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# High-refractive index, low-loss oxyfluorosilicate glasses for sub-THz and millimeter wave applications

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## ABSTRACT

Terahertz (THz) time-domain spectroscopy was used to study the optical properties of two series of oxyfluorosilicate (OFS) glasses. The experimentally measured refractive indices are analyzed by using the Clausius–Mossotti equation to retrieve information about polarizability of the glass. Compared with previously studied oxide-based glasses and chalcogenides, OFS glasses exhibit a balance of relatively low absorption coefficients ( $6\text{--}9\text{ cm}^{-1}$ ) and high refractive indices (2.9–3.7) at 0.5 THz. The value of 3.7 is the highest among silicate glasses reported to date and are comparable to those of  $\text{La}^{3+}$ :chalcogenide glasses. The relatively high values of refractive indices have been attributed to the great increase of the glass polarizability in OFS glasses, which offsets the effect of an increase in molecular volume caused by multicomponent modification of the glass structure. Comparatively low THz absorption of OFS glasses is explained by the structural relaxation effect of fluorine, which effectively suppress the charge fluctuation in the glass structure. The high refractive index and low absorption loss properties of the present OFS glasses should be useful for quasi-optic components such as lens and waveguide devices application in the sub-THz and millimeter wave region.

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## I. INTRODUCTION

Terahertz (THz) time-domain spectroscopy (THz-TDS) has been employed to study a wide variety of materials such as dielectrics,<sup>1</sup> semiconductors,<sup>2,3</sup> liquid crystals,<sup>2,4</sup> oils,<sup>5</sup> chemical mixtures,<sup>6</sup> gases,<sup>7</sup> and biological molecules.<sup>8</sup> The prominent phonon resonances of glass materials often fall in the THz frequency band. To date, however, THz properties of glasses were studied only on limited numbers of oxide-based silicate and chalcogenide glasses.<sup>9–13</sup> In some glasses, relatively high transparency in the THz frequency range has been reported.<sup>11–13</sup> Such glasses are potentially useful for quasi-optic and photonic applications in the millimeter wave and THz frequency band.

The flexibility of the glass toward forming microcrystalline or nanocrystalline structures by heat treatment allows this class of materials to exhibit superior mechanical, chemical, and optical properties.

Consequently, a variety of multicomponent silicate glasses<sup>14</sup> and some chalcogenide glasses<sup>15</sup> with high chemical/mechanical stability and desirable optical properties, such as high refractive index, high transparency, and high optical nonlinearity in visible and mid-infrared wavelength regions, have been developed. Toward THz applications, further development in glass materials with high refractive index and low loss is desired. One possibility is oxyfluoride (OF) glasses,<sup>16,17</sup> in which nonradiative transitions are suppressed with corresponding high-efficiency luminescence and transparency. They are not yet practical due to their poor chemical and mechanical durability. Recently, oxyfluorosilicate (OFS) glasses containing metal fluorides received much attention as they can exhibit combined properties of oxides and fluorides such as low melting temperature, high chemical/mechanical resistance, low phonon energy, and attractive

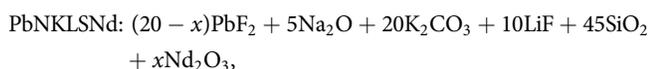
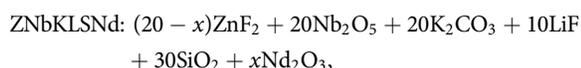
optical characteristics including high refractive index.<sup>16–18</sup> The multi-component design of these glasses allows tailoring their properties for specific applications. The THz refractive indices and dielectric properties of materials are determined primarily by their polarizabilities in the THz frequency range. The incorporation of metals with large atomic weights in OFS glasses can result in a higher polarizability to increase the refractive index in the THz frequency range.<sup>13</sup> Thus, OFS glasses incorporating appropriate metal oxides/fluorides are expected to provide essential glass materials for THz applications. The optical and dielectric properties of such OFS glasses in the THz region, however, have not been systematically investigated so far.

In this study, we extend the previous work on silicate glasses<sup>9</sup> by introducing fluorides (ZnF<sub>2</sub>, PbF<sub>2</sub>, and LiF) and rare-earth ions (Nd<sup>3+</sup>) in the silicate glass host, along with the presence of alkali ions (K<sup>+</sup> and Na<sup>+</sup>) and/or heavy metal based intermediate-network-former (Nb<sub>2</sub>O<sub>5</sub>), to further explore their potential applications in THz technology. We select two series of multi-component glasses: ZNbKLSNd and PbNKLSNd OFS glasses doped with different compositions of fluoride and rare-earth oxide. We compare THz optical properties of these series of OFS glasses with those of different multicomponent glasses such as silicates, chalcogenides, and La<sup>3+</sup>:chalcogenides. To understand the absorption loss, the effect of glass disorder structure is discussed by comparing with data of different glass groups in the literature. The experimentally measured data of THz refractive indices are also analyzed using the Clausius–Mossotti equation, which relates the dielectric constants to the polarizability. This work confirms that OFS glasses with high refractive indices and low absorption losses are potential candidates for quasi-optical components in the sub-THz or millimeter frequency range.

## II EXPERIMENTAL METHODS

### A. Sample preparation

The OFS glasses were prepared by the melt-quenching technique<sup>16–18</sup> with the following two series of chemical compositions:



where  $x = 1, 5,$  and  $10$  mol. %. The compositions were designed by taking into account our previous studies on OFS glasses including ZnF<sub>2</sub><sup>16</sup> and PbF<sub>2</sub>.<sup>18</sup> The  $x$  value was varied to see the relative contribution of the modifier (Nd) and fluorine contents. About 15 g of batch composition for each glass was thoroughly crushed in an agate mortar, and this homogeneous mixture was taken into a platinum crucible and heated in an electric furnace at 1250 °C for 3 h in an ambient condition. The melt was poured onto a preheated brass mold and annealed at 400 °C for 10 h to remove thermal strains. The glasses were slowly cooled down to room temperature and polished and formed into disks with a thickness of ~1.6 mm for the THz measurement.

### B. THz characterization and analyzing techniques

The THz optical constants of OFS glasses were determined by using a photoconductive-antenna-based THz-TDS system.<sup>2,4,19</sup> A Ti-sapphire laser (Spectra-Physics Tsunami,  $\lambda = 800$  nm) with a duration of 60 fs and an average optical power of 380 mW was used for THz generation and detection. The OFS glass sample was attached to a sample holder that had a clear aperture of ~8 mm in diameter and it was placed into the transmission type THz-TDS system.

The THz electric fields were recorded in the time domain with and without the glass sample, which was placed in the collimated THz beam path of the THz-TDS system. By Fourier-transforming the measured time-domain electric field data, we retrieved the complex amplitude and phase of the transmitted THz waves in the frequency domain. The THz absorption coefficient  $\alpha(\nu)$  and refractive index  $n(\nu)$  of the sample glasses at the frequency  $\nu$  can then be calculated by using the following equations:<sup>9</sup>

$$\alpha(\nu) = \frac{2}{d} \ln \left( \left| \frac{E_{\text{ref}}(\nu)}{E_{\text{sam}}(\nu)} \right| \frac{[n(\nu) + 1]^2}{4n(\nu)} \right), \quad (1)$$

$$n(\nu) = 1 + \frac{c}{2\pi\nu d} (\phi_{\text{sam}}(\nu) - \phi_{\text{ref}}(\nu)), \quad (2)$$

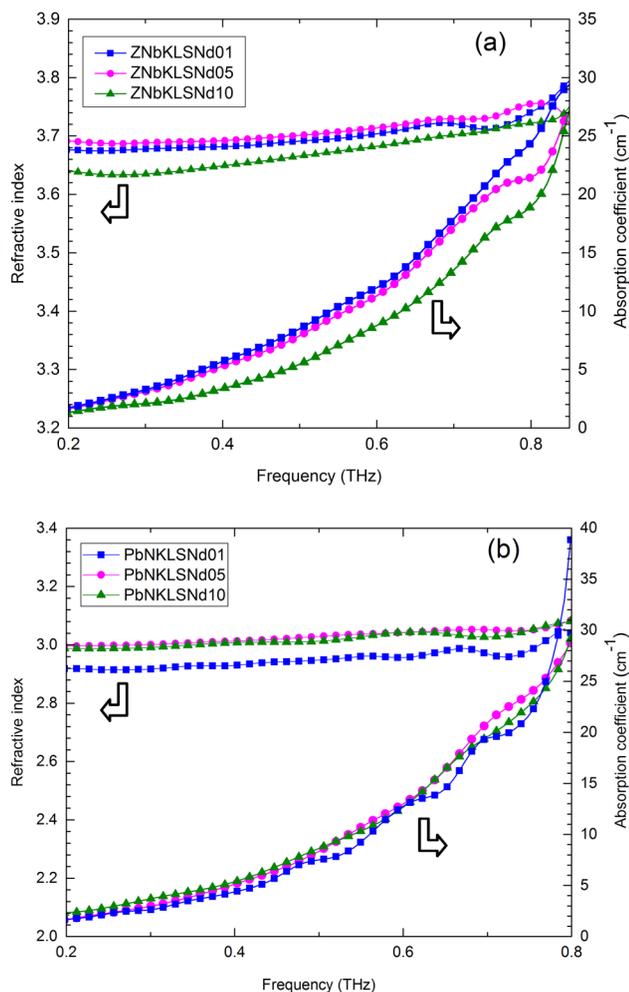
where  $E(\nu)$  and phase  $\phi(\nu)$  are amplitude and phase of the THz field transmitted through the sample (suffix: sam) and a reference (air in our case, suffix: ref);  $c$  is the speed of light, and  $d$  is the glass thickness. The second term inside the natural logarithm of Eq. (1) is a Fresnel reflection correction factor, in which the extinction coefficient is ignored because of its negligible contribution in our glass samples.

## III. RESULTS AND DISCUSSION

### A. Frequency dependence of absorption and refractive index

Figure 1 shows the absorption coefficients,  $\alpha(\nu)$ , and the refractive indices,  $n(\nu)$ , of the OFS glasses as a function of frequency in the frequency range from 0.2 to 0.8 THz. The optical constants at 0.5 THz, together with those for selected glass materials taken from Refs. 9–13, are compared in Table I. As shown in Fig. 1, the refractive index increases gradually and the absorption coefficient increases rather steeply with the frequency for both glasses. General behavior of frequency dependence as observed here is consistent with those of previously reported oxide-based silicate and chalcogenide glasses in the sub-THz frequency band.<sup>9–13</sup> The refractive indices measured in the present glasses are comparatively high. In particular, ZNbKLSNd glasses exhibit refractive indices as high as 3.70, being the highest among silicate glasses reported to date and are close to those of La<sup>3+</sup>:chalcogenide glasses. In addition, we note that the observed absorption coefficients of OFS glasses are appreciably lower than those for other high-refractive index glasses (see Table I).

The physical mechanism of THz radiation absorption in glasses has been attributed to the coupling of THz radiation into atomic vibration modes, which are associated with disorder-induced charge fluctuations in the glass structure.<sup>9,13</sup> The product of  $n(\nu)$  and  $\alpha(\nu)$  in silicate and chalcogenide glasses has been



**FIG. 1.** Terahertz refractive indices ( $n$ ) and absorption coefficients ( $\alpha$ ) of (a) ZNbKLSNd and (b) PbNKLSNd glasses with different compositions.

shown to exhibit the following power-law relationship:<sup>10,11,13</sup>

$$n(\nu)\alpha(\nu) = K(h\nu)^\beta, \quad (3)$$

where  $h$  is Planck's constant and  $K$  and  $\beta$  are material-dependent parameters of the glass. We also analyzed the present OFS glasses using this relationship. The product  $n\alpha$  of our glass samples is plotted as a function of frequency from 0.2 to 0.8 THz on a log-log scale in Fig. 2. The  $n\alpha$  values are in good agreement with the dashed lines, drawn with a slope of 2, for guiding the eye. The absorption parameter  $K$  for the present OFS glasses has therefore been defined for  $\beta = 2$ . This is consistent with the data reported for a number of glasses, including silicate and chalcogenide glasses,<sup>21,22</sup> which supports the disorder-induced charge fluctuation model for interpreting the sub-THz absorption characteristics in a wide variety of glasses. Results of  $Kh^2$  values determined at 0.5 THz are

summarized together with the values for selected glasses<sup>9–13</sup> in Table I. The value of  $Kh^2$  is associated with the magnitude of incoherent (not maintaining the local charge neutrality) atomic-charge fluctuation induced by structural disorders on intermediate and long-range scales.<sup>10</sup>

## B. Comparison of absorption and refractive indices for different glasses

The correlation between the THz absorption parameters,  $K$  and refractive indices at 0.5 THz is shown in Fig. 3 for the present OFS glasses and selected other glasses. Considering that the refractive indices of our samples do not change much in the frequency range we measured, the value of  $K$  is nearly proportional to the absorption coefficient according to Eq. (3). The larger values of  $K$  imply higher absorption loss and hence suggesting a more disordered structure in the glass samples investigated.

When alkali oxides, e.g.,  $\text{Na}_2\text{O}$ , are incorporated into the silicate oxide glass structure, covalent Si-O-Si rings are broken due to a larger difference in electronegativity between Na (0.93) and Si (1.90). This will introduce local disorder in the glass structure and produce nonbridging oxygens. As a result, the absorption parameter as well as the refractive index of the glass increases.<sup>10</sup> Naftaly *et al.*,<sup>9</sup> for example, showed that  $K$  is proportional to the fourth power of the refractive index in a series of commercial silicate-based multicomponent glasses, data of which are also included in Fig. 3. Ravagli *et al.*<sup>13</sup> found the increase in  $K$  (as well as in  $n$ ) in high-refractive-index chalcogenide glasses with high coordination number cations such as  $\text{La}^{3+}$ . Such a trend of increasing absorption with THz refractive index is observed in a variety of high-refractive-index glasses. This phenomenon is interpreted by the charge fluctuations, which are induced by the structural disorder when the glass structure is modified. Such an atomic-charge fluctuation may be enhanced particularly in multicomponent glasses including the present OFS glasses. However, as shown clearly in Table I and Fig. 3, the present OFS glasses exhibit high refractive indices yet maintaining very low absorption regardless of that their glass compositions involve alkali ions (Na, K) and intermediate oxides containing metals with large atomic weights (Nd, Nb), which would have contributed to an increase of the absorption parameter.

In order to understand this behavior in the present OFS glasses, we note that our glass samples differ from other silicate glasses in the incorporation of fluorides such as  $\text{ZnF}_2$ ,  $\text{LiF}$ , and  $\text{PbF}_2$ . In various oxide-based glasses, fluorine is known to restrict the formation of glass network due to its extremely high electronegativity (Pauling: 3.98).<sup>23</sup> The atomic polarizability ( $1.04 \text{ \AA}^3$ ) of fluorine is much lower than that of oxygen ( $3.88 \text{ \AA}^3$ ).<sup>24</sup> This is expected to reduce the refractive indices of OFS glasses. On the other hand, when the glass exhibits structural disorders and strains in its network, the introduction of fluorine is expected to relax disorder and strain. It was observed by Hosono that the introduction of a small amount (>1 mol. %) of F doping into silica glass resulted in enhanced hardening against the ultraviolet radiation.<sup>25</sup> According to their study, the strong F-Si bonding induces reconstruction of strained three-/four-membered Si-O-Si rings and makes the network more open. This eventually relaxes physical disorder in the glass structure. It is also known

**TABLE I.** THz refractive index and absorption coefficient at 0.5 THz along with the absorption parameter ( $Kh^2$ ) determined for the present and previously reported glasses.

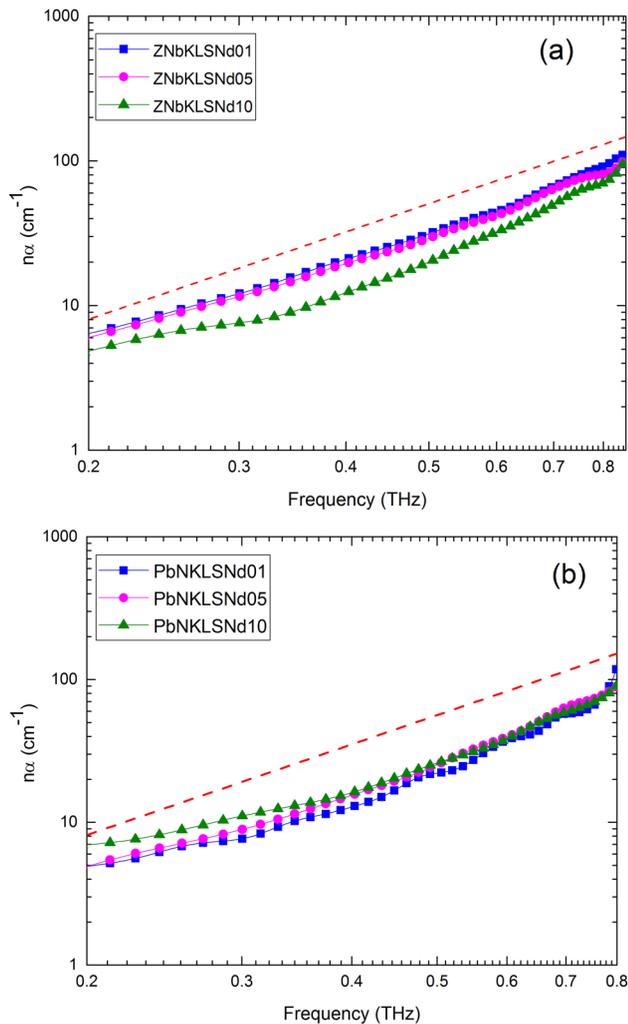
Number	Glass	Refractive index at 0.5 THz	Absorption coefficient at 0.5 THz ( $\text{cm}^{-1}$ )	$Kh^2 \times 10^{-24}$ ( $\text{cm}^{-1}\text{s}^2$ )	Reference
Oxyfluorosilicate glasses					
1	ZNbKLSNd01	3.68	8.67	128	Present work
2	ZNbKLSNd05	3.70	8.10	120	Present work
3	ZNbKLSNd10	3.65	5.62	82	Present work
4	PbNKLSNd01	2.95	7.57	90	Present work
5	PbNKLSNd05	3.02	8.60	104	Present work
6	PbNKLSNd10	3.01	8.84	105	Present work
Commercial silicate glasses (from Schott glass)					
7	Silica	1.96	$0.70 \pm 0.05$	$5.5 \pm 0.5$	9
8	Pyrex	2.11	$7.34 \pm 0.12$	$62 \pm 1$	9
9	BK7	2.51	$17.93 \pm 0.5$	$180 \pm 5$	9
10	B270	2.57	$19.45 \pm 0.5$	$200 \pm 5$	9
11	N-ZK7	2.51	$17.43 \pm 0.5$	$175 \pm 5$	9
12	SF6	3.56	$49.16 \pm 1.4$	$700 \pm 20$	9
13	SF10	3.21	$33.49 \pm 0.78$	$430 \pm 10$	9
14	SF15	3.08	$31.66 \pm 0.81$	$390 \pm 10$	9
15	SK10	2.91	$20.62 \pm 0.43$	$240 \pm 5$	9
Sodosilicate glasses					
16	NS2	2.79	25	279	10
17	NS3	2.65	25	265	10
18	NS4	2.35	25	235	10
Chalcogenide glasses					
19	$\text{Ge}_{35}\text{Ga}_5\text{Se}_{60}$	2.80	7.5	84	11
20	$\text{Ge}_{30}\text{As}_8\text{Ga}_2\text{Se}_{60}$	2.60	3.5	36.4	11
21	$\text{Ge}_{10}\text{As}_{20}\text{S}_{70}$	2.30	2.0	18.4	11
22	$\text{As}_2\text{S}_3$	2.70	6.5	70.2	12
23	$\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$	2.85	2.5	28.5	13
24	$\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$	3.19	10	127.6	13
$\text{La}^{3+}$ :Chalcogenide glasses					
25	GaLaS	3.53	23	324.76	12
26	$\text{La}_{20}\text{Ga}_{20}\text{S}_{60}$	3.89	13	202.28	13
27	$\text{La}_{16}\text{Ga}_{24}\text{S}_{60}$	3.74	11.5	172.04	13
28	$\text{La}_{12}\text{Ga}_{28}\text{S}_{60}$	3.60	13.5	194.4	13
29	$\text{La}_{12}\text{Ga}_{28}\text{S}_{48}\text{Se}_{12}$	3.50	17.5	245.0	13
30	$\text{La}_{12}\text{Ga}_{28}\text{S}_{39}\text{Se}_{21}$	3.65	19	277.4	13

that the fluorine substitutes randomly into the oxygen sites,<sup>26</sup> and this favors uniform structural relaxation. The very low absorption losses found in the present OFS glasses imply that the charge fluctuation in the glass structure is suppressed through such structural relaxation effect of fluorine.

As shown in Table I and Fig. 1, the dependence of the THz absorption coefficient of OFS glasses on the  $x$  value is weak (precisely speaking, weakly negative in ZNbKLSNd, and weakly positive in PbNKLSNd glasses). Dependence of the refractive index on  $x$  is even weaker. Such characteristics would imply that relatively small attenuation of THz waves in these OFS glasses, compared with many members of silicate and chalcogenide glasses, is predominantly determined by the basic composition of the present OFS

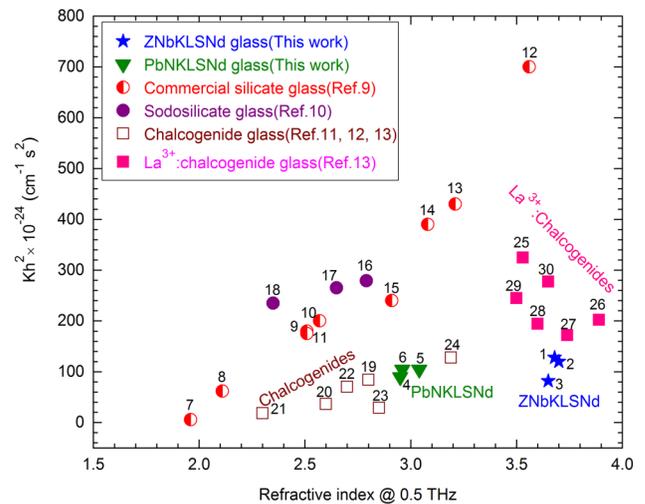
glasses which contain at least 10 mol. % of fluorine, rather than by the modifier (Nd). This is consistent with previous reports in which the structural relaxation effect emerges for fluorine fraction as small as 1 mol. % in silica.<sup>25,27</sup> Thus, we suggest that structural relaxation effect of fluorine is responsible for the observation of very low absorption coefficients in the present OFS glass systems.

To confirm this conjecture, we did a simple analysis based on our Nd composition-dependent study on THz absorption in OFS glasses. The total loss is assumed to consist of the loss of Nd-free OFS glass plus the loss due to the disorder-generating network modifier that is linearly dependent on  $x$  and negative contribution by disorder relaxation by fluorine that is also assumed to be composition-dependent, vis.,  $L_{\text{tot}}$  (total loss) =  $L(x=0) + ax - b(20 - x)$ .



**FIG. 2.** The product of refractive index and absorption coefficient ( $n\alpha$ ) as a function of frequency for (a) ZNbKLS and (b) PbNKLS glasses with different compositions. The dashed line is a guide to the eye with a slope of 2.

$L(x=0)$  was calculated by extrapolation of polynomial fitting of the composition loss data in Fig. 1 and estimated to be  $7.20 \text{ cm}^{-1}$  for the PbNKLSNd glass. The fitting coefficients,  $a$  and  $b$ , were found to be 0.15 and  $-0.02$ , respectively. That is, the loss is dominated by the PbNKLSNd ( $x=0$ ) itself, while the contribution by the Nd modifier (in the range of 1–10 mol. %) is about one order of magnitude more important than the contribution of fluorine (in the range of 10–19 mol. %) to relax the modifier-induced disorders. Similarly, we found  $L(x=0) = 8.64 \text{ cm}^{-1}$ ,  $a = -0.32$  and  $b = -0.03$  for the ZNbKLSNd glass. We note that the above analysis is preliminary and valid only as a first approximation due to limited data and the simple model used. It should be also recalled that the basic ZNbKLSNd structure involves already more than 10 mol. %  $\text{PbF}_2$  or  $\text{ZnF}_2$  in the present glass series, and this fluorine effect is likely responsible to the extremely low absorption nature of these OFS glasses.



**FIG. 3.** Relationship between the absorption parameter and refractive index for different glasses determined at 0.5 THz. Numbers denote glass numbers as shown in Table I.

As has been discussed so far, the present OFS glasses, ZNbKLSNd glasses, in particular, can be viable alternatives to the  $\text{La}^{3+}$ :chalcogenide glasses<sup>13</sup> for sub-THz and millimeter wave applications as the OFS glasses strike a balance of low absorption and high refractive index glasses in the 0.2–0.8 THz frequency range.

### C. Dielectric properties and polarizabilities of OFS glasses

According to the Clausius–Mossotti equation,<sup>9,13,28</sup> the dielectric constant,  $\epsilon$ , is related to the total polarizability,  $P_{THz}$ :

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} N_A \frac{\rho}{M} P_{THz}, \quad (4)$$

where  $N_A$  is the Avogadro number ( $6.023 \times 10^{23}/\text{mol}$ ),  $\rho$  is the density of the glass materials ( $\text{g}/\text{cm}^3$ ), and  $M$  is the average molecular weight of the glass composition ( $\text{g}/\text{mol}$ ). Since the imaginary part of the refractive index [extinction coefficient:  $\alpha c/(4\pi f)$ ] in the THz frequency band is negligibly small in our glasses (see Fig. 1 and Table I), the dielectric constant  $\epsilon$  can be approximated by  $\epsilon = n^2$ . The value of  $\rho$  was measured by the Archimedes method. The formula weights of glasses were evaluated using nominal atomic compositions. The refractive index measured in the THz region will provide the total polarizability ( $P_{THz}$ ), which is a sum of the electronic ( $P_e$ ) and ionic ( $P_i$ ) polarizabilities. To look into material dependence of the refractive indices, it is convenient to use the molar refractivity  $R_m$ , which is related to the molar volume  $V_m = M/\rho$  by the following equation:

$$R_m = \frac{\epsilon - 1}{\epsilon + 2} V_m. \quad (5)$$

The molar volume, total polarizability, and molar refractivity, together with the parameters used for their calculation, are

summarized in Table II. Figure 4 is a plot of  $R_m$  as a function of  $V_m$  in log-log scale for a variety of glasses. Combining Eqs. (4) and (5), we can see that the molar refraction  $R_m$  is directly proportional to the total polarizability, i.e.,  $R_m = (4\pi/3)N_A P_{THz}$ . The values of  $P_{THz}$  calculated in this manner are displayed by the right hand side vertical axis in Fig. 4. Straight lines display equi-slope ( $R_m/V_m$ ) contours for several fixed values of the refractive index.

From Fig. 4, we can see that the molar volumes for OFS glasses are higher than those for pure silica. This can be explained by the structural size increase by the addition of network-modifying cations, such as alkali ions (K, Li, and Na) and rare-earth ions (Nd). The open network structure caused by fluorine incorporation in the OFS glasses is also expected to contribute. The reconstruction of the silicate network due to the addition of such components enhances the production of nonbridging oxygens, making more ionic bonds.<sup>28</sup> Very large polarizability is possible for such material systems. This explains the relatively high refractive indices of the present OFS glasses. Composition ( $x$ ) dependence of the refractive index variation is found to be minimal in both the present OFS glasses. As a result, the refractive-index enhancement effect by  $Nd_2O_3$ <sup>30</sup> and the opposite effect by  $F^-$  ions<sup>25,27,29</sup> are compensating. This is consistent with the opposite trend in refractive indices with a variation of Nd and F concentrations while  $x$  varies. The particularly high refractive indices observed in ZNbKLSNd glasses are attributed to the addition of

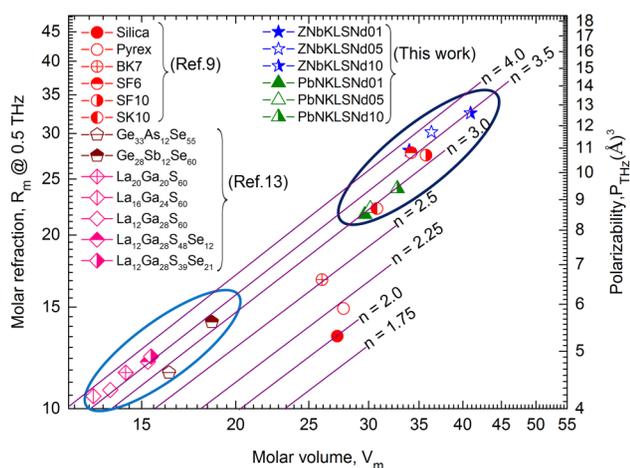
oxides with a high oxygen-to-cation ratio, such as  $Nb_2O_5$ . Taking account of these behaviors, the intermediate-network-former  $Nb_2O_5$ <sup>31,32</sup> likely plays a major role in increasing the refractive index in ZNbKLSNd glasses, though the validity of this model is subject for further study.

Other multicomponent silicate glasses that incorporate PbO (SF6 and SF10),  $B_2O_3$ , and BaO (SK10)<sup>33</sup> are found to follow the same trend of increasing refractive indices at larger molar volumes (see Fig. 4). Pyrex and BK7 glasses do not exhibit the above characteristics. This can be explained by a smaller number of oxygen atoms in the glass structure as is supported by the low density of Pyrex and BK7, as shown in Table II.

In contrast to these oxide-based glasses, chalcogenides and  $La^{3+}$ :chalcogenide glasses belong to a group with low molar refraction and low polarizability. Yet, these glass systems exhibit high refractive indices. We argue that this phenomenon can be explained by the high density of polarizable charges in these glasses. According to previous studies on LaGaS chalcogenide glasses,<sup>10</sup> as La (having higher coordination number) replaces Ga, S atoms are more strongly attracted by La. Consequently, the glass structure becomes more compact, which results in an extremely high refractive index for the chalcogenide up to 3.93 in the THz frequency range. When Se is added to LaGaS glasses, the overall polarizability does not change due to nearly equal atomic polarizabilities for Se

**TABLE II.** Molecular weight ( $M$ ), density ( $\rho$ ), THz refractive index ( $n$ ), dielectric constant ( $\epsilon$ ), molar volume ( $V_m$ ), molar refraction ( $R_m$ ), number of molecules per unit volume ( $N$ ), and total polarizability ( $P_{THz}$ ) evaluated for the present and previously reported glasses.

Glass	$M$ (g/mol)	$\rho$ (g/cm <sup>3</sup> )	$n$	$\epsilon = n^2$	$V_m = M/\rho$ (cm <sup>3</sup> /mol)	$R_m = \frac{\epsilon-1}{\epsilon+2} \times V_m$ (cm <sup>3</sup> /mol)	$N = \frac{\rho}{M} \times N_A$ ( $\times 10^{21}$ cm <sup>-3</sup> )	$P_{THz}$ (Å <sup>3</sup> )
Oxyfluorosilicate glasses (Present work)								
ZNbKLSNd01	124	3.65	3.68	13.55	33.97	27.42	17.73	10.9
ZNbKLSNd05	133	3.66	3.70	13.69	36.34	29.39	16.58	11.7
ZNbKLSNd10	145	3.54	3.65	13.32	40.96	32.94	14.70	12.6
PbNKLSNd01	110	3.72	2.95	8.70	29.66	21.34	20.30	8.5
PbNKLSNd05	114	3.78	3.02	9.24	30.15	22.10	19.97	8.7
PbNKLSNd10	119	3.62	3.01	8.76	32.75	23.62	18.39	9.4
Commercial silicate glasses (Ref. 9)								
Silica	60	2.20	1.96	3.85	27.27	13.29	22.08	5.3
Pyrex	62	2.23	2.11	4.45	27.80	14.87	21.66	5.9
BK7	65	2.51	2.51	6.30	26.02	16.62	23.25	6.6
SF6	177	5.18	3.56	12.67	34.17	27.18	17.62	10.8
SF10	153	4.28	3.21	10.30	35.75	27.03	16.85	10.7
SK10	112	3.64	2.91	8.47	30.77	21.95	19.57	8.7
Chalcogenide glasses (Ref. 13)								
Ge <sub>33</sub> As <sub>12</sub> Se <sub>55</sub> (IG2)	76	4.66	2.85	8.12	16.31	11.48	36.74	4.6
Ge <sub>28</sub> Sb <sub>12</sub> Se <sub>60</sub> (IG5)	82	4.41	3.19	10.18	18.59	14.01	32.26	5.6
$La^{3+}$ :Chalcogenide glasses (Ref. 13)								
La <sub>20</sub> Ga <sub>20</sub> S <sub>60</sub>	61	4.27	3.89	15.13	14.29	11.79	42.15	4.6
La <sub>16</sub> Ga <sub>24</sub> S <sub>60</sub>	58	4.48	3.74	13.99	12.95	10.52	46.32	4.2
La <sub>12</sub> Ga <sub>28</sub> S <sub>60</sub>	56	4.11	3.60	12.96	13.63	10.90	44.61	4.3
La <sub>12</sub> Ga <sub>28</sub> S <sub>48</sub> Se <sub>12</sub>	61	3.99	3.50	12.25	15.29	12.07	39.31	4.8
La <sub>12</sub> Ga <sub>28</sub> S <sub>39</sub> Se <sub>21</sub>	65	4.21	3.65	13.32	15.44	12.42	38.80	4.9



**FIG. 4.** Relationship of the molar refraction and total polarizability as functions of the molar volume for the present series of OFS glasses along with other groups of glasses. Straight lines are shown as guide lines for fixed refractive index values.

( $10.5 \text{ \AA}^3$ ) and S ( $10.2 \text{ \AA}^3$ ), but the increase in molar volume prevents its refractive index increase beyond that of LaGaS.

It is interesting to note that there are two distinct branches (as marked by two large circles in Fig. 4) in which high refractive indices are observed. In one branch, the polarizability is increased through the control of the silicate glass composition by allowing a limited increase in the molar volume. Our OFS glasses belong to this branch. In another branch, the molar volume is decreased through the design of chalcogenide composition, still maintaining a sufficiently high level of the polarizability. Clearly, the presently studied ZNbKLSNd and PbNKLSNd glasses belong to a class with high refractive indices among multicomponent silicate glasses. The refractive index of ZNbKLSNd05 glass is as high as 3.70. Meanwhile, its absorption coefficient is  $8.10 \text{ cm}^{-1}$  at 0.5 THz, which is impressively low for materials with such high refractive index.

#### IV. CONCLUSION

The absorption coefficients and refractive indices for two series of oxyfluorosilicate (OFS) glasses have been investigated using terahertz (THz) time-domain spectroscopy. ZNbKLSNd and PbNKLSNd glasses exhibit refractive index as high as 3.70 (3.02) and absorption loss as low as 6–9 ( $8\text{--}9$ )  $\text{cm}^{-1}$  in the sub-THz and millimeter frequency range, respectively. Compared with other silicate glasses, the OFS glasses studied in this work exhibit the highest refractive index and the lowest absorption. The very low absorption loss realized in the present OFS glasses has been interpreted by the presence of fluorine ions which contribute to reduce structural disorder in the glass. The molar volumes of the OFS glasses studied in this work are higher than those of the chalcogenide glasses, while both exhibit high refractive indices. We propose that the intermediate-network-former  $\text{Nb}_2\text{O}_5$  likely plays a major role in increasing the refractive index in ZNbKLSNd glasses. The very high polarizability of oxygen

offsets the molecular volume increase incurred under the glass composition modification. On the basis of the present study, OFS glasses, particularly ZNbKLSNd glasses, are expected to be useful as low-loss, high-refractive-index glass materials for sub-THz and millimeter wave system applications.

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