Physicochem. Probl. Miner. Process. 49(1), 2013, 323-328

www.minproc.pwr.wroc.pl/journal/

ISSN 1643-1049 (print) ISSN 2084-4735 (online)

Received May 14, 2012; reviewed; accepted July 19, 2012

UNUSUAL APPLICATION OF POROUS MATRIX MADE FROM QUARTZITE SCHIST

Tomasz MARCINISZYN

Institute of Physics, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland; tomasz.marciniszyn@pwr.wroc.pl

Abstract: Results of dielectric spectroscopy of quartzite slate are presented. New type of a porous matrix based on quartzite schist was described. The matrix was filled by a ferroelectric TGS-crystal. The phase transition of the TGS bulk was shown to occur and compared with the phase transition of the component quartzite schist filled with TGS (QSM-TGS). The resonance phenomena in the QSM were shown and described from the point of view filled material.

Key words: quartzite schist matrix, QSM, resonance

Introduction

Quartzite slates samples come from the Jeglowa mine located on the Strzelin Hills belonging to the foothills of the Sudety Block. Quartzite schists are situated about 15 meters below the ground level under the layer of quartzite (Fig. 1). The quartzite schist and quartzite occurring in the foothills of the Sudety Block was discovered and described in the XIX century (Lehmann, 1885). Properties of quartzite schist were described in the paper of Chmura (1967). Quartzite schist contains mainly SiO₂ (87–99%), Al₂O₃+TiO₂ (0.5–7%), Fe₂O₃ (0.1–2%), K₂O (0.2–3%) and Na₂O (0.02–1.5%), depending on the region of the Sudety Block and depth (Chmura, 1967). Density of quartzite schist equals 2.58–2.60 g/cm³. Quartzite schist has a wide range of effective porosity (open porosity), 0.5–9.3%, depending on depth (Chmura, 1967). Quartzite schist is a material with the temperature of the fire resistance $T = 1580-1710^{\circ}$ C. In the twenty century quartzite was used mostly to build O.H. furnaces (Piech, 1999). Presently quartzite with quartzite schist is use in the construction industry (stone interior accessories, roads and so on).



Fig. 1. Lithological profile of Jegłowa area vs depth

The aim of this work is to study dielectric spectroscopy of the empty and embedded with crystallites of tryglicine sulfate (TGS) quartzite schist matrix (QSM) and investigations of physical properties of this composite. The pores occurring in the quartzite schist matrix reduce the size of the introduced material. Embedded crystallite size reduction to nanocrystalline level results in surface effects domination which, in turns, starts to determine the physical properties of the material. There have been many theoretical and experimental studies on the size dependence of lattice dimensions of such compounds (Wang et al., 2011; Sieradzki et al., 2010, 2011; Rysiakiewicz-Pasek et al., 2010). To the authors knowledge, there is no previously documented case describing the possibility to use natural material-quartzite schist as a matrix.

The TGS has second order phase transition with the Curie point at 322 K. The TGS is applied to many applications such as infrared detectors, pyroelectric vidicon tubes operating at room temperature (Ashok et al., 2003; Balamurugan, et al., 2007). Additionally the TGS crystals are used in fabrication of capacitors, transducers and sensors.

Sample preparation and experimental

From the quartz schist, a cube of side 10 mm was prepared by cutting. Next the quartzite schist cube was heated at the high temperatures. After annealed, the matrix from the cube schist was developed. Precise chemical compositions of quartzite schist was determined using the XRF method and presented in the Table 1.

	Compound	Composition [%]
Spectral analysis (XRF)	SiO ₂	88.8
	Al_2O_3	7.07
	Fe ₂ O ₃	1.28
	CaO	< 0.01
	MgO	0.26
	Cr_2O_3	0.04
	MnO	0.02
	K ₂ O	2.27
	P_2O_5	< 0.01
	SO_3	< 0.01
	Na ₂ O	< 0.01
	TiO ₂	0.23
	ZrO_2	0.01

Table 1. Chemical composition of quartzite schist

The TGS was introduced into QSM as an aqueous solution. The QSM was soaked in the saturated aqueous TGS solution at 320 K for 3 hour. Then the sample was taken out and dried. The process was repeated twice. The QSM surfaces were polished mechanically to remove small TGS crystals. The quartzite schist matrix filled with the TGS was marked as QSM-TGS.

To describe the properties of the quartzite schist matrix dielectric spectroscopy measurements of empty and filled with the TGS crystal matrix were performed. An automatic Novocontrol Alpha impedance analyzer in the frequency range from 10^1 to $5 \cdot 10^7$ Hz and temperature from range from 273 to 360 K was used in the measurements.

Results

Measurements in wide frequency range were performed at 293 K and 373 K. The frequency dependence of the real part of permittivity for the QSM and QSM-TGS at 293 K and at 373 K is shown in the Figs 2 a) and b), respectively. It is well visible that in both QSM and QSM-TGS at both measurement temperatures about $1.7 \cdot 10^7$ Hz permittivity rapidly increases. It can be explained by resonance phenomena, like in the case of quartzite (Marciniszyn et al., in press). The piezoelectric resonance in quartzite is caused by vibrations occurring inside SiO₂ grains with average size of 0.15 mm. The value of the maximum of the real part of permittivity is twentyseven-fold much higher then for QSM in comparison to QSM–TGS at 293 K and twice higher than for QSM measured at 373 K. The difference in the value of permittivity of the empty matrix at 293 K and 373 K can be caused by absorbed water. Additionally, the peak of the real part of permittivity has become wider for QSM–TGS compared with QSM. The value of the peak of the real part of permittivity for QSM–TGS measured at 296 K exhibits the same value as for measurement at 373 K, which confirmed a good filling of QSM.



Fig. 2. Frequency dependence of the real part of the dielectric permittivity for QSM–TGS and QSM at 293 K (a) and 373 K (b)

To describe the influence of the matrix on the phase transition in TGS material dielectric spectroscopy test at different temperatures for 1 kHz frequency was performed and the result are shown in Fig. 3. From Fig. 3 it is well visible that for the bulk of TGS the second phase transition occurs at 321 K. For the QSM–TGS the phase transition become less sharp and the peak of the real part of permittivity disappears. The temperature of the phase transition is difficult to estimate. The matrix also caused reduction in the value of permittivity of the filled material.



Fig. 3. The temperature dependence of the real part of the dielectric permittivity for TGS-bulk and QSM–TGS

Conclusions

In this paper dielectric spectroscopy of the empty and filled quartzite schist matrix was described. The resonance in QSM was shown. Filling material of QSM was crystalline TGS. It was shown that the filling material has significant influence on the resonance occurring in QSM. The TGS crystal introduced into matrix decreases the value of the maximum $\epsilon'(f)$ and made the resonance peak smooth when compared to the empty quartzite schist matrix. QSM has large potential as a basic material in which we can control the resonance peak by the filling material. Additionally, is possible to get QSM with different size of pores.

Acknowledgments

The work is co-financed by the European Union as part of the European Social Fund.

References

- BALAMURUGAN N., LENIN M., BHAGAVANNARAYANA G., RAMASAMY P., 2007, Growth of TGS crystals using uniaxially solution-crystallization method of Sankaranarayanan-Ramasamy, Crystal Res. Technol. 42, 151–156.
- BATRA A.K., AGGARWAL M.D., LAL R.B., 2003, Growth and characterization of doped DTGS crystals for infrared sensing devices, Materials Lett. 57, 3943–3948.
- CHMURA K., 1967, Rozwój litograficzny Jegłowskiej serii kwarcytowej, Rocznik Polskiego Towarzystwa Geologicznego, t. XXXVII, Kraków.
- LEHMANN J., 1885, Dattelquarz von Krummendorf bei Strehlen, Jb. Schles. Ges. 63, 144.
- MARCINISZYN T., SIERADZKI A., POPRAWSKI R., (paper in press), *Electrical properties and microstructure of quartzite from Jeglowa/Poland after thermal treatment*, Journal of Applied Geophysics.
- PIECH J., 1999, Wyłożenia ogniotrwałe pieców i urządzeń cieplnych, Kraków.

- RYSIAKIEWICZ-PASEK E., KOMAR J., CIŻMAN A., POPRAWSKI R., 2010, Calorimetric investigations of NaNO₃ and NaNO₂ embeded into porous glasses, J. Non-Crystaline Solids, 356, 661–663.
- SIERADZKI A., KOMAR J., RYSIAKIEWICZ-PASEK E., CIŻMAN A., POPRAWSKI R., 2010, Calorimetric Investigations of Phase transitions in KNO₃ embeded into Porous Glasses, Ferroelectrics, 402, 60–65.
- SIERADZKI A., CIŻMAN A., POPRAWSKI R., MARCINISZYN T., RYSIAKIEWICZ-PASEK E., 2011, Electrical conductivity and phase transitions in KDP- and ADP-porous glass nanocomposites, Journal of Advanced Dielectrics, Vol. 1, No. 3, 337–343.
- WANG J., TAGANTSEV A.K., SETTER N., 2011, Size effect in ferroelectrics: Competition between geometrical and crystalline symmetries, Physical Review B, 83, 014104-5.