

THERMALLY STIMULATED PROCESS IN A CERAMIC IONIC CONDUCTOR BY TSDC TECHNIQUE

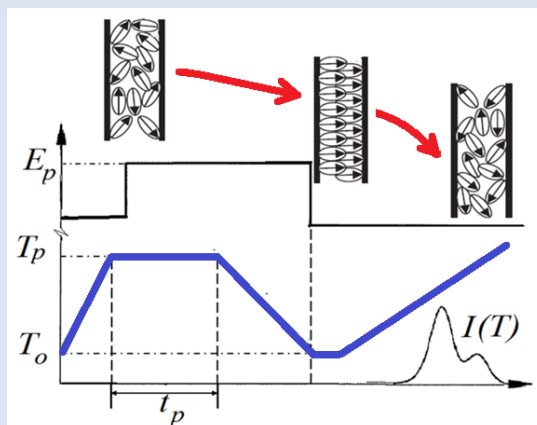
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ABSTRACT

The thermally stimulated processes in a pyrochlore-type ceramic ionic conductor were examined by the thermally stimulated depolarization current (TSDC) technique. Three polarization processes have been found in the thermogram. The first one, revealed to result from the convolution of three simple processes with approximately similar activation energies value and can be basically attributed to the reorientation of cation-anion dipoles by means of nearest-neighbor (NN) to nearest-neighbor jumps (that is to say, a NN→NN relaxation type). The second process originated most likely also from a dipolar mechanism now involving nearest-neighbor to next-nearest-neighbor relaxation processes (NN→NNN relaxation type). On the other hand, the third process has been related to a space-charge relaxation, arising from the migration of K^+ free-charge carriers. The activation energies and the pre-exponential factors for all these mechanisms were also reported.

Keywords: TSDC, Depolarization, Activation energy, Space Charge

PROCESOS ESTIMULADOS TÉRMICAMENTE EN UNA CERÁMICA CONDUCTORA IÓNICA POR LA TÉCNICA DE TSDC

RESUMEN

Los procesos térmicamente estimulados en una cerámica conductora iónica de tipo pirocloro fueron examinados por la técnica de corriente de despolarización térmicamente estimulada (TSDC). Tres procesos de polarización han sido encontrados en el termograma. El primero de ellos, revelado como resultado de la convolución de tres procesos simples con aproximadamente similar valor de energías de activación y básicamente puede ser atribuido a la reorientación de los dipolos catión-anión por medio de saltos de vecino más cercano (NN) a vecino más cercano (es decir, una relajación de tipo NN→NN). El segundo proceso se originó muy probablemente también de un mecanismo dipolar ahora involucrando procesos de relajación del vecino más cercano a los próxima vecino más cercanos (relajación del tipo NN→NNN). Por otro lado, el tercer proceso ha sido relacionado con una relajación de carga espacial, surgida de la migración de los portadores de cargas libres K^+ . Las energías de activación y los factores pre-exponenciales para todos estos mecanismos también fueron reportados.

Palabras Claves: TSDC, Depolarización, Energía de Activación, Carga Espacial

1. INTRODUCTION

The transport properties of ionic materials are usually studied by performing conductivity, diffusion or thermo-power measurements at different temperatures. An alternative method to study the transport phenomena is to employ the thermally stimulated depolarization current (TSDC) spectroscopy [1, 2]. This method can be shortly described according to the following basic steps; the sample is clamped between two electrodes and heated to a certain temperature labeled as T_p (depending on the material), and a dc electrical field (E_p) is applied for a time interval, t_p , in order to polarize it, where t_p is much longer than the relaxation time τ (T_p). By keeping the electric field turned-on, the sample is then cooled down to a low temperature T_o , and thus the polarization is frozen in. Then, the sample is heated at a constant rate in absence of the external field, and the depolarization current $I(T)$ can be recorded as a function of the temperature by using an electrometer connected in series. The TSDC spectrum can be thus obtained [3, 4]. Under the action of an external electric field, the polarization for an ionic dielectric arises from three main components [3, 5, 6]: *i*- the atomic and ionic polarization; *ii*- the dipolar polarization and *iii*- the free charge transport polarization. The latter one (*iii*) involves two phenomena, the space-charge polarization (*a*) and the interfacial polarization (*b*). The TSDC technique can successfully detect the second (*ii*) and third (*iii*) processes.

For the simplest case, that is to say, considering rotation of non-interacting dipoles, the signal $I(T)$ obeys the following expression:

$$I(T) = \frac{AP_0}{\tau_0} \exp \left[-\frac{E_a}{kT} - \frac{1}{b\tau_0} \int_0^T \exp \frac{E_a}{kT'} dT' \right] \quad (1)$$

where P_0 is the initial polarization of the dielectric, A is the area of the sample, E_a is the activation energy of the rotating dipoles and τ_0 is the usual pre-exponential factor in the time relaxation Arrhenius' relation [$\tau(T) = \tau_0 \exp(E_a/kT)$], being k is the Boltzmann's constant.

For a more general case, the activation energy is not necessarily a simple value because several types of sites, with close (but different) E_a values, may exist in the dielectric material. In such a case, the E_a

parameter is normally described by a normal distribution function $G(E_i)$ [7, 8], which is made up of several terms representing the contribution of all the involved processes. The modified depolarization current $I(T)$ appears as a convolution of several signals, according to the equations (2) and (3).

$$I(T) = \sum I(T)_i G(E_i) \quad (2)$$

$$I(T) = a_1 I_1 + a_2 I_2 + \dots + a_i I_i \quad (3)$$

The parameter a_i is a coefficient of proportionality between each type of ionic site. In the practice, the index i does not exceed three or four [4]. On the other hand, the case of the space-charge polarization is more complicated [4, 5]. The corresponding TSDC peaks are commonly sensitive to the electrode used on the sample surface. The polarization state depends on the storage condition and the electret's prehistory [4]. The competing mechanisms (e.g. bulk space charge, interfacial polarization and charge injection) also make the space-charge peaks irreproducible when experiments using different E_p intensities are performed. It makes impossible to construct an analytical equation, although several expressions have been previously suggested [4, 5, 9].

This technique has been applied to different classes of ceramic materials [5, 7, 10-13]. The aim of the present work is to explore the applicability of TSDC to KSbMoO₆ (KSM) ionic ceramic. The more general pyrochlore structure are formed by the $A^{3+}_2B^{4+}_2O_7$ and $A^{2+}_2B^{5+}_2O_7$ stoichiometry [14]. The pyrochlore structure shows varied physical properties spanning electronic insulators (e.g. La₂Zr₂O₇), ionic (Gd_{1.9}Ca_{0.1}Ti₂O_{6.9}), mixed ionic and electronic conductors, metallic conductors (Bi₂Ru₂O_{7.8}), superconducting (Cd₂Re₂O₇) and spin glass systems (Y₂Mo₂O₇). When doped appropriately, this system is particularly susceptible to be slightly oxygen deficient; e.g. A_{2-x}A'_xB₂O_{7.8} or A₂B_{2-x}B'_xO_{7.8}. The KSM present an oxygen deficient pyrochlore-type. In this material, the effect of bound water, at low temperatures range, has investigated by thermoelectric analysis and impedance spectroscopy and reported by the authors [15, 16]. The correlation between relaxation process and the variation of their electrical parameters with the state of hydration were studied to explore its application

as a humidity sensor. On the other hand, for the dehydration state (total water loss), two effects was detected, above 200 °C, which were attributed to transitions in the electrical behavior [15]. In the present work, several processes of ionic nature and charge-related are studied in the dehydrate material by the TSDC spectroscopy.

2. EXPERIMENTAL PROCEDURE

The KSbMoO_6 pyrochlore-type ceramic oxide was obtained from the conventional sintering technique, as previously reported [15]. For the TSDC measurements, the samples were pressed into disks with 10 mm in diameter and 1 mm in thickness and conductive silver paint, with its corresponding firing process, was applied on the parallel faces as electrodes. A Keithley 246 DC power supply was used for polarizing these samples with an applied electric field (E_p) of 1×10^4 V/m during 30 min (t_p). The temperature was measured by a chromel-alumel thermocouple directly connected to a temperature controller using constant heating rate (b) of 5 K/min, from room temperature up to 800 K. The depolarization current was measured using a digital Keithley Electrometer 614. The experimental set-up was controlled by a personal computer. A conventional peak cleaning technique [4] was also applied, so that a precise splitting of the involved processes was obtained, as discussed in the next section.

3. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the current (thermogram) measured over a wide temperature range. As can be seen, three peaks involving three different relaxation mechanisms were observed. A first peak was obtained at lower temperatures (LT1), with a maximum at the temperature $T_m = 515$ K, the second one (LT2) was observed at $T_m = 618$ K and the third one was obtained at higher temperatures (HT), around $T_m = 775$ K.

The first peak (LT1) was analyzed by applying the Bucci-Fieschi-Guidi (BFG) theory [1], for simple dipolar relaxation-type processes, and the parameters that characterize this relaxation process were found by the analytic initial rise and integral area methods [4]. The relaxation process parameters have been evaluated from the equation (1). A good fitting between the theoretical and experimental curves was obtained for temperatures around (above

and below) the peak, while a divergence between the experimental and theoretical curves was observed for temperature far away both sides of the peak. Thus, as shown in figure 2, the existence of three overlapped processes was assumed, and the experimental data was adjusted from the equations (2) and (3). Each one of these processes successfully responds to the equation (1) and their parameters are given in the table 1. It can be also noticed that the activation energies associated to these three processes are very close one to each other.

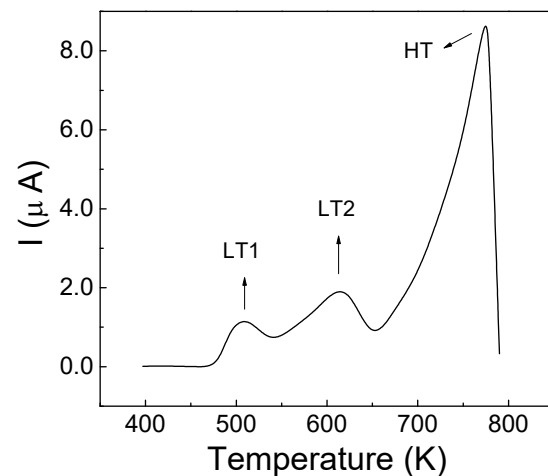


Figure 1. TSDC curve for the KSbMoO_6 system, showing the low temperature (LT1), intermediate (LT2) and high temperature (HT) peaks. The polarization conditions were $T_p = 530$ K, $E_p = 1 \times 10^4$ V/m and $t_p = 30$ min.

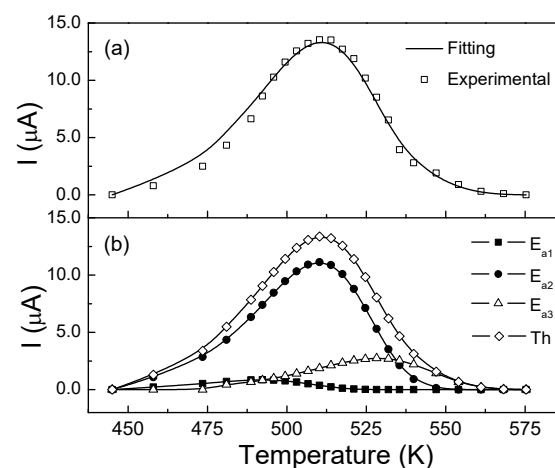


Figure 2. TSDC response for the LT1 peak showing the fitting (solid line) of the overall experimental data (symbols) (a) and the deconvolution in three contributing peaks, having different, but very close activation energies (E_a) values (b).

Table 1. Values of the activation energy (E_a) and pre-exponential factor (τ_0) obtained from the fitting of the TSDC response for the LT1 peak (involving three contributing peaks), according to the BFG Theory for simple relaxation processes.

Simple processes	E_a (eV)	τ_0 (10^{-12} s)
1	1.230	62
2	1.250	118
3	1.267	328

In order to better address this problem, several considerations previously reported in the literature have been taken into account. For instance, in a TSDC study on mordenite Na^+ zeolite [7], it has been considered that differences in the activation energy values, extracted from the material's thermogram, were related to both aspects, the cation coordination with the oxygen atoms in each site, and to the site geometry. Nevertheless, previous works conducted on pyrochlore-type materials [17-19] determined, from structural characterization, that the alkaline cations have more than one coordination number with oxygen atoms, and may thus occupy more than one nonequivalent site in the structure. Following this idea, the LT1 relaxation process can be here assumed to arise from cation-anion arrangements that should be located in three different energy positions of the framework, but with activation energy values very close one each other. From the basis of dealing with a dipolar process that normally manifests at relatively lower temperatures, the magnitude order of the calculated activation energy suggests that the cation-anion dipole relaxation involves nearest neighbor to nearest-neighbor jumps (NN \rightarrow NN relaxation type) of the K^+ cation in coordination with the neighboring oxygen atoms.

The second peak (LT2) in figure 1, was again adjusted from the Bucci-Fieschi-Guidi (BFG) theory. A good fitting between the experimental and theoretical curves was also observed, as illustrated in the figure 3. The value of the activation energy for this process, estimated from the analytic methods described above, was around 1.134 eV, while the pre-exponential factor was around 2.395×10^{-7} s. It can be noticed that the activation energy values from the LT1 and LT2 processes are relatively similar. Nevertheless, on the basis of the relatively high value of the pre-exponential factor

(10^{-7} s against 10^{-10} - 10^{-11} s for LT1), the LT2 process could be associated with a dipolar relaxation of nearest neighbor to next nearest-neighbor (NN \rightarrow NNN relaxation type) [20] in the same sublattice of K^+ cations or in the sublattice of rigid octahedron (Sb,Mo) O_4 . Further studies are required in order to accurately approach this issue.

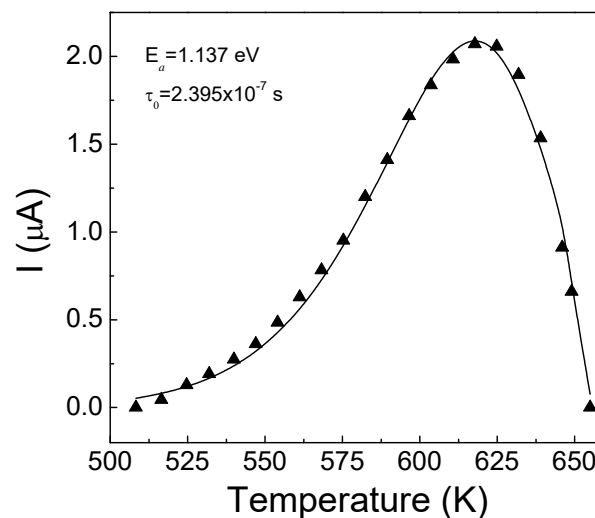


Figure 3. TSDC response for the LT2 peak showing the fitting (solid line) of the experimental data (solid symbols).

As regards the high temperature (HT) peak, as shown in the figure 4, it can be noted that both amplitude I_{\max} and position T_{\max} gradually decrease with the decrease of the polarization temperature T_p , while keeping constant the other polarization conditions (E_p , t_p and T_0). To account for such observed TSDC response, two ways may be considered. That is, this peak could result either from a dipole relaxation time distribution or from a space-charge polarization [3, 5]. The first case can be excluded because the dipolar polarization normally manifests at lower temperatures, being moreover I_{\max} and T_{\max} linear functions of T_p [3, 4], in total contrast with the results shown in figure 5.

Another important fact that should be pointed out is that quantitative characteristics of this HT peak were weakly reproducible under identical measurement conditions (T_p , E_p , t_p and T_0). This remark strongly suggests that a space-charge polarization mechanism has to be preferably considered [21, 22]. This conclusion is further supported by the calculated TSDC parameters characterizing this process: $E_a = 0.91$ eV and $\tau_0 = 6.8 \times 10^{-5}$ s, for $T_p = 530$ K, and $E_a =$

0.93 eV and $\tau_0 = 5.8 \times 10^{-5}$ s, for $T_p = 670$ K. It is worth mentioning that the temperature region over which the HT peak is activated coincides with the region where, in the KSbMoO_6 pyrochlore-type compound, an insulator-ionic conductor transition normally takes place, as previously reported in the literature [13–15], which should be promoted by highly mobile K^+ cations.

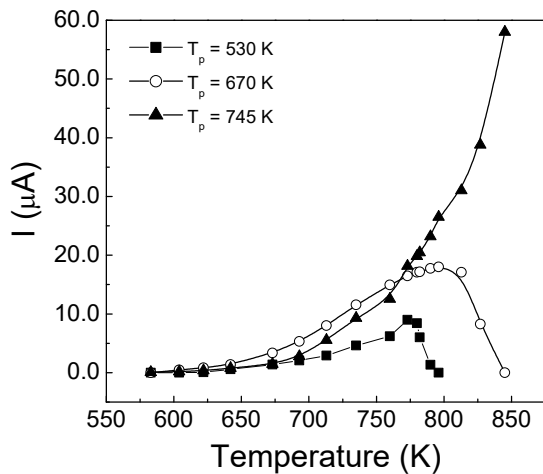


Figure 4. Evolution of the HT peak for different polarization temperatures (T_p), keeping constant the other experimental polarization conditions (E_p and t_p). The obtained values for the electrical parameters (E_a and τ_0) are presented in the text.

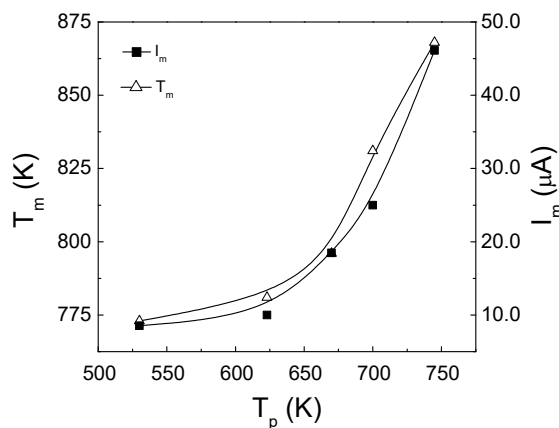


Figure 5. Polarization temperature dependence of both maximum current intensity (solid symbols) and its corresponding temperature position (open symbols) of the HT peak.

4. CONCLUSIONS

In summary, a detailed investigation on the TSDC spectra for the KSbMoO_6 pyrochlore-type ionic conductor, not previously reported in the literature,

have been carried out over a wide temperature range (300–800 °K). The study of the relaxation mechanisms in the studied system revealed an activated relaxation process at low temperatures, which can be related to the superposition of three simple dipolar processes (NN→ NN relaxation-type), and associated with different lattice sites configurations having, however, very close activation energies. A second relaxation process was also found at intermediate temperatures and has been also identified as a dipolar process, but most likely a NN→NNN relaxation-type. Toward higher temperatures, the material exhibited an insulator-ionic conductor transition, which has been ascribed to space-charge polarization and may also be manifested as a TSDC peak, depending on the polarization conditions. The present study revealed the potential of the TSDC spectroscopy for obtaining informations on the peculiarities of the relaxation processes dynamics in ionic conductor materials.

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