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Electrical properties of rare earth doped $ALPO_4$-zeolites

B.V.Suresh kumar*, H.R.Ravi, K.N.Prakash narasimha

Department of Studies in Earth Science, University of Mysore, Manasagangotri, Mysore-570006, (INDIA)

E-mail: bvsureshkumar@yahoo.com

ABSTRACT

Frequency dependence of electrical properties like conductivity, dielectric constant, and loss factor (tan δ) of rare earth doped aluminophosphate zeolites are observed in the range of 10 kHz to 100 kHz. The dielectric properties of these materials have been studied with a view to modify the properties of zeolite systems for practical applications. The conduction mechanism includes a frequency dependant process as described to the motion of rare earths in the super cages of aluminophosphate zeolites. The electrical response of a normal dielectric can be described by its Capacitance (C), dielectric constant (ε) and loss factor (tan δ). The experimental result shows that dielectric constant decreased with the addition of various rare earths in the aluminophosphates zeolites. The value of dielectric constant decreased with the increasing frequency, which indicates that, the major contribution to the orientation polarization. The present paper reports and discusses the dielectric behaviour of such rare earth doped $AlPO_4$-zeolites as a function of composition and frequency.

INTRODUCTION

In recent years, metal complexes have become of great interest because of their electrical properties in industrial applications. Zeotypes and Zeolites form an important family of solids, which are known for their application as ion exchanger and gas separation materials. In addition, zeolites are becoming more popular owing to a new range of applications in technology. Their applications are aften intimately connected with the structure and composition. The characteristic open structure of zeolites results in high surface area in them. Different additives are usually added to Aluminophosphate Zeolites in order to modify and improve their electrical properties. Inorganic additives such as transition metal salts have considerable effect on the electrical properties of Aluminophosphate Zeolites. The synthesis of rare earth doped $AlPO_4$-zeolites and characterization using XRD, FTIR, positron annihilation, SEM and BET has been reported by Byrappa et al., (2007). However, the data related to the electrical properties of these rare earth doped $AlPO_4$-zeolites were not reported earlier. The dielectric behaviour as a function of frequency was reported by Ravinder et al (2001). In the present paper properties like electrical conductivity (σ_{AC}), dielectric constant (ε) and the dielectric loss (ε') were estimated with respect to frequency at room temperature for the rare earth doped $AlPO_4$-zeolites.

EXPERIMENTAL METHODS

Following steps are adopted in the synthesis of microporous aluminophasphate zeolites.

(a) Aluminophasphate gel were prepared first by neutralizing the pseudobohemit (AlOOH-98.35mmol) homogenously in water (50ml) and

TABLE 1: Dielectric constant of rare earth doped $AlPO_4$ zeolites Vs frequency

Frequency	Dielectric Constants					
	Nd-$AlPO_4$	Gd-$AlPO_4$	Ce-$AlPO_4$	Eu-$AlPO_4$	Pr-$AlPO_4$	$AlPO_4$
8028.565	289075	282495.8	277155.5	272531.5	268341.7	261612
16836.18	277155.5	272292.7	268819.3	261156.2	255577	247696.8
28868.21	265563	262306.7	258355.7	254187.7	248427.9	242356.4
38346.68	260917.4	255577	252798.3	247696.8	243268.2	238405.5
58039.39	254882.4	249542	245591	240728.3	235986.5	230742.3
89288.03	244500	238405.5	234215.7	229591.7	225600	222000

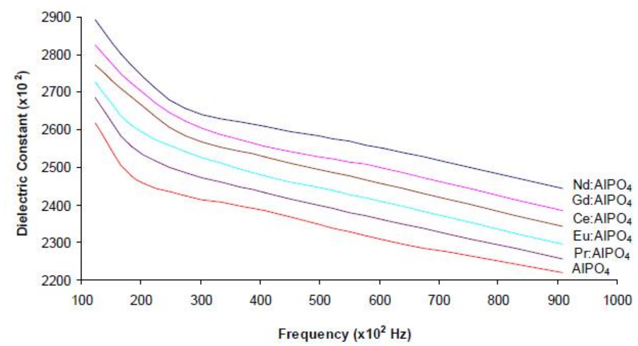
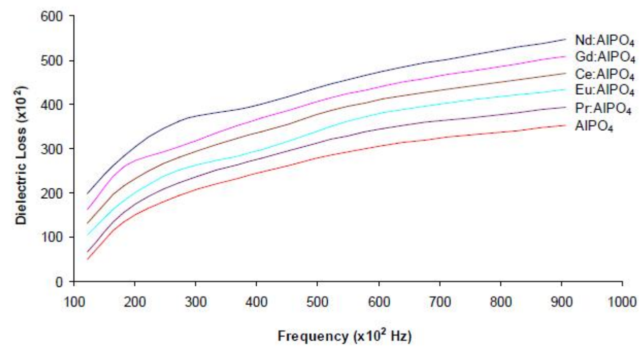


Figure 1: Variation in dielectric constant with respect to frequency for different rare earth doped $AlPO_4$-zeolites



Figuure 2 : Variation in dielectric loss with respect to frequency for different rare earth doped $AlPO_4$-zeolites

equimolar amount of dilute orthophosphoric acid (H_3PO_4-175mmol) was added with rigorous stirring. This is known as reactive gel.

(b) The reactive gel obtained was aged for 3h over a hot water bath at 50°C.

(c) Organic amine was added (dipropylamine – 36.4mmol) was added to the reactive gel, which acts as a structure directing agent. This is refereed to as precursor gel.

(d) The precursor gel is aged for 3h over a hot water bath 50°C.

(e) At this stage, 9 milli mole (mmol) of rare earths nitrates either $Ce(NO_3)_3.6H_2O$ or $Pr(NO_3)_3.6H_2O$ or $Nd(NO_3)_3.6H_2O$ or Eu $(NO_3)_3.6H_2O$ or $Gd(NO_3)_3.6H_2O$ were added.

(f) Final precursor gel was charged into 30mL capacity Teflon steel autoclave with 60% fill.

The hydrothermal runs were carried out for a period of 60 hours at 150°C in hot air oven. The runs were arrested by quenching the autoclaves in the cold water bath. The run products were carefully recovered and washed thoroughly using double distilled water and ultrasonicated to remove adhered organic amines and excess rare earths elements. Then the run products were dried in a dust proof environment at 40°C[2]. The dielectric properties like dielectric constant, tan δ and electrical conductivity (σ_{AC}) of the samples were recorded using the LCR Bridge in the frequency range 10k Hz to 100 kHz. The dielectric constant (ε), dielectric loss (ε') and conductivity has been calculated with the help of the formula $\varepsilon = Cd/A\,\varepsilon_0$; $\varepsilon' = \tan\delta * \varepsilon$; $\sigma_{AC} = 2\pi f * \tan\delta * \varepsilon * \varepsilon_0$, Where 'C' is the capacitance, 'A' is area of applied silver paste, 'd' is the thickness of the sample, 'ε_0' is absolute permittivity, 'tan δ' is the loss factor and 'f' is the frequency.

RESULTS AND DISCUSSION

Dielectric constant

The variations of dielectric constant are determined at frequency range between 10 kHz and 100 kHz with rare earth doped $AlPO_4$ zeolites (TABLE 1 and Figure1). The value of dielectric constant decreases continuously with increasing frequency. The rare earth doped $AlPO_4$-zeolites have higher dielectric constants with that of $AlPO_4$-zeolite. This is because of the rigorous vibrations of electrons at higher

TABLE 2 : Dielectric loss of rare earth doped $AlPO_4$ zeolites Vs frequency

Frequency	Dielectric Loss					
	Nd-$AlPO_4$	Gd-$AlPO_4$	Ce-$AlPO_4$	Eu-$AlPO_4$	Pr-$AlPO_4$	$AlPO_4$
11657.19	19821.75	16287.01	13125.38	10533.23	6821.752	4956.193
20491.47	28364.05	25948.64	21687.31	18152.57	15540.79	13498.49
27782.29	36356.5	30406.34	28187.31	25168.2	22237.16	19448.64
42770.11	40067.98	36925.98	33764.35	29668.82	27814.2	24829.31
62347.68	47510.57	44172.21	41187.31	38222.05	34510.57	30779.46
91165.72	54800	50800	47137.46	43500	39300	35237.16

frequencies. Iwauchi (1971) reported a strong correlation between the conduction mechanism and the dielectric behaviour starting with the conjecture that the mechanism of the polarization process which is similar to that of the conduction process[18]. The electronic exchange in local displacements which determine the polarization behaviour of the rare earth doped zeolites [15]. The decrease of dielectric constant with increase of frequency as observed in the different dopent of rare earth nitrates is a normal dielectric behaviour. This was also observed by several other investigators[3, 19, 24]. The dielectric behaviour in rare earths can be explained on the basis of the assumption that the mechanism of dielectric polarization is similar to that of conduction. Many scientists established a strong correlation between the conduction mechanism and dielectric constant of metals[9, 18]. Figure 1 depict the dispersion in dielectric constant is analogous to Maxwell–Wagner interfacial polarization[14, 10] in agreement with Koop's phenomenological theory[12].

Dielectric loss

The variation of dielectric loss with frequency for different rare earth doped $AlPO_4$-zeolites are shown in TABLE 2 and Figure 2. The dielectric loss increases with increasing frequency. A qualitative explanation can be given for the occurrence of the maximum in the dielectric loss vs. frequency curves in the case of dopent of rare earths. As pointed out by Iwauchi (1971), there is an agreeable correlation between the conduction mechanism and the dielectric behaviour. The probable conduction mechanism is considered as due to hopping of electrons between Al^{3+} and rare earths. As such, when the hopping frequency is nearly equal to that of the frequency of externally applied electric field, a maximum of loss may be observed.

Conductivity

Zeolites contain mobile cations, which are exchangeable and more weakly bonded to the adjacent atoms than the framework ions do and thus are more mobile[5, 16, 1]. This may enhances the catalytic properties of zeolites are strongly influenced by the guest molecules and ions[26, 11]. The electrical conductivity of zeolites is a function of the number of current carriers and their mobilities[13, 8, 17]. Knowledge of the conduction mechanism may be useful in view of their potential in electrochemical applications[21]. Moisture content in the pores of zeolites supports the ionic conductivity up to a temperature of 200°-375°C, depending on the type of rare earth doped. Above this the water is removed and the ionic conductivity is no longer dependent on the water absorbed[25, 5, 7, 4]. Zeolites have poor conductivity unless quenched with fairly strong bases like ammonia and other amine derivatives[22].

The variation of conductivity is determined for $AlPO_4$ doped rare earth (TABLE 3 and Figure 3).

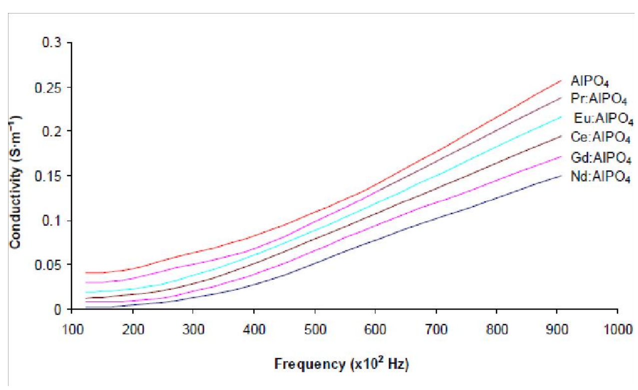


Figure 3 : Variation in conductivity with respect to frequency for different rare earth doped zeolites

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TABLE 3: Conductivity of rare earth doped $AlPO_4$ zeolites Vs frequency

Frequency	Conductivity					
	$AlPO_4$	Pr-$AlPO_4$	Eu-$AlPO_4$	Ce-$AlPO_4$	Gd-$AlPO_4$	Nd-$AlPO_4$
13586.52	0.04062	0.02962	0.01958	0.01165	0.00897	0.00249
21060.11	0.04369	0.03258	0.02159	1.51E-02	0.00858	0.00338
27782.29	0.0586	0.04665	0.03224	0.0236	0.01566	0.00964
41429.73	0.08366	0.06936	0.06199	0.05267	0.04035	0.02851
64662.88	0.1428	0.13446	0.1214	0.10932	0.09636	0.07869
91937.45	0.25709	0.237	0.216	0.194	0.172	0.14974

The conductivity gradually increases as frequency increases. Variations in the conductivity with frequency show a good contrast with that of the dielectric constant and consistent with the variation in the dielectric relaxation. The conductivity for $AlPO_4$-zeolite is more as compared with the rare earth doped $AlPO_4$-zeolites.

CONCLUSIONS

Rare earth doped $AlPO_4$ zeolites have been synthesized using closed hydrothermal method and a qualitative explanation is given for the composition and frequency dependence of the dielectric constant, dielectric loss and conductivity. The electrical property of rare earth doped $AlPO_4$ varies by the addition of different rare earths. The Dielectric constant decreases, where as the conductivity increases with respect to frequency at room temperature. This is probably due to lattice parameter seems to be dependent of the type of doped rare earth ions. This means that the rare earth ions occupy either in the zeolitic pores or hoping of electron to A- sites, Al^{3+} ions to rare earths at the grain boundaries. This is due to the fact that the tetrahedral sites are small to be occupied by the large rare earth ions which have large ionic radius. The probability of occupancy of the octahedral sites by the rare earth ions will increase with decreasing the rare earth ionic radius. Based on the present study it is concluded that the rare earth doped $AlPO_4$ zeolites have higher dielectrical constants and increase of dielectrical loss with increasing frequencies. Consequently the conductivity increases as frequency increases.

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