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Electrical and optical properties of PbO-TiO$_2$-GeO$_2$ glasses

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Glasses with the compositions $Pb_{2(1-x)}Ti_{2x}Ge_5O_{12+2x}$ ($x = 0.5, 0.4, 0.3, 0.2, 0$) were prepared in order to study their electrical and optical properties. The density decreases with increasing Ti content in the glasses, and the refractive index exhibits a maximum at $x = 0.4$. The Raman spectra show that Ge is tetrahedrally coordinated in glasses. At a given temperature, the electrical conductivity increases with increasing Ti content while the dielectric constant shows a mixing effect that exhibits a maximum at $x = 0.2$. The temperature dependence of dielectric constant was discussed by means of the Langevin theory. © *1998 Kluwer Academic Publishers*

1. Introduction

"Amorphous ferroelectricity" was first proposed by Lines [1] and experimentally demonstrated on quenched $LiNbO_3$ and $LiTaO_3$ glasses [2]. Other observations of ferroelectric phase transition in amorphous $Pb(Zr_xTi_{1-x})O_3$ [3] and $PbTiO_3$ thin films [4, 5] have been reported. Amorphous ferroelectric thin films have received increasing interest in recent years because of their high dielectric constants and because of device applications. Crystalline $PbTiO_3$ and $Pb_5Ge_3O_{11}$ are ferroelectrics. Amorphous $Pb_5Ge_3O_{11}$ was obtained both by high pressure [6] and by quenching the melt to room temperature [7]. The evolution of ferroelectricity in ultrafinegrained $Pb_5Ge_3O_{11}$ was observed by crystallization from the glass [7]. Because of unstable phases of amorphous ferroelectrics in both thin film and bulk state, however, it is difficult to study the temperature-dependent electrical and optical properties of such glasses and the mixing effect of different components. PbO-TiO$_2$-GeO$_2$ is a good glass-forming system. Glasses with the compositions $Pb_{2(1-x)}Ti_{2x}Ge_5O_{12+2x}$ ($x = 0.5, 0.4, 0.3, 0.2, 0$) were prepared in the present work in order to study the electrical and optical properties of the bulk glasses by means of dielectric and Raman spectroscopy.

2. Experimental

PbO (Aldrich, 99.9%), TiO$_2$ (Aldrich, 99.99%), and GeO$_2$ (Heraeus, 99.999%) were used as starting materials. The powders were mixed and then melted in a Pt crucible in an electric furnace at 1623–1723 K for 1 h. The melt was then quenched in a Ni crucible and annealed at 623 K for 20 h. The prepared glasses are transparent and yellowish in color and are homogenous when examined with a petrographic microscope. For the impedance measurements the glass specimens were cut into thin slices and diamond polished. Gold electrodes were sputtered onto the disclike samples in vacuum. The relative error of the thickness of samples was 2%. Dielectric measurements were performed in Ar gas with a 1260 impedance gain-phase analyzer and a Chelesea dielectric interface. During the impedance measurements the variation of temperature is controlled within 1 K. The relative error of the impedance measurements was 10^{-3}. The glass densities were determined by an immersion method with the accuracy of 5×10^{-4} (g/cm^3), and Raman scattering experiments were carried out with a Perkin–Elmer spectrometer (System 2000 NIR FT-Raman). The samples were excited with the 1064 nm line of a Nd-YAG laser. The refractive indices were determined by ellipsometry with a He-Ne laser at 632.8 nm.

3. Results

Fig. 1 shows the Raman spectra of $Pb_{2(1-x)}Ti_{2x}Ge_5O_{12+2x}$ glasses ($x = 0.5, 0.4, 0.3, 0.2, 0$). With decreasing Ti content, the main band near 429 cm^{-1} shifts to higher frequencies with a gradual loss of intensity. This band is comparable with the Raman band at $\sim$420 cm^{-1} of vitreous GeO$_2$ [8, 9] and indicates that Ge is tetrahedrally coordinated in these glasses. The Raman band in the range from 786 to 810 cm^{-1} is comparable with the peak at 784 cm^{-1} in $Na_2O1.78\ GeO_2$ glass [8]. As discussed previously [8], this band arises from stretching-motions of the non-bridging oxygens. Both frequency and intensity of this band increase with decreasing Ti content, indicating that the non-bridging oxygen is closely correlated with the addition of TiO$_2$ in the glass. This is because the number of oxygens in glasses is proportional to the Ti content. A very broad fluorescence band between 1500 and 3500 cm^{-1} is observed for the glasses with compositions of $x = 0.5$ and $x = 0.3$.

The refractive indices and the densities of the glasses determined by ellipsometry and immersion method are listed in Table I. Both the refractive index and the density of the glass vary non-linearly with Ti content.

Fig. 2 illustrates the temperature-dependent real part of electrical conductivity for $Pb_{2(1-x)}Ti_{2x}Ge_5O_{12+2x}$

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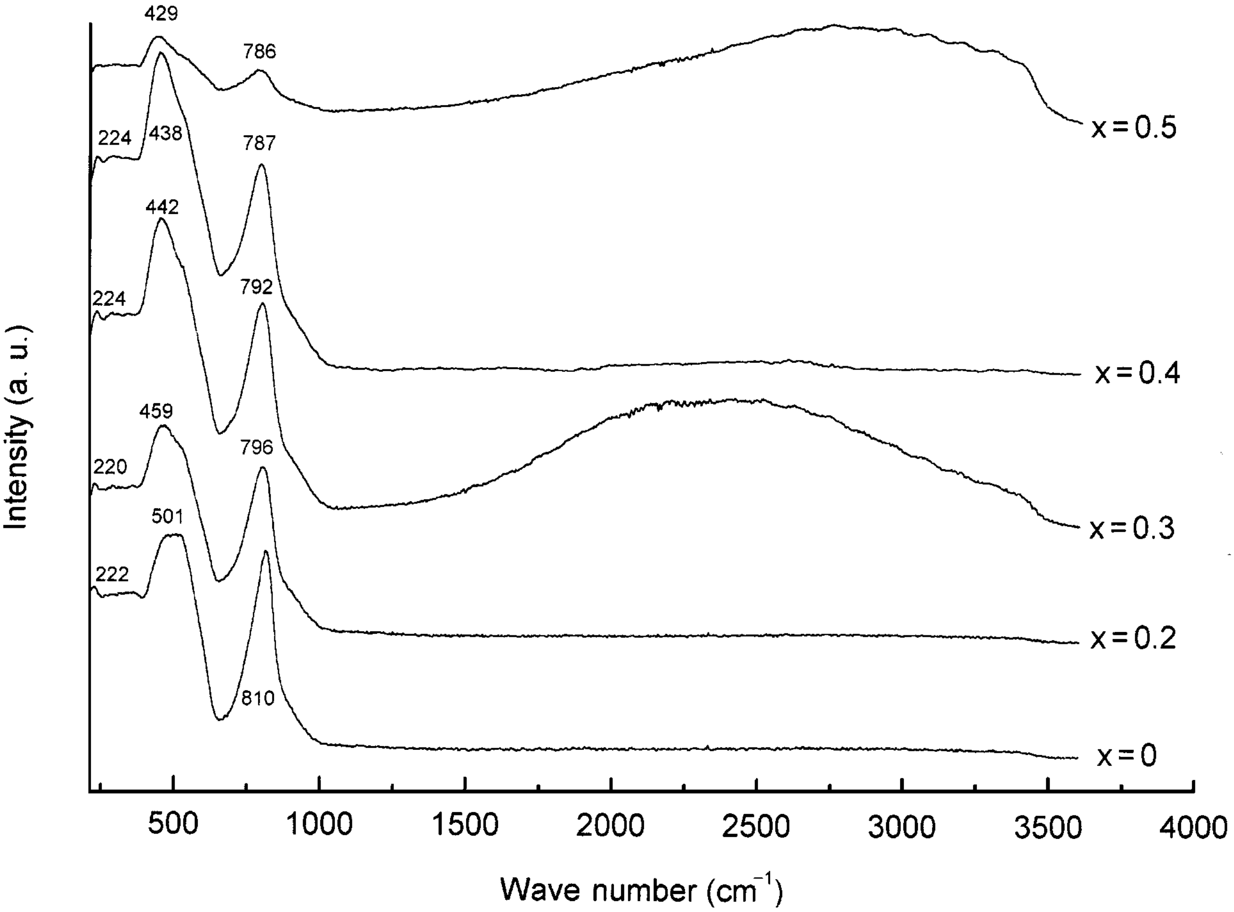

Figure 1 Raman spectra of $Pb_{2(1-x)}Ti_{2x}Ge_5O_{12+2x}$ glasses.

glasses at the frequency of 0.1 Hz. A frequency-independent dc conductivity is observed in the frequency range from 0.1 to ~1000 Hz for all glasses. Thus the electrical conductivity (in $\Omega^{-1}m^{-1}$) shown in Fig. 2 represents the dc value of the glasses. It increases with rising temperature, showing that the electrical conduction of the glass is a thermally activated process. At a given temperature, the electrical conductivity increases with increasing Ti content in glasses.

For dielectric materials in which the electrical conduction is produced through hopping of the charge carriers, the temperature dependence of electrical conductivity σ can be expressed by the form

$$\sigma = \sigma_0 \exp\left(-\frac{E_\sigma}{k_B T}\right), \qquad (1)$$

where σ_0 is a pre-exponential constant, k_B is the Boltzmann constant, E_σ denotes the activation energy, and T is the absolute temperature [10]. The dc electrical conductivity of $Pb_{2(1-x)}Ti_{2x}Ge_5O_{12+2x}$ glasses can be described by means of Equation 1. The fitting results are also plotted in Fig. 2, and the evaluated σ_0 and E_σ are listed in Table I. The activation energy increases with decreasing Ti content, and the pre-exponential factor σ_0 also shows the same tendency, except for the glass with $x = 0.4$.

The temperature-dependent real part of dielectric constants of the glasses at 13 110 Hz are plotted in Fig. 3. In order to monitor the effect of electrode polarization at low frequencies, the dielectric constants are measured from 0.1 to 10^6 Hz, and the selected dielectric constants shown in Fig. 3 are determined at 13 110 Hz. The contribution of electrode polarization to the

TABLE I Physical parameters of $Pb_{2(1-x)}Ti_{2x}Ge_5O_{12+2x}$ glasses

x	0.5	0.4	0.3	0.2	0
Density ρ (g/cm^3)	4.428	4.853	5.065	5.265	5.582
Refractive index n (632 nm)	1.842	1.928	1.918	1.913	1.892
Activation energy E_σ (eV)	1.10 ± 0.01	1.14 ± 0.01	1.24 ± 0.01	1.31 ± 0.01	1.36 ± 0.01
Pre-exponential constant σ_0 (1/($\Omega \times$ m))	559 ± 5	332 ± 3	731 ± 7	1483 ± 15	2232 ± 21
s (cm^3)	2465 ± 23	2617 ± 17	3276 ± 13	3875 ± 20	3147 ± 37
$i/10^6$ (K $\times$ cm^3)	-2.6 ± 0.1	-2.2 ± 0.1	-2.8 ± 0.1	-4.0 ± 0.1	-3.6 ± 0.2

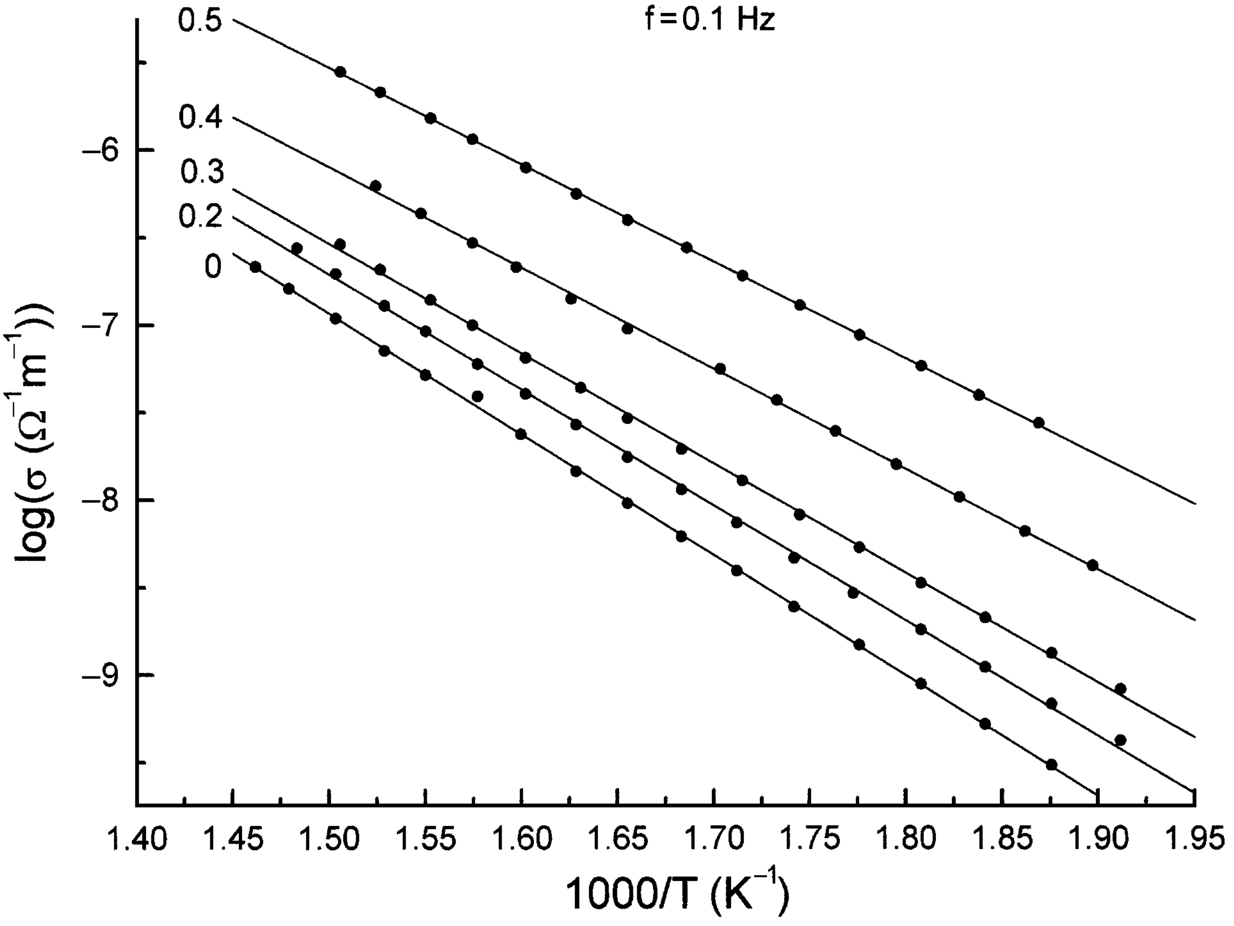

Figure 2 Electrical conductivity σ $(\Omega \times \mathrm{m})^{-1}$ of $\mathrm{Pb}_{2(1-x)}\mathrm{Ti}_{2x}\mathrm{Ge}_5\mathrm{O}_{12+2x}$ glasses at different temperatures. Electrical conductivity is determined at 0.1 Hz. The solid circles are experimental results, and the solid lines represent the fitting results by Equation 1. The fitting parameters are listed in Table I.

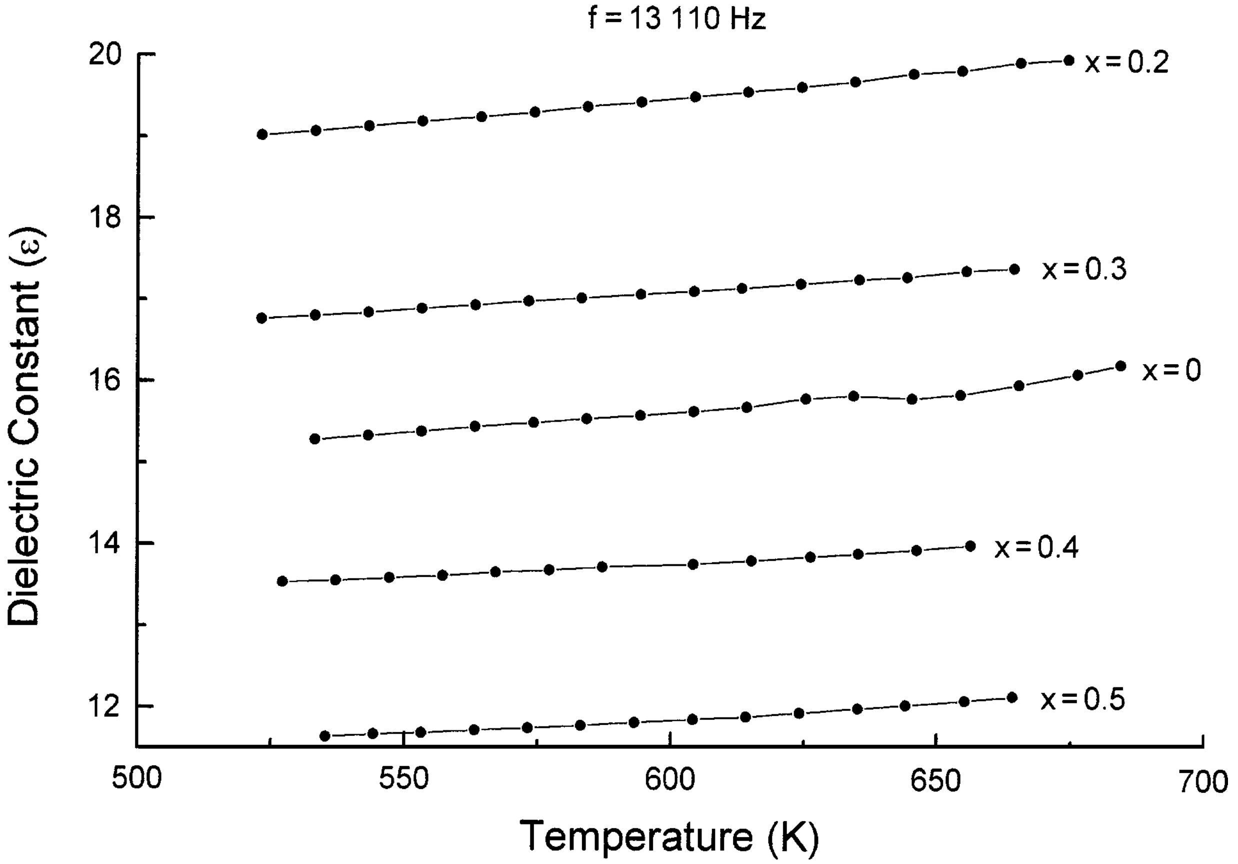

Figure 3 Temperature dependence of the real part of dielectric constant ϵ at 13 110 Hz for $\mathrm{Pb}_{2(1-x)}\mathrm{Ti}_{2x}\mathrm{Ge}_5\mathrm{O}_{12+2x}$ glasses.

dielectric constant can be neglected at this frequency. As can be seen, the dielectric constant increases with increasing temperature for all glasses. At a given temperature, a mixing effect can be observed. The dielectric constant exhibits a maximum at $x = 0.2$.

4. Discussion

The mixing effect can be observed in both optical and electrical properties of $Pb_{2(1-x)}Ti_{2x}Ge_5O_{12+2x}$ glasses. The refractive index, Raman band frequencies, and pre-exponential constant σ_0 all exhibit an anomaly at $x = 0.4$. A mixing effect may be induced by the variation of glass structure. As for other polar glasses [11], no ferroelectricity is observed in the temperature-dependent dielectric constant data, such as the phenomena reported in $Pb_5Ge_3O_{11}$, $LiNbO_3$, and $LiTaO_3$ glasses. This observation indicates that no spontaneous ferroelectric grain exists is the presently investigated bulk glasses. The high dielectric constants and refractive indices of the glasses are due to the high polarizabilities of Pb^{2+} and Ti^{4+} ions.

The dielectric constants, as the results show in Fig. 3, are related with two polarization processes. One is the deformation polarization, which results from deformation of the charge distribution of the molecule, and another is the orientation of polarization, which is due to the dipole movement [11–13]. For $Pb_{2(1-x)}Ti_{2x}Ge_5O_{12+2x}$ glasses, we can assume that the bonds Pb^{2+}–O^{2-} and Ti^{4+}–O^{2-} produce a permanent dipole moment. According to the Langevin theory, the temperature-dependent dielectric constant can be described by the following equation [14, 15]:

$$\varepsilon - 1 = \frac{\mathrm{N_A}}{\varepsilon_0}\frac{\rho}{M}\left(\alpha + \frac{\mu^2}{3\mathrm{k_B}T}\right), \qquad (2)$$

where α is deformation polarizability, μ is the average dipole moment, $\mathrm{N_A}$ is the Avogadro number, M and ρ are the molecular weight and density of the glass, respectively.

If we neglect the thermal expansion of glasses and let the density in Equation 2 be equal to its value at room temperature, the temperature-dependent dielectric constants shown in Fig. 3 can be described by Equation 2. The experimental and fitting results are shown in Fig. 4. In the plot of $(\epsilon - 1)MT/\rho$ versus T, Equation 2 is demonstrated to be a straight line, the slope of which, s, is equal to the term of $\mathrm{N_A}\alpha/\epsilon_0$, and the intercept i gives $\mathrm{N_A}\mu^2/(3\mathrm{k_B}\epsilon_0)$. The evaluated values are listed in Table I. Note that the slope also exhibits a maximum at $x = 0.2$. Unexpectedly, the evaluated intercepts for all glasses are found to be negative. An explanation of such results appears to be the temperature-dependent deformation polarizability, α, which is described by the equation of

$$\alpha = \alpha_0 - \frac{\mathrm{c}}{T}, \qquad (3)$$

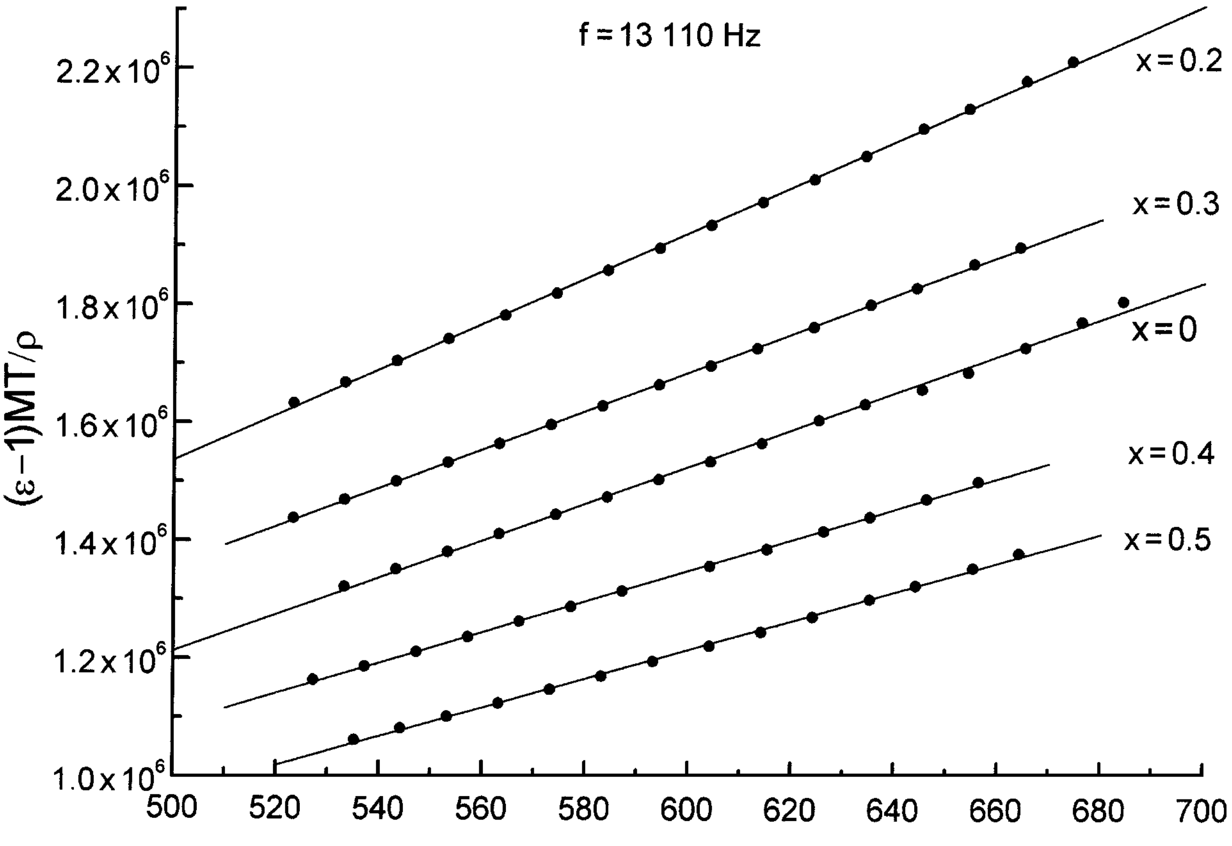

Figure 4 $(\epsilon - 1)MT/\rho$ versus temperature. The values of the dielectric constant are from Fig. 3, and the densities of glasses are listed in Table I. The solid circles are experimental results, and the solid lines are the fitting results by Equation 3. The fitting parameters are listed in Table I.

where α_0 and c are the two constants. In this case, the slope s is expressed by the relation of $s = N_A\alpha_0/\epsilon_0$, and the intercept i is given by $i = N_A\mu^2/(3k_B\epsilon_0) - c$.

The deformation polarization can respond to the applied electric field even at optical frequencies, whereas the orientation of dipoles possesses the distribution of relaxation times and thus disappears at high frequencies [13]. Therefore, the evaluated intercept i is mainly related with the constant c at 13 110 Hz.

5. Conclusions

Glasses with the compositions $Pb_{2(1-x)}Ti_{2x}Ge_5O_{12+2x}$ ($x = 0.5$, 0.4, 0.3, 0.2, 0) were prepared to study electrical and optical properties. The Raman spectra show that Ge is tetrahedrally coordinated in glasses. The refractive index, dielectric constant, deformation polarizability, and frequencies of Raman bands all exhibit a mixing effect. The electrical conductivity increases with increasing Ti content. No ferroelectricity is observed in the temperature-dependent dielectric constant data. The deformation polarizabilities of all glasses are found to depend on temperature.

Acknowledgements

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