Electrical Properties of $Sr_2InV_3O_{11}$

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The electrical conductivity $\sigma(T)$ and thermoelectric power $S(T)$ measurements of $Sr_2InV_3O_{11}$ showed the insulating state and the change of sign of thermopower from p to n at $T_{n-p} = 400$ K. The I–V characteristics provided the evidence of symmetrical and non-linear behaviour typical of strong emission of charge carriers induced by temperature and voltage. Relative dielectric permittivity ε_r as well as loss tangent ($\tan \delta$) strongly depend both on the temperature in the range of 295–400 K and the frequency in the range of 5×10^2 to 1×10^6 Hz, showing the broad maximum at 320 K. These effects are considered as a relaxation process like in the Maxwell–Wagner or Jonscher model as well as the conduction of electric current, as determined by the Joule–Lenz law.

1. Introduction

The last few decades, intensification has been observed in the field of research on multicomponent oxide systems, which is frequently aimed at obtaining new materials of interesting electric, magnetic or catalytic properties. Investigations dealing with systems based on the oxides of divalent and trivalent metals have allowed among others to prove an existence of a series of compounds with the general formula $A_2BV_3O_{11}$ (where A(II) and B(III) — metals), e.g. $Zn_2FeV_3O_{11}$, $Mg_2CrV_3O_{11}$, $Ni_2FeV_3O_{11}$, $Pb_2BiV_3O_{11}$, $Sr_2BiV_3O_{11}$. It can be concluded from bibliographic data that these compounds are likely to find an application for example as cathode materials in high-energy cells or as components of effective catalysts for the oxidation processes of light hydrocarbons.

This paper presents the electrical properties of $Sr_2InV_3O_{11}$ compound as well as the considerations on the electron emission over the potential barrier.

2. Experimental details

The investigations of reactions occurring in the SrO–V_2O_5–In_2O_3 system have permitted a statement that also in this system a new compound of the formula $Sr_2InV_3O_{11}$ is formed [1–3]. Hitherto performed works have shown that a synthesis of $Sr_2InV_3O_{11}$ can be conducted by heating the mixture of $SrCO_3$ /In_2O_3/V_2O_5 (in molar ratio 4:1:3) in the atmosphere of air and in the temperature range 450–800 °C [1, 2]. X-ray diffraction measurement of $Sr_2InV_3O_{11}$ shown in Fig. 1 and the indexing of diffractogram confirmed that compound under study crystallizes in the triclinic system with the following unit cell parameters: $a = 0.7007(4)$ nm, $b = 0.6909(3)$ nm, $c = 1.1110(6)$ nm, $\alpha = 97.62(5)°$,

$\beta = 118.1(1)°$, $\gamma = 84.97(7)°$, $V = 0.4705$ nm³, $Z = 2$ (Fig. 1). The experimental density of $Sr_2InV_3O_{11}$ is equal to 4.36 ± 0.05 g/cm³ [3]. The energy gap calculated from the ultraviolet–visible and near-infrared measurements gave $E_g = 3.5$ eV [3].
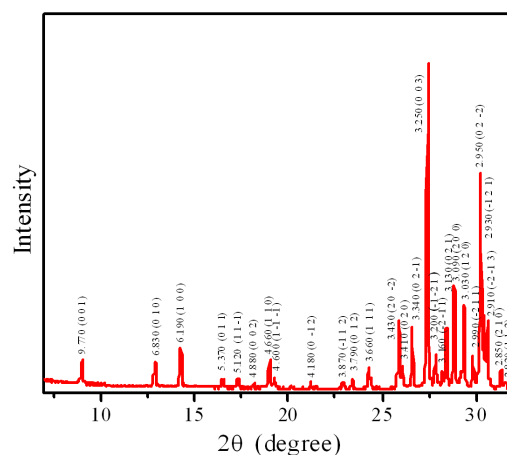

Fig. 1. Fragment of X-ray diffraction pattern of $Sr_2InV_3O_{11}$: d [Å] (hkl).

The sample morphology was observed on the scanning electron microscopy (SEM) images. SEM study was performed on JSM-1600, JEOL, Japan with an X-ray energy dispersive analysis — EDX (ISIS-300, Oxford). The crystals of $Sr_2InV_3O_{11}$ visible in Fig. 2 are similar in morphology to the crystals of this compound shown in the paper [3] but slightly differ in size. Crystals of the compound are irregular polyhedra and their average size is about 1–5 µm.

The electrical conductivity $\sigma(T)$ and the I–V characteristics have been measured via a four-probe dc method [4–6] in the temperature range 300–400 K using a KEITHLEY 6517B Electrometer/High Resistance Meter. The thermoelectric power $S(T)$ was measured in
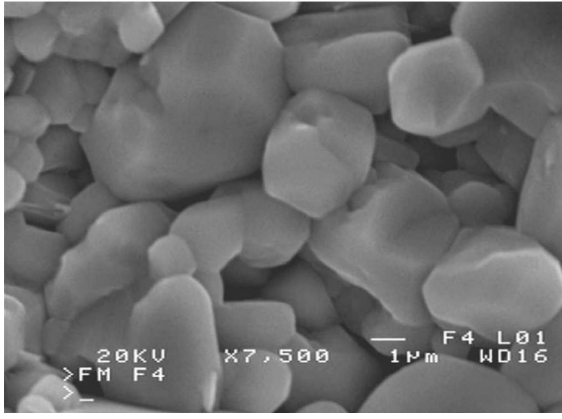
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Fig. 2. SEM image of $Sr_2InV_3O_{11}$. Magnification — 7,500.

Fig. 3. Electrical conductivity ($\ln \sigma$) vs. reciprocal temperature ($10^3/T$) and thermoelectric power S vs. temperature T.

Fig. 4. The I–V characteristics at 300 and 400 K.

the temperature range 300–600 K with the aid of a Seebeck Effect Measurement System (MMR Technologies, Inc., USA). Broadband dielectric spectroscopy measurements were carried out using pellet, polished and sputtered with ($\approx$ 80 nm) Ag electrodes in the frequency range of 5×10^2 to 1×10^6 Hz with a Novocontrol Alpha Impedance Analyser and in the temperature range 295–400 K. The sample electrode surface and thickness were 5 mm^2 and 1.0 mm, respectively. For measuring $\varepsilon_r = C/C_0$ [7], where C_0 is the capacity of the empty capacitor and $\tan \delta = \varepsilon''/\varepsilon'$ [7], where ε'' and ε' are imaginary and real part of complex dielectric permittivity, respectively.

3. Results and discussion

In $Sr_2InV_3O_{11}$ the electrical conductivity of less than 3.4×10^{-9} S/m in the temperature range 300–400 K was observed (Fig. 3). Such small values of electrical conductivity are characteristic of insulators having the value of the energy gap $E_g \approx 3.5$ eV [3]. Thermopower measurements in the range of 300–600 K (Fig. 3) revealed a sign change of thermoelectric power from p-type to n-type at 400 K in a presence of both the vacancy acceptor levels activated at lower temperatures, and the vacancy donor ones activated at higher temperatures. This is the result of ionic bonding of the oxide under study whose the electrical conductivity is nonzero and increases strongly with increasing temperature. At the same time a change of the conductivity type from p to n at $T_{n-p} = 400$ K is observed (Fig. 3). Similar behaviour was found in $AgY_{1-x}(Gd,Nd)_x(WO_4)_2$ [4, 5], $MRE_2W_2O_{10}$ (M = Cd, Co, Mn; RE = Y, Nd, Sm–Er) [4, 5] and $RE_2W_2O_9$ (RE = Pr, Sm–Gd) [6] tungstates as well as $Cd_{1-3x}Gd_{2x}\square_xMoO_4$ molybdates [4, 5].

Measurements of current–voltage, I–V, characteristics, both at 300 and 400 K revealed linearity and symmetry depending on the electric current as a function of voltage (Fig. 4) by almost two orders of magnitude difference. Such strong emission of charge carriers may be caused by reduced the potential barrier under the influence of
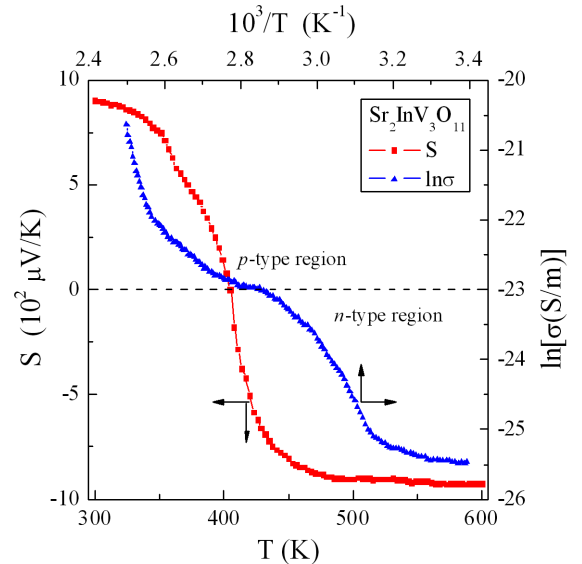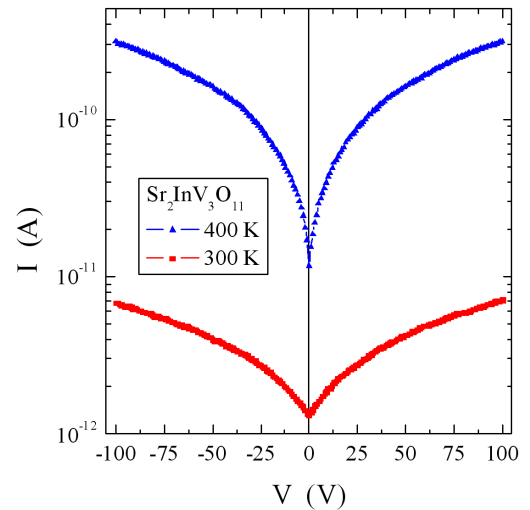
an applied electric field because our compound is the insulator with the energy gap of 3.5 eV [3]. Therefore it is unlikely that the thermal energy kT is able to activate the electrons to the conduction band.

Dielectric study revealed a strong dependence on the temperature and frequency of both the relative dielectric constant ε_r (Fig. 5) and the loss tangent $\tan \delta$ (Fig. 6) of the broad maximum of 320 K. Such behaviour could be considered as a relaxation process like in the Maxwell–Wagner [8] or Jonscher [9] model, which is strongly obscured by dc conductivity with the variable activation energy. Usually also the high values ε_r and $\tan \delta$ slightly at lower temperature may be due to the heat loss caused by the flow of electric current, described by the Joule–Lenz law [10, 11]. However, in this case, the effect is not so strong.
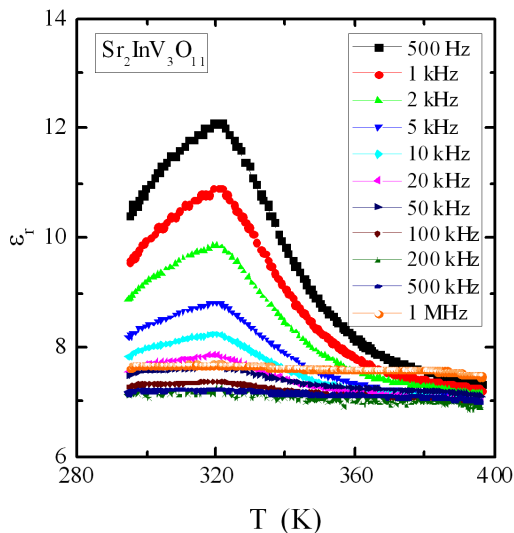
Fig. 5. Dielectric constant ε_r vs. temperature T in the frequency range 500 Hz–1 MHz.
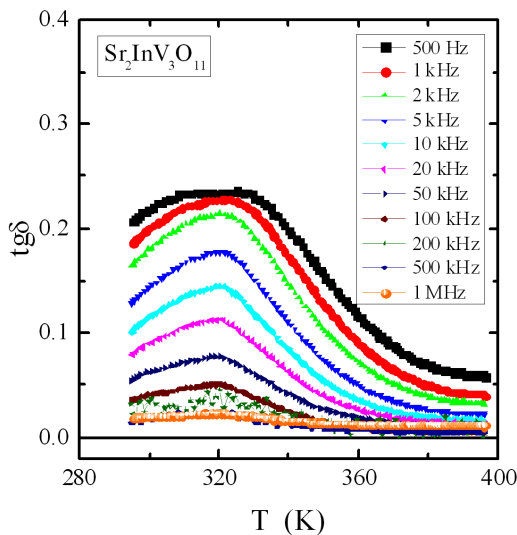

Fig. 6. Loss tangent $\tan\delta$ vs. temperature T in the frequency range 500 Hz–1 MHz.

4. Conclusions

The results of $Sr_2InV_3O_{11}$ ceramic characterization by dielectric spectroscopy, electrical conductivity, thermoelectric power, the I–V characteristics measurements have shown the insulating properties of this material with the band energy gap of 3.5 eV [3]. Moreover, the maximum values of dielectric permittivity and loss tangent slightly above room temperatures are characteristic of the relaxation process like in the Maxwell–Wagner [8] or Jonscher [9] model. A strong emission of charge carriers forced by the temperature and voltage supports the above results. Almost constant and low values at higher frequencies of relative permittivity and loss tangent of the ceramic material under study can be useful for electronic applications.

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