Optical Engineering

RESEARCH PAPER

Infrared lens units using chalcogenide glass with high transmission properties

Yoshimasa Matsushita,[a,*] Fumio Sato,[a] Noriaki Masuda,[a] and Masafumi Kimata[b]
[a]Nippon Electric Glass Co., Ltd., Otsu, Japan
[b]Consultant, Kawanishi, Japan

ABSTRACT. Germanium and chalcogenide glasses are used as infrared lens materials, but there is no one that combines both excellent optical properties and mass production. Against this background, we worked on the development of a new infrared lens material, and a novel infrared lens material named FI-02 has been developed. FI-02's most useful feature is its infrared transmission property. It can transmit up to 20-μm-wavelength infrared light and has a vast transmittance spectrum in the infrared region compared to germanium and conventional chalcogenide glass. In addition, FI-02 has a high refractive index of 3.47 (at a wavelength of 10 μm). This enables the fabrication of thin and high-performance infrared lenses. Furthermore, FI-02 can be processed through press molding. This enables making of high-performance lenses with high productivity. In an infrared lens unit using FI-02, infrared images are captured with better contrast as compared to those captured using the germanium or conventional chalcogenide glass lenses. This could be attributed to the good infrared transmission property of FI-02. In addition, we confirmed that using FI-02 with a high refractive index as an aspheric lens, it is possible to design a lens unit with unprecedented characteristics, such as a low-distortion ultra-wide-angle lens.

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1 Introduction

Recently, infrared technology and products have drawn significant attention. Far-infrared light imaging using more than 8-μm-wavelengths has been vital for many applications, such as security, thermography, and automotive-night vision system.[1]

As common optical glass materials used in the visible to near-infrared wavelength range cannot transmit far-infrared light, a special material is required for infrared optics. Generally, crystal materials (e.g., germanium, zinc sulfide, and zinc selenide) or chalcogenide glasses are widely used as infrared lens materials. Germanium crystals have good infrared transmission properties and a high refractive index of 4.0 at 10 μm. It is possible to fabricate aspherical lenses with germanium by point diamond turned. However, considering the future increase in the number of infrared cameras, lens materials that have high productivity through press molding are essential. Therefore, chalcogenide glass has been regarded as a desirable material with the expansion of the infrared optics market owing to its infrared transmission properties and productivity. The composition of commercially available conventional chalcogenide glass is Ge-As-Se, As-Se,

*Address all correspondence to Yoshimasa Matsushita, ymatsushita@neg.co.jp

Table 1 Advantages and disadvantages of conventional infrared lens materials.

Material	Germanium	Conventional chalcogenide glass (commercially available)
Pros	High infrared transmission property High refractive index	Can be formed through press molding
Cons	Only processed through machining	Lower infrared transmission property than germanium
		Lower refractive index than germanium
	Expensive	Constitute highly toxic elements

Ge-Sb-Se, Ge-As-Se-Te, As-S, Ge-Sb-Sn-S, etc. Chalcogenide glass can be formed into any shape through press molding. Using chalcogenide glass, we can make complex shape optics, such as aspherical lenses, with high productivity. However, it does not have as good optical properties as germanium. As its infrared transmission property is lower than germanium, lenses using chalcogenide glass tend to reduce the contrast of infrared images. A lower refractive index than germanium may increase lens thickness and limit the types of lenses that can be designed. In addition, most commercially available conventional chalcogenide glass is composed of highly toxic elements, such as arsenic and selenium.

Table 1 summarizes the advantages and disadvantages mentioned above. As no material has the advantages of excellent optical properties and high productivity, we aim to develop a novel chalcogenide glass that has excellent optical properties, can be press-formed, and does not contain highly toxic elements. Furthermore, we aim to develop an infrared lens unit using it.

2 Development of Novel Lens Material: FI-02

Chalcogenide glass is composed primarily of chalcogen elements belonging to group 16 of the periodic table of elements, e.g., sulfur, selenium, and tellurium. As chalcogen elements form bonds with lower binding energy than oxides, chalcogenide glasses can transmit light at longer wavelengths than typical oxide-based glasses.[2] Unlike crystal materials, chalcogenide glass comprises multiple elements. Therefore, the optical properties, such as transmission range, refractive index can be tuned by changing the types of components or their ratios. The maximum wavelength that a chalcogenide glass can transmit is determined by the vibrational frequencies of the bonds between the atoms that make up the glass. This is expressed by the following equation:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{\mu}}, \tag{1}$$

where ν is the vibrational frequency of light absorbed, μ is the converted mass of two atoms connected by a bond, and f is the spring constant determined by the binding energy. This means that chalcogenide glasses consisting of heavy elements and weak bonds have longer transmission limit wavelengths and better transmission properties. Thus we chose tellurium as the primary component. Tellurium is toxic, but it is much safer than arsenic and selenium. The primary component of commercially available conventional chalcogenide glass is sulfur or selenium because telluride glass tends to crystallize easily and is very difficult to vitrify. However, by adding Ge and other elements, we have found the compositions that allow for stable vitrification and developed a new chalcogenide glass, FI-02. In the development process, we also made effort not to contain arsenic and selenium, which is highly toxic and is often found in conventional chalcogenide glass.[3]

3 Experimental Procedures

3.1 Material Development

Chalcogenide glasses, mainly composed of Te, were prepared by the melt-quench process shown in Fig. 1. First, reagent-grade metals, Te, Ge, and other components were weighed and mixed to obtain the designed proportions. Then to avoid contamination by oxygen, the mixture was placed

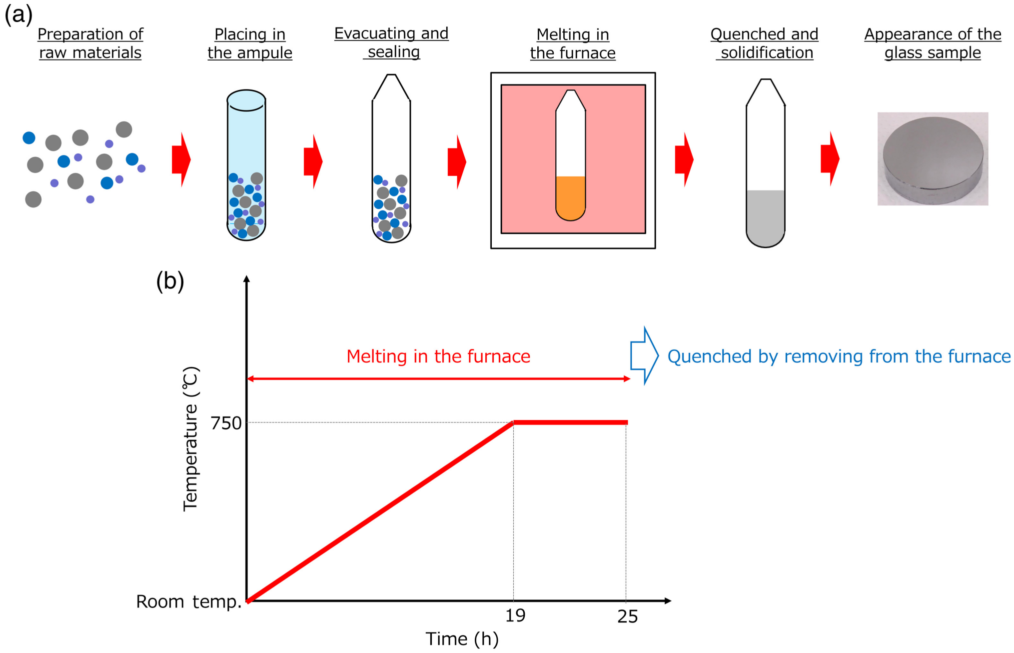

Fig. 1 (a) Procedure of making glass samples and (b) temperature profile of melting.

in the evacuated fused silica ampoule. Next, melted samples were made by placing the ampoules in the furnace, and subsequently, the melt was quenched to room temperature and solidified. The temperature profile during melting is shown in Fig. 1(b).

The composition of FI-02 was determined by examining the glass stability of glass samples made with Te 50% to 90%, Ge 5% to 30%, and other elements 5% to 20%. Glass stability was evaluated from the difference between the glass transition temperature (T_g) and crystallization temperature measured by thermogravimetry-differential thermal analysis (TG-DTA).

The infrared transmittance of the sample was measured by a Frontier IR Perkin Elmer FT-IR. We evaluated the internal transmittance to remove the effect of reflections on the sample surface. The internal transmittance can be calculated using two samples of different thicknesses and the following formula:

$$\log \tau = -\frac{\log T_1 - \log T_2}{d_2 - d_1} \times 10 \qquad d_2 > d_1, \tag{2}$$

where τ is the internal transmittance of glass at 10 mm, d (mm) is the thickness of samples 1 and 2, and T is the transmittance of samples 1 and 2, including surface reflection loss.

The refractive index was measured by the minimum deviation method. We made a prism sample and measured the refractive index in the infrared region using NRI-100 manufactured by Bunkoukeiki.

3.2 Making Lens Unit Procedure

Figure 2 shows the procedure of making lens units. First, we created an optical design using Zemax Opticstudio and determined the lens shape and structure of the lens barrel. Next, we formed FI-02 into the shape of an aspherical lens through press molding. Press forming was performed at temperatures of 150°C to 250°C and pressures of 0.05 to 0.45 MPa. We next created an anti-reflection (AR) coating on both surfaces of the lenses. AR coating is multilayer thin films composed of germanium or zinc sulfide, commonly used in AR coatings for infrared applications. Finally, we assembled the infrared lens unit by building the lenses into a lens barrel. To evaluate the infrared lens unit performance, we attached the lens unit to a commercially available far-infrared camera (ULVIPS PICO 384 manufactured by Vision Sensing).

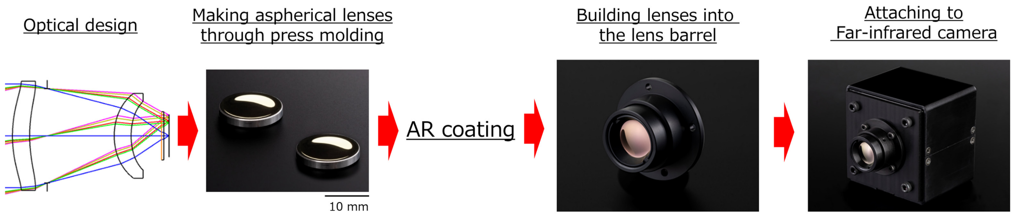

Fig. 2 Procedure of making lens units.

4 Results and Discussion

4.1 Evaluation of Glass Stability

The correlation between composition and ΔT is shown in Table 2. ΔT is the value obtained by subtracting the glass transition temperature from the crystallization temperature of the glass material. The larger the value is, the higher the glass stability will be. ΔT varied greatly with the ratio of Ge to Te, and glass was obtained without devitrification when $\mathrm{Te/Ge} = 4$ to 6. When the Te/Ge ratio was greater than this range, crystallization occurred, and telluride-dominated crystals were produced. When the ratio was smaller than this range, crystals consisting mainly of germanium telluride were produced. This suggests that Te and Ge constitute the main frame of the glass. The other elements at higher than 10 at. % made glass formation unstable and crystallization occurred but did not significantly affect the glass stability below 10 at. %. When crystallization occurs, infrared light is scattered and cannot be used as a material for infrared lenses.

4.2 Properties of FI-02

The most effective feature of FI-02 is its infrared transmission property. The measured internal transmittance spectra of the infrared transmitting materials are shown in Fig. 3. The transmittance of conventional chalcogenide glass shown in Fig. 3 is the measured value of the Ge-As-Se

Table 2 Correlation between composition and ΔT.

Te (at. %)	Ge (at. %)	Others (at. %)	Te/Ge	T_g (°C)	ΔT
82.5	10.0	7.5	8.3	Devitrified	
80.0	12.5	7.5	6.4	149	72
77.5	15.0	7.5	5.2	153	89
75.0	17.5	7.5	4.3	155	75
72.5	20.0	7.5	3.6	Devitrified	

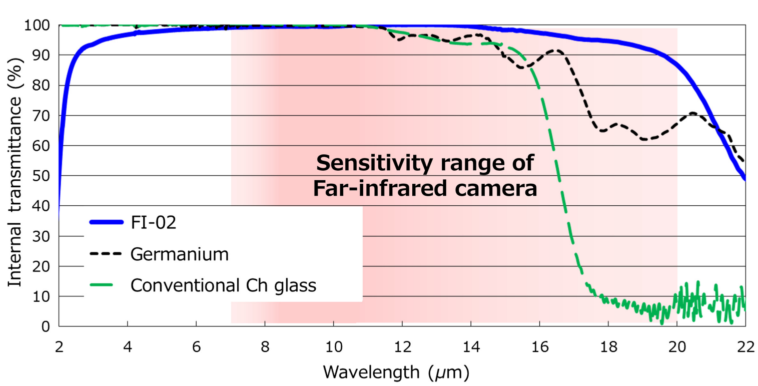

Fig. 3 Internal transmittance of infrared lens materials (sample thickness: 2 mm).

system, which is the most common typical composition on the market. It can be observed that FI-02 can transmit up to 20-μm wavelengths of infrared light and has a vast transmittance spectrum in the infrared region compared to the germanium single crystal and conventional chalcogenide glass. Therefore, it can be considered that FI-02 exhibits the best-infrared transmission performance of all infrared lens material. This excellent transmission property is expected to improve the brightness and clarity of infrared images.

The energy of infrared light that each material can transmit was estimated. Assuming a sample thickness of 2 mm and a subject temperature of 35°C, FI-02 is estimated to be capable of transmitting 107% of the energy of germanium and 123% of the energy of conventional chalcogenide glass at wavelengths from 7 to 20 μm. For long-range imaging, wavelengths between 8 and 14 μm are used, but at close range, wavelengths above 14 μm also affect imaging. From Planck's law, the energy of infrared radiation emitted from an object at temperature T is expressed by the following equation:

$$I'(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}, \tag{3}$$

where λ is the wavelength of light, h is Planck's constant (6.626×10^{-34} Js), c is the speed of light (3.0×10^8 ms^{-1}), and k is Boltzmann's constant (1.380×10^{-23} JK^{-1}).

The refractive index is a critical property of the lens material. As it is determined by the interaction between light and the electrons that make up the material,[4] it tends to be higher when the material contains more elements with high polarization rates. Tellurium, the primary component of FI-02, has a higher polarization rate than other chalcogen elements (S, Se).[5] Therefore, FI-02 has a very high refractive index of 3.47 (at a wavelength of 10 μm). This is much higher value than Ge-As-Se-Te system, which has the highest refractive index in commercially available chalcogenide glass (2.79 at 10 μm). High refractive index of FI-02 enables to create thin, high-performance infrared lenses. Figure 4 shows the refractive indices and estimated lens thickness when we design focal length (FL) = 10 mm spherical lens. The estimated lens thickness of FI-02 is 4.6 mm. This is thinner than the 6.3 mm thickness of conventional chalcogenide glass and very close to germanium.

Unlike crystalline materials, many glass materials can be press-formed using molds because their viscosity varies continuously with temperature.[6,7] We confirmed that aspherical lenses could be fabricated by press molding in FI-02. Aspherical shapes effectively reduce optical aberrations and may improve the performance of the lens unit and reduce the number of lenses that make it up. Figure 5 shows a case of optical design using FI-02 aspherical lenses. Assuming mass production of lenses for automotive applications, etc., it is not practical to manufacture germanium aspherical lenses by the point diamond-turned process. For this reason, in Fig. 5, we compare spherical Ge lenses and molded aspherical chalcogenide lenses, which can be mass-produced. Three lenses are required when the optical design uses only germanium spherical lenses.

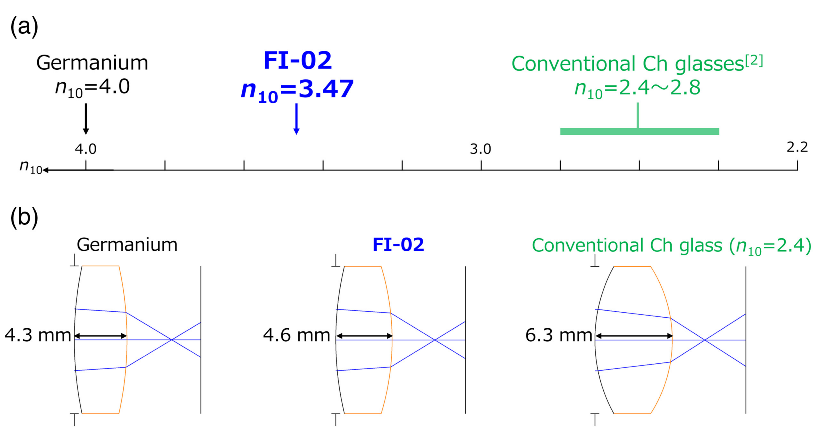

Fig. 4 (a) Comparison of refractive indices of materials at 10 μm. (b) Simulated lens thickness value (FL 10 mm spherical lens, optimization was done by Zemax).

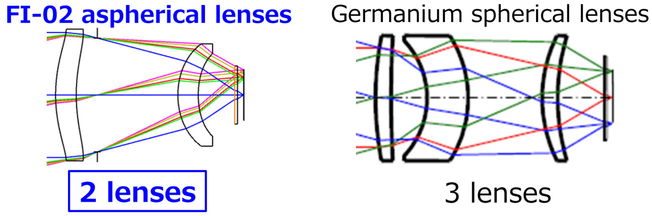

Fig. 5 Verification of the advantages of aspheric lenses (optical design with the same target; $f/1.0$, FL = 20 mm).

Table 3 Summary of material properties.

	FI-02	Germanium	Conventional Ch glasses
Maximum transmission wavelength	20.5	17.1	15.9
Refractive index at 10 μm	3.47	4.00	2.4 to 2.8
Dispersion ν_{10}	253	942	30 to 175
dn/dT ($\times 10^{-6}$, −40°C to 80°C)	294	396	20 to 103
Press molding	Possible	Impossible	Possible
Highly toxic substances (As, Se)	Free	Free	Contain

However, when FI-02 aspherical lenses are used, the design can be performed with only two lenses. Reducing the number of lenses helps reduce the weight and cost of the lens unit.

The properties of FI-02 compared with those of other materials are summarized in Table 3. “Maximum transmission wavelength” means the wavelength in which internal transmittance falls below 80% in Fig. 3. The optical dispersion ν_{10} was calculated according to the following equation:

$$\nu_{10} = \frac{n_{10} - 1}{n_8 - n_{12}}, \tag{4}$$

where n_λ is the refractive index at λ μm. The larger the value of ν_{10} is, the lower the dispersion in FIR region will be. FI-02 has a low dispersion, which is not found in conventional glass materials, and it is possible to design an optical system with low chromatic aberration using only FI-02. As dn/dT of FI-02 is smaller than germanium, it is possible to be athermalized. In addition to the unique optical properties previously mentioned, its capability to be press molded is distinctly advantageous. This enables aspherical lenses to be made with high productivity. In addition, unlike commercially available conventional chalcogenide glass, FI-02 does not contain highly toxic substances, such as arsenic or selenium. Hence, FI-02 is an innovative infrared transmitting material for infrared optics with excellent optical properties and productivity.

4.3 Development of Far-Infrared Lens Unit Made of FI-02

To investigate FI-02’s performance as an infrared lens material, we developed two types of infrared lens units: FL 10.5 and FL 2.04 mm. Both lens units were designed using only FI-02. FL 10.5 mm lens unit is made as the standard type presented in Fig. 6.

Using this lens unit, we compared the lens units made of other materials with equivalent F values and angles of view. Figure 7 shows the infrared images taken with each lens unit. The comparison images were taken with same camera settings of gain and integration time. Lens units made of FI-02 could capture infrared images that have better contrast than those obtained using germanium or conventional chalcogenide glass lenses. We evaluated the contrast of infrared images quantitatively. Here, contrast is defined as the difference between signal values when looking at the 50°C object and 20°C object with each lens unit. A black body was used as the object to avoid the influence of differences in the emissivity of the objects on the signal values.

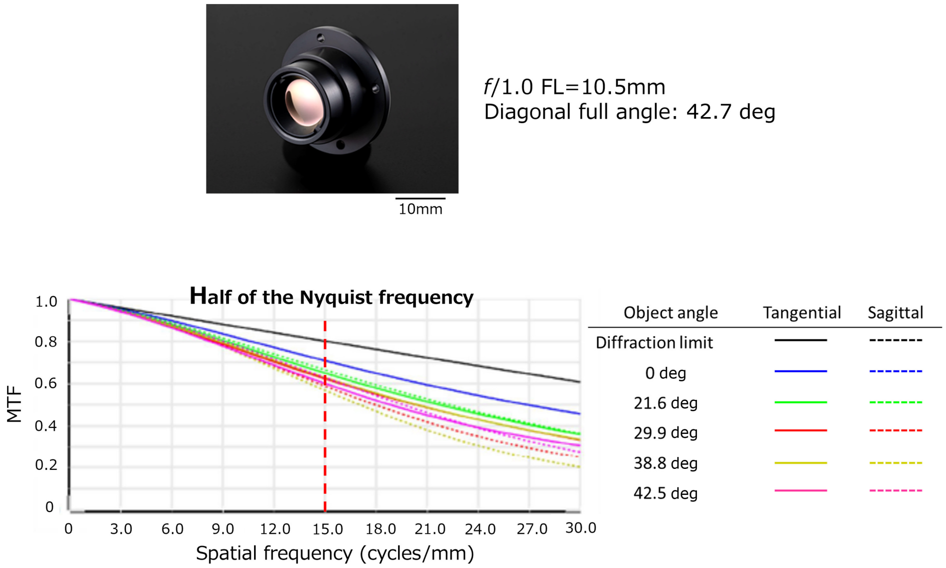

Fig. 6 Appearance of the standard-type lens unit and its MTF.

Fig. 7 Comparison of infrared images taken with lens units of different materials.

In this way, we confirmed that the contrast of the infrared image was improved by 8% and 22% for the germanium and conventional chalcogenide glass lenses, respectively. The greater the energy of the infrared light entering the sensor is, the greater the contrast of the infrared image will be. The use of FI-02, which has excellent transmission characteristics, is thought to have allowed more energy to be captured by the sensor, resulting in improved image contrast.

To take advantage of the unique features of FI-02, including its high refractive index and aspherical shape, we designed an FL 2.04 mm lens unit: super wide-angle type, as shown in

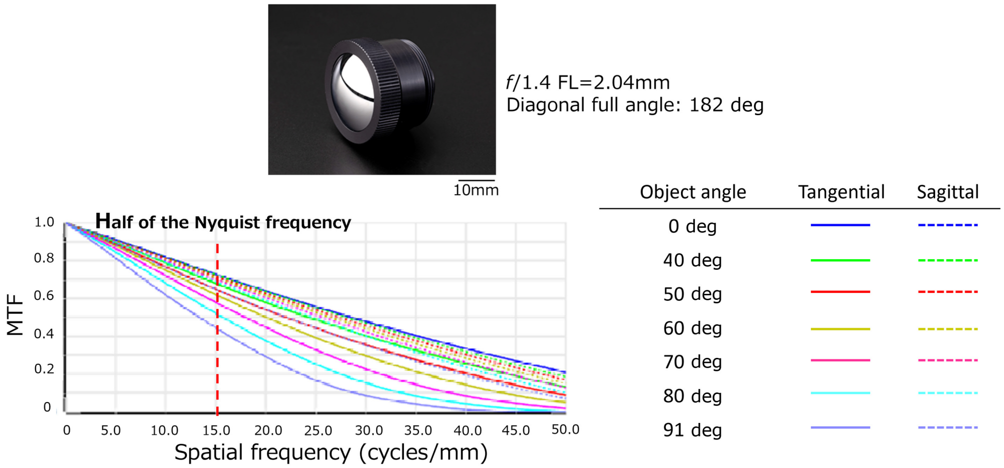

Fig. 8 Appearance of the super wide-angle-type lens unit and its MTF.

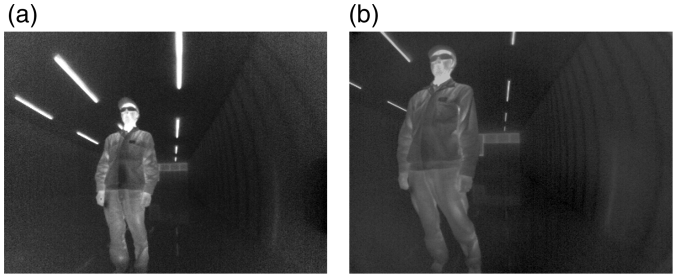

Fig. 9 (a) Infrared image taken by FI-02 super wide-angle type lens unit. (b) Infrared image taken by a typical wide-angle lens unit.

Fig. 8. Generally, wide-angle lenses have significant image distortion, but we have found an optical design that can solve this problem by adding an aspherical shape to FI-02, which has a high refractive index. Its diagonal field of view is 182 deg, which is an unprecedented wide field of view in far-infrared lenses. Although it has a wide field of view, it can capture far-infrared images with low distortion. Figures 9(a) and 9(b) compare the infrared image with a typical wide-angle lens unit, which is made of germanium with FL 2.6 mm. While a typical wide-angle lens unit produces distorted images in which the center of the image seems to be magnified, the FI-02 super-wide angle lens unit was confirmed to be able to capture images with low distortion while capturing a wider area.

5 Conclusion

We developed a new infrared transmitting glass material called FI-02 and a far-infrared lens unit made of FI-02. The main feature of FI-02 is its wide infrared transmittance range. In addition, compared to the commercially available conventional chalcogenide glass material, FI-02 has distinct features, including its high refractive index and absence of highly toxic substances. We confirmed that various unique lens units could be designed and fabricated with high productivity through press molding by taking advantage of these properties. We believe that FI-02 is a superior infrared optical material and can improve the performance and productivity of infrared optics.

Code, Data, and Materials Availability

The data that support the findings of this study are available from the corresponding author, Yoshimasa Matsushita, upon reasonable request.

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Yoshimasa Matsushita is a senior engineer at Nippon Electric Glass Co., Ltd. He received his BS and MS degrees in chemistry from Kyoto University in 2010 and 2012, respectively, and entered Nippon Electric Glass Co., Ltd. in 2012. He is currently engaged in the development of chalcogenide glass materials and infrared lenses in the Research and Development Division.

Biographies of the other authors are not available.