ISSN 0030-400X, Optics and Spectroscopy, 2021, Vol. 129, No. 6, pp. 872–876. © Pleiades Publishing, Ltd., 2021.
Russian Text © The Author(s), 2021, published in Optika i Spektroskopiya, 2021, Vol. 129, No. 6, pp. 773–777.

OPTICAL MATERIALS

Transmittance of CsI, AgCl, KRS-5, and KRS-6 Crystals in the Terahertz Range

I. A. Kaplunov[a], **, G. I. Kropotov[b], *, V. E. Rogalin[c], *, and A. A. Shakhmin[b]**

[a] *Tver State University, Tver, 170100 Russia*
[b] *Tydex LLC, St. Petersburg, 191015 Russia*
[c] *Institute of Electrophysics and Electric Power Engineering, Russian Academy of Sciences, St. Petersburg, 191186 Russia*
**e-mail: grigorykropotov@tydex.ru*
*** e-mail: kaplunov.ia@tversu.ru*
**** e-mail: v-rogalin@mail.ru*

Received January 19, 2021; revised February 3, 2021; accepted February 10, 2021

Abstract—Spectral dependences of the transmittance of CsI, AgCl, KRS-5 (TlBr–TlI), and KRS-6 (TlCl–TlBr) single crystals in the infrared (IR) and terahertz (THz) spectral ranges are measured. Spectral dependences of the absorption (attenuation) coefficient of these crystals in the spectral range of 200–3000 μm are calculated. It is found that these crystals are transparent in the millimeter range, which makes it possible to use them in THz devices. It should be noted that, in contrast to the IR spectral range, the optical quality of the surface of crystal samples barely affects the transmittance in the millimeter range.

Keywords: THz range, CsI, AgCl, KRS-5, KRS-6, transmittance, absorption, refractive index, spectrophotometer, single crystal

DOI: 10.1134/S0030400X21060059

INTRODUCTION

In XXI century, the interest in terahertz (THz) electromagnetic range increased significantly [1–3]. This range (30–3000 μm or 0.1–10 THz) is located between the infrared (IR) spectral range and radio frequencies. It turned out to be much more poorly studied than the neighboring ranges because of the following simple reasons: high transmission loss in atmosphere and the absence of good radiation sources and sensitive detectors. Quite acceptable (although narrow) transmission bands in atmosphere were found during studies, and rather efficient radiation detectors were designed. Various high-power radiation sources (including lasers [4–8]) were also developed.

Many fairly important possible applications of THz radiation were found, including in safety systems, astronomy, spectroscopy of dielectric and semiconductor materials, and medicine. In this range, clothes are transparent and the photon energy is extremely small, which made it possible to apply THz radiation for inspecting passengers and luggage in airports and train stations, instead of harmful X rays [1–3]. Relict radiation has a strong THz component, while launching of astronomical instruments into space allows one to avoid atmospheric loss. The use of THz radiation in medical diagnostics and for treating oncological diseases is being actively studied [9, 10].

However, there occurred another problem: deficit of optical materials for this spectral range [11–13]. It was found that there are only few crystals and plastics that are transparent in the THz range. While transparent elements (plates, lenses, wedges, etc.) made of organic plastic materials (e.g., polymethylpentene, polyethylene, Teflon, etc.) are quite applicable for low-power emitters, power optics requires the use of materials with high optical durability.

Such materials are being actively sought for; they mainly belong to crystalline semiconductors and insulators (silicon, sapphire, and quartz) [11]. A relatively new optical material (polycrystalline diamond, which has already been commercialized) turned out to be very promising [14–17]. However, the above materials are insufficient to satisfy all requirements for the operating and optical characteristics of THz devices.

This study continues a series of publications devoted to transparent crystalline materials for THz spectral range [11, 18, 19]. Here, we consider the optical properties of a group of plastic ionic single crystals: cesium iodide (CsI), silver chloride (AgCl), and solid solutions of thallium halides KRS-5 (bromide–iodide, TlBr–TlI) and KRS-6 (bromide–chloride, TlBr–TlCl).

Table 1. Main physicochemical properties of the crystals

Property	CsI	AgCl	KRS-5	KRS-6
Molecular weight	259.83	143.34	312.9	257.0
Density, g/cm^3	4.51	5.56	7.371	7.192
Mohs hardness	1–2	2.5	2.4	2.2
Melting temperature, °C	621	457.7	414.5	423.5
Solubility, g/100 g water	44	0.000089	0.05	0.32
Specific heat, J kg^{-1} K^{-1}	200.9	354.5	150.7	201.8
Thermal expansion, K^{-1} 10^{-6}	48.6	35	61	55
Thermal conductivity, W m^{-1} K^{-1}	1.13	1.15	0.54	0.72

The data for KRS-5 are given for the composition of 42% TlBr and 58% TlI; the data for KRS-6 are given for the composition of 40% TlBr and 60% TlCl.

EXPERIMENTAL

A characteristic feature of the ionic single crystals under study is their tendency to plastic deformation and extremely low hardness: the Mohs hardness is 1–2 for cesium iodide and 2.2–2.5 for other crystals.

Two crystals under study (KRS-5 and CsI) are transparent up to 50 μm, which overlaps with the formally limited and generally accepted THz range (30–3000 μm). AgCl and KRS-6 are transparent up to 25 and 30 μm, respectively; these ranges are adjacent to the THz range. The properties of these crystals in the range up to 50 μm were investigated in detail, which is indicative of their wide application in this range.

Cesium iodide is popular for IR devices [20, 21]. This material is convenient for alignment of related optical systems, because it is transparent in the visible spectral range and nontoxic; however, it is very soft and sensitive to atmospheric moisture. Since cesium iodide is one of the few materials that are transparent up to 50 μm, it is used in devices operating in the far IR range (in particular, in spectrophotometers).

Silver chloride is transparent in the IR range up to 25 μm. An advantage of this material is that AgCl optical elements can operate even when contacting with sea water, while its drawback (along with plasticity) is high sensitivity to ultraviolet (this effect can partially be compensated for by doping the crystals with mercury [22]). Silver halide crystals are used for fabricating mid-IR fibers [23]. Concerning the mechanical properties, crystals of silver chloride are similar to copper, though tenfold weakened, and are readily subjected to mechanical treatment. Due to the strong piezo-optic effect, these crystals are often used for simulating various problems of applied mechanics by the photoelasticity method [24].

Single crystals of solid solutions of thallium halides KRS-5 and KRS-6 were developed during World War II for night viewing devices (actively designed at that time). They are transparent for the IR range (KRS-6 up to 30 μm and KRS-5 up to 50 μm) [25, 26]. KRS-5 crystals are in more demand: along with high transparency, they exhibit piezo-optic properties and thus are applied in IR acoustooptics. Currently, KRS-5 is used for fabrication of fibers operating in the range of 1–45 μm. On the whole, the application of thallium halides is limited in many respects by harmful effect of thallium on a human organism, which should be taken into account at material treatment.

Thus, two crystals under study (KRS-5 and CsI) are transparent up to 50 μm, which overlaps with the formally limited and generally accepted THz range (30–3000 μm). AgCl and KRS-6 are transparent up to 25 and 30 μm, respectively; these ranges are almost adjacent to the THz range. The main physicochemical properties of the crystals under study (according to the data in the literature [26–32]) are listed in Table 1.

Instruments for spectral measurements included a Photon RT spectrophotometer (range 185–1700 nm, absolute error of the wavelength scale 1 nm), a Bruker Vertex 70 Fourier spectrometer (range 1.3–670 μm, error in determining the wave number 0.3–0.5 cm^{-1}), and a TeraK8 terahertz time domain spectrometer (MenloSystems) (measurements in the range of 150–3000 μm). The error in measuring transmittance was ~0.5% for all the devices. The measurement techniques, calculation of the absorption (attenuation) coefficient, and determination of the absolute calculation error were discussed in [18, 19, 33, 34].

The reflectance values for the crystals under study were obtained by us; the measurement results from [21, 35, 36] were also used.

RESULTS AND DISCUSSION

The results obtained show that the plastic ionic crystals under investigation (CsI, AgCl, KRS-5, and KRS-6) are transparent in the millimeter range. Figures 1–4 show the measured transmission spectra for CsI, AgCl, KRS-5, and KRS-6 single crystals from the near-IR region to 3000 μm. Complex measurement of the transmittance in such a wide range (including thoroughly studied IR range [18–20, 23]) is necessary for comparing the optical properties of these materials in the IR and THz ranges.

Figure 5 shows the spectra of the absorption (attenuation) coefficient in the millimeter spectral range, which are calculated for the investigated single crystals based on the data obtained. Attenuation coefficients α were calculated taking into account multiple reflections according to the technique described in [19, 34]. The attenuation coefficient was calculated using the

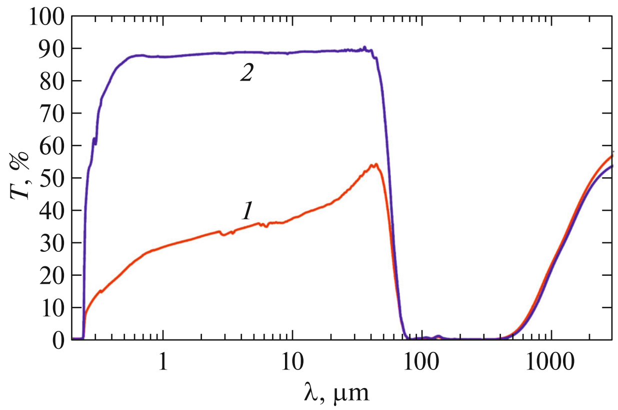

Fig. 1. Spectral dependences of the transmittance of the CsI single crystal: (*1*) sample with surface defects (thickness 4.0 mm) and (*2*) as-polished sample (thickness 4.2 mm).

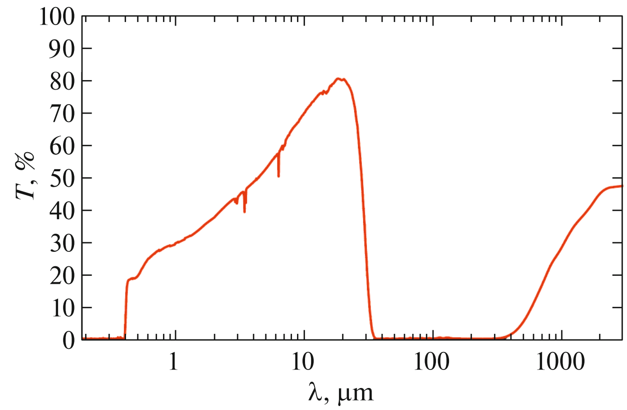

Fig. 2. Spectral dependence of the transmittance of the AgCl single crystal (thickness 1.16 mm, sample with poorly polished surfaces).

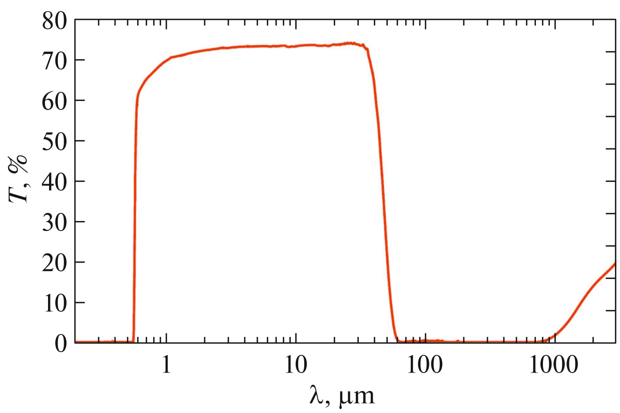

Fig. 3. Spectral dependence of the transmittance of the KRS-5 single crystal (thickness 2 mm).

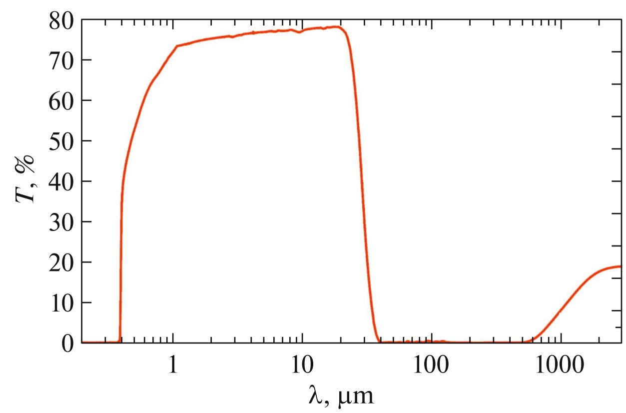

Fig. 4. Spectral dependence of the transmittance of the KRS-6 single crystal (thickness 2 mm).

data on the dependences of the Fresnel reflection on the wavelength (frequency), obtained for the spectral range of 150–3000 μm using the TeraK8 MenloSystems spectrometer. The measurements were performed taking into account single reflection on specially prepared samples.

Figure 1 shows the spectral dependence of the transmittance for two CsI single crystals. Curve *1* corresponds to the spectrum of a crystal, which has been previously in use and is characterized by turbid regions on the surface in the operating area (it was used in the optical scheme of a spectrophotometer). One can see in the spectral dependence of the transmittance that the sample transparency in the IR range decreased several times, in comparison with an as-polished sample. The transmittance of the turbid sample in the IR range increased monotonically with an increase in the wavelength to be as high as 55% at a wavelength of 40 μm, which is, nevertheless, much lower than the value for the as-polished sample (~90%). However, in the millimeter spectral range, the transmittances of both samples barely differ.

We observed similar results when studying the transparency of silver chloride crystals. Figure 2 shows the spectral dependence of the transmittance of one of the investigated samples.

Spectral dependences of the transmittance of KRS-5 and KRS-6 single crystals are shown in Figs. 3 and 4. These crystals also exhibit transparency in the millimeter range; however, it should be noted that the transmittance of these materials is low. For example, the transmittance in the vicinity of 3 mm does not exceed 20%, which is evidently insufficient for the use of this material in optical schemes of the corresponding spectral range.

However, since there are hardly any acousto-optic crystals that are transparent in the millimeter spectral range, a limited use of KRS-5 crystals (which are widely used in the IR range for this purpose) is possible.

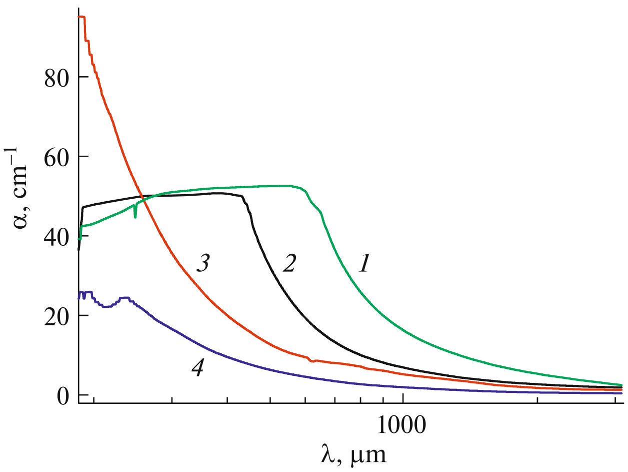

Fig. 5. Spectra of the attenuation coefficient in the range of 200–3000 μm for the following single crystals: (*1*) KRS-5, (*2*) KRS-6, (*3*) AgCl, and (*4*) CsI.

Figure 5 shows the spectra of the absorption (attenuation) coefficient of the investigated crystals in the millimeter spectral range.

CONCLUSIONS

Spectral dependences of the transmittance of CsI, AgCl, KRS-5, and KRS-6 single crystals were measured and spectral dependences of the absorption (attenuation) coefficient in the spectral range of 200–3000 μm were calculated. It was found that the crystals under study are transparent in this spectral range; however, the transmittance of the crystals is low and they can hardly be efficient optical materials in this range. It should also be noted that, in contrast to the IR spectral range, the optical quality of the surface of these crystal samples barely affects the transmittance in the millimeter range. Despite their low transmittance, KRS-5 crystals can be used to a limited extent in acousto-optic devices of the millimeter range.

ACKNOWLEDGMENTS

This study was performed using the equipment of the Tydex facilities and the Shared Research Center of the Tver State University.

FUNDING

This study was supported by State research contracts nos. 0057-2019-0005 and 0817-2020-0007.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Xi-Cheng Zhang and Jingzhou Xu, *Introduction to THz Wave Photonics* (Springer, Berlin, 2010). https://doi.org/10.1007/978-1-4419-0978-7
2. E. Brundermann, H. W. Hübers, and M. F. Kimmit, *Terahertz Techniques* (Springer, Heidelberg, 2012).
3. Y. S. Lee, *Principles of Terahertz Science and Technology* (Springer, New York, 2009).
4. A. A. Vedenov, G. D. Myl'nikov, and D. N. Sobolenko, Sov. Phys. Usp. **25**, 833 (1982). https://doi.org/10.1070/PU1982v025n11ABEH004662
5. S. Ya. Tochitsky, Chieh Sung, S. E. Trubnick, Chan Joshi, and K. L. Vodopyanov, J. Opt. Soc. Am. B **24**, 2509 (2007). https://doi.org/10.1364/JOSAB.24.002509
6. S. Ya. Tochitsky, J. E. Ralph, C. Sung, and C. Joshi, J. Appl. Phys. **98**, 26101 (2005). https://doi.org/10.1063/1.1957123
7. D. Haberberger, S. Tochitsky, and C. Joshi, Opt. Express **18**, 17865 (2010). https://doi.org/10.1364/OE.18.017865
8. N. A. Vinokurov and O. A. Shevchenko, Sov. Phys. Usp. **61**, 435 (2018). https://doi.org/10.3367/UFNe.2018.02.038311
9. K. I. Zaytsev, I. N. Dolganova, N. V. Chernomyrdin, G. M. Katyba, A. A. Gavdush, O. P. Cherkasova, G. A. Komandin, M. A. Shchedrina, A. N. Khodan, D. S. Ponomarev, I. V. Reshetov, V. E. Karasik, M. Skorobogatiy, V. N. Kurlov, and V. V. Tuchin, J. Opt. **22**, 013001 (2020). https://doi.org/10.1088/2040-8986/ab4dc3
10. I. N. Dolganova, P. V. Aleksandrova, N. V. Chernomyrdin, S.-I. T. Beshplav, A. V. Kosyrkova, P. V. Nikitin, A. A. Gavdush, I. V. Reshetov, V. V. Tuchin, and K. I. Zaytsev, Proc. SPIE **11073**, 110730 (2019). https://doi.org/10.1117/12.2526759
11. V. E. Rogalin, I. A. Kaplunov, and G. I. Kropotov, Opt. Spectrosc. **125**, 1053 (2018). https://doi.org/10.1134/S0030400X18120172
12. Md Saiful Islam, M. B. Cristiano, Cordeiro, J. Md Nine, J. Sultana, A. L. S. Cruz, A. Dinovitser, B. Wai-Him Ng, H. Ebendorff-Heidepriem, D. Losic, and D. Abbott, IEEE Access. **8**, 97204 (2020). https://doi.org/10.1109/ACCESS.2020.2996278
13. R. T. Ako, A. Upadhyay, W. Withayachumnankul, M. Bhaskaran, and S. Sriram, Adv. Opt. Mater. **8**, 1900750 (2020). https://doi.org/10.1002/adom.201900750
14. V. G. Ral'chenko and A. P. Bol'shakov, in *Carbon Photonics,* Ed. by V. I. Konov (Nauka, Moscow, 2017) [in Russian].
15. V. E. Rogalin, M. I. Krymskii, and K. M. Krymskii, J. Commun. Technol. Electron. **63**, 1326 (2018). https://doi.org/10.1134/S1064226918110098
16. V. E. Rogalin and S. M. Aranchii, Integral, No. 5 (67), 7 (2012).
17. The Element Six CVD Diamond Handbook. https://e6cvd.com/media/wysiwyg/pdf/E6_CVD_Diamond_Handbook.pdf.

18. I. A. Kaplunov, A. I. Kolesnikov, G. I. Kropotov, and V. E. Rogalin, Opt. Spectrosc. **126**, 191 (2019). https://doi.org/10.1134/S0030400X19030093

19. I. A. Kaplunov, G. I. Kropotov, V. E. Rogalin, and A. A. Shakhmin, Opt. Spectrosc. **128**, 1583 (2020). https://doi.org/10.1134/S0030400X20100136

20. Window Crystal. http://bjpcrystal.ru/.

21. *Handbook of Optical Constants of Solids* (Academic, New York, 1997), Vol. 3, p. 857. https://doi.org/10.1016/B978-012544415-6.50136-9

22. M. P. Shaskol'skaya, *Crystallography* (Vysshaya Shkola, Moscow, 1984) [in Russian].

23. L. N. Butvina, O. V. Sereda, A. L. Butvina, E. M. Dianov, N. V. Lichkova, and V. N. Zagorodnev, Quantum Electron. **39**, 283 (2009). https://doi.org/10.1070/QE2009v039n03ABEH013982

24. V. E. Rogalin, A. V. Shalimova, and M. P. Shaskol'skaya, Izv. Akad. Nauk SSSR, Ser. Fiz. **41**, 1537 (1976).

25. I. S. Lisitskii, G. V. Polyakova, V. F. Golovanov, and M. S. Kuznetsov, Tsvet. Met., No. 6 (882), 74 (2016). https://doi.org/10.17580/tsm.2016.06.10

26. Giredmet. http://www.giredmet.ru/en/production-and-service/haloidtl/.

27. A. A. Blistanov, V. S. Bondarenko, N. V. Perelomova, F. N. Strizhevskaya, V. V. Chkalova, and M. P. Shaskol'skaya, *Acoustic Crystals, The Handbook* (Nauka, Moscow, 1982) [in Russian].

28. D. D. Salimgareev, Cand. Sci. (Tech.) Dissertation (Ural. Fed. Univ., Ekaterinburg, 2018).

29. L. V. Zhukova, A. S. Korsakov, and D. D. Salimgareev, *Infrared Crystals. Theory and Practice* (UMTs UPI, Ekaterinburg, 2015) [in Russian]. http://hdl.handle.net/10995/36046.

30. Yu. V. Voroshilov and V. I. Pavlishin, *Fundamentals of Crystallography and Crystal Chemistry. X-Ray of Crystals* (KNT, Kiev, 2011) [in Russian].

31. *Short Reference Book of Physical and Chemical Quantities,* Ed. by A. A. Ravdel' and M. A. Ponomareva (Khimiya, Leningrad, 1983) [in Russian].

32. E. M. Voronkova, B. N. Grechushnikov, G. I. Distler, and I. P. Petrov, *Optical Materials for Infrared Technology* (Nauka, Moscow, 1965) [in Russian].

33. M. V. Kurik, J. Appl. Spectrosc. **4**, 199 (1966). https://doi.org/10.1007/BF00612152

34. I. A. Kaplunov, A. I. Kolesnikov, I. V. Talyzin, L. V. Sedova, and S. L. Shaiovich, J. Opt. Technol. **72**, 564 (2005). https://doi.org/10.1364/JOT.72.000564

35. *Handbook of Optical Constants of Solids* (Academic, New York, 1997), Vol. 3, p. 857. https://doi.org/10.1016/B978-012544415-6.50136-9

36. Refractive Index. INFO. https://refractiveindex.info/about.

Translated by A. Sin'kov