Study of Leucite-type Glass-ceramics by Thermally Stimulated Depolarization Current

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Two different ingots of leucite-type glass-ceramics were studied by integral and by partial thermally stimulated depolarization current (TSDC) in the range from 173 to 370 K. Partial measurements showed distributed dipolar relaxation (P_1) with a maximum at 256 K, caused by the interaction between alkali ions and nonbridging oxygen atoms. The following relaxation, observed at a higher temperature (P_2), was attributed to the decay of the space charge dipoles. Only the beginning of P_2 was studied because the development of the process was overlapped by the conductivity current. Addition of different oxides to the original material decreased the P_1 and increased the P_2 relaxation, due to the increase of the interface area.

Key words: leucite, glass-ceramics, thermally stimulated current, TSDC.

INTRODUCTION

The significant growth in the applications of glass-ceramics in recent years is based on the unique properties of these materials. Glass-ceramics show many advantages over traditional powder-processed ceramics. For example, glass-ceramics can be produced by high speed processes such as rolling, pressing, blowing and drawing. They are characterized by high electri-

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cal resistance and corrosion resistivity, and, like all ceramics, they are also stable at high temperatures. Furthermore, glass-ceramics have no internal porosity, and they have low thermal expansion coefficients.

Glass-ceramics are partially polycrystalline solids produced by the controlled crystallization within a glass matrix. Volume fraction of the crystalline phase is generally over 50% and the crystal sizes in some cases can reach 10 μm. The crystal growth must be controlled to avoid large crystals that serve as planes for the propagation of fractures, which eventually result in cracking. Glass-ceramics are conveniently classified by their bulk chemical composition, or specifically by the composition of the major crystalline phase. According to the bulk chemical composition, they can be classified, very generally, as silicate, phosphate or oxide glass-ceramics.

Leucite ($KAlSi_2O_6$) belongs to the feldspathoid group of minerals. At room temperature, leucite is tetragonal (space group $I4_1/a$) with three tetrahedral sites, whereas, above 878 K, natural leucite also becomes cubic ($Ia3d$). A wide range of elements can be substituted into the tetrahedrally coordinated framework sites of leucite. This fact is very important for the production of leucite glass-ceramics, because by changing the chemical composition of the material it is possible to control some of its chemical and physical properties. England *et al.*[1] used Mössbauer and X-ray absorption spectroscopies to investigate incorporation of iron ions into the leucite-type framework. Microstructure of leucite-type dental glass-ceramics was investigated by X-ray powder diffraction, Fourier transform infrared and laser Raman spectroscopies, scanning electron microscopy and energy dispersive X-ray spectrometry. [2,3]

The aim of this work was to investigate the electric polarization of the leucite-type glass-ceramics by thermally stimulated depolarization current (TSDC) measurements. Generally, TSDC measurements are very important for the investigation of molecular motions in various nonconductive materials. This allows a high resolution and separation of the relaxation processes.[4] A more sophisticated application is the partial TSDC, which is based on polarization within a narrow temperature window (ΔT) and isolation of the narrow relaxation part. It is therefore possible to divide the wide relaxation into a series of elementary processes[5–7] and determine the actual distribution of the relaxation parameters.

EXPERIMENTAL

The original ingots of leucite-type glass-ceramics, denoted G_1 and G_2 in this paper, were obtained by courtesy of Ivoclar-Vivadent, FL-9494 Schaan, Liechtenstein. The chemical composition of samples investigated was given by the manufacturer

and presented in Table I. X-ray powder diffraction (XRD) performed at room temperature with Cu-Kα radiation showed the presence of leucite crystals and amorphous fraction due to the glass matrix.[2]

TABLE I

Composition of glass-ceramics

Oxide	G_1	G_2	$(G_2 - G_1)^a$
	Mass fraction, $w \times 100$		
SiO_2	59.0–61.0	59.0–63.0	+1.0
Al_2O_3	17.0–21.0	12.5–16.7	−4.4
K_2O	10.0–14.0	10.0–14.0	0
Na_2O	3.5–6.5	5.8–8.0	+1.9
B_2O_3	0.0–1.0	0.5–2.0	+0.75
CeO_2	0.0–1.0	0.5–2.0	+0.75
CaO	0.5–2.5	1.0–3.5	+0.75
BaO	0.0–1.5	0.5–3.0	+1.0
TiO_2	0.0–0.5	0.0–0.5	0

[a] Difference $G_2 - G_1$ was calculated using the mean values for G_1 and G_2.

The samples for TSDC measurements were discs of 11.5 mm in diameter and 1 mm thick. Silver electrodes, 7 mm in diameter, were evaporated on both sides. The samples were placed into a cell filled with dry nitrogen. For integral measurements, polarization was performed by the electric field E_p = 6 kV cm^{-1} at the temperature T_p = 370 K for 2 min. Cooling to the storage temperature T_o = 173 K under E_p was at a rate of about 6 K min^{-1}. Storage in the short-circuited state (SCS) at T_o lasted 30 min. Depolarization by heating was performed at the rate of 4 K min^{-1}.

Partial runs were carried out in two ways. First, polarization by E_p = 6 kV cm^{-1} at a chosen T_p for t_p = 5 min. Then, the sample was cooled down to $T_p - \Delta T$ under E_p for 5 min. The temperature window ΔT was equal to 5 K and the runs were performed from 173 to 370 K in steps of 10 or 5 K. Cooling to T_o in SCS and the storage at T_o in SCS took together 20 min. T_o was equal to 173 K or at least 30 K below T_p. The cooling rate in SCS was about 6 K min^{-1}. The heating rate during depolarization was 4 K min^{-1}. Modified partial (MP) runs were performed by extremely narrow temperature windows.[8] The samples were polarized at T_p for 2 min and immediately cooled to T_o in SCS. Therefore, the actual temperature window was equal to the thermal gradient in the sample. A Keithley 617 electrometer was used for current measurements. The temperature was controlled by an LFE model 2012 controller.

RESULTS

Integral TSDC Measurements

The TSDC curve obtained without previous poling of sample G_1 is shown in Figure 1a. The exponential rise of current caused by conductivity appeared at about 250 K. The experiment, carried out by the usual integral methodology with poling in a wide temperature range, is shown in Figure 1b. It is not possible to see any relaxation, except for the increased background current in the whole range from 173 to 370 K. The current is caused by intensive storage of charge during poling and it is released by conductivity.
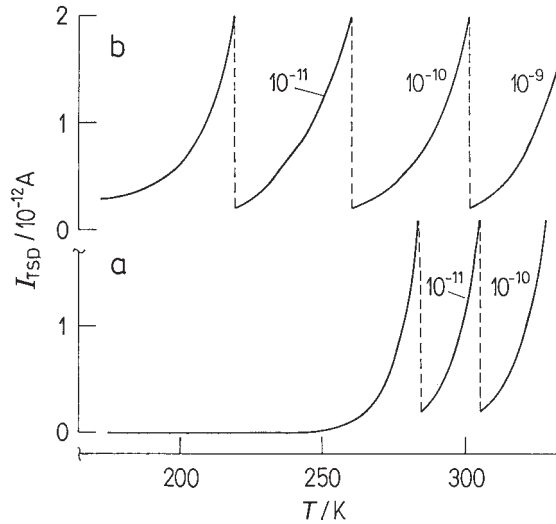

Figure 1. Integral measurements of TSDC *vs.* temperature for potassium aluminium silicate glass-ceramics G_1: a) without poling, b) poling 5 kV cm^{-1} at 368 K.

Partial TSDC Measurements

In order to reduce the storage of charge, a MP poling was applied with the reduced temperature window and time of poling.[8] The partial TSDC peaks obtained in such a way for sample G_1 are shown in Figure 2. For the first curve, the background current (BC) that appeared at its end can be neglected. For the other curves, the BC increases. For consideration of the results, the peaks have to be normalized by subtracting the BC. The normalization trend is shown in the inset of Figure 2. BC was approximated by an
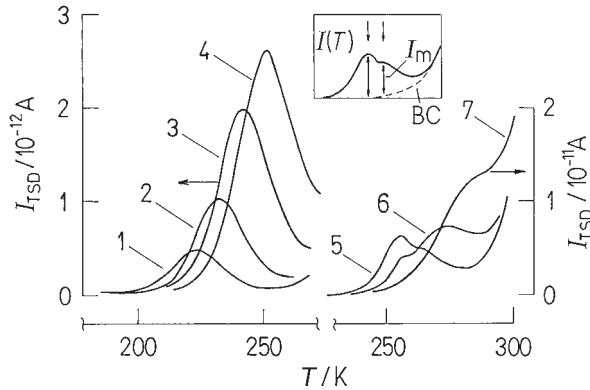
Figure 2. TSDC peaks obtained by partial polarization for sample G_1. $E_a = 6$ kV cm^{-1}. Inset: Normalization trend. BC, estimated background current; I_m, maximum current; vertical arrows show the maxima of two different relaxation processes in one partial peak.

exponential extrapolation of the ending part of the curves.[9] The curves at lower temperatures, numbered 1 to 4, represent one broad relaxation process P_1. In the following curves, 5 and 6, an additional higher temperature process P_2 appears. In the last curve 7, P_1 disappears and the only peak belongs to P_2. Analogous results for sample G_2 are shown in Figure 3. The appearance of two successive peaks in the runs numbered 5, 6 and 6' is due to
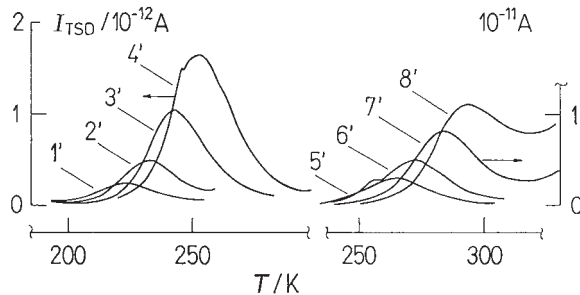

Figure 3. Partial peaks for sample G_2.

the temperature gradient in samples during the poling. Also, this is a temperature range in which two different, but close, mechanisms of relaxation are in operation.

For better comparison, the main parameters of the partial peaks are shown in Figure 4. The I_m's are the normalized maximum currents and T_m's

TABLE II

Parameters of partial TSDC peaks

Sample	Process	Curve no.[a]	$\dfrac{T_m{}^b}{K}$	$\dfrac{I_m{}^b}{10^{-12}\ A}$	$\dfrac{T_p{}^b}{K}$	$\dfrac{t_m{}^b}{min}$
G1	P1	1	223	0.44	213	2
		2	232	0.99	223	
		3	242.5	1.89	233	
		4	252	2.54	243	
		5 [c]	256	5.9	253	
		6	258	4.1	263	
	P2	5	264	4.8	253	
		6	273.5	6.1	263	
		7	280	7.0	273	
G2	P1	1'	223	0.19	213	
		2'	232	0.45	223	
		3'	242.5	1.03	233	
		4'	253	1.59	243	
		6' [c]	256	2.60	263	
	P2	5'	265	3.00	253	
		6'	273.5	4.90	263	
		7'	284.5	8.10	273	

[a] Curve numbers are related to the curves in Figures 2 and 3.
[b] T_m, temperature of peak maximum; I_m, maximum current; T_p, temperature of poling; t_p, time of poling. Errors: T_m's for P1 ± 1 K; P2 ± 2 K; I_m's ± 6 %.
[c] Curves with the maximum I_m.

are the temperatures of the peaks maxima. The numbers correspond to the peaks in Figures 2 and 3. The numerical data are given in Table II. The I_m's of P_1 in sample G_1 are higher than the related maxima in G_2. It means that system G_2 is less polarizable. The temperature of the maximum partial peak in P_1 is equal for both systems, for G_1 as well as for G_2, and amounts to 256 K.

Only three partial runs were recorded (dashed lines) for the higher temperature relaxation P_2 because the development of the process was greatly interfered by BC. Nevertheless, it is possible to see that the initial rise of I_m's for G_2 is higher than the corresponding rise in G_1. Such an increase of P_2 is contrary to the behavior of P_1 in G_2, which is reduced. Comparison of P_1 and P_2 in samples G_1 and G_2, respectively, led to the conclusion that the

changes in sample composition influence differently the relaxation mechanisms. Obviously, both relaxations are different in origin.
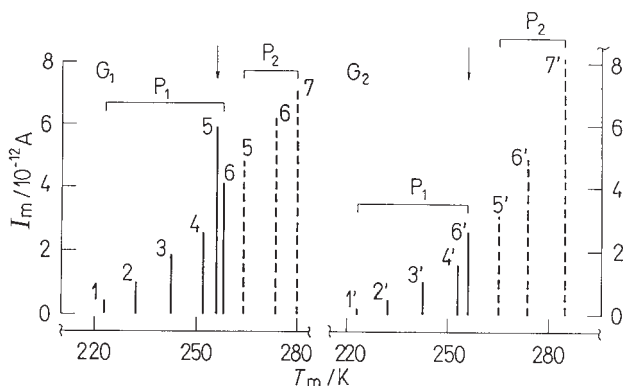

Figure 4. Main parameters of the partial peaks for samples G_1 and G_2. I_m, normalized maximum current; T_m, temperature of peak maxima; P_1, group of peaks related to lower temperature relaxation; P_2, group related to higher temperature relaxation. Arrows show maxima of the entire P_1. Numbers are related to the peaks in Figures 2 and 3.

Distribution of Activation Energy

In order to evoluate the activation energies (E_a), partial runs had to be performed by sampling with $\Delta T = 5$ K rather than by the modified procedure MP. Figure 5 contains E_a's *versus* T_m's for samples G_1 and G_2. E_p was equal
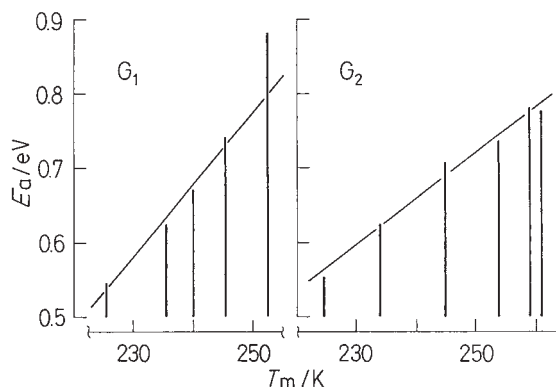

Figure 5. Activation energy E_a *vs.* T_m of the partial peaks related to P_1 for two different samples G_1, and G_2.

to 6 kV cm^{-1}. E_a's were obtained from the normalized partial peaks of relaxations P$_1$ by the initial rise method.[10] Determination of E_a for the higher temperature peaks of the P$_2$ process was not considered due to the possible uncertainty in estimation of the BC, which greatly influences the calculation of E_a's.[11] One can see that the function E_a (T_m) for both systems is practicaly linear, with one exception that appeared in G$_1$ for the maximum in T_p. The linear dependence means that a unique but distributed process is in operation. The slopes in the E_a (T_p) functions are measures for the change of P$_1$ entropy. The obtained slope for G$_2$ is decreased in comparison with G$_1$, indicating that the width of the distribution in G$_2$ is reduced. It is indicative of the hindered motions. The data for E_a's are given in Table III.

TABLE III

Activation energy

Sample	Process	T_m/K	ΔT_p/K	t_p/min	E_a/eV
G1	P1	225.5	213-208	10	0.55
		235.5	223-218		0.63
		240	228-223		0.67
		245.5	233-228		0.74
		252.5	243-238		0.88
G2	P1	224.5	213-208		0.55
		234	223-218		0.63
		245	233-228		0.71
		254	243-238		0.74
		259	253-248		0.78
		261	263-258		0.78

T_m, temperature of peak maximum; ΔT_p, temperature window for poling; t_p, time of poling. Errors for E_a's vary from $\pm$ 0.02 to 0.03 eV.

Characterization of TSDC Peaks

The electric origin of peaks has been studied by the dependence of I_m *versus* E_p for the G$_1$ system. The results are shown in Figure 6. For characterization of the lower temperature process P$_1$, the partial peaks obtained by MP procedure at T_p = 243 K were used. For characterization of the P$_2$ process, as representatives, the partial peaks obtained with T_p = 263 K were taken into consideration. In both cases, the dependences I_m (E_p) were

mainly linear with a zero intercept. Such a behavior is characteristic of linear dielectrics, showing induced polarization that is only dependent upon the external field applied (up to 11 kV cm^{-1}). The zero intercepts show the absence of any remanent dipole that might exist in the samples. As regards the I_m for peaks at lower temperature (L), one can see some exception in linearity. The exponential rise of I_m for the positive E_p could be attributed to the interference with the charge coming out from the electrode-sample interface.[7] All current values in Figure 6 were normalized against BC.
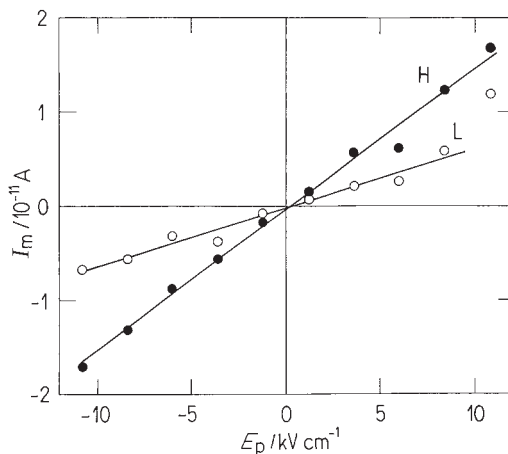

Figure 6. Characterization of relaxation processes by $I_m(E_p)$ plots. L, obtained by partial runs with poling at 243 K in the range of P_1 relaxation; H, obtained by the runs with poling at 263 K, representing the P_2 relaxation.

DISCUSSION

Appearance of two successive relaxations close to the beginning of the exponential rise of the conductivity is typical behavior that is often observed in many amorphous polymers[12–15] and glasses.[16–19] In polymers, the lower temperature process, P_1, coincides with the glass transition T_g caused by the cooperative motions of the main chains, and thus the decay of the previously induced dipolar state. In glasses, P_1 is also caused by dipolar relaxations but does not coincide with T_g.

In order to interpret the results of this paper, one can take into account the model dealing with the mixed alkali silicate glasses described in the literature.[16–18] P_1 is attributed to a dipolar relaxation caused by the motion of the localized alkali ion around the nonbridging oxygen ions. P_2 is a space charge relaxation caused by a longer range motion of the alkali ions, which

move along limited conduction pathways. BC is caused by a long range thermal motion of alkali ions.

The assumption that P_1 are caused by the dipolar relaxation is supported by the linear function of $I_m (E_p)$ drawn in Figure 6. For the higher temperature space charge relaxations like P_2, the $I_m (E_p)$ functions are usually not completely linear and are less reproducible.[14,20] In our case, $I_m (E_p)$ for P_2 is completely linear, showing an interfacial Maxwell-Wagner effect, which is related to the localized motion of charges and exhibits dipolar features.[4]

As regards the P_1 relaxations, it has been found that the motions of the localized alkali ion in G_2 are reduced. An opposite situation occurs in the range of the P_2 events where the relaxation is more intensive in G_2 than in G_1. Considering the contents of both materials (Table I), one may regard the system G_1 as a matrix and G_2 as a matrix with addition of Na_2O, B_2O_3, CeO_2, CaO and BaO. While addition of Na_2O should increase the intensity in both relaxations, P_1 and P_2, addition of other oxides seems to hinder the motions related to P_1. At the same time, addition of new components increases the grain boundary interfaces in G_2, which increases the concentration of the space charge dipoles and consequently produces the released current in the P_2 region.

CONCLUSION

TSDC measurements in the range from 173 to 370 K show three kinds of relaxation. The first one, P_1, which is widely distributed with a maximum at 256 K, is a dipolar relaxation caused by the localized motion of the alkali ions. The second relaxation, P_2, is a space charge relaxation attributed to the longer distance motion of the alkali ions. The third phenomenon is the conductivity caused by the thermal activities of many charge carriers including the alkali ions, beginning at approximately 250 K.

Comparison of the two investigated systems shows that P_1 is less pronounced in G_2 because the motions of the alkali ions are disturbed by the presence of new oxides. In contrast, the higher temperature relaxation P_2 is more intensive in G_2 due to the increase of the interface area between the matrix and the added oxides.

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SAŽETAK

Studij leucitne staklo-keramike metodom termički stimulirane depolarizacije

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Dva različita odljevka leucitne staklo-keramike istraživana su metodom integralne i parcijalne termički stimulirane depolarizacije u području od 173 do 370 K. Parcijalna mjerenja pokazuju proširenu relaksaciju (P$_1$) s maksimumom na 256 K koja je uzrokovana međudjelovanjem alkalijskih iona i nepremošćenih kisikovih atoma. Druga relaksacija, uočena na višoj temperaturi (P$_2$), pripisuje se termičkom raspadu dipola prostornog naboja. Moguće je ispitivati samo početak relaksacije P$_2$, jer je nastavak u znatnoj mjeri prekriven strujom zbog rastuće vodljivosti. Dodatak različitih oksida smanjuje P$_1$, a povećava P$_2$, zbog povećanja međufaznih površina i povećanja koncentracije prostornog naboja.