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Optical properties of some crystalline fluorides in the terahertz region of the spectrum

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ABSTRACT

The transmission in the terahertz spectral range of crystalline fluorides of Lithium (LiF), Calcium (CaF_2), Barium (BaF_2) and Magnesium (MgF_2), which are widely used in ultraviolet and infrared spectral optics, was studied. The spectral dependences of the absorption coefficient of these materials were obtained, in the region of 200–3000 μm a transparency zone was registered. This is of interest for the possible use of fluorides in THz devices in the millimeter range.

1. Introduction

At the end of the 20th century, active development of the terahertz (THz) range, occupying an intermediate position between infrared (IR) radiation and the radio range, began. Currently, the THz spectral range is much less studied than the neighboring ranges, due to significant absorption in the atmosphere, as well as the lack of good emitters and photodetectors. Therefore, this situation was even called the "THz gap" [1]. With the exit of mankind into space, there was a significant need to use this range in order to obtain the necessary information for the study of astronomical objects. In addition, in the THz range, important data can be obtained when studying the spectra of complex organic molecules, including such as explosive, poisonous and narcotic substances, harmful substances - atmospheric pollutants, as well as proteins, DNA.

Careful study of the THz range allowed detecting atmospheric windows, although narrow. Subsequent studies initiated the creation of a variety of radiation sources, including laser ones. Significant power levels (up to 10^9 W per pulse) have already been obtained with THz lasers [2–7], which raises the question of necessity to use transparent materials with high optical damage. Very sensitive photodetectors have been developed to detect radiation [1,8,9]. It was found out, that many of the materials, including textiles, plastics and biological tissues are transparent in THz range. At the same time, due to the low THz photon energy, the radiation does not cause damages that are characteristic of ionizing radiation, even at significant intensity [1,8,9]. This stimulated the search for new interesting non-destructive applications in spectroscopy, medical diagnostics, as well as for quality control and/or for security assurance; the list of such applications is constantly updated.

For optical materials used in the visible and IR ranges there is a large selection of transparent materials with an absorption coefficient at the operating wavelength of 10^{-4} cm^{-1} or even less [10]. For the THz range, in which only a few crystals and a number of plastics are transparent [11–13], absorption at a level of 0.5 cm^{-1} is considered quite acceptable. The most commonly used crystals are: silicon, sapphire and quartz; as well as polymeric materials: polymethylpentene, polyethylene, fluoroplastic [11,14–16]. Great prospects have a relatively new optical material - polycrystalline diamond, already produced by industry [17–20]. But at present, the high cost and processing difficulties in many cases prevent its widespread use. For applications in the THz region, optical antireflection methods have been developed [21,22].

These materials are widely used in various THz range devices. However, all of them are not free from flaws, which were discussed in detail in Ref. [11]. The growing demand for rapidly developing applications of THz range of the spectrum stimulates the search for new materials that would allow the development of numerous technologies, used in the visible and IR ranges, in the THz region.

Multi-range devices, which require the use of transparent optics, both in THz and in traditional ranges, are also created. This was the

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Table 1
The main physicochemical properties of fluorides.

Properties	LiF	CaF_2	BaF_2	MgF_2
Molecular weight	25.94	78.08	175.36	62.32
Density, $g \cdot cm^{-3}$	2.64	3.18	4.83	3.18
Mohs hardness	3	4	3	5–6
Melting point, °C	846	1360	1280	1255
Solubility, g/100 g of water	0.27	0.0016	0.17	0.0076
Specific heat, $J \cdot kg^{-1} \cdot K^{-1}$	1562	9	436	920
Thermal expansion, $K^{-1} \cdot 10^{-6}$	35	18	18.4	8.8
Thermal conductivity, $W \cdot m^{-1} \cdot K^{-1}$	4.01	9.17	7.1	3.15
Refractive index n (at $\lambda = 5$ μm)	1.32	1.399	1.45	1.33

* Data for $\lambda = 5$ μm are given for reference.

reason for the statement of this work. It is devoted to studying the transmission in the THz range (up to 3000 μm) of Lithium fluorides (LiF), Calcium (CaF_2), Barium (BaF_2) and Magnesium (MgF_2), which are widely used in the optics of the ultraviolet (UV) and infrared spectral ranges. This work continues our previous studies of transparent materials for the THz range [11,23,24].

2. Materials and experimental procedure

Compared with alkali halide crystals [24], fluorides have significant advantages. They almost do not dissolve in water (see Table 1), which is essential when working in conditions of high humidity, are well processed, do not represent environmental danger. Their disadvantages include fragility along cleavage planes and high sensitivity to thermal shocks. Earlier these materials practically were not used in the THz range. In the IR and UV ranges, fluorides are applied very widely, due to their good optical properties. The optical properties of fluorides in these ranges are well studied.

For example, Lithium fluoride has the best transparency in the vacuum ultraviolet region of the spectrum. Therefore, it is a non-alternative optical material for the optics of molecular fluorine lasers ($\lambda = 0.157$ μm) [25]. Most common are optical single crystals of Calcium and Barium fluorides, which are widely used in modern photolithography [26]. For the manufacture of optical elements of a photolithographic installation, optical material with extremely high requirements for optical characteristics in the vacuum ultraviolet region of the spectrum is required. Therefore, high requirements are placed on materials in terms of optical uniformity, birefringence, crystalline orientation and resistance to excimer laser exposure. It is known, that Calcium fluoride is used to record highly stable holograms [27]. Also, these crystals are actively used in optics of the mid-IR range, including laser optics [28].

Magnesium fluoride, as well as crystalline quartz, which is widely used in the THz range, is a birefringent crystal, unlike other isotropic fluorides considered by us. This disadvantage is overcome by cutting out the sample along the crystallographic axis, along which both beams propagate in the same direction.

The spectral dependences given below were measured on samples of single crystals grown from a melt by the Bridgman-Stockbarger method. The main physicochemical properties of the studied crystals are given in Table 1 [29–31].

Spectral transmission of samples was recorded using a Photon RT spectrophotometer from Essent Optics, a Bruker Vertex 70 Fourier spectrometer in the spectral range 0.185–670 μm. Measurements were carried out at room temperature. For Photon RT in the range 185–1700 nm, the absolute error of the wavelength scale was 1 nm; for Bruker Vertex 70, the accuracy of determining the wave number was 0.3–0.5 cm^{-1}. The error in measuring the transmittance with these devices was 0.5%. In the range of 150–3000 μm, measurements were carried out on a TeraK8 MenloSystems device, the error in determining the transmission and refractive index was 0.5%.

The calculation of absorption (attenuation) coefficients α was carried out according to the standard methods that takes into account multiple

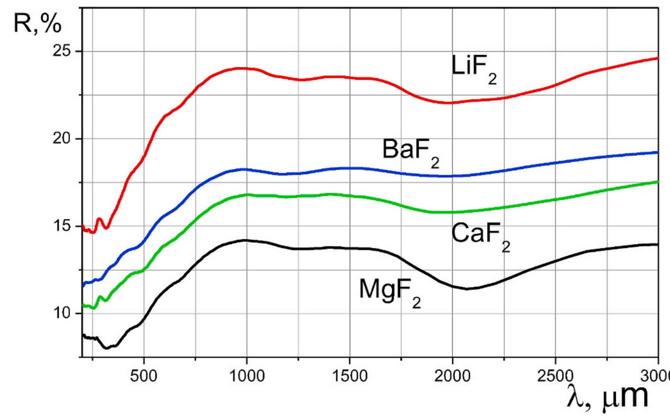

Fig. 1. Reflection spectra of fluorides of magnesium, lithium, calcium and barium in the THz range.

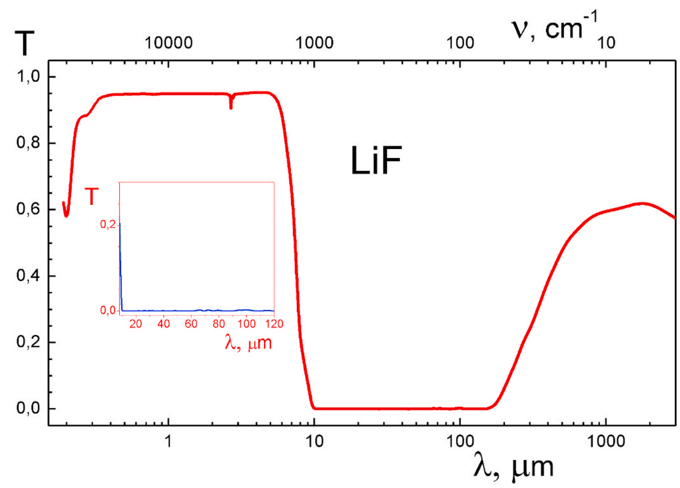

Fig. 2. The spectral dependence of the transmittance of LiF crystal with a thickness of 2 mm.

reflections [32,33]. To calculate and plot the spectral dependences of the absorption coefficient, we used the data on the dependences of the reflection on the wavelength (frequency) obtained for the spectral range of 150–3000 μm using a TeraK 8 MenloSystems spectrometer. The

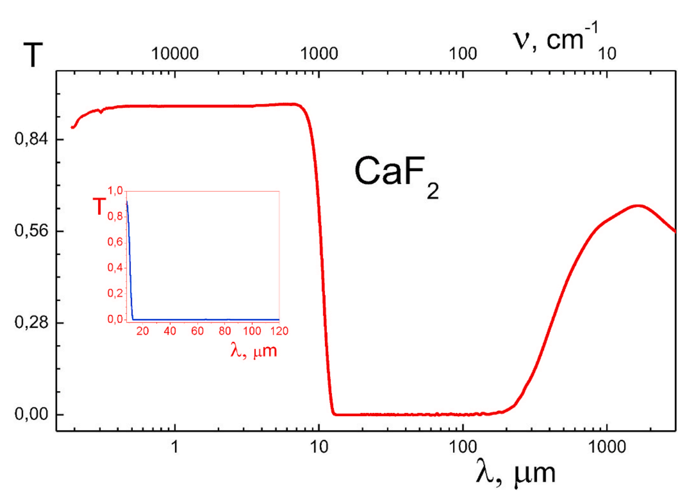

Fig. 3. The spectral dependence of the transmittance of CaF_2 crystal with a thickness of 2 mm.

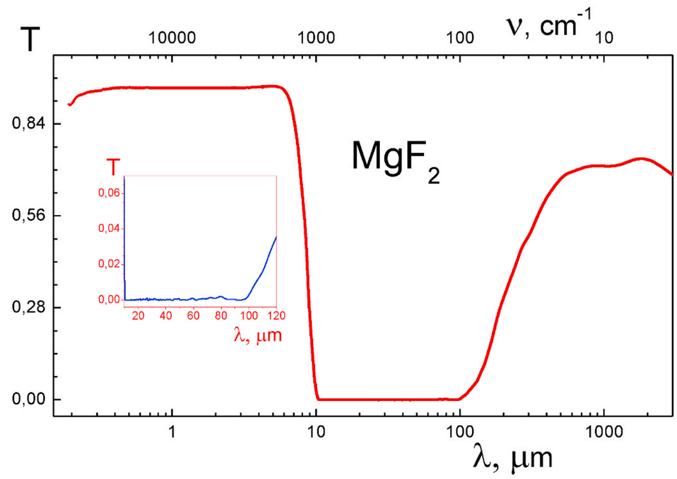

Fig. 4. The spectral dependence of the transmission of MgF_2 crystal with a thickness of 2 mm.

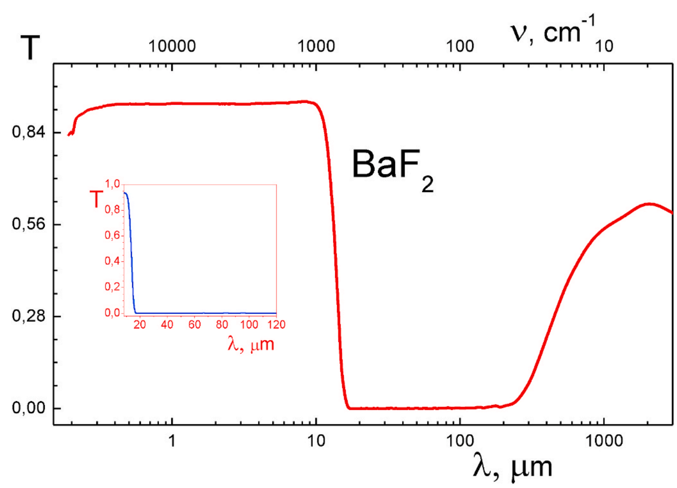

Fig. 5. The spectral dependence of the transmission of BaF_2 crystal with a thickness of 2 mm.

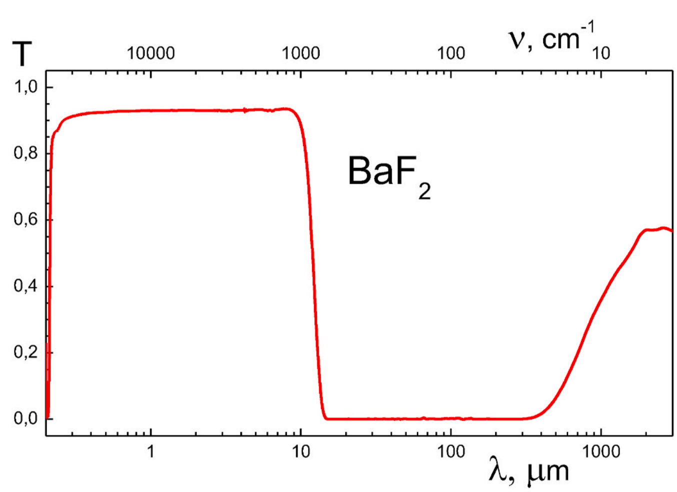

Fig. 6. The spectral dependence of the transmission of BaF_2 crystal with a thickness of 7.29 mm.

reflectance values were used in the form of a discrete dependence of the reflectance values on the wavelength. In the range of 200–3000 μm, 298 corresponding values were obtained. Reflection coefficient measurements were made on specially prepared samples, the geometry of which excluded the entering photodetector of the device by the beam reflected from the second face. For the visible and infrared ranges, we used the results of works [29,30,34]. The absolute calculation error - Δα was determined according to Refs. [23,33], using the data from Ref. [33].

3. Experiment results

Fig. 1 shows the dependences of reflection (R) on the wavelength for the crystals under study in the terahertz spectral range. These values were used to calculate the absorption coefficients of the studied fluorides.

Figs. 2–5 show the measured transmission spectra for single crystals of LiF, CaF_2, BaF_2 and MgF_2 from the near-IR range to 3000 μm; the thickness of the samples was 2 mm. In order to illustrate the effect of crystal thickness on its transmission, the spectral dependence of the transmission of a BaF_2 single crystal with a thickness of 7.29 mm is presented (Fig. 6). A significant difference in transmission was observed. For example, at a wavelength of 1000 μm, a crystal 2 mm thick transmitted 55% of the radiation, and a crystal 7.29 mm thick transmitted only 36%.

Fig. 8 shows the calculated spectra of attenuation coefficients for single crystals of LiF, CaF_2, BaF_2 and MgF_2 in the range 200–3000 μm MgF_2 crystals have the minimum absorption in the range 200–800 μm. For them, the absorption coefficient in this range is 0.35–4.90 cm^{-1}. LiF crystals have the minimum absorption in the range of 800–3000 μm; for them the absorption coefficient in this range is 0.02–0.20 cm^{-1} and the minimum absorption (0.02–0.03 cm^{-1}) occurs in the range 1550–1650 μm. Of the crystals studied, MgF_2 has the highest transmission in the THz range. This material already at a wavelength of 200 μm transmits 30% of the radiation, and at 1000 μm - 70%, while other crystals at 200 μm transmit only a few % of the radiation. At 1000 μm, LiF and CaF_2 transmit about 60%, while BaF_2 only - 55%. However, LiF crystals in the terahertz spectral range have a higher refractive index and correspondingly higher reflection losses. The calculation of the errors (according to Ref. [33]) shows the values of the absolute error Δα in the wavelength range of 500–2000 μm for fluorides: $BaF_2 \pm 0.034$ cm^{-1}; LiF $\pm$ 0.014 cm^{-1}; $CaF_2 \pm 0.030$ cm^{-1}; $MgF_2 \pm 0.012$ cm^{-1}.

4. Discussion of results

The IR and UV transmission spectra (up to 50 μm) of the crystals, studied in this work, are well known. However, we found it necessary to show them in Figs. 2–6, so that the reader can make a complete picture of the transparency of these crystals. As the results of this work show, the studied fluoride single crystals have a transparency band in the spectral range of 200–3000 μm. Figs. 2–6 show that after the transmission band in the IR range, in all described crystals, a region of intense absorption, due to phonon processes, is observed [29]. The range of phonon absorption of these crystals (from ~8 μm to ~ 300 μm) is noticeably smaller than in alkali-halide single crystals - (from ~15 μm to ~ 800 μm) [24].

For use in the millimeter range, fluorides are much more promising, because in the range of 300–3000 μm these crystals are transparent and can be used in THz devices. It should be noted that, although our experimental capabilities were limited by a wavelength of 3000 μm, the shape of the transmission curves indicates the transparency of the studied crystals at longer wavelengths.

When comparing the data in Figs. 5 and 6, it can be seen that, in the THz range, BaF_2, like almost all known crystals, has noticeable absorption. Therefore, for example, at a wavelength of 1000 μm, the absorption is 1.11 cm^{-1}. The same applies to the rest of the fluorides studied by us: for LiF - 0.13 cm^{-1}, CaF_2 - 0.87 cm^{-1} and MgF_2 - 0.26

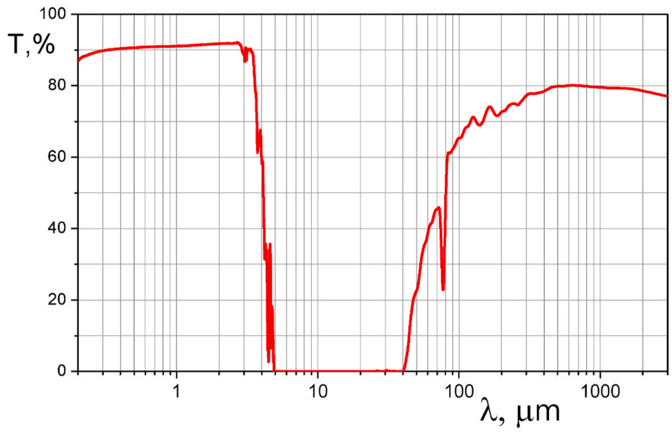

Fig. 7. Transmission spectrum of crystalline quartz Z cut.

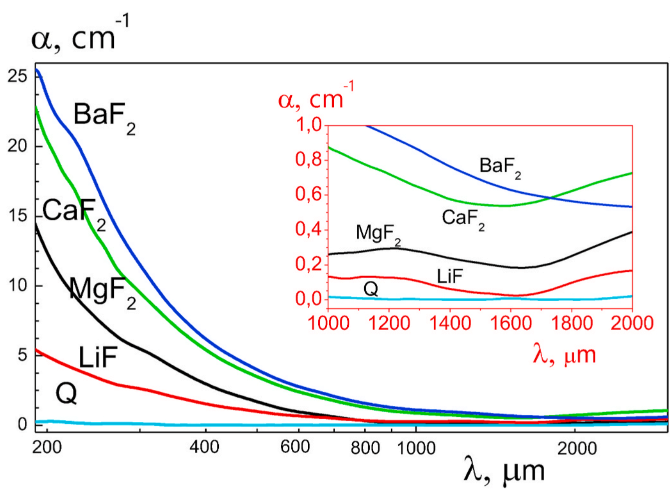

Fig. 8. Calculated spectra of attenuation coefficients for single crystals of LiF, CaF_2, BaF_2, MgF_2 and crystalline quartz (Z cut) in the range 200–3000 μm.

cm^{-1}.

Let us compare the properties of fluorides with the properties of one of the actively used THz material - crystalline quartz. Fig. 7 shows the well-known transmission spectrum of Z cut crystal quartz, 2 mm thick, measured by us under the same conditions. Fig. 8 shows the attenuation curves of for the fluorides compared with that of a crystalline quartz. Of course, the absorption in quartz is much lower than that of fluorides, although in some parts of the spectral range it is quite comparable. It is clearly seen that the phonon absorption zone in quartz is much narrower than in fluorides and is located in the spectral range 4–100 μm. Because of this quartz is practically inapplicable in multiband devices that combine the IR and THz ranges. In addition, one should take into account the significantly larger technological problems of growing these crystals. They are grown by the hydrothermal method; the growth cycle lasts for several months at a strictly maintained and controlled around the clock temperature of about 400 °C and pressure up to 1000 atm. Whereas fluorides are grown from the melt with significantly fewer problems.

5. Conclusion

In this work, we measured the spectral dependences of the transmittance coefficients and calculated the spectral dependences of the absorption coefficient of single crystals of LiF, CaF_2, BaF_2 and MgF_2 for the THz range. It was found that a transparency zone is observed in these crystals in the range 300–3000 μm. In order to characterize the overall picture of the transparency of these materials over a wide range of the spectrum and to compare the transmission with the results for the THz region, the transmission dependences were obtained and presented for these samples also in the IR range.

The fluorides studied in this work are well-studied optical materials, widely used in various UV and IR optical devices. They are commercially produced by the industry and therefore can be recommended for use in devices that combine their optical and THz properties. In some parts of the THz range, optical properties of fluorides are quite comparable with traditionally used materials. When developing specific devices, fluorides can be considered as optical elements, due to their wider availability and advanced optical processing technologies.

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CRediT authorship contribution statement

Ivan A. Kaplunov: Conceptualization, Ideas, Methodology, Development, Writing – review & editing, Writing-Reviewing; Editing. **Grigory I. Kropotov:** Investigation, Validation, Verification. **Vladimir E. Rogalin:** Writing – review & editing, Writing - reviewing; Editing. **Alexey A. Shakhmin:** Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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