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STRUCTURAL TRANSFORMATIONS IN Tl_4HgI_6 AND Tl_4CdI_6 CRYSTALS AS EVIDENCED BY DIELECTRIC PROPERTIES AND CONDUCTIVITY

We present the results of experimental studies of the temperature-dependent real part of the dielectric constant and the electrical conductivity for Tl_4HgI_6 and Tl_4CdI_6 crystals. We show that the crystals under study manifest anomalous behaviors of the both physical properties in the same temperature regions. The latter facts, together with some other recent experimental data, can evidence the presence of structural transformations in those regions.

Keywords: dielectric permittivity, electrical conductivity, ionic conductors, phase transformations.

1. Introduction

Searching for new functional materials and methods for controlling their properties based on external influences is one of the important problems in electronics and optoelectronics. For a long time, a considerable portion of attention of researchers has been focused on wide-gap semiconductors, including single crystalline materials. One of the interesting and promising objects is a group of A_4BX_6 crystals, with A = In, Tl, ..., B = Mg, Zn, Cd, Hg, Ge, Pb, ..., and X = Cl, Br, I, ... Although the reports on the growth and the determination of a structure and some physical properties of many of those compounds have been known for a long enough time [1], we have witnessed recently an upsurge of the interest in the ternary halides, in particular, those with A = Tl, B = Hg, Pb and Cd, and X = I (see, e.g., [2–9]). Among many reasons, one can recall the promising ionic conductivity, good nonlinear optical characteristics, high optical anisotropy, and scintillating properties promising for, e.g., the radiation detection.

According to some of the recent data [2, 8, 9], one cannot exclude a possibility for structural transformations in the Tl_4HgI_6 and Tl_4CdI_6 crystals. Although their characteristics and the underlying mechanisms are not understood yet, the previous data indicate that it would be natural to link them with the conductivity. In this respect, it seems to be useful to investigate basic electro-physical properties of the crystals mentioned above. In this work, we report the results on the electrical conductivity and the dielectric permittivity of Tl_4HgI_6 and Tl_4CdI_6, with a particular emphasis on possible phase transformations.

2. Experimental

For the synthesis of Tl_4HgI_6 and Tl_4CdI_6 crystals, we used the salts of metal halides of industrial production. The initial components were taken according to equimolar ratios. The preliminary purification of the salts was carried out by repeatedly (about 20 times) recrystallizing them from the melt inside quartz ampoules.

Single crystals of $\mathrm{Tl_4HgI_6}$ and $\mathrm{Tl_4CdI_6}$ were grown by the standard Bridgman–Stockbarger technique in quartz crucibles having a conical bottom and a diameter of 12 mm. The crucibles containing a mixture of purified initial halides of a required molar composition were kept at a pressure of 5 Torr and then annealed during 3 h, while their temperature was increased up to $T = 470$–570 K. Then the crucibles were placed into a furnace. During the growth, the ampoule was moved through a crystallization zone with a speed of 0.5 mm/h. The optimal regime of crystallization corresponded to the conditions, under which the crystal growth rate exactly matched the speed of movement of the crucible through the crystallization zone (see also [8, 9]). The temperature of a heater was kept stable with a controlling electronic scheme, which provided an accuracy of ±1 K for the temperature stabilization.

After the crystal growth process was finished, the temperature in a furnace was lowered down to 520 K, and a crystal was annealed during a day. In this way, we have managed to obtain single crystals of a fairly good optical quality with a typical volume somewhat larger than 1 cm^3.

The dielectric and conductivity properties were investigated on a number of plane-parallel slabs of single crystals, with their thicknesses of the order of 1 mm and the areas of about 1 cm^2. The surfaces of the slabs were polished to a sufficiently good quality in order to remove undesirable edge- and surface-related effects. The samples prepared for the measurements were covered by a silver paste. Copper wires were used to connect the crystalline capacitors with the external electric circuit.

The real part of the dielectric constant ε and the electrical conductivity σ were studied, by using the standard ac measurement technique and an LCR device HP4284A. The measurements were performed in an autonomous chamber at the atmospheric pressure, various temperatures, and various frequencies of the applied electric field. The heating of samples was provided, by using a spiral furnace coiled around the experimental chamber. The refrigerating technique included gaseous nitrogen flowing inside thin channels around the chamber.

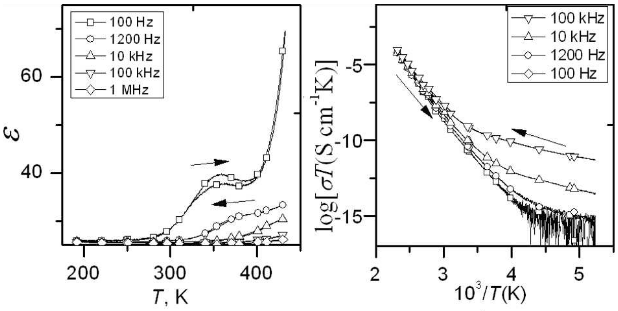
In general, our apparatus allowed us to make measurements in a temperature range of about 100–600 K. While the origin of the lower limit was quite evident, the upper one was associated with the fact that the silver paste could not withstand higher temperatures. Depending on the particular crystals and the regions of interest, the temperature range of our measurements was typically from 100–200 K to 430–480 K. The temperature change rate was about 1 K/min, and the temperature circling was carried out in order to check a possible hysteretic behavior of the properties under study. The crystal temperature tolerance was approximately equal to ±0.1–0.2 K, depending on the number of additional conditions. To make the results more reliable, we repeatedly performed the measurements, by using several samples for each crystal. As a rule, the electric-field frequencies studied in this work were 20 Hz, 100 Hz, 1.2 kHz, 10 kHz, 100 kHz, and 1 MHz.

3. Results and Discussion

Figures 1 and 2 show some of the results obtained by us for $\mathrm{Tl_4HgI_6}$ and $\mathrm{Tl_4CdI_6}$ crystals at various electric-field frequencies. Here, panels (*a*) and (*b*) correspond to the temperature dependences of the real part of the dielectric permittivity $\varepsilon(T)$ and the electrical conductivity $\sigma(T)$, respectively. Since there are clear indications that the ionic part of the conductivity associated with Tl^+ should exceed significantly the electronic contribution (see [12]), the conductivity data in Figs. 1, *b* and 2, *b* are represented in the Arrhenius coordinates modified for the case of ionic conductivity, $\log(\sigma T)$ versus $1/T$. They are associated with the well-known expression (see, e.g., [3–6])

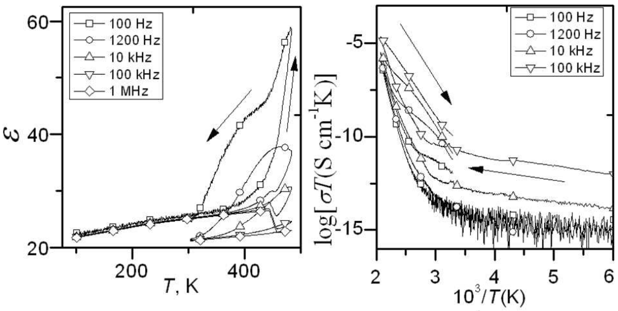
$$\sigma(T) = \frac{A}{T} \exp - \frac{E_a}{kT}, \tag{1}$$

where T is the absolute temperature, A the constant, k the Boltzmann constant, and E_a the activation energy. It is worth mentioning that the dependences $\log(\sigma T) = f(10^3/T)$ for $\mathrm{Tl_4HgI_6}$ and $\mathrm{Tl_4CdI_6}$ are almost linear so that formula (1) should represent a good enough approximation. Some weak nonlinearities may indicate more complex conductivity mechanisms. In particular, a nonnegligible electronic contribution to the conductivity cannot be ruled out completely (see the discussion in [12]).



a *b*

Fig. 1. Temperature dependences of the real part of the dielectric permittivity (*a*) and the electric conductivity (*b*) for Tl_4HgI_6 crystals measured at various frequencies indicated in the legend. The arrows indicate the heating or cooling run



a *b*

Fig. 2. Temperature dependences of the real part of the dielectric permittivity (*a*) and the electric conductivity (*b*) for Tl_4CdI_6 crystals measured at various frequencies indicated in the legend. The arrows indicate the heating or cooling run

Note that the experimental data have not been smoothed and reveal some noise, which is mainly typical of the low-temperature conductivity. This represents a combined effect of temperature stabilization issues and “expanded” temperature scale in panels (*b*) at low temperatures. Furthermore, Figs. 1 and 2 are only typical examples of all the data measured by us. Note that some of finer details of these dependences (e.g., the exact positions of the regions of anomalies) are slightly sample-dependent.

As far as the orders of magnitude of the dielectric constant and the conductivity are concerned, our results correlate fairly well with the data of previous studies of the dielectric properties (see, e.g., [2] for Tl_4HgI_6) and the conductivity (see [2, 6, 11, 12] for Tl_4HgI_6 and [10] for Tl_4CdI_6). However, our values of conductivity are somewhat higher. We also observe a fair correlation of our results with the literature data for the most general regularities of the $\varepsilon(T)$ and $\sigma(T)$ dependences (increasing/decreasing, the average temperature slopes, *etc.*). The only exception is the absence of a low-temperature region in Fig. 2, *b*, where the conductivity decreases with increase in the temperature, as found for Tl_4CdI_6 in [2]. However, this finding of the study [2] represents a feature that seems unlikely for semiconductors. Furthermore, our data seem to be notably more precise, since they reveal a number of fine features, which have not been resolved in the preceding studies. First of all, this is a non-monotonic character of most of the temperature curves seen in Figs. 1 and 2. These points will be the main subject of our further discussion.

Let us pass to the detailed analysis of the dielectric permittivity data. As seen from Fig. 1, *a*, the dependence $\varepsilon(T)$ at 100 Hz for Tl_4HgI_6 crystals is characterized by a broad maximum in the temperature interval 325–400 K and by a hysteresis between the heating and cooling temperature runs. The both phenomena become less pronounced for higher frequencies, and, in general, the main features of the anomalous behavior of the $\varepsilon(T)$ function somewhat depend on the measuring frequency. This also remains true for Tl_4CdI_6. Note that the only attempts to check the hysteresis effect in Tl_4HgI_6 and Tl_4CdI_6 have been made in [6] and [2], respectively. However, the corresponding results [6] call in question the effect, whereas the results [2], though confirming it, are inconclusive. In the rest of the works on the subject, the authors have not studied the hysteresis and performed their measurements only in the heating run [11] or even have not indicated the temperature regime at all [12].

The other crystal under test, Tl_4CdI_6, manifests qualitatively similar results for the dielectric constant (see Fig. 2, *a*). The data on Tl_4CdI_6 are specific in several aspects. First, unlike Tl_4HgI_6, the experimental curves $\varepsilon(T)$ reveal “humps” (i.e., a non-monotonic changes in the temperature derivative of the $\varepsilon(T)$ functions) in a very wide temperature region (300–480 K, which are centered at ∼400 K), rather than maxima themselves (see Fig. 2, *a*). Second, this anomalous 'hump-like' behavior of the dielectric permittivity is observed only in the cooling runs. Third, a hysteretic character of the $\varepsilon(T)$ dependences seems to be indisputable, since it is clearly seen almost for all of the frequencies. However, the hysteresis becomes more pronounced with lowering the frequency. Finally, we should point out that the peculiarities of the dielectric permittivity discussed above can evidence some phase transformations in our ternary halides. At least, an evident structural instability should occur in the temperature regions mentioned above. As for $\mathrm{Tl_4CdI_6}$, our results confirm the data in [2], where the anomalies have also been found approximately at 400 K.

As seen from the data of Figs. 1, *b* and 2, *b*, $\mathrm{Tl_4CdI_6}$ is a rather poor conductor, unlike $\mathrm{Tl_4HgI_6}$ crystals. This conclusion confirms the results in [10]. The analysis of our data on the temperature dependences of the electrical conductivity corroborates the structural transformations found from the dielectric permittivity data. No jumps or discontinuities are observed in the conductivity, which have been found in ionic conductors under order-disorder phase transitions (see, e.g., the results in [10]). To be more precise, these peculiarities have been found for the isostructural $\mathrm{In_4CdI_6}$ compound at somewhat higher temperatures (~500 K (see [10])), which are unreachable in the present experiments. In general, the main features of the anomalous temperature $\varepsilon(T)$ and $\sigma(T)$ dependences correlate fairly well, although some differences are also seen. So, the hump-like and hysteretic behaviors of the $\sigma(T)$ curves for the $\mathrm{Tl_4HgI_6}$ crystal are less evident (see Fig. 1, *b*), when compared to the $\varepsilon(T)$ curves. Instead of maxima peculiar for the $\varepsilon(T)$ curves, one can see only the weak $\sigma(T)$ humps. On the other hand, there appear "bends" in the dependences $\log(\sigma T) = f(10^3/T)$, which occur in the same temperature region where the $\varepsilon(T)$ anomalies have been seen (cf. with Fig. 1, *a*).

The experimental dependences $\sigma(T)$ for $\mathrm{Tl_4CdI_6}$ crystals reveal a close resemblance with the $\varepsilon(T)$ ones, with both the region and the structure of the temperature curves preserved (cf. Fig. 2, *a* with Fig. 2, *b*). In particular, the $\sigma(T)$ curve for $\mathrm{Tl_4CdI_6}$ acquires a hump-like anomaly only under the cooling. Like the case of the dielectric properties, the presence of a thermal hysteresis in the $\sigma(T)$ dependences for $\mathrm{Tl_4CdI_6}$ seems to be undoubtful.

Earlier, the authors of the present work have reported some experimental evidences of the phase transformations occurring in the ternary halides under test. In particular, the anomalous thermal expansion and photoinduced second harmonic generation effects have been found for $\mathrm{Tl_4HgI_6}$ [8], while the photoinduced second harmonic generation effect has been shown to reveal anomalies for $\mathrm{Tl_4CdI_6}$ [9]. Note that the temperature regions of the anomalies found in those studies correlate well with that obtained in the present work. This fact testifies that the mentioned anomalies can quite possible be associated with the structural transformations. Revealing the nature of the transformations will be a subject of forthcoming studies.

4. Conclusions

We have performed the synthesis and the growth of single crystals $\mathrm{Tl_4HgI_6}$ and $\mathrm{Tl_4CdI_6}$, using the Bridgman–Stockbarger method. The investigations of the dielectric parameters and the electrical conductivity have shown anomalies in the temperature dependences $\varepsilon(T)$ and $\sigma(T)$. These are a non-monotonic behavior and a thermal hysteresis. Although the both crystals are usually considered to be isostructural, one can see some quantitative differences in the $\varepsilon(T)$ and $\sigma(T)$ curves typical of $\mathrm{Tl_4HgI_6}$ and $\mathrm{Tl_4CdI_6}$. Despite these differences, we have obtained, in general, some additional experimental evidence of that the crystals under test should reveal structural transformations. Their nature and physical mechanisms require additional studies.

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СТРУКТУРНІ ПЕРЕТВОРЕННЯ В КРИСТАЛАХ Tl_4HgI_6 ТА Tl_4CdI_6, ПРО ЩО СВІДЧАТЬ ДІЕЛЕКТРИЧНІ ВЛАСТИВОСТІ ТА ПРОВІДНІСТЬ

Резюме

В цій роботі ми представляємо результати експериментальних досліджень температурної залежності дійсної частини діелектричної проникності та електричної провідності кристалів Tl_4HgI_6 і Tl_4CdI_6. В результаті досліджень було виявлено, що речовинам притаманна аномальна поведінка обох фізичних параметрів в аналогічному температурному діапазоні. Дані факти разом з попередніми дослідженнями можуть свідчити про наявність структурних перетворень у даних речовин.