Preparation and characterization of silver nanoparticles within silicate glass ceramics via modification of ion exchange process

Salwa A.M. Abdel-Hameed [a,*], Ahlam M. Fathi [b]

[a] Glass Research Department, National Research Center, Dokki, ElBehoos St., Cairo 126222, Egypt
[b] Physical Chemistry Department, National Research Center, Dokki, ElBehoos St., Cairo 1, Egypt

ARTICLE INFO

ABSTRACT

This work pointed out the preparation of glass-ceramic based on fluoramphibole using different alkalis. Phases were crystallized using heat-treatment at 850 °C/2.5 h and were identified using XRD. Fluorophlogopite, fluorrichterite, enstatite and cristobalite were found in the heat-treated glasses. Crystallization of fluorophlogopite or fluorrichterite was detected in samples containing high K and Na, respectively, accompanied with crystallization of enstatite in the last sample. Cristobalite was crystallized only in equal alkali-containing glass beside enstatite and richterite. Nanoparticles of silver have grown within a silicate glass via modification of ion exchange process. The metal particle diameters were detected using XRD and TEM. The particles size ranges from 4 to 10 nm. The amount of silver ions exchanged was varied according to type and amount of alkali on fluoramphibole compositions. The composites show low values of dielectric permittivity (10–30) due to the formation of interconnected metal nanoparticle chains. The resistivity of the specimen dropped from 10^8 to 10^{10} Ω cm^2 to 10^4 to 10^8 Ω cm^2 after ion exchange process which shows metallic and semiconducting behavior according to the reduction temperature.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Glass-ceramic materials based on fluoramphibole are very important because they have a wide range of compositions and they can be crystallized easily from melt quench glasses. Glass ceramics containing fluorrichterite phase exhibit excellent mechanical properties, chemical durability and resistance to slow crack growth; therefore it can be used in the manufacture of computer hard disks [1,2].

The stiochiometric fluoramphibole formula is $A_{0-1}B_2Y_5T_8$ O_{22} (OH, F, Cl)$_2$, where A is a vacancy usually occupied by Na or K; B-site is occupied by either Na, Li, Ca, Mn, Fe, or Mg; while Y-site is occupied by Mg, Fe, Mn, Al, Fe^{+3} or Ti, and T or the tetrahedral-position is occupied by either Si or Al. The B-site occupancy is a key feature in amphibole crystal chemistry, and is the base of amphibole classification and nomenclature [3].

The solid solution between (Fe, Mg, Mn) and Na amphiboles in B-site is restricted in natural samples [4], whereas recent work showed nearly complete solid solution between Li and Na amphiboles in B-site [5,6]. Substitution of Na$^+$ by Li$^+$ or Ca^{2+} in K-fluorricterite indicated that the presence of one sodium atom per formula unit is necessary for fluorrichterite crystallization [3]. Sub-stitution of K$^+$ and Li$^+$ for Na$^+$ in Mg-fluorricterite enhanced the formation of fluormica or protoamphibole [7].

In recent years, nanostructured materials have attracted considerable attention because of their interesting physical properties and applications they exhibit, for example, they can be used in the nanofabrication of devices and the preparation of interelement wiring by growing metallic nanowires. Preparation and study of quantum dots and wires have been reported extensively [8–13]. The most suitable host for growing these dots or wires is oxide glasses and glass ceramics containing crystal channels. Oxide glasses have a random network structure with physical void spaces and, therefore, can be exploited as nanotemplates in which nanowire structures can be generated. On the other hand, glass ceramics containing fluorophlogopite mica phase were exploited to grow nanofilaments of metallic silver within the crystal channels of the former.

Physical and chemical methods have been used to grow nanometals in different forms [9,14,11,15–17]. Silver nanowires can be grown within silicate glasses and glass ceramics containing flourophlogopite mica phase by the electrodeposition process [17–19]. Arrays of nanoparticles of silver and copper grown within silicate glass exhibited diode-like voltage characteristics [20].

Detailed work on the electrical properties of such composites was reported earlier [10,21,22]. Nanoparticles of silver of diameters ranging from 6 to 10 nm were grown in glass–ceramic samples containing lithium niobate and zinc orthosilicate. These nanocom-

* Corresponding author.
E-mail address: Salwa_NRC@hotmail.com (S.A.M. Abdel-Hameed).

Table 1
Chemical composition of glasses under investigation.

Sample code	Stoichiometric fluorrichterite formula	Batch composition (wt%)						
		SiO$_2$	MgO	CaO	MgF$_2$	Na$_2$O	K$_2$O	Li$_2$O
GNKL	Na$_{0.65}$K$_{0.65}$Li$_{0.65}$CaMg$_5$Si$_8$O$_{22}$F$_2$	58.57	19.64	6.83	7.59	2.46	3.73	1.18
GK	Na$_{0.5}$K$_2$Li$_{0.5}$Ca$_{0.5}$Mg$_5$Si$_8$O$_{22}$F$_2$	56.59	18.98	3.30	7.34	1.82	11.08	0.88
GN	Na$_2$K$_{0.5}$Li$_{0.5}$Ca$_{0.5}$Mg$_5$Si$_8$O$_{22}$F$_2$	58.25	19.54	3.40	7.55	7.15	2.85	0.91

posites exhibit about four orders of magnitude dc resistivity change when the relative humidity varies from 35 to 95% [23]. On the other hand Na$^+$/Ag$^+$ ionic exchange can be used in preparation of antibacterial glass. Tests and analyses revealed that 6 wt.% of AgNO$_3$ in the ionic medium was the critical concentration [24]. Also Ag$^+$- and Zn^{2+}-exchanged zeolites and clays have been used as coatings and in composites to confer broad-spectrum antimicrobial properties on a range of technical and biomedical materials [25].

A number of studies were reported on switching in discontinuous metal films and metal ceramics composites. In the former, electrical conduction was explained as arising due to electrons traveling from one island to other impurity levels of the substrate surface with electrons emitted into a vacuum by a Fowler–Nordheim tunneling mechanism [10,26].

In the present work, growing silver nanoparticles via modification of ion exchange process within the pores of fluoramphibole glass ceramics was pointed out. Also, the effects of alkali position occupation on fluoramphibole glass, its crystallization behavior and ion exchange process of three different alkali contents were also studied.

2. Experimental

The glass batch compositions used are that used earlier viz. the corresponding author [27] depending on the stiochiometric formula of the fluorrichterite (NaNaCaMg$_5$Si$_8$O$_{22}$F$_2$).

Substitutions in A- (or vacancy or may filled by Na) and B-site of the stiochiometric fluorrichterite with K and Li were calculated, weighted and well mixed (Table 1). All compositions were prepared from ingredient chemicals. Calcium, magnesium, sodium, potassium or sodium was added as carbonate. Silica and fluorine were added as quartz sand and MgF$_2$. The glasses were produced after melting processes in a covered platinum crucible at 1350–1450 °C temperature for 2 h with occasional swirling every 30 min to ensure homogenization. The melts were then cast into hot steel moulds in the form of rods which were transferred to a muffle furnace at 450 °C for annealing as recorded in previous work [27].

The heat-treatment was carried out at 850 °C/2.5 h according to our previous DTA data [27]. At this temperature maximum crystallization of the desired phases were observed. The heat-treated glasses were subjected to powder X-ray diffraction using Ni-filled Cu Kα rays for determination of the types and contents of the crystalline phases precipitated in the glasses.

The alkali/silver ion exchange treatment was carried out by immersing the glass samples (5 mm × 5 mm × 3 mm) in a molten bath of silver nitrate at a temperature of 583 °C for 8 h. After the interdiffusion reaction the samples were washed in distilled water to remove any silver nitrate adhering to their surfaces. The ion-exchanged specimens were covered by activated carbon and then subjected to a reduction treatment at 590 °C/0.5 h and 1 h, 650 °C/1 h, 750 °C/1 h and 900 °C/1 h.
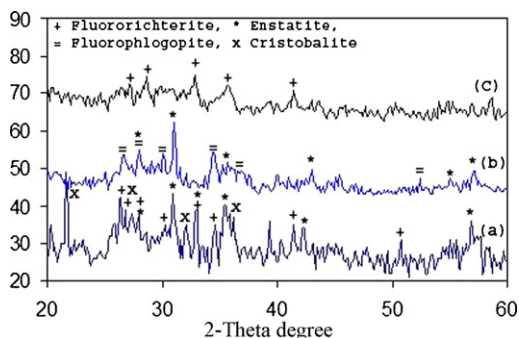

Fig. 1. XRD patterns of glasses (a) GNKL, (b) GK and (c) GN heat-treated at 850 °C/2.5 h.

The modifications here are (1) increasing the ion exchange and reduction temperatures by about 275 °C than that used in previous works (2) using activated carbon for reduction reaction instead of hydrogen gas, which was a reason of making the experiment easier.

The crystallite size of silver metal, in the reduced samples, for the most intense peak of silver (1 1 1, 2 0 0 and 3 1 1) was determined from the XRD data on the surface of glass ceramics using Debye–Scherrer formula: $D = k\lambda/B\cos\Theta$, where D is particle size, k is constant, λ for Cu is 1.54 Å, B is full half wide and $2\Theta = 4°$. The heat-treated glasses were crushed and sonically suspended in ethanol, few drops of the suspended solution were placed on an amorphous carbon film held by a copper microgrid mesh and then observed using JEM 2010 transmission electron microscope to study the microstructure of the ion-exchanged and reduced glass-ceramic samples. The relative amounts of alkali/silver ion exchange were obtained via XRD on the surface by comparing the relative intensity of silver peaks for different samples.

Electrical measurements were carried out on the specimens with an area of 0.5 cm^2 and thickness of ~0.3 cm, the samples were polished in silicon carbide grit of different mesh sizes and finally in 0.5 mm size alumina powder to an optical finish. The electrochemical characteristics of different samples were studied over the temperature range 30–300 °C by a Keithley 617 electrometer.

3. Results and discussion

Crystallization of fluoramphibole glasses containing high concentration of specified alkali depends on the kind of alkali. In samples containing high K (GK) sample, fluorophlogopite becomes the dominant phase in the entire heat-treatment schedule with enstatite. In samples containing high Na (GN) sample, fluorrichterite was the main phase developed as shown in Fig. 1.

Generally, the heat-treatment parameters of triplet alkalis-containing glass samples, as well as its content, efficiently control the developed phases. This is due to that Li$^+$ has lower melting point and higher field strength, than Na$^+$ and K$^+$ (m.p. Li$_2$O = 618 °C, field strength Li = 0.23 Å, K = 0.13 Å and Na = 0.19 Å [28]), therefore, it increases the mobility of ions during heat-treatment of glasses and consequently facilitates their crystallinity. In the case of equal alkalis-containing glass GNKL, enstatite, richterite and cristobalite were developed at 850 °C/2.5 h.

Crystallization of fluorrichterite follows the presence of Na ions and it becomes dominant in the sample of highest Na content. However, K ions in the highest percent hinder the crystallization of fluorrichterite and enhance the formation of fluormica, i.e. fluorophlogopite.

The pre-mentioned results show that, in fluorosilicate glass-ceramic, K$^+$ is preferably accommodated in a layer structure [29]. Therefore, in high K-containing glass-ceramic a sheet structure fluormica was developed, while in high Na-containing samples the amphibole synthesis was sluggish [30].

The TEM micrograph of the ion-exchanged (with silver) glass-ceramic samples subjected to a reduction treatment at the optimum reducing temperature for the studied samples is shown in Fig. 2. It can be seen that TEM of GN and GK glass-ceramic reduced at 750 °C/1 h and 900 °C/1 h, respectively, shows uniform distribution of high density, nanosize silver metal particles in an insulating matrix, while GNKL glass ceramics reduced at 750 °C/1 h shows coagulation of net like structure of silver metal.

The crystallite size of silver metal calculated from XRD data (on the surface of glass ceramics) for the most intense peak analysis of silver present in the glass ceramics reduced at 590 °C/1/2 h are shown in Table 2 and Fig. 3. (It can be noticed from Fig. 3 that, the crystallized phases are not affected by ion exchange process and
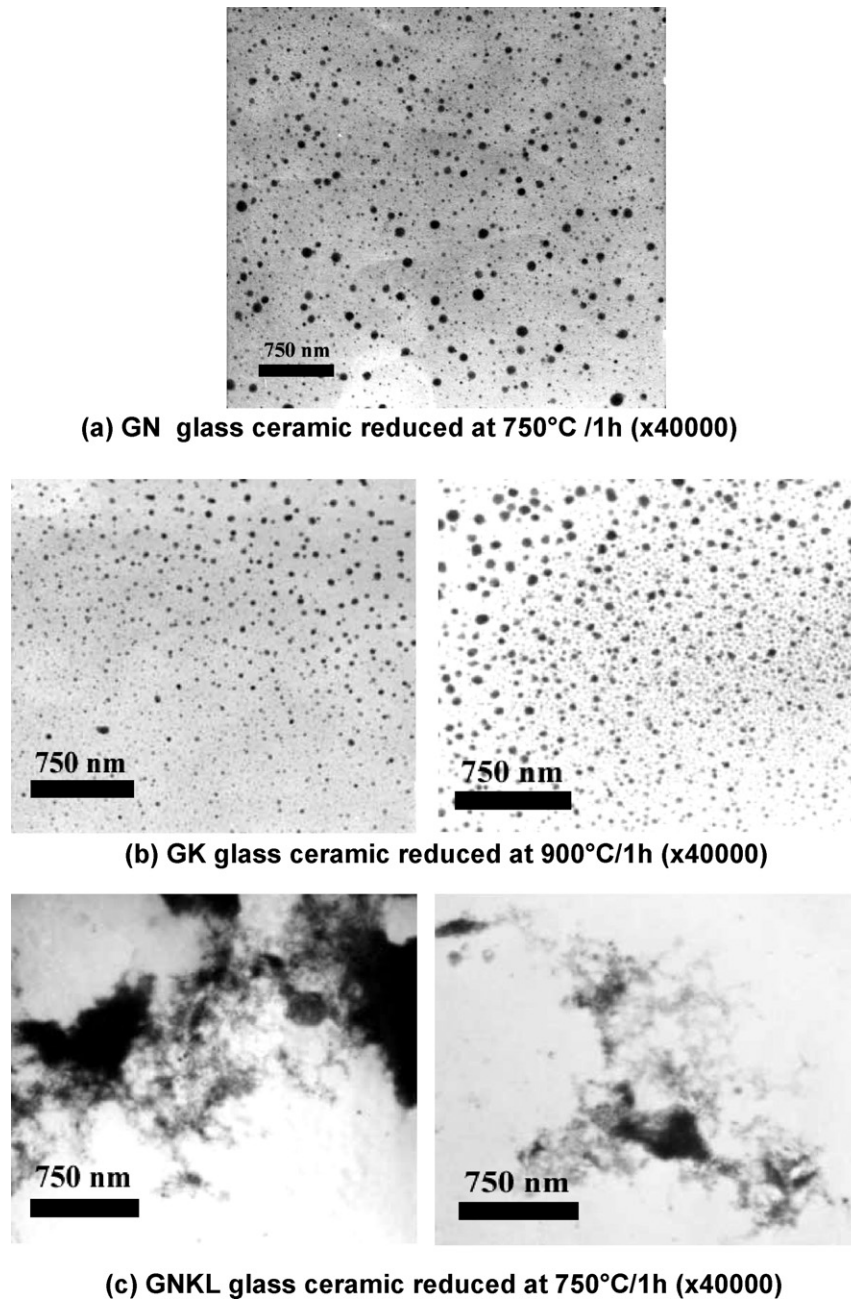
(a) GN glass ceramic reduced at 750°C /1h (x40000)

(b) GK glass ceramic reduced at 900°C/1h (x40000)

(c) GNKL glass ceramic reduced at 750°C/1h (x40000)

Fig. 2. Transmission electron micrograph of the ion-exchanged (with silver) glass-ceramic samples at different reduction temperatures. (a) GN glass ceramic reduced at 750 °C/1 h (40,000×). (b) GK glass ceramic reduced at 900 °C/1 h (40,000×). (c) GNKL glass ceramic reduced at 750 °C/1 h (40,000×).

still as it is.) The results indicate the precipitation of nanoparticles from silver metal, the grain size of silver is relatively larger in GN sample than in GK and GNKL. Fig. 3 also clarifies that, comparing the intensity of silver peaks in different samples, the amount of silver metal precipitated in the glass-ceramic samples is higher in GK then decreases in GNKL and reaches minimum value in GN. This can be explained as follow; the silver ion prefer to exchange with K$^+$ ions

than with Na$^+$ and Li$^+$ ions, as the amount of K$^+$ ions increases from GN, GNKL and GK, respectively, the amount of ion exchange with silver increases and thus the amount of precipitated silver metals increases.

The particle size distribution obtained from Fig. 2(b) is shown in Fig. 4. The points in this figure represent the experimental data. These were fitted to a polynormal distribution function and the solid line in Fig. 4 is the theoretically fitted curve. The median diameter extracted from this fitting is 5.4 nm and the geometric standard deviation is 1.4 nm. A similar analysis of sample GN and GNKL reduced at 750 °C/1 h give a median diameter of 10.1 and 5.6 nm and geometric standard deviation are 1 and 1.3 nm, respectively. It is noticed that, the particles size obtained by this way is slightly higher than that calculated from XRD which can be related to coagulation of particles and personal error.

Table 2
The crystallite size of silver nanoparticles precipitated in samples reduced at 590 °C/1/2 h (nm).

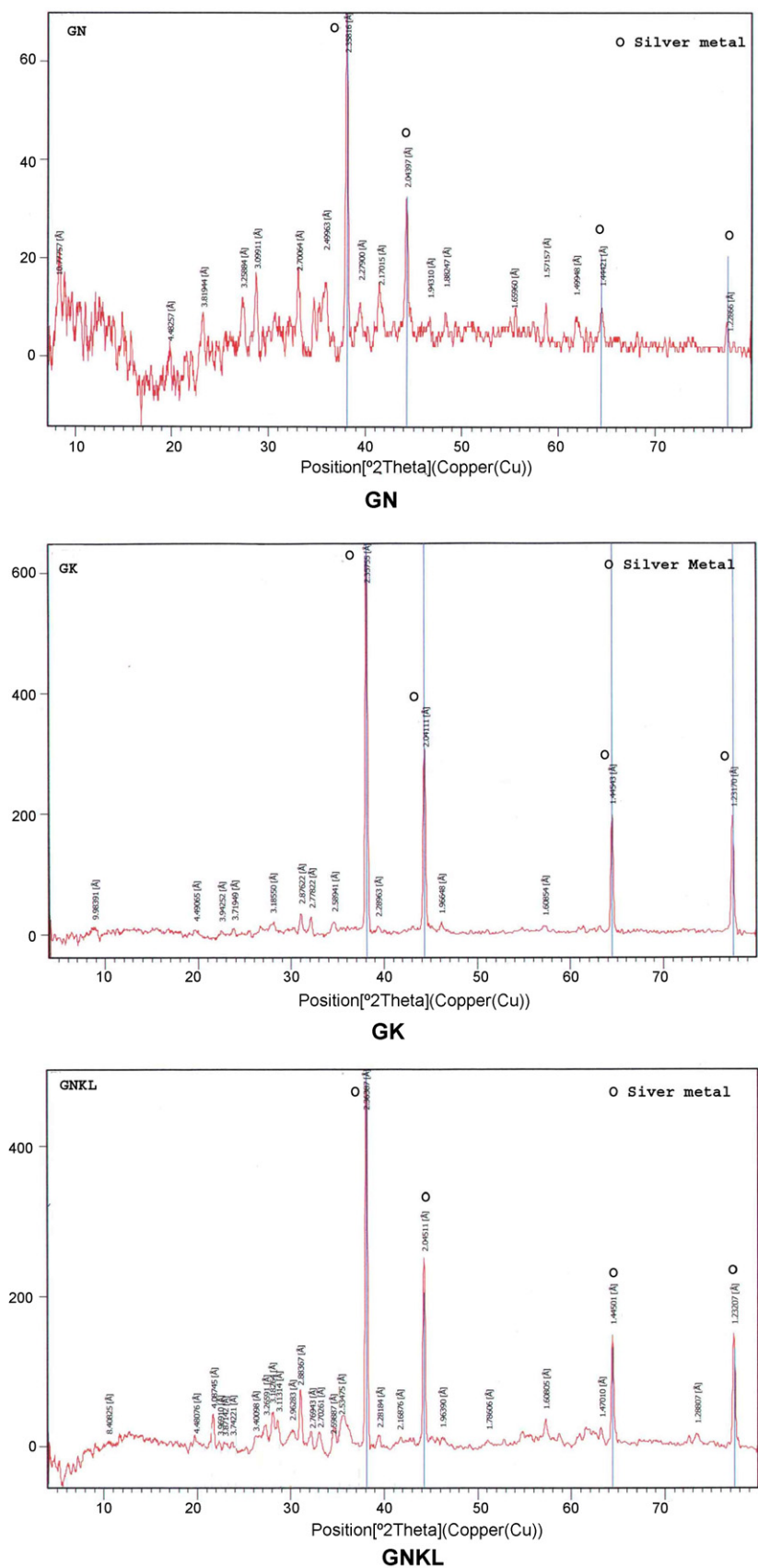| Sample	Crystal size (nm)
GN	9.66
GNKL	3.82
GK	3.92

Fig. 3. XRD data on the surface of GN, GNKL and GK glass ceramics after ion exchange with silver and reduced at 590 °C for 1/2 h.
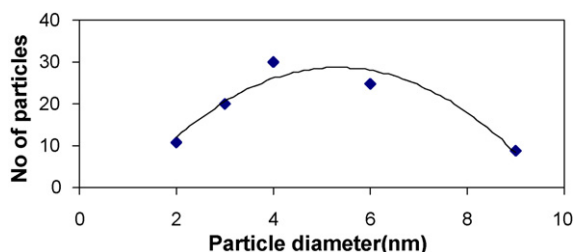
Fig. 4. Particle size distribution of silver atoms in GK sample from Fig. 2b.

The variation of dielectric constant of glass-ceramic samples (reduced at different temperatures 590 °C for 1/2 h and 900 °C for 1 h as a function of frequency at temperatures ranging from 50 to 300 °C was studied. The behavior of all samples (GK, GN and GNKL) at different temperatures is qualitatively similar. Gk sample will be depicted as an example for this study at 50 °C (Fig. 5(a and b)). Values of dielectric constant for the entire samples at different temperatures ranges from 10 to 30, the low values of dielectric constant indicates the formation of interconnected metal nanoparticle chain [31] and accordingly, samples under investigation are considered as ion conducting.

Fig. 6 shows the variation of surface resistivity as a function of inverse temperature for specimen GN reduced at different temperatures. It is clear that the behavior of the specimen reduced at 590 °C for 1/2 h and 900 °C for 1 h shows nonlinear variation. The presence of more than one line in the represented data was a sign of presence of more than one conduction mechanism [32]. It is known that alkali oxide glasses containing transition metal oxide exhibit mixed conductivity (electronic and ionic) [33]. As shown from Fig. 6, the resistivity increases in the first temperature region from 25 to 175 °C, while in the second region above 175 °C the resistivity decreases.

On the other hand, for GK specimen, the variation of surface resistivity as a function of inverse temperature shows nonlinear behavior as shown in Fig. 7. For the sample reduced at 590 °C,

Fig. 6. Variation of resistivity as a function of temperature for specimen GN reduced at different temperatures.

Fig. 7. Variation of resistivity as a function of temperature for specimen GK reduced at different temperatures.

the resistivity increases as the temperature increases from 25 to 150 °C and the resistivity decreases above 150 °C, while for sample reduced at 900 °C the resistivity is approximately constant over the first temperature range and then it decreases.

The increase in resistivity as a function of temperature in the first region (25–175 °C) for the three samples confirmed the presence of metallic phase [34], and indicated that the conductivity is ionic due to the mobility of alkali metal. At higher temperature the conductivity is electronic due to the excitation of electrons of silver, and this was confirmed by the presence of semiconducting state. A transition from metallic conductivity state to semiconducting state occurred at around 175 °C for GN and 150 °C for GK, this transition has been ascribed to the effect of high pressure generated by mismatch of thermal expansion [16]. For GNKL specimen, resistivity is directly proportional to temperature as can be seen from Fig. 8. As the size of metal particles reaches nanoscale, the electrical resistivity increases [35].
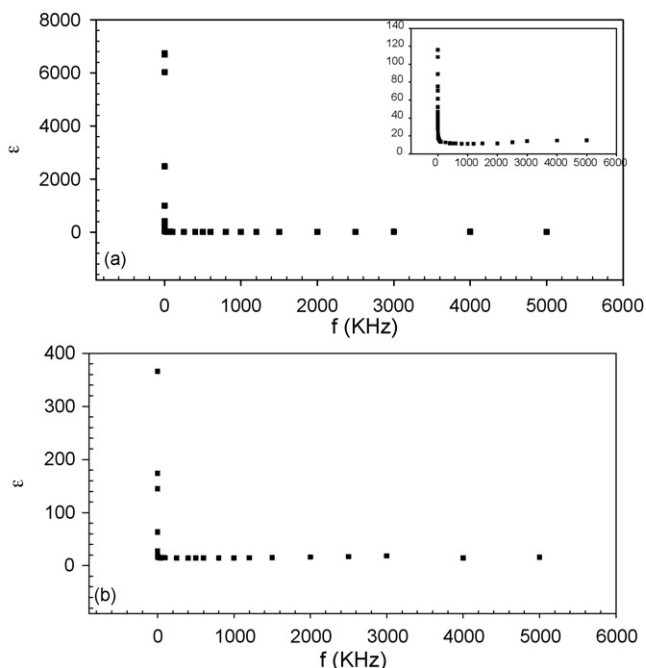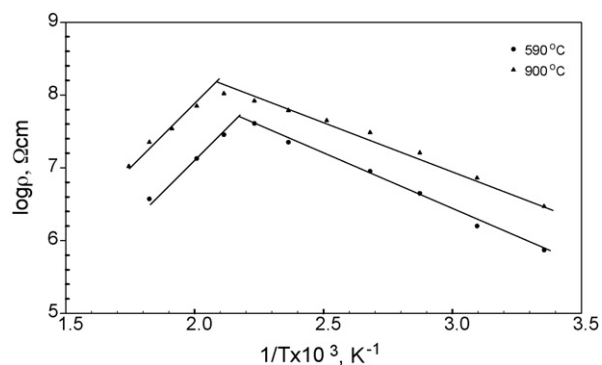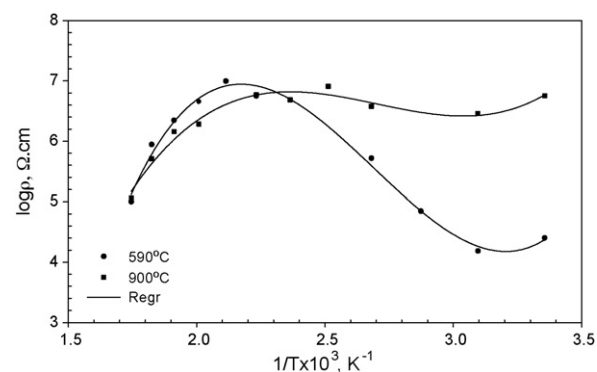

Fig. 5. Variation of dielectric constant as a function of frequency at 50 °C for specimen GK after ion exchange with silver and reduced at (a) 590 °C for 1/2 h and (b) 900 °C for 1 h.
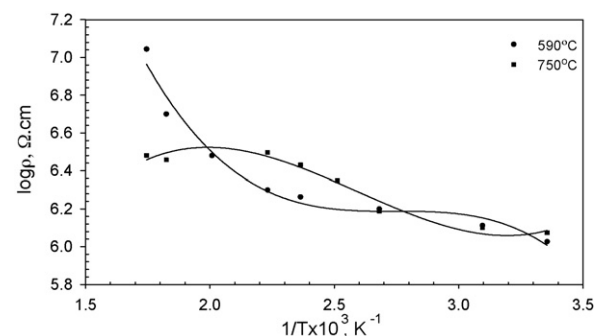

Fig. 8. Variation of resistivity as a function of temperature for specimen GNKL reduced at different temperatures.

The activation energy calculated by Arrhenius formalism reveals at least two activation energies. One between 25 °C (298 K) and 175 °C (448 K) (metallic region) which is in the range from 0.5×10^{-4} to 3×10^{-4} eV, while the other is between 175 and 300 °C (573 K) (semiconducting region) and is in the range 1.5×10^{-4} to 3.3×10^{-4} eV. The detected activation energy is very small indicating transport by electron tunneling.

As shown from Figs. 6–8, it is evident that the resistance level is in direct relation with the heat-treatment. This result is consistent with the fact that, increasing heat-treatment decreases the pore diameter [36,37] which in turn gives rise to nanowires of smaller diameter. It has been reported earlier that silver–glass nanocomposite containing silver particle with diameter of 3 nm showed an electric conductivity less than Mott's minimum metallic conductance [35,38].

The values of measured resistivity for the samples before ion exchange ranges from 10^8 to 10^{10} Ω cm^2, while for nanocomposite samples, they range from 10^4 to 10^8 Ω cm^2 which shows metallic or semiconducting behavior according to the reduction treatment given to the specimen and to the amount of K$^+$ ions present in the specimen. It is noticed that inducing surface conductivity arises from the percolation of the silver metallic phase in the glass–crystal boundary region. The glass–crystal interface is believed to act as heterogeneous nucleation sites [39]. Thus it becomes easier for the metal phase to percolate through the insulating medium and generate higher surface conductivity values.

Comparing the values of resistivity in the whole range of temperature, it can be clearly seen that GK (containing large ratio of potassium) have the least values of resistivity. This is in accordance with the results mentioned above, which indicates that the amount of silver precipitated in GK is larger than the amount of silver in GN and GNKL. Therefore, the K$^+$ ions play an important role on the silver ion exchange process and the conductivity of these glasses.

4. Conclusions

Nanoparticles of silver have been grown within a silicate glass via modification of ion exchange process. Particle sizes ranges from 4 to 10 nm. The amount of silver ions exchanged varied according to type and amount of alkali on fluoramphibole compositions. The silver ion prefers to exchange with K$^+$ ions than with Na$^+$ and Li$^+$ ions. As the amount of K$^+$ ions increases from GN, GNKL and GK samples, respectively, the amount of ion exchange with silver increases and accordingly the amount of precipitated silver metals increases.

The composites show low values of dielectric permittivity (10–30) due to the formation of interconnected metal nanoparticle chains. The resistivity of the specimen dropped from 10^8 to 10^{10} Ω cm^2 to 10^4 to 10^8 Ω cm^2 after ion exchange nanocomposite which shows metallic and semiconducting behavior according to the reduction temperature.

References

[1] W. Holand, G. Beall, Glass-ceramic Technology, first ed., The Amer. Ceram. Soci., Westerville, OH, 2002.
[2] I.L. Denry, J.A. Holloway, J. Dent. Mater. 20 (2004) 213–219.
[3] A.A. Omar, E.M.A. Hamzawy, M.M. Farag, Ceram. Int. 35 (2009) 301–307.
[4] W.A. Deer, R.A. Howie, J. Zussman, Rock forming minerals, in: Double-chain Silicates, Longman Scientific & Technical, New York, 1999, pp. 692.
[5] R. Oberti, J.M. Caballero, L. Ottolini, S. Lopez-Andres, V. Herreros, Am. Mineral. 85 (2000) 578–585.
[6] J.M. Caballero, R. Oberti, L. Ottolini, Am. Mineral. 87 (2002) 976–982.
[7] E.M.A. Hamzawy, C. Leonelli, Glass Technol. 48 (2007) 316–321.
[8] D. Chakravorty, S. Basu, P.K. Mukherjee, S.K. Saha, B.N. Pal, A. Dan, S. Bhattacharya, J. Non-Cryst. Solids 352 (2006) 601–609.
[9] H. Fan, K. Yang, D.M. Boye, T. Sigmon, K.J. Malloy, H. Xu, G.P. Lopez, C.J. Brinker, Science 304 (2004) 567.
[10] H. Chik, J. Liang, S.G. Clontier, N. Kouklin, J.M. Xu, Appl. Phys. Lett. 84 (2004) 3376.
[11] T.W. Kim, T. Kawazoe, S. Yamazaki, M. Ohtsu, T. Sekiguchi, Appl. Phys. Lett. 84 (2004) 3358.
[12] S. Eliezer, N. Eliaz, E. Grossman, D. Fisher, I. Gouzman, Z. Henis, S. Pecker, Y. Horovitz, M. Fraenkel, S. Maman, Y. Lereah, Phys. Rev. B 69 (2004) 144119.
[13] G. Lakshminarayana, J. Qiu, J. Alloys Compd. 478 (2009) 630–635.
[14] H. Chik, J. Liarg, S.G. Clontier, N. Kouklin, J.M. Xu, Appl. Phys. Lett. 84 (2004) 3376.
[15] P. Dutta, A. Manivannan, M.S. Seehra, N. Shah, G.P. Hffman, J. Appl. Phys. 99 (2006), 08H105.
[16] D. Chakravorty, S. Basu, B.N. Pal, P.K. Mukherjee, B. Ghosh, K. Chatterjee, A. Bose, S. Bhattacharya, A. Banejee, Bull. Mater. Sci. 31 (2008) 263.
[17] S. Banerjee, A. Dan, D. Chakravorty, J. Mater. Sci. 37 (2002) 4261.
[18] P.K. Mukherjee, D. Dutta, S. Battacharyy, A. Ghosh, D. Chakravortya, J. Phys. Chem. C 111 (2007) 3914.
[19] P.K. Mukherjee, D. Chakravortya, J. Mater. Res. 17 (2002) 3127.
[20] A. Dan, B. Satpati, P.V. Satyam, D. Chakravortya, J. Appl. Phys. 93 (2003) 4794–4800.
[21] M. Boscaa, L. Popa, G. Borodib, P. Pascutaa, E. Culeaa, J. Alloys Compd. 479 (2009) 579–582.
[22] H.Y. Koo, J.H. Yi, Y.C. Kang, J. Alloys Compd. 489 (2010) 456–460.
[23] B.N. Pal, D. Chakravorty, Sens. Actuators B 114 (2006) 1043–1051.
[24] M.A. Fiori, M.M. da Silva Paula, A.M. Bernardin, H.G. Riella, E. Angioletto, Mater. Sci. Eng. C 29 (2009) 1569–1573.
[25] N.J. Coleman, A.H. Bishop, S.E. Booth, J.W. Nicholson, J. Eur. Ceram. Soc. 29 (2009) 1109–1117.
[26] T. Ziegler, A. Neubrand, S. Roy, A. Wanner, R. Piat, Compos. Sci. Technol. 69 (2009) 620–626.
[27] E.M.A. Hamzawy, S.A.M. Abdel-Hameed, Crystallization of triplet alkalies (Li, K, Na)-containing fluorrichterite glasses, Ceram. Int. 35 (2009) 2139–2144.
[28] H. Scholze, Glass, Structure and Properties, Springer Verlag, New York Inc., 1991.
[29] H.R. Shell, J.E. Comefero, Eitel, U. S. Bureau of Mines, 4517, 1958.
[30] R.W. Charles, Am. Mineral. 60 (1975) 367–374.
[31] M.J. Rice, J. Bernasconi, Phys. Rev. Lett. 29 (1972) 113–116.
[32] V.C. Veeranna Gowda, R.V. Anavekar, Solid State Ionics 176 (2005) 1393–1401.
[33] S. Muthupari, S. Lakshmi Raghavan, K.J. Rao, J. Phys. Chem. 100 (1996) 4243.
[34] S. Banerjee, D. Chakravorty, Appl. Phys. Lett. 72 (1998) 1027.
[35] K. Chatterjee, S. Banerjee, D. Chakravorty, Phys. Rev. B 66 (2002) 085421.
[36] G.W. Scherer, S. Clas, R. Sempere, J. Non-Cryst. Solids 240 (1998) 118–130.
[37] Z.J. Li, C.R. Liu, Q.S. Zhao, J. Non-Cryst. Solids 265 (2000) 189–192.
[38] S. Bhattacharryya, S.K. Saha, D. Chakravorty, Appl. Phys. Lett. 77 (2000) 3770.
[39] G.C. Das, T.K. Reddy, D. Chakravorty, J. Mater. Sci. 13 (1978) 2211.