisms underlie the dielectric relaxation in β-CdP_2. The same is evidenced by the temperature dependence of the peak-loss frequency (Figs. 2, 3, insets). The temperature effects on the dielectric properties of β-CdP_2 can be interpreted in terms of several models [7, 8]. The model proposed by Zhukovskii *et al.* [7] describes the temperature-dependent permittivity of defect-rich semiconductors in terms of hopping transport. Electron exchange between neighboring neutral defects leads to the formation of dipoles, thereby increasing polarization. We believe that the present experimental results are best described by the isolated defect model [8].

CONCLUSIONS

Optically homogeneous single crystals of tetragonal cadmium diphosphide were prepared by vapor-phase growth, and their electrical conductivity, dielectric permittivity, and loss tangent were measured between 78 and 400 K. The electrical properties of β-CdP_2 were shown to be anisotropic.

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