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Conductivity of composite calcium fluoride–silica solid electrolytes

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Abstract

Calcium fluoride based composites containing 1 to 15 $^{m}\!/\!_{o}$ SiO_2 disperse phase were prepared. The electrical conductivity of the samples was measured in the temperature range 400–700°C by both the d.c. four-probe and the impedance spectroscopy method. The conductivity values for the samples with SiO_2 in the range 1 to 10 $^{m}\!/\!_{o}$ were significantly higher than those of pure CaF_2 and they were dependent on the preparation method of the sample. The maximum conductivity values were observed for 5.0 $^{m}\!/\!_{o}$ SiO_2 content. The ($CaF_2 + SiO_2$) composites appeared to be purely ionic conductors. The materials prepared were applied as electrolytes in solid-state oxide galvanic cells. In this way the Gibbs free energy of formation of calcium silicates, $CaSiO_3$ and Ca_2SiO_4, at 700°C was determined. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved

Keywords: Conductivity; $CaF_2 + SiO_2$; Solid electrolytes

1. Introduction

Calcium fluoride, CaF_2, has been extensively used as a solid electrolyte to measure fluorine chemical potentials at high temperatures, and thus, to determine the Gibbs free energies of formation of metal fluorides, oxides, carbides and sulfides [1,2]. From an electrical properties point of view CaF_2 belongs to the best known and widely studied materials. Measurements indicated that its electrical conductivity is purely ionic and fluorine ion transport may be effected by both vacancy and interstitial mechanism [3]. Its ambient and moderate temperature conductivities are relatively low (e.g. $10^{-8}\ \Omega^{-1}\,cm^{-1}$ at 500°C) [3]. That is a limitation of the use of CaF_2 as a practical electrolyte for low temperature operations. Numerous papers report significant enhancement in ionic conductivity by the dispersion of fine insulating and insoluble oxide particles into an ion conductor phase [4–6]. These so-called dispersed solid electrolyte systems or composite solid electrolytes are interesting materials for solid state technology.

Our previous work concerned the $CaF_2 + Al_2O_3$ composite electrolytes [7]. This work, however, was initiated to study the ceramic samples of CaF_2 containing SiO_2 as a disperse phase. No systematic investigation on this system has been reported, to date. In the present work SiO_2 was introduced in CaF_2 in two ways: as a commercial fumed silica powder and as an organic precursor, tetraethyl orthosilicate (TEOS), $(C_2H_5O)_4Si$. The purpose of our investigation was to examine, how the presence of SiO_2 heterophase in CaF_2 matrix would influence electrochemical properties of the composite prepared.

2. Experimental

2.1. Preparation and characterization of the materials

The material used as a dispersoid for enhancing ionic conductivity should be chemically inert with respect to a matrix. In order to decide if SiO_2 reacts with CaF_2, appropriate thermodynamic calculations have been performed. The potential reaction would cause the growth of an insulating CaO layer in the grain boundaries of CaF_2, and decrease its electrical conductivity. Moreover, SiF_4 as a gaseous reagent of the reaction would generate pores in the specimen during sintering, and decrease the mechanical strength of the material. The calculations indicated that at 1 atm partial pressure of SiF_4 the reaction of SiO_2 with CaF_2 would be able to proceed at temperatures higher than 2530°C. However,

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the calculated equilibrium SiF_4 partial pressure at 1000°C assumes a very small value, 2.43×10^{-11} atm. Thus, it can be concluded that the reaction should not occur if SiF_4 gas is not continuously removed from the reaction environment. It is worth mentioning that the quasi-binary CaF_2-SiO_2 system shows complete immiscibility of its components [8]. Thermodynamics of the interaction of CaF_2 with moisture and oxygen in surrounding atmosphere has already been discussed by us [7]. Heat treatment of CaF_2 must be performed in a dry, inert gas, with low levels of impurity.

In the present work two preparation methods were used. In the first, the starting substances were commercial ultrapure anhydrous calcium fluoride (Merck) and fumed silica (Degusa, a trademark: Aerosil) powders. Appropriate amounts of CaF_2 and SiO_2 (previously dried at 250°C for 6 h) were weighed and dry mixed in an agate mortar. The resulting powders were uniaxially pressed at 350 MPa. Cylindrical pellets thus obtained were 12 mm in diameter and 2 mm in thickness. The pellets were placed in a quartz-glass support and sintered under dried argon at 1000°C for 2 h. Seven preparations containing 0, 1.0, 2.0, 3.0, 5.0, 10.0 and 15.0 $^{m}/_{o}$ were obtained in this way. In the second method as a source of SiO_2 an organic precursor, tetraethyl orthosilicate $(C_2H_5O)_4Si$ (Merck p.a., a trademark: TEOS) was used. First a suspension of CaF_2 in a solution of TEOS in ethyl alcohol was obtained. Then silica gel in the solution via TEOS hydrolysis at 50°C was prepared. The resulting slurry was dried, ground and pulverized. The powder was pelletized and then isostatically pressed under pressure of 350 MPa. The pellets were sintered at 1000°C for 2 h. Six preparations of different SiO_2 content: 1.0, 2.0, 3.0, 5.0, 10.0 and 15.0 $^{m}/_{o}$ were prepared in this way. The sintered samples were examined by X-ray diffraction and scanning electron microscopy.

2.2. Electrical conductivity

A simple d.c. four-probe method was applied for determining of electrical conductivity. Its application to the conductivity measurements of an ionic conductor was described in Ref. [9]. Four platinum wires were wrapped around the regular shape of 10×5×3 mm cut from the appropriate pellet. A small current was passed between the outer probes in both directions and the potential between the inner probes was measured. The electrical conductivity was calculated directly from the measured resistance and from the dimensions of the sample. The measurements were performed in the temperature range of 400–700°C. Another method used was impedance spectroscopy. The bridge systems Tesla 507 and Tesla 508 were used over a frequency range 500 Hz to 100 MHz. Both faces of the pellet were polished on SiC paper, washed in acetone, dried and then sputtered with Pt in a vacuum chamber. Electrical contacts were made via Pt wires connected with the platinized outer surfaces of a pellet. Each sample was held under slight spring tension in a conductivity cell. Then the dry argon was passed through the cell. The measurements were made in the temperature range 400–700°C.

2.3. E.m.f. measurements

The samples were tested as electrolytes in solid-state galvanic cells, which may be shown schematically:

$$\mathrm{Pt|Ni,\ NiO|(CaF_2+SiO_2)|Cu_2O,\ Cu|Pt} \tag{1}$$

$$\mathrm{Pt|O_2|CaO|(CaF_2+SiO_2)|CaSiO_3,\ SiO_2|O_2|Pt} \tag{2}$$

$$\mathrm{Pt|O_2|CaO|(CaF_2+SiO_2)|Ca_2SiO_4,\ CaSiO_3|O_2|Pt} \tag{3}$$

From the e.m.f. of cell (1) a contribution of the ionic conductivity in the (CaF_2+SiO_2) samples was determined. A similar type of a galvanic cell involving $(CaF_2+Al_2O_3)$ composites was investigated by us previously [7]. The two-phase mixtures (Ni, NiO) and (Cu_2O, Cu) with known equilibrium oxygen partial pressures (p_{O_2}) were used as the half-cells (1). If an electrolyte separating both the half-cells has pure ionic conduction and only one kind of ion is transported, the e.m.f. (E_t) of the cell (1) under thermodynamic equilibrium is given by the Nernst equation:

$$E_t=\left(\frac{R\times T}{4\times F}\right)\times\ln\left(\frac{p_{O_2}(\mathrm{Cu,\ Cu_2O})}{p_{O_2}(\mathrm{Ni,\ NiO})}\right) \tag{4}$$

In the case of an electrolyte which contains two (or more) mobile charged species, the e.m.f. of the cell (1) can be expressed as:

$$E=t_i\times E_t \tag{5}$$

where t_i denotes an effective ionic transference number of ions in the sample under study.

Taking the respective E_t values from Ref. [10], the ion transference numbers in the (CaF_2+SiO_2) samples were determined on the basis of e.m.f. measurements of the cell (1). Knowing these ion transference numbers, the e.m.f. of cells (2) and (3) were measured and the standard Gibbs free energy of formation of the calcium silicates, $CaSiO_3$ and Ca_2SiO_4, was calculated. The e.m.f. measurements were performed at 700°C. The details of the experimental procedures were similar to those described in Ref. [10] (for cell 1) and in Ref. [11] (for cells 2 and 3).

3. Results and discussion

3.1. Characterisation of the composites

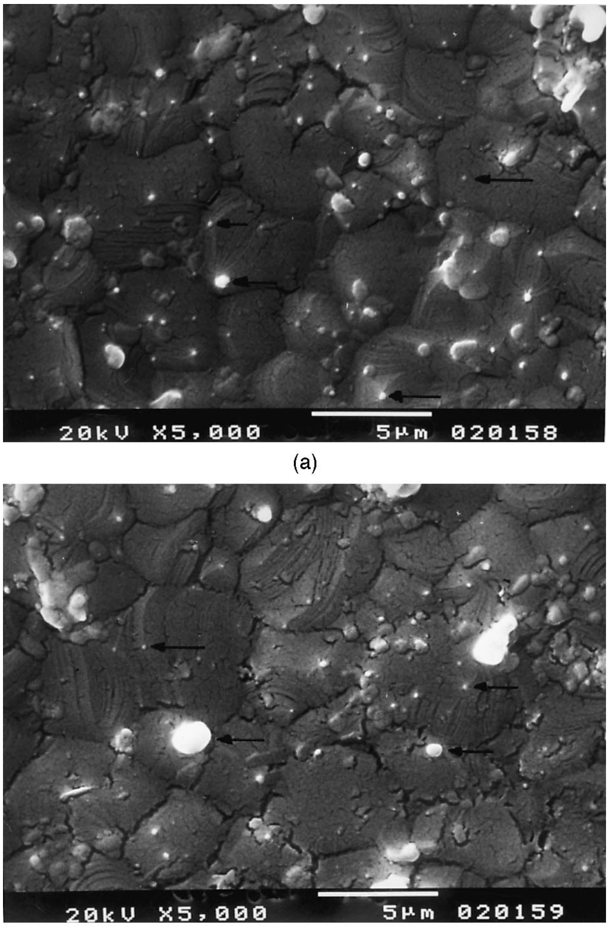
X-ray diffraction analysis of all samples shows that no reaction has taken place between CaF_2 and SiO_2 powders during their sintering. In the samples obtained from the mixture of CaF_2 and fumed silica powders most of the SiO_2 inclusions occur as a quartz phase and the rest as crystobalite. On the contrary, mainly crystobalite and only a small amount of quartz phase are present in samples prepared with the use of TEOS reagent. Fig. 1a and b illustrates typical SEM microstructures of the composites obtained by the two methods. Some SiO_2 inclusions detected by the EDS technique are indicated by arrows. It can be seen that in both cases the grains of the CaF_2 matrix have regular shapes and sizes of about 5 μm. The SiO_2 grains also have regular shapes and exhibit a nearly uniform distribution among the matrix grains. The distributions of SiO_2 grain sizes whose microstructures are presented in Fig. 1a and b, are shown in Fig. 2a and b, respectively. The average size of SiO_2 grains in the sample prepared using fumed silica powder is about 0.25 μm. The distribution of the SiO_2 inclusion in the sample prepared using TEOS is similar to the previous one but the average size of the SiO_2 grains, 0.15 μm, is distinctly smaller than those of the samples prepared using fumed silica. In both cases the inclusions larger than 1.2 μm are not observed.

3.2. Electrical conductivity

In solid electrolytes the electrical conductivity, σ, generally obeys the Arrhenius equation:

$$\sigma \times T = A \times \exp\left(\frac{-E_{\mathrm{a}}}{R \times T}\right) \qquad (6)$$

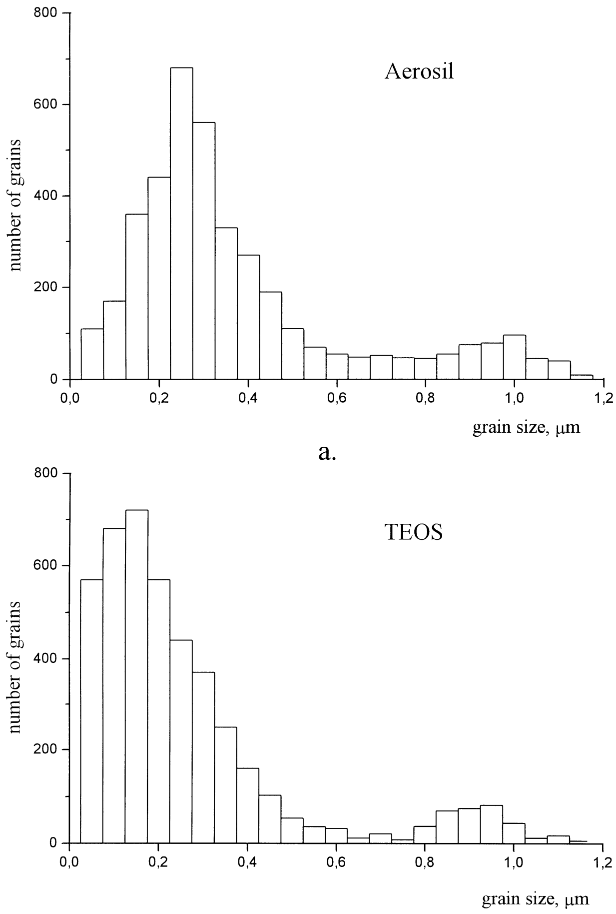
where T is absolute temperature, E_{a} is the activation energy and R is the gas constant. A is called the pre-exponential factor. It is dependent on a defect structure



(a)

(b)

Fig. 1. Microstructure of the (CaF_2+SiO_2) composite containing 5.0 m/o SiO_2 prepared (a) from the CaF_2 and fumed silica mixture, and (b) by the use of TEOS.



a.

b.

Fig. 2. SiO_2 inclusion size distribution for the (CaF_2+SiO_2) composite containing 5.0 m/o SiO_2 prepared (a) from the CaF_2 and fumed silica mixture, and (b) by the use of TEOS.

in a solid electrolyte and related to a conduction mechanism [12].

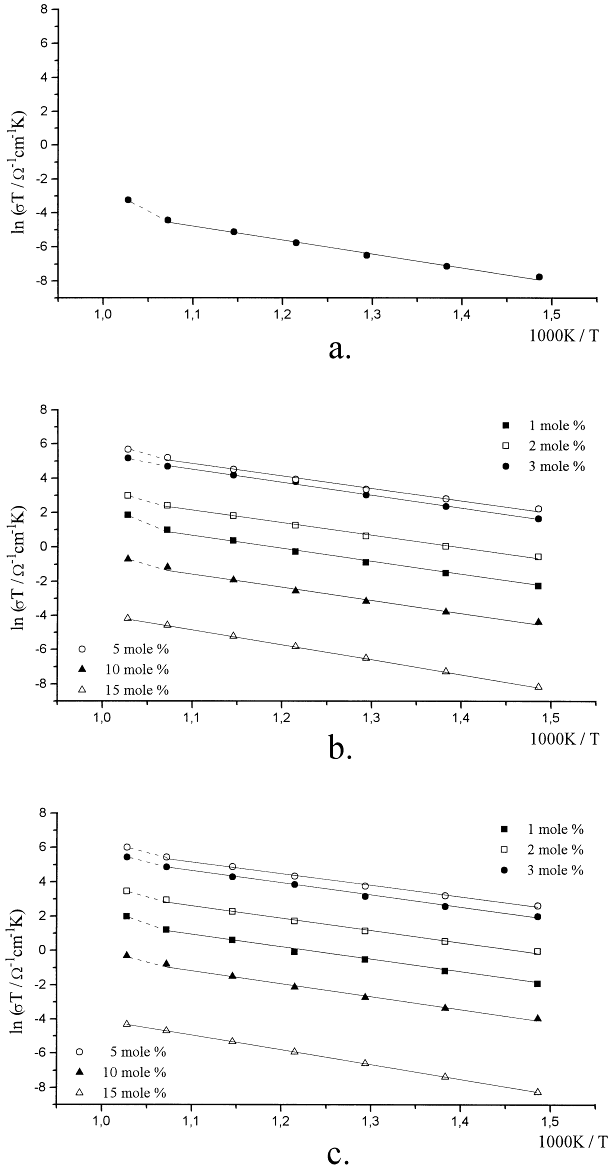
As it results from the Arrhenius equation, an increase in A or a decrease in E_a should lead to an increase in σ, but for the ionic conductors it has been shown that the two terms are often related by the Meyer–Neldel rule:

$$\ln(A) = a \times E_a + b \tag{7}$$

where a and b are straight-line coefficients.

Consequently, a decrease in E_a may not necessarily lead to an increase in σ (as it would be expected from the Arrhenius equation) due to the corresponding decrease in A in the Meyer–Neldel equation. Thus, in order to elucidate the conduction process both A and E_a should be determined from conductivity experiments.

Fig. 3a–c show the $\ln(\sigma \times T)$ vs $1/T$ plots obtained on the basis of d.c. measurements for both series of $(CaF_2 + SiO_2)$ samples as well as for the pure CaF_2, respectively. For all the samples containing up to 10 $^{\rm m}/_{\rm o}$ SiO_2 no break in the straight line, $\ln(\sigma \times T) = \ln(A) - (E_a/R \times T)$, is recognized up to temperatures above 660°C. For the pure CaF_2 the activation energy calculated for a low temperature region is equal to 67.4 kJ/mol. However, the break temperature and the activation energy for pure CaF_2 single crystal has been reported as 560°C and 86.5 kJ/mol, respectively [13]. The conductivity values at 400°C and the corresponding pre-exponential factor and activation energy values calculated for a low temperature region are given in Table 1. Because of experimental limitations we have not been able to determine conductivities over 700°C, and thus to calculate the conductivity parameters for a high temperature region. From Table 1, it can be seen that both the conductivity and the pre-exponential factor increase with composition up to 5.0 $^{\rm m}/_{\rm o}$ SiO_2 for each of two series of preparations, whereas the activation energy decreases in the same direction. The samples obtained by the method using an organic precursor exhibit higher conductivity and lower activation energy values than those of the same composition prepared from the mixture of CaF_2 and SiO_2 powders. However, the pre-exponential factor assumes comparable values for the relevant composites with equal SiO_2 content. Thus, the differences in conductivity are mainly due to those in activation energy. Fig. 4a and b show the plots of natural logarithm of A against activation energy for two series of the samples under study. Assuming Eq. (7) is valid in our case, a correlation factor for the straight line representing the Meyer–Neldel rule was calculated as 0.94 and 0.92 for each series of the samples, respectively. The influence of SiO_2 on conduction properties of the composite is illustrated by the plot of the relative total conductivity (σ/σ_0, σ_0 being the conductivity of pure CaF_2) at 400°C vs SiO_2 content (Fig. 5). The inclusion of 5.0 $^{\rm m}/_{\rm o}$ of SiO_2 causes an enhancement in the conductivity by a factor 17 200 for



a.

b.

c.

Fig. 3. The $\ln(\sigma \times T)$ vs $1000/T$ plots obtained from d.c. measurements (a) for the pure CaF_2, (b) for the samples prepared from the CaF_2 and fumed silica mixture, and (c) by the use of TEOS.

Table 1
The d.c. conductivity at $T = 400°C$ (σ_{400}), natural logarithm of the pre-exponential factor (A) and the activation energy (E_a) values for the samples prepared by two preparation methods

$^{\rm m}/_{\rm o}$ SiO_2	σ_{400} $(\Omega \times cm)^{-1}$		$\ln A/(\Omega\,cm)^{-1} \times K$		E_a (kJ/mol)	
	Fumed silica	TEOS	Fumed silica	TEOS	Fumed silica	TEOS
0	6.27×10^{-7}		4.147		67.4	
1.0	1.55×10^{-4}	2.18×10^{-4}	9.280	9.260	64.9	62.7
2.0	8.51×10^{-4}	1.45×10^{-3}	10.61	10.95	63.4	62.3
3.0	7.78×10^{-3}	1.10×10^{-2}	12.90	12.81	63.2	61.4
5.0	1.38×10^{-2}	2.06×10^{-2}	13.19	13.26	62.4	60.4
10.0	1.83×10^{-5}	2.86×10^{-5}	7.394	7.621	67.0	65.8
15.0	4.14×10^{-7}	3.84×10^{-7}	4.718	4.500	72.2	71.4

the samples in which SiO_2 has been precipitated from an organic precursor, and 11 500 for those in which SiO_2 has been introduced as a fumed silica powder.

In the second method the electrical conductivity values have been calculated on the basis of impedance measurements. The overall impedance of a polycrystalline ceramic sample may be modelled by the bulk resistivity of individual crystallites in series with impedance due to parallel resistance–capacitance effects associated with crystallite grain boundaries [14]. Data obtained by the complex impedance method may be approximated to a characteristic shape of a partial semicircle on a complex impedance plane. Fig. 6 shows impedance plots obtained at 400°C for several composites prepared using an organic precursor. In every case, two arcs separated from each other are observed. Similar plots are obtained for other series of samples. The arc at the left hand frequency side is referred to as the bulk resistance. The other one at the right hand side is related to the grain boundaries. Thus, the intersection of the left arc with the real axis is attributed to the bulk resistivity, and that of the right arc is the sum of the bulk and the grain boundary resistivity. So, both the grain boundary and the bulk conductivity of the sample under study could be calculated. The grain boundary and the bulk conductivity at 400°C as well as the corresponding pre-exponential factor and the activation energy values calculated from the Arrhenius equation for a low temperature region (400–660°C) are presented in Table 2 for both series of samples with 1.0, 2.0, 3.0 and 5.0 $^{\mathrm{m}}/_{\mathrm{o}}$ SiO_2 content. The Arrhenius plots for the samples exhibiting the highest conductivity are shown in Fig. 7. Similar plots were obtained for other samples under study. From Table 2, it can be seen that the conductivity as well as the pre-exponential factor for the grain boundary and for the bulk increase and the activation energy decreases with increasing SiO_2 content. The above results appear to be consistent with those obtained from d.c. measurements. The samples prepared via an organic precursor have both the grain boundary and the bulk conductivity values higher and the activation energy values lower than those prepared via mixing CaF_2 and SiO_2 powders. However, the relevant samples containing equal SiO_2 amount have nearly the same values of respective pre-exponential factor. The grain boundary conductivities are comparable with those for the bulk in the samples having the same composition except that one containing 5.0 $^{\mathrm{m}}/_{\mathrm{o}}$ SiO_2 obtained with the use of an organic precursor; in the latter case the grain boundary conductivity exceeds markedly that one for the bulk. However, for each sample the pre- exponential factor for the bulk assumes higher value than that for the grain boundary.

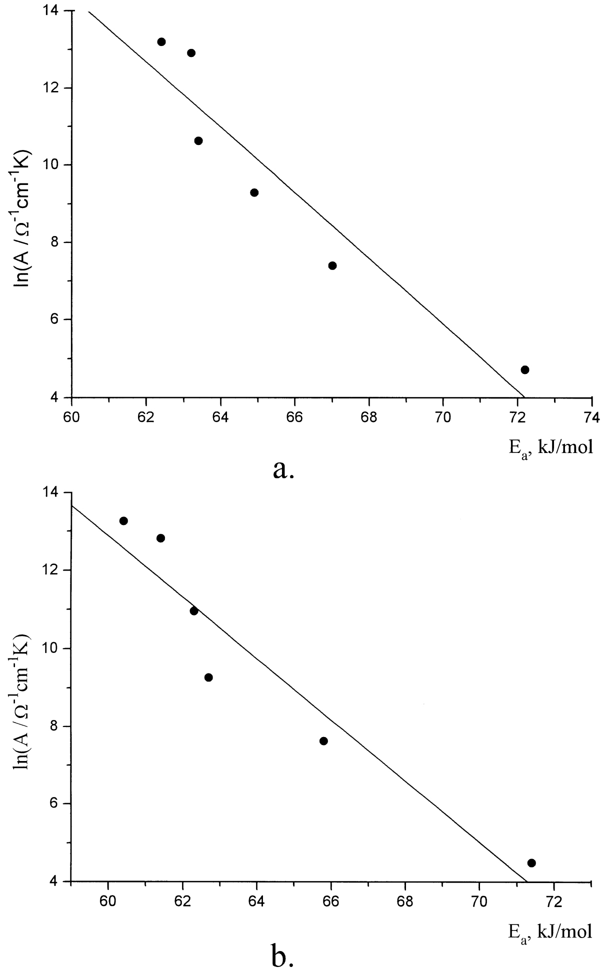


Fig. 4. The ln(A) vs E_a plots for the samples prepared (a) from the CaF_2 and fumed silica mixture, and (b) by the use of TEOS.

In order to interprete the fact of the changes in conductivity of the composites with the SiO_2 content the effect of enhanced carrier concentration within the

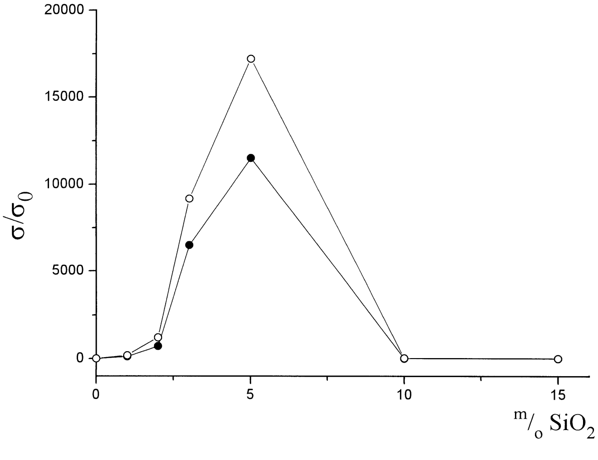


Fig. 5. The relative total d.c. conductivity (σ/σ_0, σ_0 being the conductivity of pure CaF_2) at $T=400°C$ vs the SiO_2 content: (a) the samples prepared by sintering the powders obtained by mixing of CaF_2 and fumed silica; (b) the samples prepared with the use of tetraethyl orthosilicate (TEOS) as a precursor of SiO_2.

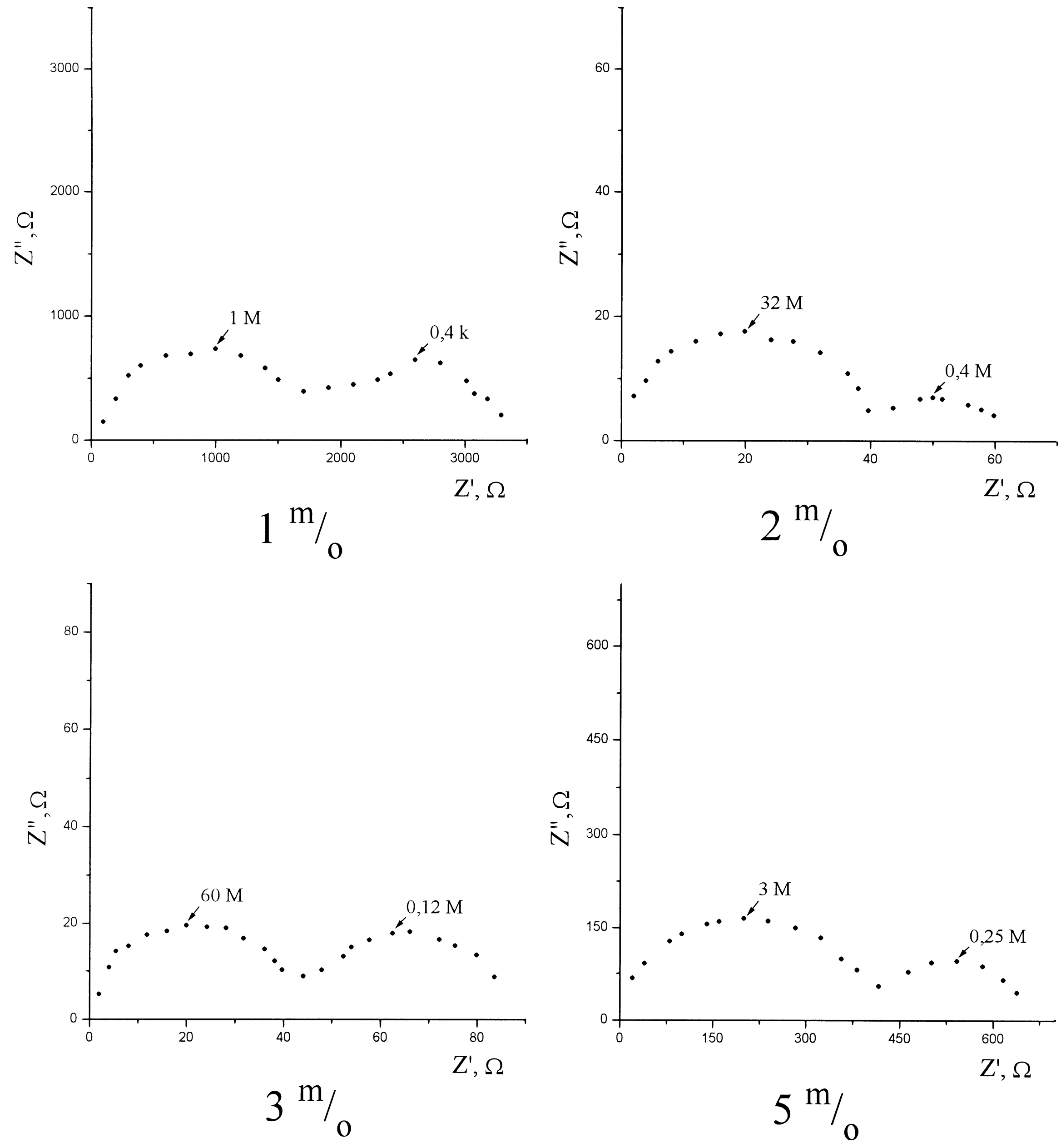


Fig. 6. Impedance plots at $T=400$°C for some samples prepared with the use of TEOS as a precursor of SiO_2, containing 1.0, 2.0, 3.0 and 5.0 ^{m}/% SiO_2.

interfacial space–charge layers, caused by a presence of particles of an SiO_2 insulating phase, may be taken into account [6]. As a result of the interaction at the interface between the ionic species in CaF_2 and SiO_2, fluorine ions will be enriched on the surface. Thus, the bulk concentration of the fluorine vacancies will increase. The vacancies there formed will provide additional conducting paths for F^- ions. As a consequence, the pre-exponential factor for the bulk should be higher than that for the grain boundary. This interpretation is consistent with our experimental results. Obviously, the activation energy for the bulk must be higher than that for the grain boundary. The activation energy for grain boundary could be related to the area of interfaces between CaF_2 matrix grains and SiO_2 particles. The conductivity of dispersed solid electrolyte systems has been found to increase with increasing volume fraction of a dispersoid [4]. The larger is SiO_2 content and the smaller is the size of SiO_2 particles, the higher is a volume fraction of the dispersoid, and thus, the larger is a total surface area available for adsorption of F^- ions. As a result, the activation energy for grain boundary should decrease with an increase in the total surface area of the SiO_2 grains. In this way, the influence of microstructure of the composite sample on its conduction properties can be explained. However, at higher concentrations the SiO_2 particles may block conduction paths in the composite, and thus, they may decrease its conductivity, as it was observed for the samples containing 10 and 15 $^m/_o$ SiO_2.

3.3. Transference number

The half-cell reactions in cell (1) are:

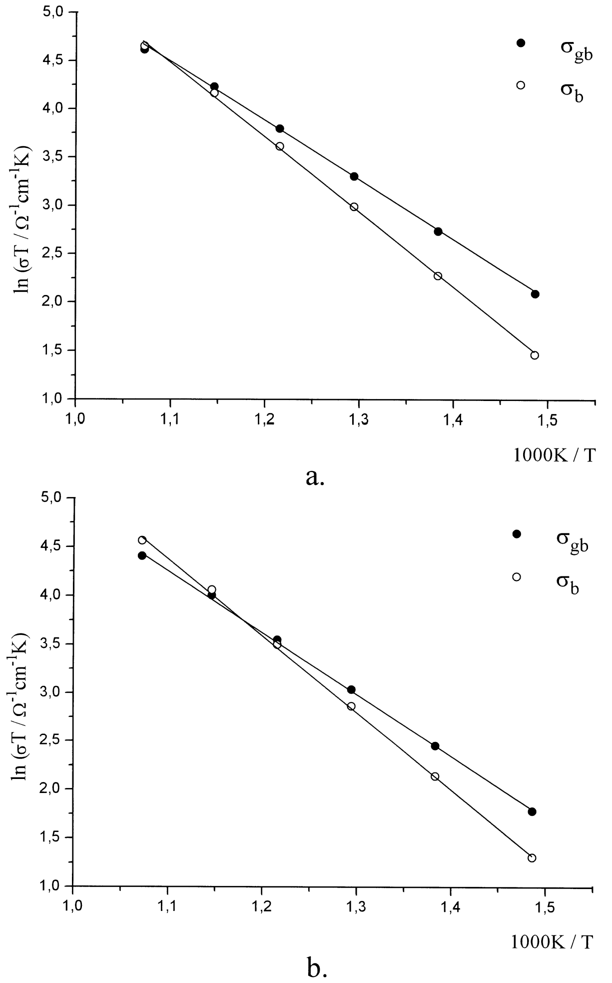
$$NiO + CaF_2 + 2e^- = CaO + Ni + 2F^- \tag{8a}$$

$$CaO + 2Cu + 2F^- = Cu_2O + CaF_2 + 2e^- \tag{8b}$$

The fluorine ions move from the right half-cell to the left one through the calcium fluoride electrolyte. For the passage of two faradays of charge, the virtual cell reaction is:

$$NiO + 2Cu = Ni + Cu_2O \tag{8}$$

The half-cell reactions (8a) and (8b) depend on the formation of CaO at the electrolyte–electrode interfaces; the CaO phase relates the oxygen activity to the calcium activity which in turn produces a defined fluorine activity. The e.m.f. measurements were performed for the samples from both series, exhibiting the highest electrical conductivities, i.e. for those containing 5 $^m/_o$ SiO_2. The values measured at 700°C were 268.3 and 262.8 mV, respectively. The measured e.m.f. (E) of the cell (1) involving calcia fully stabilized zirconia electrolyte (in which the oxygen ion transference number equals 1) amounted to 271.0 mV as reported in Ref. [10]. Thus, the fluorine ion transference numbers, calculated from formula (5), are 0.99 and 0.97 in the samples under study which implies almost exclusively ionic conduction.



a.

b.

Fig. 7. The grain boundary (σ_{gb}) and bulk (σ_b) a.c. conductivities of the ($CaF_2 + SiO_2$) sample containing 5.0 $^m/_o$ SiO_2 prepared (a) from the CaF_2 and fumed silica mixture, and (b) by the use of TEOS.

3.4. The determination of the Gibbs free energy of formation (from oxides) for $CaSiO_3$ and Ca_2SiO_4

The CaF_2 composite with the highest ionic conductivity was used as the solid electrolyte in the cells (2) and (3). The overall cell reactions are:

$$CaO + SiO_2 = CaSiO_3 \tag{9}$$

$$CaO + CaSiO_3 = Ca_2SiO_4 \tag{10}$$

respectively. Reaction (9) describes $CaSiO_3$ formation (from CaO and SiO_2) whereas the formation of Ca_2SiO_4 from its respective oxides is derived from the sum of reactions (9) and (10):

$$2CaO + SiO_2 = Ca_2SiO_4 \tag{11}$$

Table 2
The conductivity at $T = 400°C$ (σ_{400}), natural logarithm of the pre-exponential factor (A) and the activation energy (E_a) in the temperature range 400–660°C for grain boundary (gb) and for bulk (b) for the samples prepared by two methods

$^m/_o$ SiO_2	σ_{400} $(\Omega\times cm)^{-1}$		ln $A/(\Omega\times cm)^{-1}\times K$		E_a (kJ/mol)	
	gb	b	gb	b	gb	b
Fumed silica						
1.0	8.5×10^{-5}	8.3×10^{-5}	7.380	9.843	57.3	69.2
2.0	4.4×10^{-4}	4.7×10^{-4}	8.756	11.06	55.8	68.3
3.0	2.9×10^{-3}	3.5×10^{-3}	10.57	12.94	55.4	67.6
5.0	8.8×10^{-3}	5.5×10^{-3}	11.29	13.10	53.2	65.9
TEOS						
1.0	1.4×10^{-4}	1.2×10^{-4}	7.557	9.530	55.5	67.4
2.0	7.3×10^{-4}	5.1×10^{-4}	8.905	10.91	53.8	67.0
3.0	5.6×10^{-3}	5.3×10^{-3}	10.69	13.09	52.4	66.1
5.0	1.2×10^{-2}	6.4×10^{-3}	11.25	13.03	51.2	64.6

Table 3
The standard Gibbs free energies of formation (from oxides), $\Delta_f G^0(i)$, for calcium metasilicate, $CaSiO_3$, and calcium orthosilicate, Ca_2SiO_4, at $T = 700°C$

Reference	$\Delta_f G^0(CaSiO_3)$ (kJ/mol)	$\Delta_f G^0(Ca_2SiO_4)$ (kJ/mol)
This work	89.0	134.0
[7]	89.0	–
[11]	89.7	135.1
[15]	88.8	135.6

Taking into account that the the respective standard molar Gibbs free energies of reactions (9) and (10) are connected with the e.m.f. of cells (2) and (3), the standard Gibbs free energies of the calcium silicates formation (from oxides), $\Delta_f G^0(CaSiO_3)$ and $\Delta_f G^0(Ca_2SiO_4)$ can be calculated on the basis of the e.m.f. values according to the equations:

$$\Delta_f G^0(CaSiO_3) = -2 \times F \times E_2 \tag{12}$$

$$\Delta_f G^0(Ca_2SiO_4) = -2 \times F \times (E_2 + E_3) \tag{13}$$

In Table 3 the respective $\Delta_f G^0$ values at 700°C are in good agreement with other published data [7,11,15].

4. Conclusions

The ionic conductivity of CaF_2 is enhanced by the introduction of silica as a disperse phase. The samples in which SiO_2 was deposited from an organic precursor exhibited higher electrical conductivities than those of the same composition, prepared by direct sintering of the mixture of CaF_2 and SiO_2 powders. The conductivities appeared to be almost purely ionic with a strong dependence on the SiO_2 content. An increase in conductivity up to four orders of magnitude was observed for both series of samples. Although the materials prepared were fluorine ion conductors, they were applied successfully for solid-state galvanic cells involving calcium silicates. In this way the applicability of the CaF_2 based composites for thermodynamic investigations of oxide systems was demonstrated.

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