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# Effect of the addition of $MgF_2$ and NaF on the thermal, optical and magnetic properties of fluoride glasses for sensing applications

Yujie Wang, Shuangbao Wang*, Saifu Deng, Jianting Liu, Jiahui Zhang

*School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan, 430074, China*

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Optical glass was very important for the development of optical fiber sensor. In this paper, a new type fluoride glass of ZrF4-BaF2-AlF3-NaF-MgF2(ZBANM) was synthesized for sensing application which has low loss and high magneto-optical coefficient, and it was found that the glass system had at least 60% transmittance from 3.5 μm to 7 μm and smallest verdet constant of $4.628E^{-5}/(\text{rad A}^{-1})$ at 632.8 nm. The relationship among the compositions of sample glass with its thermal property, optical absorptivity and magnetic-optical coefficients was respectively studied with Thermal Gravimetric-Differential Thermal Analyzer, Fourier Transform infrared spectroscopy and a home-made magneto optical bench. The study indicated that transmittance of fluoride glass structure had been obviously improved after moderate content of Mg2+ and Na+ was doped. Simultaneously, with the molar ratio of alkaline-earth ions Mg increased, the Verdet constant of fluoride glass was increased. And the glass structure with composition of 48%ZrF4-24%BaF2-6%AlF3-8%NaF-14%MgF2 exhibited a small molar absorptivity and the largest Verdet constant of $2.853E^{-4}/(\text{rad A}^{-1})$.



## 1. Introduction

The optical fiber sensor was an emerging sensor technology, which was known for its wide application prospects in biology, chemistry and environment fields. Silicon glass was commonly used for the material of optical fiber, due to its ultraviolet–visible spectra, it could hardly perform good in infrared. On the other hand, facts proved that the silicon glass was gradually reached its theory loss limits (0.02 dB/km), so people were badly in need of finding one glass material which had low cost with good optical-magnetic properties in the infrared wave band. Fluoride glass was considered that it has a wider spectral range [1] (about 0.2–7 μm) and lower theory loss limits [1,2] (0.001 dB/km). It was the ideal material for the application of optical fiber sensor in the infrared band. Based on the Faraday rotation effect, the optical glasses could be made for current sensor. Literatures on oxide glasses for current sensor applications have been reported [9,11], and we learned that the presence of heavy metal ions in glass structure and a long wave shift for the working wavelength will both lead to the increase of optical-magnetic coefficient. Compared with traditional oxide glasses, high transmissivity of heavy metal fluoride glasses in the middle infrared waveband makes it potential in sensing field.

As a diamagnetic and optical window material, Fluoride glass have a great performance in electrical, optical and magnetic field. The glasses based on ZrF4-BaF2-LaF3-NaF–AlF3 (ZBLNA) or ZrF4-BaF2-LaF3-NaF (ZBLN) have been reported a lot [1–3]. Considering the high cost of rare earths (La) and the simplification of glass itself, the alkali and alkaline-earths were chosen to replace rare earths. Meanwhile, the magneto-optical coefficients of fluoride glasses in the middle infrared band was essential for the sensitivity and accuracy of current sensor, so it was significant to analysis the effects of doping cations on the magneto-optical property of fluoride glasses. Based on the researches carried out by author, a $ZrF_4$-$BaF_2$-AlF3-NaF-$MgF_2$ (ZBANM) based glass system was chosen for this study with the aim of obtaining a candidate with low loss and good magneto-optical properties for optical fiber sensor. The test on thermal, optical and magneto-optical properties of the sample glass was carried out via Thermal Gravimetric-Differential Thermal Analyzer (TG-DSC), Fourier transform infrared microscope instrument (FT-IR) and a home-made magneto-optical modulation platform respectively.

* Corresponding author.
*E-mail address:* shuangbaowang@126.com (S. Wang).

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## 2. Experiment

### 2.1. Sample preparation and tests

High-purity fluoride raw materials and auxiliary reagents $NH_4HF_2$ in accordance with Table 1 was used to make for several groups of sample. After stirred for 1 h, the mixture was poured into a Corundum Crucible with a crucible lid, and then taken into the muffle furnace for melting.

In order to study on the thermal stability of fluoride glass, the mixed fluoride materials were given a Thermal Gravimetric and Derivative Thermogravimetry test respectively, and the result was shown in the Fig. 1(a) and (b). According to heat loss curve of fluoride weight in Fig. 1(a), we learned that there are two mainly weight loss stages in the melting process of fluoride glasses, which took place respectively in the melting temperature range of 200–400 °C and 850–950 °C. When temperature increased from 200 °C to 400 °C, ZBANM lost 11.2 wt% of the weight. It was attributed to auxiliary reagents $NH_4HF_2$ thermal decomposition. When temperature increased from 850 °C to 950 °C, ZBANM lost 13.38 wt% of the weight. It was attributed to the thermal evaporation of fluoride material. According to Derivative Thermogravimetry curve in Fig. 1(b), the temperature in the first stage was set at 350 °C in practice, and this step is called fluoride stage [3]. Similarly, the melt temperature in the second stage was set at 900 °C and kept for 30min, this stage is called melting [4,5].

Then we removed the Crucible from the furnace and poured the glass liquid quickly into self-made metal mold, and finally glass liquid was sent into the furnace again for a later annealing. The annealing temperature was set at 150 °C and performed for 30min.

Glass samples which have regular shape and good transparency was prepared and selected for several groups, then cut, grinding and polishing each of them. The absorption coefficients and verdet constants of selected glasses was achieved by the measurements with a Fourier Transform infrared spectroscopy and a home-made system in magneto-optical Faraday principle.

**Table 1**
Optical properties of the ZBANM glass samples.

| Sample number | Sample composition/mol% | Density/ (g cm$^{-3}$) | Verdet constant/ (rad A$^{-1}$) |
|---|---|---|---|
| ZBLNM00 | $58ZrF_4$-$28BaF_2$-6AlF3-8NaF-$0MgF_2$ | 4.690 | 1.132E-5 |
| ZBLNM01 | $56ZrF_4$-$26BaF_2$-6AlF3-8NaF-$4MgF_2$ | 3.956 | 1.057E-4 |
| ZBLNM02 | $48ZrF_4$-$24BaF_2$-6AlF3-8NaF-$14MgF_2$ | 5.596 | 2.853E-4 |
| ZBLNM03 | $48ZrF_4$-$24BaF_2$-6AlF3-18NaF-$4MgF_2$ | 4.607 | 4.628E-5 |

Experiment conditions: incident wavelength (632.8 nm), magnetic field (100 mT).

### 2.2. Magneto-optical properties test

#### 2.2.1. Setup optical platform

As the light path shown in Fig. 2, a magneto-optical modulation system [6] was self-made, which used the He-Ne laser with the central wavelength $\lambda = 632.8\ nm$. Laser beam (with an Original intensity I0 collimated by lens) traveled successively over polarizer P1, sample glass magnetically modulated by DC coil and polarizer P2, and finally the emergent light intensity Iout was detected by a power meter. According to Malus law [6] we can conclude that:

$$\mathrm{Iout} = \mathrm{I_0}{*}\cos^2(\theta + \alpha + \theta_0) \overset{\alpha+\theta_0=\frac{\pi}{2}}{\approx} \mathrm{I_0}{*}\theta^2 \quad (1)$$

In formula (1), $\theta_0$ is the angle between P1 and P2 transmission axis, $\alpha$ is the polarization rotation angle caused by glass linear birefringence. θ refers to the faraday rotation angle of samples glass in the presence of external magnetic field, it generally givens by the consists of faraday rotation effect [6] and Biot-Savart law [7]:

$$\theta = \mathrm{VBL} \quad (2)$$

$$\mathrm{B} = \frac{\mathrm{u_0NI}}{2\mathrm{R}} \quad (3)$$

In the upper formula (2) and (3), V is the unknown Verdet constant of fluoride glass, B is the magnetic induction produced by the DC coil, N is the number of turns of the coil, and R is the radius of the coils, the $u_0$ is the permeability of vacuum.

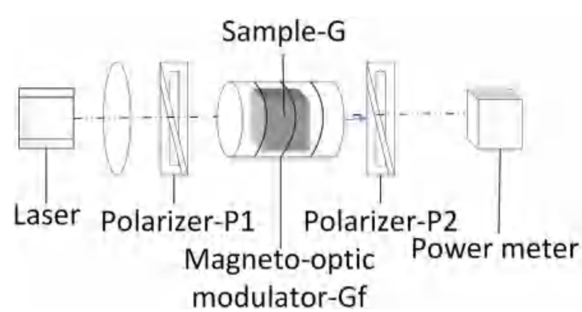


**Fig. 2.** The system of magneto-optical modulation.

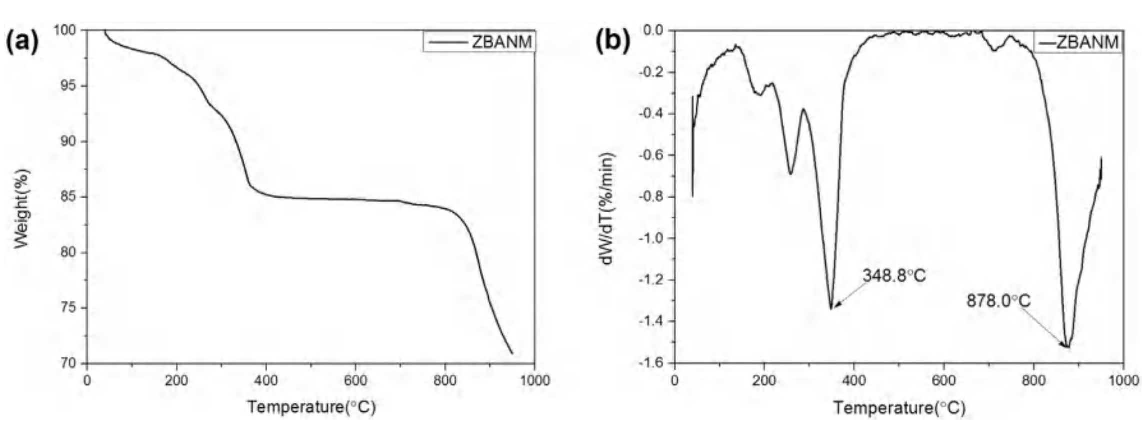


**Fig. 1.** (a). TGA curve of ZBANM samples. Fig. 1(b). DTG curve of ZBANM samples.

*2.2.2. Calculate Verdet constant*

In order to simplify the experiment, we used standard Tesla meter (HT20) to measure the magnetic induction B in the presence of external current I at the sample position in the coil. In addition, using standard silicon glass (Verdet constant is known to 0.01352 min $G^{-1}$ $cm^{-1}$ [8,9]) to check the magnetic-optical modulation system is needed. Commonly, the value of polarization rotation caused by own linear birefringence was bigger than the angle of Faraday rotation in one glass structure, so we had to try to eliminate the phase delay caused by own linear birefringence in the glass. Concrete means were performed as follows:

At first, it was essential to eliminate the impact of background light. HT20 probes and silica samples were both set at the central position of modulated coil in the optical path of Fig. 2. Polarizer P2 was rotated in a darkroom, afterwards, the maximum intensity I1 was measured by the power-meter. Extinction process for light path was made before add the external magnetic field, then the minimum intensity I2 was obtained when $\theta_0 + \alpha = \frac{\pi}{2}$. A static magnetic field was produced by a constant current-constant voltage source (HT-1721) which supplied a steady current I from 0A to 5A on the modulated coil. Due to the Faraday effect, the light path was no longer extinct in the presence of steady magnetic field, thus a new transmission light of I3 was obtained, accordingly, $I_{out} = I3 - I2$. The measurement was timely performed and finally the Verdet constant of sample glass was calculated by formula (1) and (2).

Following the above steps, the Verdet constant of silica was obtained. It was found that the experiment value was closed to the theoretical value of 0.01352 min $G^{-1}$ $cm^{-1}$, which proved that the magnetic-optical modulation system make sense. Under the same condition, the Verdet constant of the fluoride glasses was measured.

## 3. Results and analysis

### *3.1. FT-IR spectra*

Fig. 3. (a) shows the FT-IR spectra analysis on the prepared samples. There were three mainly absorption peaks shown in the FT-IR spectra. And ZBLNM03 showed more than 80% of transmittance during 3500 nm to 5500 nm. The peak around 3484cm-1 was due to the OH absorption. The peak around 2913 $cm^{-1}$ was correspond to the non-bridging modes of Zr-F. The peak around 1654 $cm^{-1}$ was attributed to the stretch motion of Mg-F. And it could be found that the peak around 1654 $cm^{-1}$ was gradually enhanced with the increase of $Mg^{2+}$ content.

Based on principle of FT-IR absorption spectra and Langevin-law [7], a relationship between the absorbance A of sample and its optical transmission T can be inferred:

$$A = -\log T = -\log(\mathrm{Is}/\mathrm{I}) = \mathrm{K} \cdot l \cdot \rho \quad (4)$$

From formula (4) it can be seen that the transmittance of sample is related to the thickness L of the sample. In fact, we need a parameter who regardless of the sample size and thickness but only associated with the glass structure to evaluate the quality of fluoride glass. In formula (4), K names molar absorptivity, which refers to the optical absorption coefficient of sample, it is only related to the sample material when the test wavelength $\lambda$ is determined, so we chose the molar absorptivity K as the parameter to evaluate sample's quality. Accordingly, groups of K-λ curves of sample glass were obtained by formula (4), as is shown in the Fig. 3(b).

It can be seen from Fig. 3(a) and (b) that all the five-fluoride glass structures have good transmittance from 2 μm to 7.5 μm wave band, and sample of ZBLNM03 series exhibited more than

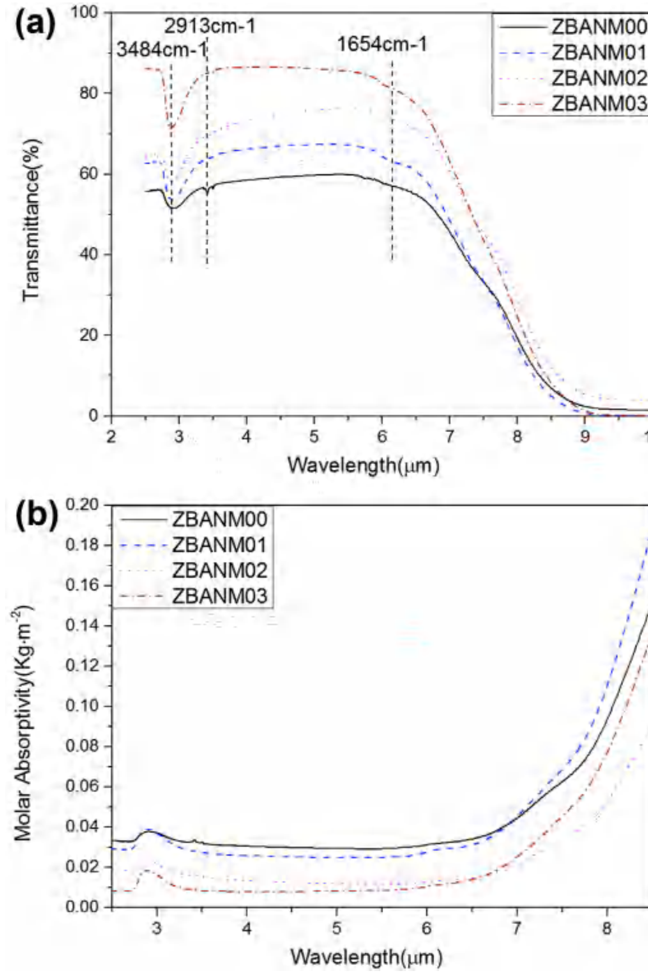


**Fig. 3.** Transmission Spectra (a) and K dependent λ curves (b) of ZBANM samples.

85% transmittance and the lowest molar absorptivity in middle infrared. Compared with ZBLNM00, 01 and 02 samples, it can be found that the optical transmittance of fluoride glasses in the infrared wave band gradually increased with the increase of Mg ion content. It was mainly attributed to the combination of $Mg^{2+}$ with the “non-bridge-anion” $F^-$, which formed a polyhedron $[MgF_x]$. Thus, the non-symmetric stretch motion of Zr-F around 2913 $cm^{-1}$ exhibited a weaker peak. As one kind of glass-forming intermediate, the $MgF_x$ polyhedron can hinder the recombination of $Zr^{4+}$, $Ba^{2+}$, $F^-$, et al. plasm to form crystal in the glass structure, namely, restrained the crystallization phenomenon of glass, which is similar to the point of A. Lu et al. in the paper of formed the network impact on the heavy metal oxide glasses [8,9]. It also can be found by the comparison of ZBLNM02 and ZBLNM03 samples that the increase of doping content of $Na^+$ can also improve the optical transmittance of fluoride glass in infrared band. As a outside network body in fluoride glass system, NaF has weak Ionic, and $Na^+$ can combined easily with F which came from the original adjacent bond of fluoride glass, namely, the presence of NaF would provide a bigger amount of “free $F^-$” in the glass system. Based on the presence of NaF, other cations like $Mg^{2+}$, $Al^{3+}$ could get into the network structure of fluoride glass, which would improve the optical and chemical stability of fluoride glass. It indicated that the presence of alkali metal ion could strengthen the reconstruction ability of glass structure, and $Na^+$ mainly played the role of broking network in glass system.

In addition, it was observed that the five fluoride glasses structure have a distinct absorption peak near 2.75 μm, which attributes to the characteristic peak of $OH^-$ group [10–12]. It mainly consists of the moisture introduced by the environment and materials during glass melting-casting process. For the low transmission spectrum after 8 μm, it can be interpreted that in the long-wavelength band, due to the smaller energy of light wave has little contribution to the electronic transitions within the structure of glass, molecular vibration and lattice heat-absorption takes the leading role in this stage, consequently, the fluoride glass structure exhibits low transmission after 8 μm wave band.

### 3.2. Raman spectra

The Raman spectra of ZBANM00 and ZBANM03 samples was obtained with a infrared Raman spectrometer at 1024 nm shown in Fig. 4. In order to study the change of structures for samples, we also have tests on the ZrF4 and BaF2 crystal.

From the spectra, the peak near 576 $cm^{-1}$ was sharp and strong, which was attributed to the high local symmetric stretch motion of F-Zr-F, independent with the change of bond angle. The sharp peaks lied in the range of 400 $cm^{-1}$ to 512 $cm^{-1}$ were attributed to the “bridge-anion” motion duo to symmetric stretch motion of Zr-F-Zr [21]. Similarly, the peak near 302 $cm^{-1}$ was correspond to the “bridge-anion” motion due to symmetric stretch motion of Ba-F-Ba. Based on the peaks of BaF2 crystal, the Raman peak of Al-F and Mg-F should appear in the region of low frequency (near 200 $cm^{-1}$) duo to their mass were smaller than $Ba^{2+}$’ s [21], thus the peaks near 186 $cm^{-1}$ was attributed to the stretch motion of Al-F and Mg-F.

Compare to the ZBANM03 sample, the spectra of ZBLNM00 glass mainly exhibits an increase in intensity at 576 $cm^{-1}$, indicating a weaker symmetric stretch motion of F-Zr-F in ZBANM03. It was mainly attributed to the combination of $Mg^{2+}$ with the “non-bridge-anion” F which come from the bond of F-Zr-F. On the other hand, the spectra of ZBANM00 and ZBANM03 was almost coincide expect a slight difference at intensity, which reflected that the composition of two samples are basically same but only the ZBANM00 sample shows a higher backgrounding scattering. It is possibly coming from the denser scattering cross-section of the later.

### 3.3. Magneto-optic measurement on fluoride glass

The experimental data of Verdet constants of ZBANM samples were shown in Table 1.

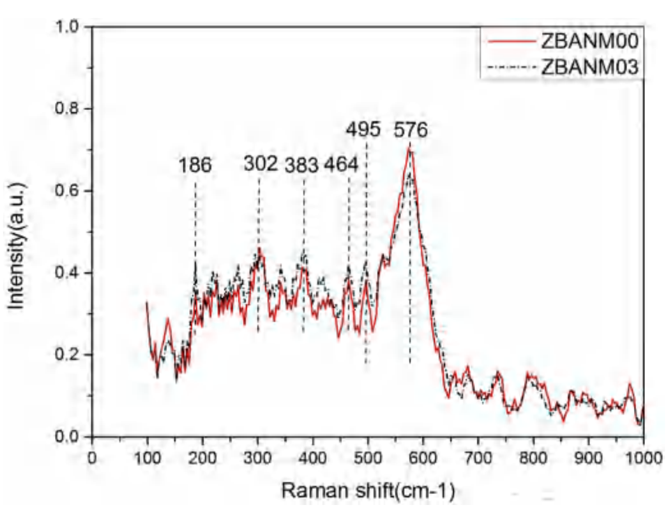


**Fig. 4.** Raman spectra of ZBANM samples.

The Verdet constant of silicon glasses is about 1.132$E^{-5}$/(rad A-1), which was obtained by the magneto-optical measured system diagrammatically shown in Fig. 2 in the presence of laser wavelength $\lambda = 632.8$nm, static magnetic field B = 100 mT. And the data's volume was same with the value of C.Z.Tan proposed in the paper of Faraday Effect in silica glasses [9,10], which proved that the magneto-optical measured system was feasible. Based on the system, the tests on the polished samples was performed from ZBANM00 to ZBANM03, and the related Verdet coefficient was obtained as shown in Table 1. From Table 1, it can be seen that ZBANM02 sample exhibited the best magneto-optical properties, namely, had the highest Verdet coefficient of 2.853$E^{-4}$/(rad A-1), and similar values was proposed by G. Zhang et al.'s paper [13]. From the comparison of ZBANM00, 01 and 02 samples, it can be seen that the Verdet coefficient of fluoride glass rose with the increase of doping content of Mg ion. What's more, it found that a bigger molar proportion of heavy metal ions like $Zr^{4+}$, $Ba^{2+}$ in glass structure could also help increasing its Verdet coefficient [9].

For most materials, basing on the well known Becquerel formula for the dispersion of the Verdet constant [14–19], the Verdet coefficient and material structure satisfies the following relationship [10]:

$$V(\lambda) = u_0 \cdot r \cdot \frac{e}{2mc} \cdot \lambda \cdot \frac{dn}{d\lambda} \tag{5}$$

Here, $u_0$ is the permeability of vacuum, e is the electron charge, m is the electron mass, and n is the refractive index of the material, dn/dλ is the dispersion of the material. Normally, r is the magneto-optical anomaly factor, which is a function of the wavelength, increasing slightly from the red to the violet. For the material consisted mainly of covalent type bond, r is close to 0.28, and for the material mainly consisted of ionic type bond, r is close to 1 [13,14,16]. From our Faraday rotation data, as a function of the wavelength and the index of refraction dispersion given in the literature [20], it is possible to calculate, through use of formula (5), the value of r for each sample. The term dn/dλ at the given wavelength can be evaluated with a known V and the term e/2mc. For fluoride glass, the constant (e/2mc) = 293.8 rad$\cdot T^{-1} \cdot m^{-1}$ [16], the evaluated dn/dλ at 632.8 nm for ZBLNM02 is 0.00122 $nm^{-1}$.

In the frame of the dispersion theory, the frequency-dependence of the refractive index, n, can be described by Sellmeir's dispersion formula [10],

$$n^2 = 1 + \frac{Ne^2}{m\varepsilon_0} \sum_k \frac{f_k}{w_k^2 - w^2} \tag{6}$$

where N is the number of the dispersion electrons per unit volume, $\varepsilon_0$ is the permittivity of space, and $f_k$ is known as the oscillator strength at the resonance frequency $w_k$. As we said in 3.1, the Mg ion was easy to form Mg-Fnb in the fluoride glass structure. In fact, the radius of $Mg^{2+}$ was smaller than $Zr^{4+}$ and $Ba^{2+}$, which means the number of the dispersion electrons per unit volume in fluoride glass would be increased, and it would be lead to a slight increase of optical dispersion of fluoride glass. Therefore, the Verdet coefficient of fluoride glass rose with the increment of doping content of Mg ion from ZBANM00 to ZBANM02 in Table 1.

## 4. Conclusion

In this paper, a new fluoride glass system of $ZrF_4$-$BaF_2$-AlF3-NaF-$MgF_2$ was studied, and the structure of ZBANM02 exhibited more than 70% transmittance from 3500 nm to 7000 nm band and the largest verdet constant of 2.853$E^{-4}$/(rad $A^{-1}$). In addition, the relationship among the composition of fluoride glasses with their thermal, optical and magnetic properties was studied. It could be concluded that the alkali metal ion could strengthen the reconstruction ability of glass structure, and Na ion mainly played the role of broking frame network in the glass system. Based on the presence of $Na^{+}$, $Mg^{2+}$ and $Al^{3+}$ could get into the network structure to forming polyhedrons, which restrained the crystallization phenomenon and increased the optical dispersion of fluoride glasses.

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