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Some physical properties of anhydrous and hydrated Brownmillerite doped with NaF

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Abstract

Different samples of Brownmillerite (the ferrite phase of cement clinker) doped with 0, 1 or 3 wt.% NaF were prepared. At first, the oxide mixture of Brownmillerite was prepared according to the following composition: 4 mol CaO, 1 mol Al_2O_3 and 1 mol Fe_2O_3 in addition to 1 or 3 wt.% NaF. Each mixture was mixed very well, introduced into an electric furnace at 1300 °C for 1 h in a platinum crucible, and then quenched in air. The product was divided into four portions mixed with 40 wt.% distilled water to form Brownmillerite paste, except for one portion which was left dry. Each paste was molded into two molds; after 24 h, they were immersed in a distilled water and withdrawn after 1 or 3 days of hydration, respectively. The pastes were ground again. The anhydrous powders of Brownmillerites and the hydrated samples were prepared for a.c. conduction measurements by pressing it to be in pellets form. The two surfaces of each pellet were coated with silver paste. The a.c. conductivity and dielectric constant for different samples were measured using four-probe method. The data was collected from 320 up to 670 K. Mössbauer spectra and X-ray diffraction patterns were measured for each sample (anhydrous and hydrated) to confirm the formation of Brownmillerite, identify the iron states and the magnetic properties. The results showed that NaF addition to Brownmillerite expedites the hydration reaction rate. The superparamagnetic relaxation, which appeared in the anhydrous Brownmillerite spectra due to the small particle size, decreases with increasing the hydration time. Also, the Fe^{3+}(Oh) state increases while Fe^{3+}(Td) decreases with the time of hydration. The a.c. conductivity value at fixed frequency for anhydrous and hydrated samples was found to increase with NaF addition. The a.c. conductivity and Mössbauer measurements can be used as good tools to verify the purity of Brownmillerite phase and, accordingly, the purity of cement.

Keywords: Mössbauer; Brownmillerite; Physical properties

1. Introduction

Portland cement is composed of a number of compounds whose reaction with water leads to the setting and hardening of the cement [1], through which these compounds are all attacked or decomposed forming hydrated compounds.

Although the ferrite phase in Portland cement, which is called Brownmillerite, is not necessarily C_4AF[1] as such, but solid solution of composition lying between C_6AF_2 and C_6A_2F, the hydration behaviour of the ferrite phase is typified by that of the C_4AF composition. When mixed with water, hexagonal-plate crystals occur mostly as foliated masses. Hydration of C_4AF in the presence of sulphate and of calcium ions, as in the case of hardening cement paste, may differ considerably.

The presence of fluorides in cement influences the mechanism of C_3S and C_2S formation in the cement clinker. As CaF_2 doping in cement clinker was increased, the phase C_3A is gradually replaced by the phase $C_{11}A_7{\cdot}CaF_2$, while the β- to γ-C_2S polymorphic transition is enhanced and the average particle size of the clinker minerals decreases [2]. Hassaan et al. [3] found that doping impurities produces small particle size, in particular LiF doping, which gave the smallest particle size and, hence, the highest blocking temperature. The structure and properties of Portland cement clinker doped with zinc oxide was studied by Odler and Schemidt [4]. Shortly, Mössbauer effect was applied in different investigations in cement and its phases [5–22].

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[1] Cement nomenclature: C = CaO, S = SiO_2, A = Al_2O_3 and F = Fe_2O_3.

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Wittmann et al. [13] made the earliest investigation about the cement by Mössbauer effect; they established a new method to estimate the degree of hydration of cement. Vertes et al. [14] studied the hydrated Brownmillerite at different times of hydration. Tamas and Vertes [15] concluded that the hydration of the Brownmillerite can be easily studied by Mössbauer effect, due to the significant difference existing between the spectra of anhydrous and hydrated Brownmillerite. Harchand et al. [16,17] also studied the hydration of calcium aluminoferrite phase of cement clinker. Hassaan and Eissa [18] made a review article on the applications of Mössbauer effect in cement studies over the period 1965–1984. Ekimov et al. [19] studied the Mössbauer spectra of solid solutions of calcium aluminoferrites; they revealed that, below the Néel temperature, there are two iron states existing in the spectra; each one showed six absorption lines characterizing ferric iron in octahedral and tetrahedral coordinations. Above the Néel point, the spectra showed that two quadrupole-splitting doublets have the same coordinations, which are mentioned above. Eissa et al. [20] followed up the iron states in cement pastes during the hydration process using Mössbauer effect. They demonstrated the possibility of the determination of the degree of hydration using Mössbauer technique. As impurities inside the ferrite phase of cement clinker, the alkalis were studied also by Hassaan et al. [21] using Mössbauer effect.

This work was carried out in order to elucidate the influence of doping NaF on the formation and hydration of the ferrite phase of cement clinker.

2. Experimental

The pure ferrite phase of cement clinker was prepared from a mixture composed of: 4 mol CaO + 1 mol Al_2O_3 + 1 mol Fe_2O_3. The ferrite mixtures were doped with 0, 1 or 3 wt.% NaF. All chemicals used were of high purity grade.

Each mixture was fired in a platinum crucible in an electric furnace at 1300 °C for 1 h and rapidly cooled in air. Each sample was ground and then mixed with water at room temperature. The water ratio to the C_4AF ratio was equal to 0.4. After 24 h, the samples were immersed in distilled water for 1 or 3 days of hydration. Each sample was dried and then ground and measured using X-ray diffraction and Mössbauer spectroscopy. The samples were pressed into pellets. The two surfaces of each pellet were coated with silver paste for the conductivity measurement.

X-ray diffraction measurements were done at room temperature using CuK_α radiation. The Mössbauer effect measurements were performed at room temperature using a source of Co-57 in Rh matrix and a constant acceleration transducer interfaced to a based PC-MCA; metallic iron was used for calibration. The a.c. conductivity and permittivity measurements were obtained by using RLC bridge (Stanford model SR 720 RLC Meter) at temperature range from 320 to 670 K.

3. Results and discussions

3.1. X-ray diffraction data

The C_4AF formation is confirmed by the X-ray diffraction data. As the time of hydration increased, the intensity of C_4AF peaks decreased gradually, together with the formation of hydrated compound with most intense peak that appeared at $2\theta = 29.5$. This peak increased with increasing the time of hydration. The rate of decreasing of C_4AF phase and the rate of increasing the hydrated phase were found to increase as NaF percentage increased in the C_4AF [3].

3.2. Mössbauer data

The Mössbauer spectra of the anhydrous and hydrated C_4AF (Fig. 1) and C_4AF doped with NaF (Fig. 2) gave the same general features, which represent the C_4AF of very small particle size, from 30 to 100 Å [3,22]. That is where a superparamagnetic relaxation in addition to two central doublets was observed (Figs. 1 and 2). The analyses of these doublets exhibit two phases of iron: Fe^{3+} ions in the octahedral state (Oh) having quadrupole splitting equal to 0.73 mm/s and isomer shift equal to 0.38 mm/s, while the other state of iron is the tetrahedral state (Td) having quadrupole splitting equal to 0.98 mm/s and isomer shift equal to 0.11 mm/s for the hydrated samples. These values are in agreement, with a little deviation, with that observed for hydrated cement [16,20]. This deviation may be due to the presence of C_4AF phase in these samples as a unique phase and not a solid solution of the four main phases of cement clinker, which are C_4AF, C_2S, C_3S and C_3A.

Another important feature that has been observed in the Mössbauer spectra (Figs. 1 and 2) is the gradual decrease of the intensity of Fe^{3+}(Oh) doublet as the time of hydration increased with a simultaneous increase in the intensity of Fe^{3+}(Td). The Fe^{3+}(Td)/Fe^{3+}(Oh) ratio was calculated for all the spectra and was found to be about 0.53 for the anhydrous samples and 0.33 for the 3 days hydrated samples. This gives an indication to the amount of hydration products that has been formed [12,15]. It should be noted that the parameters of the two doublets of the anhydrous samples are different than that of the hydrated samples [16,20]. The gradual decrease in the paramagnetic relaxation with increasing the time of hydration indicates a gradual growth in the particle size, which is called blocking of the product compound due to the entrance of water molecules to the crystal structure [22]. This means that when the hydration reaction comes to an end, the Fe^{3+}(Td) and the paramagnetic relaxation are expected to disappear completely [20]. It has also been observed that, as NaF content was increased up to 3 wt.%, more than 50% of the hydration reaction process of C_4AF phase took place within the first 3 days of hydration. Therefore, the increasing content of NaF in C_4AF expedites the hydration reaction rate. The para-

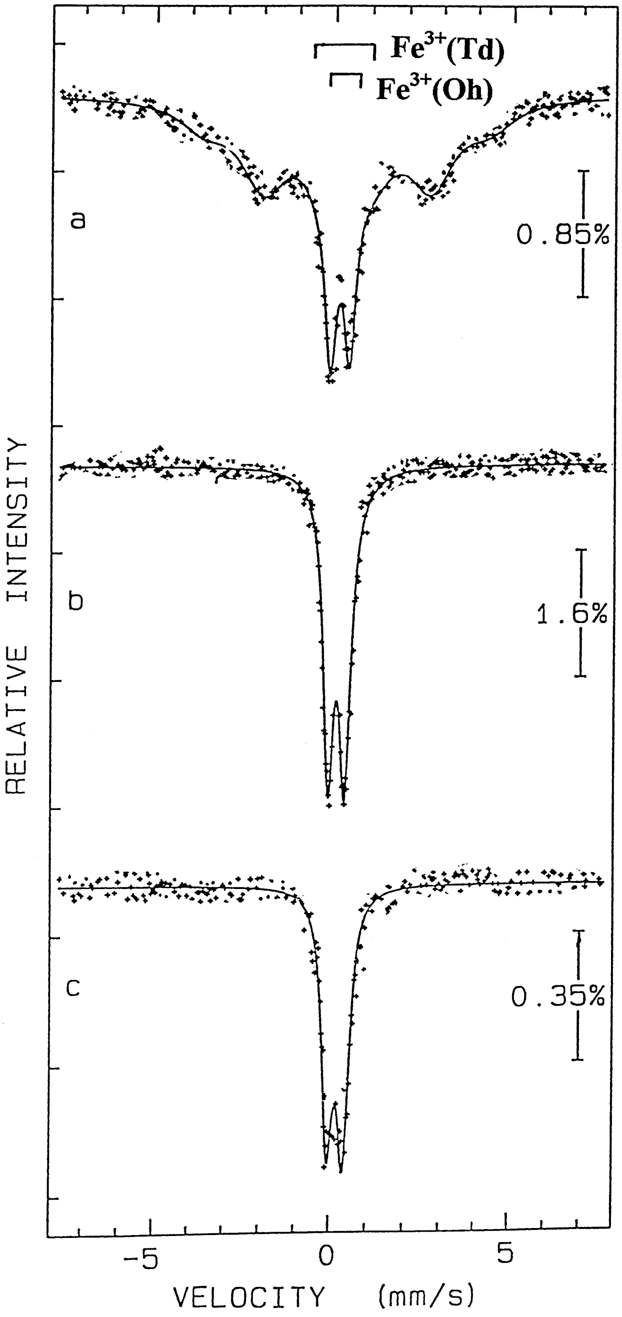

Fig. 1. Room temperature Mössbauer spectra of pure C_4AF. (a) Anhydrous, (b) hydrated for 1 day and (c) hydrated for 3 days.

magnetic relaxation will disappear on measuring the sample at blocking temperature [3,22].

3.3. a.c. conductivity data

A common feature of all semiconductors materials is the frequency-dependent conductivity $\sigma_{ac}(\omega)$, which increases almost linearly with frequency at least in the frequency range $10<\omega<10^8$ Hz, i.e.,

$$\sigma_{ac}(\omega)=\sigma(\omega)-\sigma_{dc}.$$

Where σ_{dc} is the d.c. part of the total conductivity $\sigma(\omega)$. The phenomenon has variously been ascribed to the relaxation caused by the motion of electrons or atoms, hopping or tunneling between the equilibrium sites. The complex dielectric constant of a material medium is represented by

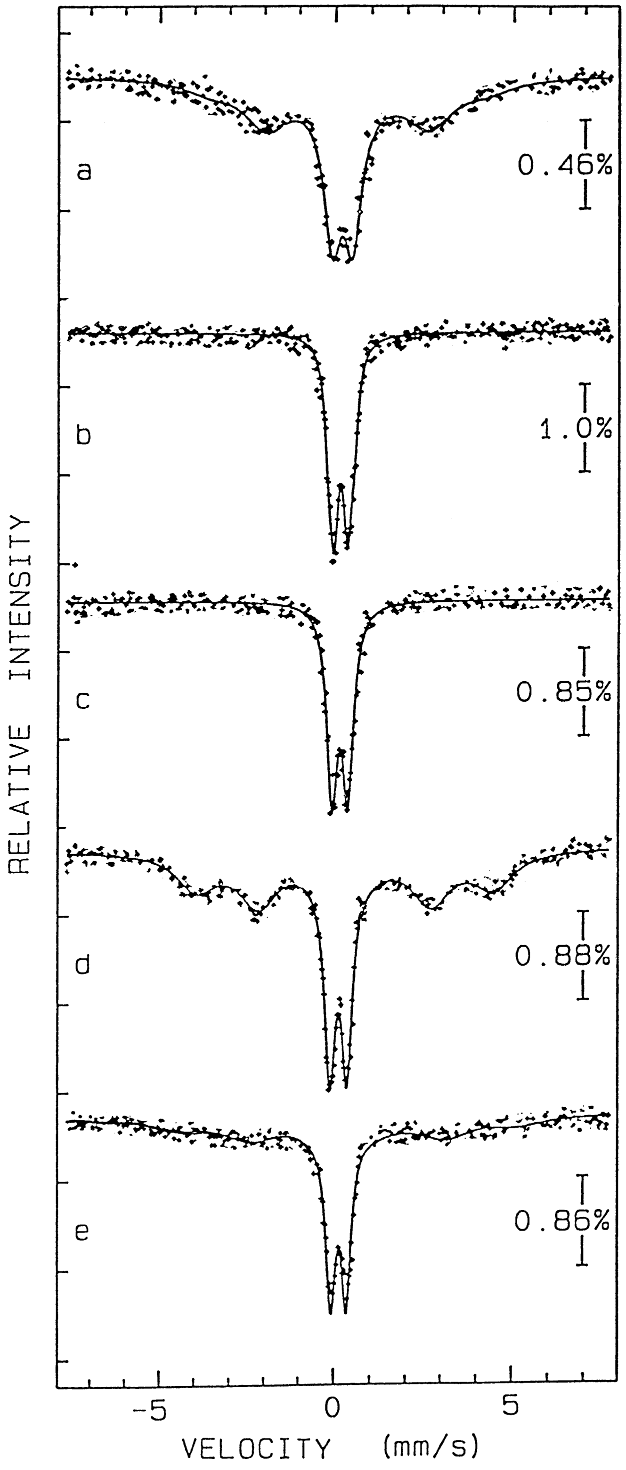

Fig. 2. Room temperature Mössbauer spectra of anhydrous and hydrated C_4AF containing different concentrations of NaF. (a) 1 wt.% NaF anhydrous, (b) 1 wt.% NaF hydrated for 1 day, (c) 1 wt.% NaF hydrated for 3 days, (d) 3 wt.% NaF anhydrous and (e) 3 wt.% NaF hydrated for 3 days.

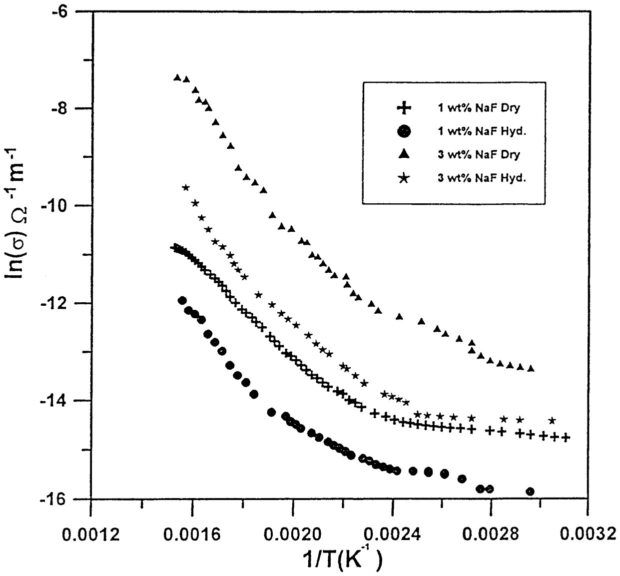

Fig. 3. Temperature dependence of a.c. conductivity at fixed frequency (1 kHz) for anhydrous and hydrated C_4AF containing different concentrations of NaF.

two parts $\varepsilon = \varepsilon' + i\varepsilon''$, where ε' is the real part (dielectric constant or permittivity) and ε'' is the imaginary part (loss). The relation between ε' and ε'' defines a dielectric loss tangent: $\tan\delta = \varepsilon''/\varepsilon'$.

The a.c. conductivity and permittivity of C_4AF and its compounds with NaF at different concentrations 1 or 3 wt.% for either anhydrous or hydrated samples are measured at room temperature up to 700 K. Generally, the d.c. conductivity σ_{dc} and a.c. conductivity σ_{ac} as a function of $1/T$ can be studied according to the following relation $\sigma = \sigma_o \exp(-w/kT)$, where σ_o is constant, w is the activation energy and k is the Boltzmann constant.

The measured temperature dependence of a.c. conductivities at fixed frequency (1 kHz) are shown in Fig. 3 in the form of ln σ vs. $1/T$ of the above compounds at concentrations 1 and 3 wt.% NaF for anhydrous and hydrated samples. It is obvious that there is a linear relation consisting of two linear sections connected by a range of transition. The transition temperature T_c between the two conduction mechanisms, as well as the activation energies for low (w_1) and high (w_2) temperatures, are calculated and listed in Table 1.

Table 1
Transition temperature and activation energy at low (w_1) and high (w_2) temperatures for C_4AF samples doped with different NaF

Sample	Transition temperature (T_c), K	Activation energy	
		w_1 (low), eV	w_2 (high), eV
1 wt.% NaF anhydrous	422	0.044	0.41
1 wt.% NaF, 3 days hydration	414	0.09	0.36
3 wt.% NaF anhydrous	428	0.15	0.57
3 wt.% NaF, 3 days hydration	408	0.036	0.43

From the above data, it was found that the investigated samples of C_4AF with different concentrations of NaF have activation energies ranging from 0.036 to 0.15 eV below T_c and from 0.36 to 0.57 eV above T_c. The observed T_c in all the samples may be attributed to a change in the lattice structure and it may be due to a change in magnetic order from the superparamagnetic state to an antiferromagnetic one [22,23]. The activation energies at lower temperatures, given in Table 1, lay around 0.1 eV for different samples. This means that, at low temperatures, there is no change in the a.c. conductivity of different samples. Above the transition temperature, the activation energies varied markedly. This means that the effect of NaF addition appears only at high temperatures.

Fig. 4 shows the relationship between ln σ vs. different concentrations of NaF in anhydrous and hydrated C_4AF. From the figure, one can observe the conductivity values of the anhydrous samples, which are more than that of the hydrated samples. This may be attributed to the growth of the particle size (blocking process) of the product compound due to the presence of water molecules in the crystal lattice. This growth decreases the ions' mobility and, accordingly, decreases the conductivity. On the other hand, the presence of water molecules in the lattice structure led to the removal of the magnetic relaxation and to the decrease of the Fe^{3+}(Td)/Fe^{3+}(Oh) ratio. This is confirmed by Mössbauer results. Whereas from Fig. 4, it was found that the increase in the conductivity by increasing NaF concentrations is attributed to the lattice holes, which are filled completely by NaF ions [21].

The temperature dependence of the permittivity ε' at different concentrations (1 and 3 wt.% NaF) at fixed frequency (1 kHz) is shown in Fig. 5. The values of

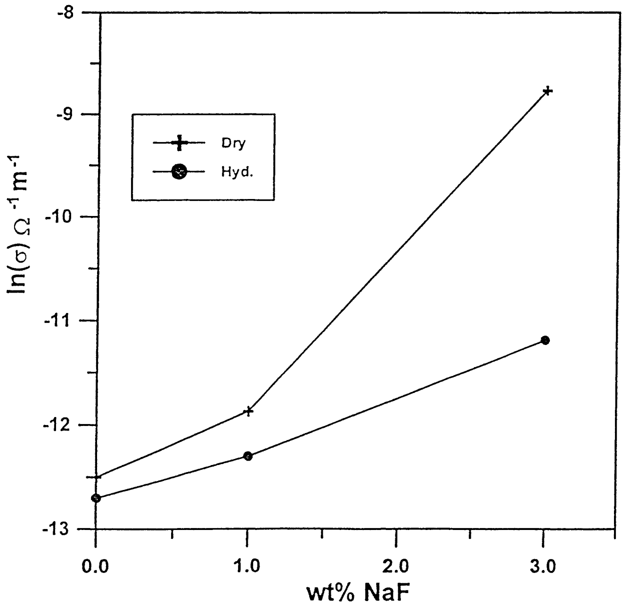

Fig. 4. Variation of a.c. conductivity at fixed temperature of anhydrous and hydrated C_4AF containing different NaF concentrations.

permittivity for different samples gradually increase with increasing temperature as well as the concentration of NaF. The sharp increase in the permittivity at 1 kHz and above 600 K is due to dielectric relaxation, which can be clearly observed in Fig. 6. This behaviour indicates a Debye-type dielectric dispersion [22], which is confirmed by a.c. conductivity results.

The variations of the dielectric loss tangent (tan δ) with temperature for different samples of C_4AF containing different concentrations of NaF at fixed frequency (1 kHz) are shown in Fig. 6. From this figure, it is clear that there is a maximum peak, which appears in all curves indicating the characteristic feature of a Debye-type relaxation process [23] with a relaxation frequency f_o, i.e., $1/2\pi\tau$, where τ is the relaxation time. The relaxation time, which is necessary to describe the present dielectric loss data, is not only due to the distribution of molecular processes, but arises also from a cooperative relaxation processes in which the motion of a given molecule depends upon its neighbours. Also from Fig. 6, it is clear that the dielectric loss tangent increases by increasing the concentration of NaF in C_4AF and the position of the peak is not affected by the hydration process, but only affected by the NaF concentration.

This result demonstrates that a.c. conductivity and Mössbauer measurements can be considered as effective methods to investigate the purity of the Brownmillerite phase of cement clinker from any foreign ions such as alkali or fluorine ions, which could be found naturally in the raw materials.

Moreover, from the above results, we can observe that the addition of fluorine ions to C_4AF affects its structure, which changes from orthorhombic to tetragonal or monoclinic according to the NaF concentration.

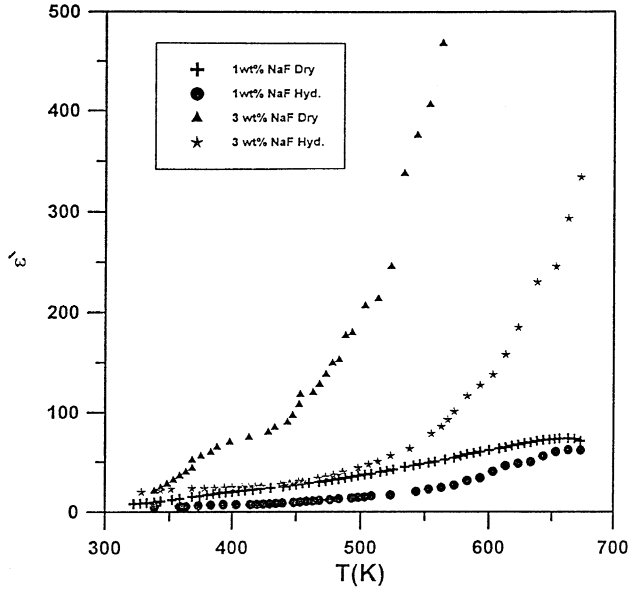

Fig. 5. Temperature dependence of permittivity ε′ at fixed frequency (1 kHz) anhydrous and hydrated C_4AF containing different concentrations of NaF.

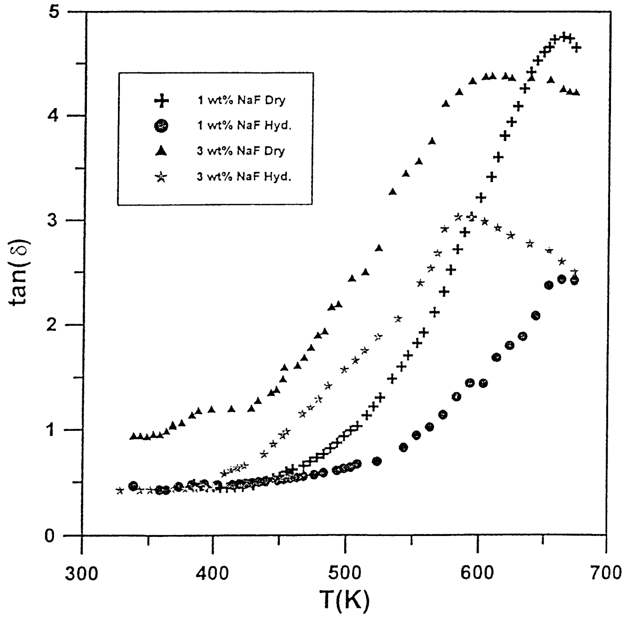

Fig. 6. Temperature dependence of dielectric loss tangent (tan δ) at fixed frequency (1 kHz) anhydrous and hydrated C_4AF containing different concentrations of NaF.

4. Conclusion

The above results reveal that NaF addition to C_4AF expedites the hydration reaction rate. The superparamagnetic relaxation, which appeared in the anhydrous C_4AF spectra, decreases as the time of hydration increases. The Fe^{3+}(Oh) increases and Fe^{3+}(Td) decreases also as the time of hydration increases. More than 50% of the hydration reaction occurs during the first 3 days of hydration. As the NaF content was increased, this percentage of the hydration reaction was found to increase. The temperature dependence of a.c. conductivity at fixed frequency (1 kHz) for different anhydrous and hydrated samples increases with increasing NaF addition to the C_4AF. This is attributed to the lattice holes, which may be filled by NaF. The conductivity decreases in hydrated samples more than the decrease in the anhydrous samples. This is attributed to the change in the lattice structure and it may be due to a change in the magnetic order from the superparamagnetic to antiferromagnetic state. The activation energy values exhibits that the effect of NaF additions on the a.c. conductivity data appears only at high temperatures. The a.c. conductivity and Mössbauer measurements can be used as good methods to verify the purity of the Brownmillerite phase of cement clinker from any foreign ions such as NaF ions, which may be found naturally in the raw materials of cement industry.

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