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Thermally stimulated depolarization currents in γ-irradiated β-spodumene solid solution ceramic

H. S. RAGAB
Department of Physics, Faculty of Education, Suez Canal University, El-Arish, Egypt
R. A. ABD ELLAH
Department of Physics, Faculty of Industrial Education, High Education Ministry, Cairo, Egypt
M. S. ABO ELLIL, A. SHEHAB, A. F. BASHA, F. H. ABD EL-KADER
Department of Physics, Faculty of Science, Cairo University, Giza, Egypt

Thermally stimulated depolarization currents (TSDC) in unirradiated and γ-irradiated press prepared β-spodumene solid solution ceramic have been investigated within the wide temperature range 20–160°C. Doses in the range 10–10^5 Gy were used. The TSDC spectrum at relatively high polarizing fields shows two relaxation peaks whose positions and intensities depend on the polarization conditions and γ-doses. Discussion of data is given on the basis that dipolar and space-charge polarization coexist in the used ceramic material. Activation energies for space-charge peak are determined from the initial rise of thermal current peak under different γ-doses. Aging effect clearify that the longer the aging time, the smaller the polarization. Pyroelectric current data provide further support to space charge effects.

1. Introduction

Ceramic dielectric materials are typically used in dielectric circuits as either capacitors or insulators. Capacitors act as electrical buffers, diverting spurious electrical signals and storing surges of charge that could damage circuits and disrupt their operation [1, 2]. In addition, the traditional use of ceramics as insulators in high-power applications is still a substantial economic activity.

The thermally stimulated depolarization current (TSDC) technique is a powerful tool for understanding the molecular relaxation mechanism, trapping parameter and charge storage behaviour of insulating materials [3–8]. All peaks found in TSDC spectra have a counterpart in conventional dielectric loss measurements except for space charge, which is likely to appear in TSDC measurements. The TSDC method is characterized by its high resolving power, allowing a separate investigation of the effects caused by various types of relaxation of a given material.

Gamma rays are expected to make large chemical and physical changes of the materials, either by direct damage or by reaction with any oxygen present. To our knowledge, little work [9] has been done on the TSDC of ceramic materials. On the other hand, no attempt has been made before to study the effect of γ-irradiation on depolarization behaviour of ceramics. Hence, in the present work, it is planned to apply relatively low doses of γ-rays for a thoroughly understanding of radiation-induced damage on β-spodumene solid solution ceramics.

2. Experimental

β-spodumene solid solution $Li_2O:Al_2O_3:6SiO_2$ was prepared using chemically pure materials. The lithium carbonate ($Li_2 CO_3$, purity 99.5%) as a source of Li_2O, local quartz from Aswan (Upper Egypt) as a source of SiO_2 and pure Kaolin from Montcatiene S.E.A. Millano as a source of Al_2O_3 and SiO_2 too. Batches composition percent are 12.90% Li_2CO_3, 45.10% Kaolin and 42.00% quartz. Batches were wet mixed, dried. calcined at 950°C with heating rate 10°C/min and then finely ground. Bodies in the form of discs were shaped using Semi-dry pressing technique (100 kg/cm^2) using polyvinyl alcohol (5%) as a binder and vitrified by firing in an electric furnace at temperature 1350°C. Optimum vitrification parameters are bulk density 1.6 g/cm^3 and apparent porosity 31.

Sample of 0.2 cm thickness were irradiated by different doses of γ-rays in the range 10–10^5 Gy using ^{60}Co source at room temperature and a constant dose rate. Thermally stimulated depolarization current studies were carried out using a sandwich configuration of samples holder of two copper electrodes with an effective area of 0.95 cm^2. Silver paste was used for sample coating to achieve ohmic contacts. Samples were exposed to a poling process, prior to TSDC measurements. This was done by first heating them to a specific polarization temperature (T_p) of 45, 65, 85, 100 and 125°C and then applying an electric polarizing field (E_p) of 0.8, 1.1, 1.6, 2.4 and 4 kV/cm for a polarizing time of 2 h. After polarization, the field was switched off at room temperature and the samples were shorted for about 30 min to remove frictional and remanent charge [10], if any. The depolarization current were recorded by a Keithley Electrometer Model 616, by heating the sample at a linear heating rate 1°C/min from room temperature to about 140°C. The pyroelectric currents were measured at different polarizing fields. All measurements were carried out 24 h after irradiation.

3. Results and discussion

3.1. TSDC of unirradiated samples

When the stored charges are released during the reheating cycle, after the poling process, one can measure the discharge current as a function of temperature to obtain the so-called thermally stimulated depolarization current (TSDC). The TSDC technique, due to its low equivalent frequency, has an inherently high resolution and low noise level [11].

The experimental measurements of TSDC were done on several virgin samples, and only reproducible data were reported. In order to determine some suitable starting conditions for measurements, Figs 1 and 3 were obtained to illustrate the mutual effects of different polarization conditions, namely field intensity and polarization temperature, on TSDC for β-spodumene solid solution samples.

Fig. 1 shows the effect of electric field strengths from 0.8 to 4 kV/cm on the TSDC spectra of β-spodumene solid solution samples while the other polarizing conditions of temperature and time are kept unchanged at 100°C and 2 h, respectively. It can be seen that each spectrum consists of a single pronounced broad peak corresponding to a nearly constant T_m of 65 ± 2°C independent of E_p. The occurrence of a maximum does not necessarily mean that a single thermally activated process is involved. Competing thermally activated processes or a temperature-dependent structure may be advocated as well. A small additional peak is also observed around 50°C for 2.4 and 4.0 kV/cm polarizing field strengths. The effect of glassy phases cannot be ignored as lithia-alumina-silicate glasses were reported to have exceptionally higher values than their crystalline phases [12]. The differential scanning calorimetry (DSC) thermogram obtained at heating rate of 10°C/min for the investigated sample shown in Fig. 2, indicates a glass transition at about 50°C. At the glass transition temperature, interatomic restraints are reduced sufficiently to permit a non-elastic displacement of neighbouring molecules under an applied electric stress. This may be the reason for the small current peak in the thermal-current spectra. The inset of Fig. 1 shows that field strength up to 1.6 kV/cm cause an increase in the peak current (I_m). The total charge stored increases linearly with the applied field for uniform polarization and non-linearly for space charge [13]. Thus, one can expect that the large relaxation peak which appears in β-spodumene solid solution may be suggestive of the existence of space charge effects [14, 15].

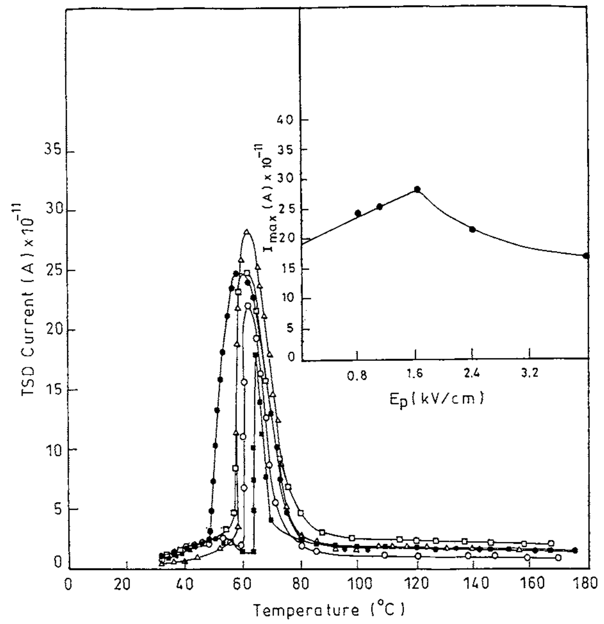

Figure 1 Effect of polarized (E_p) on TSDC for β-spodumene solid solution samples. Polarization temperature T_p = 100°C; polarization time t_p = 2 h; polarization field E_p (kV/cm): □ 0.8; ● 1.1; △ 1.6; ○ 2.4 and ■ 4.0.

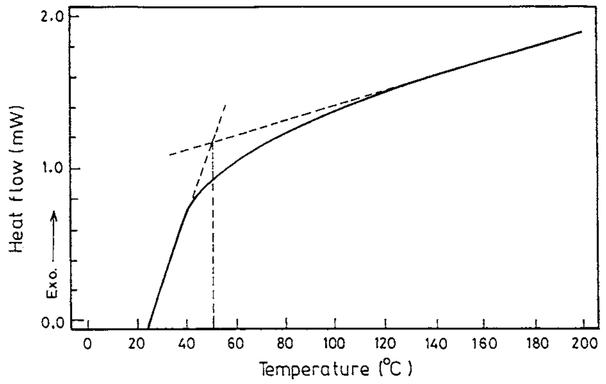

Figure 2 DSC thermogram of β-spodumene solid solution ceramic sample. Heating rate; 10°C/min.

The current released during a TSDC run is a measure of the degree of polarization of the sample which in turn is conditioned by several microscopic mechanisms including the degree of molecular mobility [16]. The decrease of peak current (I_m) at polarizing field strength higher than 1.6 kV/cm can be explained on the basis that under these conditions more polarization is activated and/or space charge polarization due to charge generation at the electrode-sample interface. These charges are neutralized by conduction current in opposite directions, which means that the observed charge release will be less than the initially stored charge [17]. In addition, partial compensation of heterocharge by charge injected from electrodes (homocharge) seems a more probable mechanism for the decrease of the charge released in the discharge.

The microstructure of β-spodumene solid solution is previously reported [18] that Li atoms, in one of the four channel per unit cell, are ordered and coplanar with silica. Our group previously established that Li^+ ions are considered solely to be the mobile ones on account of their lower equivalent weight (6.9 g/mol) compared to Al^{3+} (26.08 g/mol) or Si^{4+} (28.08 g/mol) [19]. Relevant studies [20] on LAS glass ceramic system showed that the dielectric relaxation is due to single particle hopes of Li^+ ions on local double-well potential presenting a well known structural feature of several crystalline compounds of LAS system. A comparison of TSDC with dielectric loss data, particularly those in the low frequency range, may therefore be helpful to identify the origin for a peak. The first small peak around 50°C which appeared at higher polarizing fields 2.4 and 4.0 kV/cm in TSDC spectra is consistent with that found in our previous work [19] of dielectric loss tangent for the same material. Therefore, this peak is attributed to dipolar relaxation. It is partly related to the effect of water unavoidably trapped in ceramic samples as noticed by infrared spectrum analysis [21]. On the other hand, the peak appeared around 65°C in TSDC spectra has no correspondence in our dielectric loss tangent measurement confirming that it is due to space charge polarization, consistent with the former explanation.

Fig. 3 depicts the TSDC spectra obtained after poling of 2 h in 0.8 kV/cm at different polarization temperatures $T_p = 45, 65, 85, 100$ and 125°C. It is clear from the figure that the increase of temperature up to 85°C is associated with shift of the peak position towards higher temperatures. The peak position is kept unchanged for further increase of T_p at 100 and 125°C, while it shows a slight shift at temperature lower than at $T_p = 85$°C. In addition, the polarizing temperature 100°C is apparently enough for reaching the nearly filling state of polarized sample, and consequently to cause the generation of highest depolarization current. A higher polarizing temperature of 125°C is found to entail general decrease in TSDC, suggesting space charge polarization due to charge injection from electrodes [22].

Figs 1 and 3 thus indicate that values of $t_p = 2$ h, $T_p = 100$°C and $E_p = 1.6$ kV/cm may be considered as appropriate polarization conditions for obtaining appreciable TSDC from β-spodumene solid solution samples under investigation.

Fig 4 shows TSDC spectra of five repeated depolarization cycles of β-spodumene solid solution under identical conditions; 100°C in a d.c. field of 1.6 kV/cm for a time 2 h. The first run provides an irreversible current owing to the released space charge injected during poling process. The amplitude of this current is reduced in subsequent runs. Since aging markedly increases relaxation times, the depolarization current resulting for a given time is expected to be smaller the longer the sample has been aged. This remarkable decrease in TSDC suggests that special consideration should be given to the thermal history and aging effects in standard TSDC measurement of such ceramic material [23]. The aging effect can be explained by a reduction of the free volume, so that ions mobility may be reduced and then less polarization is achieved. The TSDC peak position and shape are not affected by aging. This agrees with the fact that the shift of relaxation times occurs without an appreciable change in the shape of distribution function [24]. The relaxation peak appearing during the repeating heating cycles of the sample (as shown in Fig. 4) is assumed to arise from space-charge build-up associated with the migration of ions inside the dielectric over macroscopic distances [25].

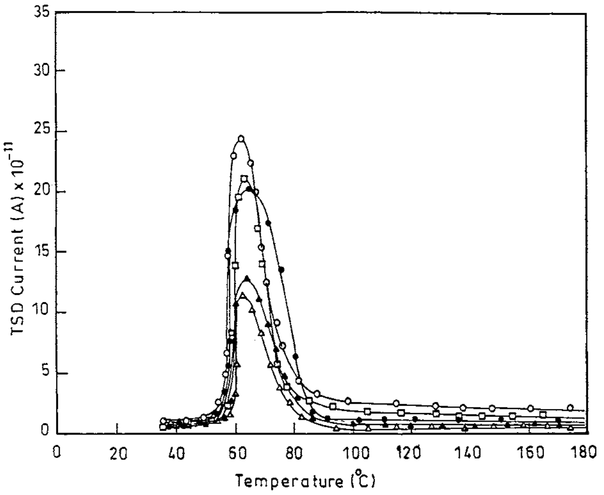

Figure 3 Effect of polarization temperature (T_p) on TSDC for β-spodumene solid solution samples. Polarization field $E_p = 0.8$ (kV/cm); polarization time $t_p = 2$ h; polarized temperature T_p (°C): △ 45; ▲ 65; ● 85; ○ 100 and □ 125.

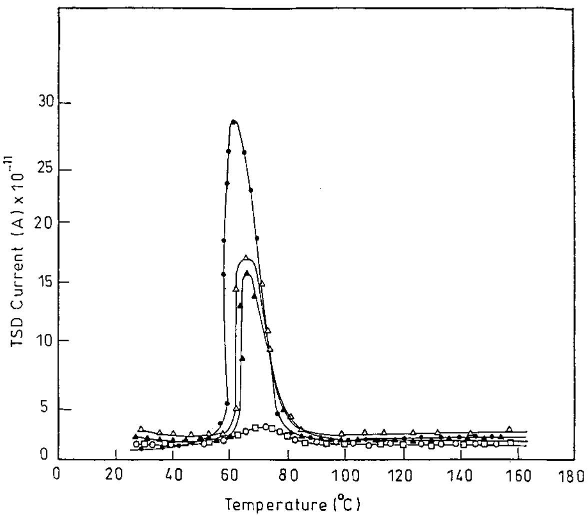

Figure 4 Effect of aging time on the TSDC for β-spodumene solid solution samples. Polarization field $E_p = 1.6$ (kV/cm); polarization temperature $T_p = 100$°C; polarization time $t_p = 2$ h; aging time (days): ● 1.0; △ 2.0; ▲ 3.0; ○ 7.0 and □ 12.0.

3.2. TSDC of irradiated samples

Fig. 5 shows TSDC thermogram of β-spodumene solid solution samples before and after irradiation with various γ-doses (10, 10^2, 10^3, 10^4 and 10^5 Gy). The sample irradiated with 10 Gy shows an anomaly of two peaks, the lower of which may be considered as a secondary peak. The samples irradiated with 10^2 and 10^3 Gy are characterized by the occurrence of one distinct discharge gaussian peak. The thermogram due to 10^4 Gy shows slight shoulder. The exposure to a relatively higher γ-dose 10^5 Gy leads to the disappearance of the relaxation peak which may be due to the slowly decaying space charge. The inset in Fig. 5 shows a monotonic decrease up to 10^3 Gy, followed by a rapid increase at 10^4 Gy.

As a result of γ-irradiation, ions and free radicals are formed and trapped in the bulk of the material. Further, the irradiation was carried out in air and hence, the

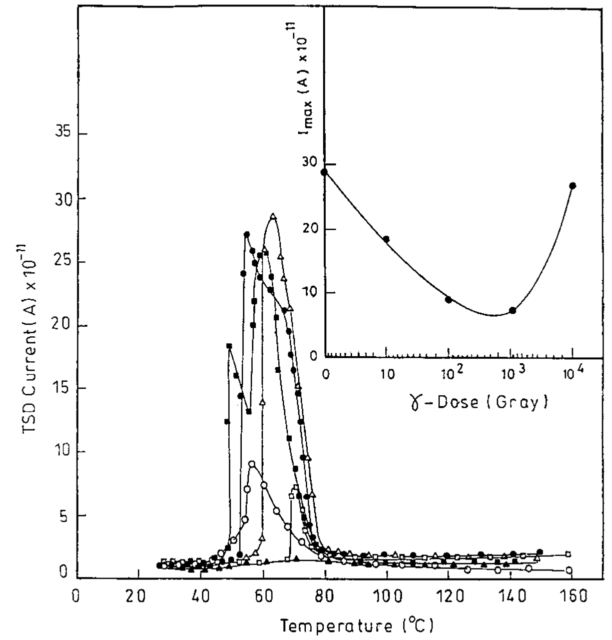

Figure 5 Effect of γ-radiation on TSDC for β-spodumene solid solution samples. Polarization field $E_p = 1.6$ (kV/cm); polarization temperature $T_p = 100°C$; polarization time $t_p = 2$ h; irradiation dose (Gy): △ unirradiated; ■ 10; ○ 10^2; □ 10^3; ● 10^4 and ▲ 10^5.

formed gaseous ions around the samples may produce homocharge on the surface of the specimen [26]. The change in shape, position and the area of relaxation peak on irradiation may result from a variation in the distribution function of the associated relaxation times. This suggests that the average relaxation time has been irregularly changed due to structural modification. The minimum of the inset curve of Fig. 5 elucidates the existence of competition between induced processes of opposite nature. In all cases, it has become evident that β-spodumene solid solution ceramic have much higher sensitivity to radiation damage.

β-spodumene solid solution having derivative quartz structure with a tetragonal symmetry, the degree of anisotropy is comparatively lower, and the change in cell volume is accompanied by a change in both a- and c-axes [27]. Thus, radiation damage induced in this material illuminates the role that lattice imperfections played in influencing the structural and physical characteristics of solids [28].

The spectra of Fig. 5 are analyzed in terms of the initial rise method [29] and the Bucci-Fieschi theory [30]. Using the initial rise method, the activation energies are found to be 0.47, 0.95, 0.34, 0.55 and 0.82 eV for unirradiated, 10, 10^2, 10^3 and 10^4 Gy, respectively. From the relatively high values of activation energies, it has been suggested that the ceramic grains suppress the mobility of ions at low temperatures. Also, it is partly related to that γ-irradiation induces aggregation and causes a decrease in polarizability, but sometimes new dipolar defects are found [31].

3.3. Pyroelectric current

Although pyroelectricity in composite materials has been studied for a long time, the interest in new materials for use in electronics industry has motivated the continuing work on this topics [4, 9, 32–36].

The pyroelectric coefficient, $P(T)$ can be evaluated using the relation

$$P(T) = -\frac{I(T)}{AB} \tag{1}$$

where $I(T)$ is the short-circuit pyroelectric current, A is the sample's area and B is the heating rate (1°C/min). The sign of $P(T)$ was taken as positive for the pyroelectric currents with the same polarity as the first depolarization currents.

Using Equation 1 and the thermally stimulated discharge current we can obtain the pyroelectric coefficient as a function of temperature. Fig. 6 shows the variation of the pyroelectric coefficient for β-spodumene solid solution at different polarizing fields from 0.8 up to 4.0 kV/cm and fixed polarizing temperature (100°C) and period 2 h. It is interesting to note that at field strength 4.0 kV/cm the pyroelectric coefficient is very small in addition to the disappearance of a peak. However, the magnitude of pyroelectric coefficient peak is large at field strength 1.1 kV/cm in the sense that reaching its maximum value at a much lower temperature. It is believed that the origin of pyroelectricity is due to the injection of charge carriers from the electrodes into the dielectric and also due to displacement of ions [37], both are termed as space charge dominated processes. The positive values of pyroelectric coefficient in the range of temperature investigated under different polarization field support this view [35]. Moreover, the pyroelectric properties of this ceramic sample will result from nonuniform temperature dependence of electrical permittivity or thermal expansion coefficient [19, 21].

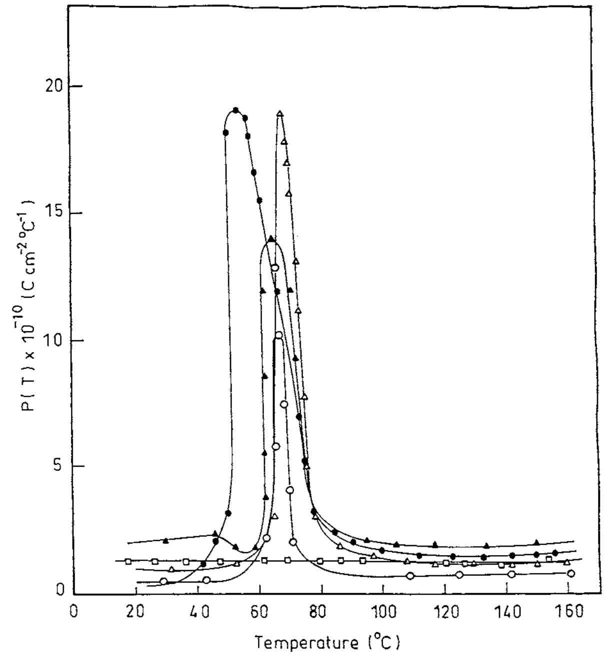

Figure 6 Temperature dependence of pyroelectric coefficient of β-spodumene solid solution polarized at 100°C for different polarizing fields. Polarization temperature $T_p = 100°C$; polarization time $t_p = 2$ h; polarization field E_p (kV/cm): ▲ 0.8; ● 1.1; △ 1.6; ○ 2.4; and □ 4.0.

4. Conclusions

Although most ceramic materials, in general, are temperature independent highly resistive polar dielectrics, β-spodumene solid solution material is found to be noticeably temperature dependent resistive material and highly sensitive to the relatively low level γ-irradiation. The TSDC spectra of the sample show the combined effect of hetero- and homo-charges. At high polarization fields, the first small peak is due to dipolar relaxation while the second large peak arises due to space charge polarization. The structure and magnitude of the space charge relaxation peak are mainly determined by polarization conditions and the level of γ-doses. The whole experimental evidence suggests that a special consideration should be given to aging effects and polarization conditions in addition to further studies for the use of this material in dosimetry.

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