ACERP: Vol. 2, No. 1, (Winter 2016) 1-4

Advanced Ceramics Progress

Research Article

Journal Homepage: www.acerp.ir

Electrical Resistivity Measurement of the Molten Cordierite Glass Using Two-wire Method

F. Soleimani*, A.R. Aghaei, M. Zakeri, M.J. Eshraghi

Ceramics Department, Materials and Energy Research Center, P.O. Box 31787/316, Karaj, Iran

PAPER INFO

Paper history:
Received25 April 2015
Accepted in revised form February 16 2016

Keywords:
Lead free piezoceramics
Potassium sodium niobate
Nano and micron WO$_3$
Microstructure
Electrical properties

ABSTRACT

Lead free potassium sodium niobate (KNN) piezoceramics were synthesized via conventional solid state sintering route. Tungsten oxide (WO$_3$) with nano and micron particles was used as a donor dopant. Dielectric and piezoelectric properties of samples sintered in the temperature range of 1110°-1145°C were measured by precision LCR-meter and APC d_{33}-meter devices. SEM results revealed that micron WO$_3$ inhibited the grain growth of KNN ceramics and led to a finer microstructure. KNN with micron WO$_3$ had much finer microstructure and the sintering process terminated at higher temperature compared to pure KNN and KNN with nano WO$_3$. Nano and micron sized WO$_3$ affected the densification and electrical properties of KNN considerably. Additionally, KNN with nano WO$_3$ reached the maximum density at lower temperature compared to its counterpart. Finally, at 1125ºC KNN with 0.3 mol% nano sized WO$_3$ showed d_{33}, ε_r, tanδ, and Q_m of 75 pC/N, 345, 2%, and 50, respectively. For KNN sample with 0.3 mol% micron WO$_3$ at 1135ºC these values were 81 pC/N, 773, 3.3%, and 30, respectively.

1. INTRODUCTION

In glass production industry, measuring the ER of molten glass is of great importance [1,2]. For example, when a glass is melted with high frequency induction method, a new method for glass melting, it is necessary to know the ER of the molten glass. In this process, choosing the frequency of the induction generator depends on the ER of the material [3].It was reported that the glass melt absorbs induction current if the ER be below 10 Ω.cm [4]. Cordierite glasses are used as insulators, optic, refractory, etc. [5-7]. For example, non-stoichiometric cordierite glass was used as radome in the missile industry [8].The ER of cordierite glasses was previously measured for temperatures lower than its glass transition temperature [9, 10]. There are several methods to measure the ER of molten glasses [11-13]. In general, they may be classified into three groups: 1) The absolute, calibration-free methods; 2) The methods based on low-temperature calibration using solid glass; and 3) The methods based on room temperature calibration using aqueous solutions. The absolute method was introduced by Baucke et al. [14]: Two parallel electrodes are immersed into the glass melt and the resistivity can be determined directly according to Equation (1). This straightforward does not require calibration using reference materials at lower temperatures. But, the accuracy of the results is generally in the range of 5–10%. On the other side, the methods of accurate measuring of the ER are complicated and not suitable for industrial usages. In this study the two-wire method was chosen for measuring the ER. The two-wire method is a low accuracy and calibration free method but for making quick laboratory measurements or monitoring an industrial process stream, a low-accuracy technique is often most appropriate [13, 15]. In this research, the ER of cordierite glasses was measured in the range of 1100 to 1550 ˚C which to the authors' best knowledge has not previously been reported.

2. EXPERIMENTAL PROCEDURE

2.1. GLASS BATCHING

The chemical composition of the cordierite base glasswas chosen based on a previous report [5]. The composition was $56SiO_2$-$20Al_2O_3$-$15MgO$-$9TiO_2$ by weight percent. Na_2O was added to the cordierite base glass about 0.5 and 1 wt.% considered Sample 2 and 3, respectively. The raw materials were SiO_2, $MgCO_3$, Al_2O_3, TiO_2 and Na_2CO_3

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*Corresponding Author's Email: F-soleimani@merc.ac.ir powders and all were reagent grade. The raw materials were well mixed together using a wet ball mill and dried in an oven. 100 g of raw materials were charged into the platinum crucible and were used to measure ER.

2.2. ELECTRICAL RESISTIVITY ASSESSMENT

The schematic view of the setup was shown in Fig. 1. The crucible and the wires consisted of Platinum. An HCl (4wt. % concentration) solution, with known resistivity (ρc), was used for determination of the cell constant. By using a power supply, the loaded voltage was changed and the induced current was measured.The loaded voltage and the induced current, total resistivity of the cell (Rc) was determined.

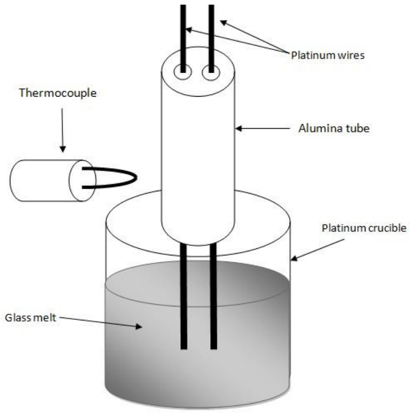

Figure 1. Schematic view of the setup of measuring the electrical resistivity

Using equation (1), the cell constant (C) was calculated. The cell constant was 294 cm-1. The wires were placedinto an alumina tube. Then, the tube was placed in the furnace from the top and the wires were immersed in the melt. The probe immersing in the melt was performed after finishing the heating period and melting. In fact, measurement of the ER was performed in the cooling cycle. The depth of immersion was carefully controlled to 5 mm. After that, by using equation (1), the ER of the melt was measured.

$$R=\rho C \qquad (1)$$

In this equation R is resistivity, ρ is the specific electrical resistance of the glass melt and C is the cell constant.

3. RESULT AND DISCUSSION

The ER of cordierite base glass previously reported at temperatures lower than its glass transition temperature [9]. The electrical resistivity which was measured in this study was much lower because the temperature of the experiments was above the T_g. In the glass samples of this study, because ofthe high mobility of ions in high temperatures (especially at the melting point), the ER decreased once temperature increased. In the diagram in Fig. 2 the variation of induced current against loaded voltagewas displayed. It is obvious that the variation was linear and there is very good agreement between the data (the linear regression was about 0.99 for all samples data). Measurements of the induced current at the lowertemperatures had some errors because of the sensitivity of the ampere meter. Figs. 3 and 4 show the variation of induced current against loaded voltage for samples (2) and (3). The diagrams depicting the variations of the ER of the melt against temperature for all samples were shown in Fig. 5. The values of the ER were listed in Table. 1. It is clear that in all samples the ER of the glass decreased exponentially asthe temperature increased. But, this decreasing in rate in samples 2 and 3 was higher than the base glass (See fig.5). Below 1100 °C, all samples crystallized so the data achieved in this temperature rangeare not reliable [11].

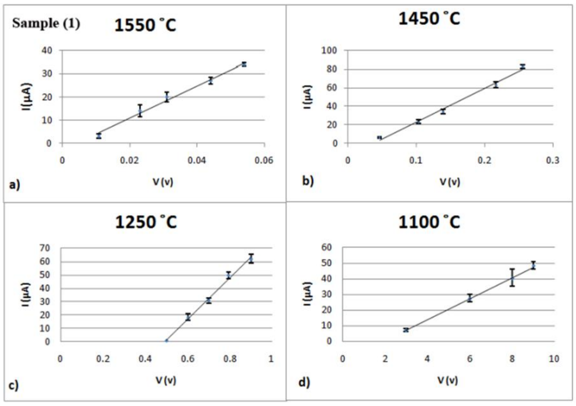

Figure 2. Diagram of variation of voltage vs. current for cordierite glass at:a) 1550, b) 1450, c) 1250 and d) 1100 °C

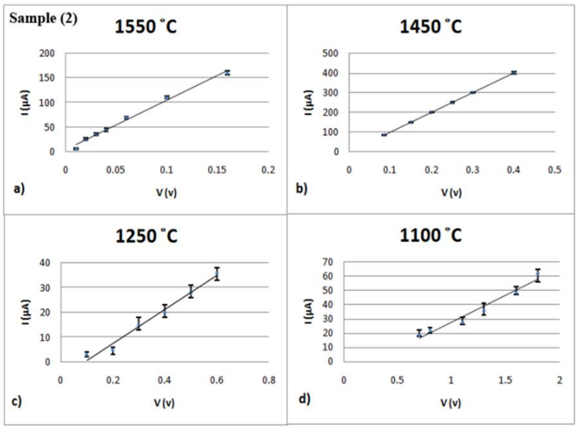

Figure 3. Diagram of variation of voltage vs. current for cordierite glass with 0.5 % Na_2O at: a) 1550, b) 1450, c) 1250 and d) 1100 °C

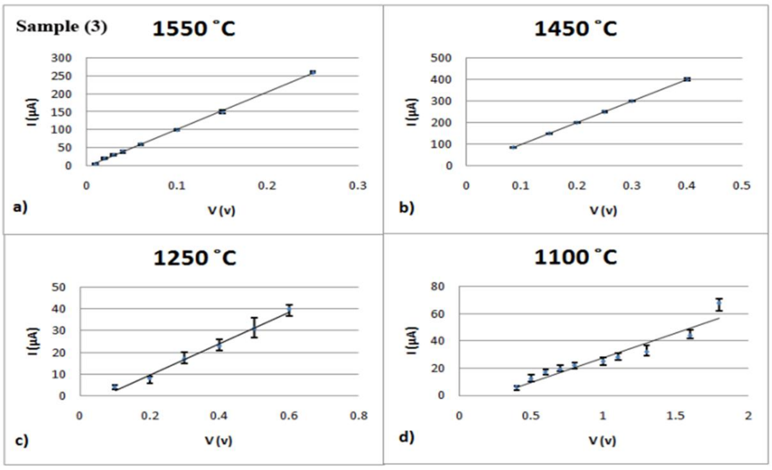

Figure 4. Diagram of variation of voltage vs. current for cordierite glass with 1 % Na_2O at: a) 1550, b) 1450, c) 1250 and d) 1100˚C.

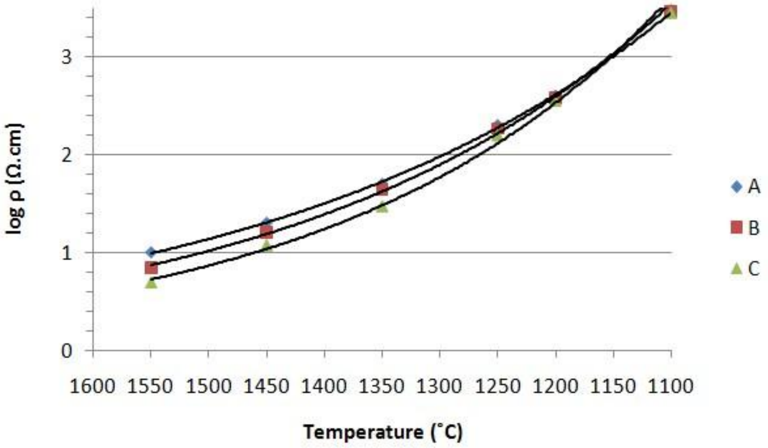

Figure 5. Diagram of variation of electrical resistivity of the samples vs. temperature: A) Cordierite glass, B) Cordierite glass with 0.5 %wt Na_2O, C) Cordierite glass with 1% wt Na_2O

For the samples containing Na_2O, it was observed that in high temperatures, compared to the base glass the ER was decreased (for example at 1500˚C, the ER of sample (1) was about 25 Ω.cm while that is 15Ω.cm for sample (3)).

Table 1. Electrical resistivity (ohm.cm): A) Base glass, B) Sample(2) and C) Sample (3)

1550	1500	1450	1350	1250	1100	Temp. (˚C)
8±2	25±3	55±15	323±26	825±83	4010±105	B
5±2	8±3	39±8	301±16	803±83	3965±105	C
4±1	7±2	27±3	277±11	803±13	4001±15	A

This phenomenon has previously been reported for silica glasses [16]. Adding alkali oxide to the silica glass resulted in more decreasing in the ER by increasing temperature. In this research, this phenomenon was observed for cordierite glass. Monovalent ions have high mobility in glasses and melts. Accordingly, anincrease in the concentration of alkali oxides leads to an intensive decrease in the electrical resistivity. The high mobility of Na+ ions in the glass melt is the most important cause for ER reduction; furthermore, when temperature decreases, the mobility of Na+ ions also decreases. Thus, the ER of the samples was close together at lower temperatures (~3000 Ω.cm at 1100 ˚C). It should be noted that the presence of Mg2+ along with Na+ result in a mechanism so called the "mixed alkali effect". Adding monovalent alkali oxide to a glass containing bivalent oxide results in a greater decrease in ER in high temperatures [11]. Some researchers [17] had proposed a defect model for mixed alkali effect where alkali cations in foreign sites were defined as 'mixed alkali defects'. According to this model, mechanical and electrical strains localized on the defect sites are causing strains in, and weakening of the network former – bridging oxygen bonds. Mixed alkali defects thus reduce electrical resistivity and account for the observed minimum with compositional variations. In the transition region, stress and structural relaxation causes mixed alkali defects to convert to normal sites with time. Diffusion/conductivity behavior in the mixed alkali defect model is predicted by assuming to be site preferred; alkali cations may diffuse along the foreign sites, though, but at reduced rate. Anyway, there is no a promise model for interpreting of the mixed alkali effect in glasses until now.The ER of the samples (2) and (3),were below10 Ω.cm at above1550˚C and 1500 ˚C, respectively (Fig. 5). So if we want to melt the glass by induction melting, with the addition of Na_2O, the temperature of absorbing of the induction current can be reduced.

4. CONCLUSION

The ER of cordierite base glass samples was measured at temperatures between 1100 to 1550 ˚C using the two-wire method. The results showed that ER decreases as temperature increases. The ER of the cordierite glass was 10 Ω.cm at 1550 ˚C, approximately. In order toreduce the ER, Na_2O was added to the base glass. The results showed that the ER is decreased by adding Na_2O. This was attributed to the high mobility of Na+ ions and the mixed alkali effect mechanism.

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