

Characterization of LiZnVO₄ ceramics prepared by two different methods

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Recently, vanadium oxide based materials have been intensively studied due to their unique structural, optical, electrical and magnetical properties. In this work, LiZnVO₄ ceramics were obtained by the conventional solid-state reaction method or by the sol-gel technique. We report on the compositional and morphological characterization of LiZnVO₄ samples, as well as on the influence of the preparation method on the photoluminescence and dielectric properties. The highest emission intensity was attained for the sol-gel LiZnVO₄ powder thermally treated at 600 °C, while the best microwave dielectric properties ($\epsilon_r \sim 7.5$ and $Q \times f \sim 37900$ GHz) were achieved for the conventional LiZnVO₄ resonator sintered at 700 °C.

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1. Introduction

Currently, the production of luminescent materials with higher efficiency is a continuous concern of researchers in order to improve the performance of different applications, such as light sources and display screens [1-3]. LiZnVO₄ (LZV) compound is widely used in electrochemical devices [4, 5] and as humidity sensors [6-9]. Moreover, in recent years, the interest of scientific field for the luminescence properties of this vanadate, generated by the [VO₄]³⁻ group, has considerably increased [10-12]. LZV crystallizes with a rhombohedral phenacite-type structure (R3 space group), where the cations occupy three tetrahedral sites; however, a definitive ion position assignment was not reported [13-15]. Grandhe *et al.* [10, 11] indicated for LZV phosphor prepared by the solid-state reaction method a bright green emission at 533 nm ($\lambda_{\text{ex}} = 359$ nm). Hsiao *et al.* [12] obtained LZV by the vibrating milled solid-state reaction method and reported a band-gap energy of 3.0 eV for the sample thermally treated at 500 °C. Ram [16] prepared LZV ceramic by a solution-based chemical route and investigated the electrical conduction, which was found to be a thermally activated process.

In this paper, we report on LZV powders and ceramics obtained by two different methods, the conventional and sol-gel techniques, their phase composition and morphology being analysed in detail. The photoluminescence properties were also investigated. The sol-gel synthesis particularities and the dielectric characterization of LZV ceramics, at low or microwave frequencies, represent the novelties of our work.

2. Experimental

In the first case, LiZnVO₄ (LZV) ceramics were prepared by the conventional solid-state reaction method, using Alfa Aesar lithium carbonate (Li₂CO₃; 99 %), zinc oxide (ZnO; 99.9 %) and vanadium pentoxide (V₂O₅; ≥ 99.6 %) as starting materials. The precursor powders were weighted according to LZV stoichiometry, homogenised by ball milling in ethanol, for 1 h, using zirconia jar and balls, then dried at 80 °C. The dry precursor mixture was uniaxial pressed at 50 MPa into discs and calcined at 600 °C, for 5 h, in air, then the discs were ball milled and dried in the same conditions as earlier mentioned. The resulting powder was granulated using a camphor solution and uniaxial pressed at 50 MPa into pellets. The pellets were sintered at 700 °C, for 5 h, in air.

In the second case, LZV ceramics were prepared by a solution-based chemical route, a sol-gel method, using Sigma-Aldrich lithium acetate dihydrate (LiOOCCH₃·2H₂O; ≥ 97 %), zinc acetate dihydrate (Zn(OOCCH₃)₂·2H₂O; ≥ 99 %) and ammonium metavanadate (NH₄VO₃; ≥ 99 %) as starting materials. The corresponding amount of NH₄VO₃ was dissolved in distilled water, heating at 90 °C and adjusting the pH = 8.5 with 25 % ammonia solution. Separately, the predetermined amounts of LiOOCCH₃·2H₂O and Zn(OOCCH₃)₂·2H₂O were dissolved in distilled water and the resulting solutions were added to the previous one, with a permanent pH control, so that a clear solution was achieved. After 1 h of solution stirring and heating at 90 °C, the temperature was gradually increased at 450 °C and maintained at this value for 4 h in order to burn the organic part; a residue powder was obtained. In order to attain single phase crystalline LZV powder, a calcining treatment at 500 or 550 °C, for 2 h, in air, was performed. LZV ceramics were obtained after granulating, uniaxial pressing

and sintering at 600 °C (the powder calcined at 500 °C) or 700 °C (the powder calcined at 550 °C), for 5 h, in air.

In the case of the sol-gel method, the precursor powder was investigated by thermal analysis (DTA-TG), using a Shimadzu DTG-60 equipment, in the 20 - 800 °C temperature range, in air. The sol-gel powders were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). A PANalytical X'Pert PRO MDB PW 3040/60 diffractometer was used to identify the phase composition and crystal structure and a Hitachi S-2600N scanning electron microscope was employed to analyse the morphology.

LZV ceramics were investigated by XRD and SEM. The photoluminescence (PL) spectra were recorded with a Edinburgh Instruments FLS920 spectrometer equipped with a Hamamatsu H5773-03 detector. For the investigation of the dielectric properties (capacitance and dielectric loss) at low frequencies (1 kHz, 5 kHz, 10 kHz, 50 kHz, 100 kHz, 500 kHz, 1 MHz), an Agilent E4980A LCR Meter equipment endowed with a Cryostat System was used, on a temperature range between 10 K and room temperature. Hakki-Coleman method was applied for the microwave dielectric properties (dielectric constant and dielectric loss) measurement at room temperature. A computer aided measurement system containing an HP 8757C scalar network analyser and an HP 8350 B sweep oscillator was used.

3. Results and discussions

The precursor powder (a fluffy, mesoporous and carbon-rich mass) obtained in the case of the sol-gel method was subjected to thermal analysis from room temperature to 800 °C (figure 1) in order to study the evolution of LZV compound formation process. The thermogravimetric data show four weight loss steps in the 130 - 510 °C temperature range. The first two endothermic effects, with maxima at 200 and 240 °C, can be assigned to the solvent loss and surface adsorbed water release. The strong exothermic effect in the 280 - 370 °C temperature range, with maximum at 350 °C, can be attributed to the combustion of most of the organic component contained by the precursor, with LZV oxide powder formation, fact confirmed by the residue XRD pattern (Fig. 3a). The fourth small exothermic effect, with maximum at 480 °C, can be associated with the completion of the organic part combustion. Above 510 °C, no other weight loss is noticed.

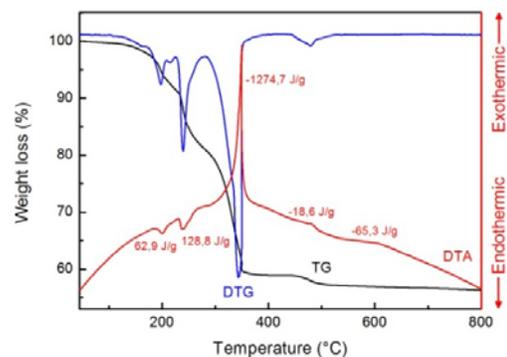


Fig. 1. Thermal analysis of LZV precursor powder, in the case of the sol-gel method.

The XRD patterns of LZV powder calcined at 600 °C and LZV ceramic sintered at 700 °C (figure 2a), both obtained by the conventional method, present intense and sharp diffraction peaks attributed to the rhombohedral structure of LZV (JCPDS 00-038-1332). The crystallinity degree is high from the calcined powder stage.

Fig. 2b displays a SEM image of the conventional LZV ceramic sintered at 700 °C. The microstructure does not involve well defined grains, but extended domains, separated by pores; the general appearance can be associated rather with a crystallized melt than a sintered ceramic. Moreover, the presence of some pores with much smaller sizes can be observed inside these domains. Unfortunately, the sintering time can not be extended in order to eliminate the inner pores because this will lead to lithium volatilization and secondary phases formation.

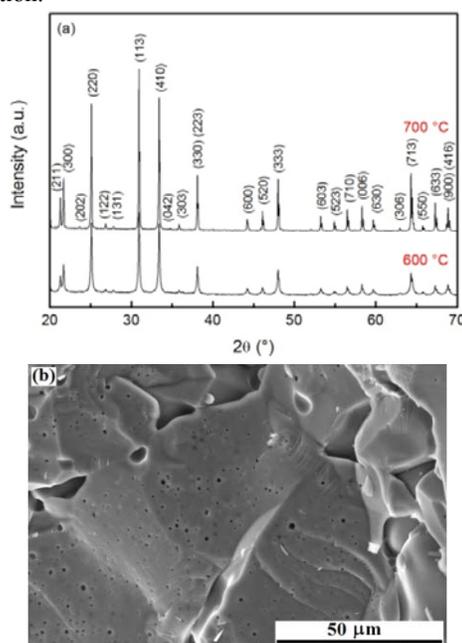


Fig. 2. (a) XRD patterns of LZV powder and ceramic and (b) SEM image of LZV ceramic, in the case of the conventional method.

The XRD patterns of LZV residue and powders calcined at 500 or 550 °C are presented in figure 3a. The powders contain small amounts of secondary phases, two of them being identified as LiVO_3 (JCPDS 00-025-1100) and $\text{Zn}_2\text{V}_2\text{O}_7$ (JCPDS 01-070-1532) binary compounds. The diffraction peaks specific to LZV rhombohedral structure can be observed from the residue stage, which suggests that LZV compound formation takes place at a temperature lower than 450 °C. LZV powder calcined at 500 °C shows a particle average size of 0.4 μm (Fig. 4a), while the one calcined at 550 °C has a sintered body appearance (Fig. 4b). The XRD patterns of the sol-gel LZV ceramics sintered at 600 or 700 °C (Fig. 3b) indicate LZV rhombohedral single phase (JCPDS 00-038-1332), with a high crystallinity degree; the sintering process leads to the secondary phases evanescence. Their microstructure is similar (figures 4b and 4c), but different from the one of the conventional LZV ceramic (Fig. 2b); well defined polyhedral grains, with a relatively large size distribution, and a higher inter-granular porosity can be noticed.

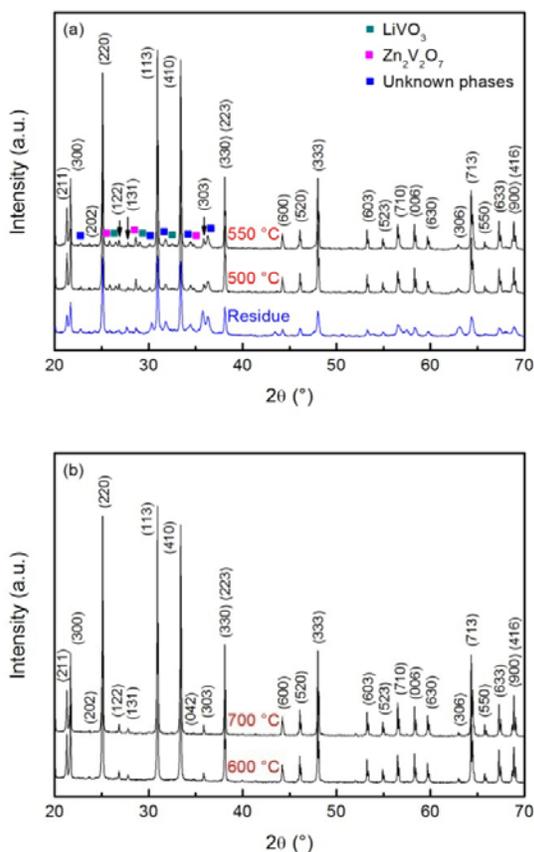


Fig. 3. XRD patterns of: (a) LZV residue and powders and (b) LZV ceramics, in the case of the sol-gel method.

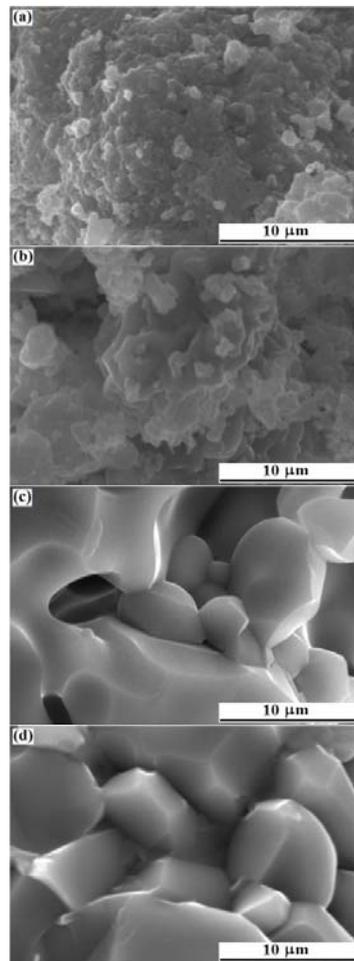


Fig. 4. SEM images of LZV powders calcined at: (a) 500 °C and (b) 550 °C and LZV ceramics sintered at (c) 600 °C and (d) 700 °C, in the case of the sol-gel method.

The excitation and emission spectra of LZV powders are shown in figure 5. For both preparation methods, the excitation spectra ($\lambda_{em} = 560 \text{ nm}$) present a broad band having its maximum at 340 nm, except the conventional LZV powder calcined at 600 °C, which exhibits maximum at 330 nm ($^1\text{A}_1 \rightarrow ^1\text{T}^1$) [10, 11]. This absorption band is attributed to $[\text{VO}_4]^{3-}$ anionic group, namely to the charge transfer from the oxygen ligands (O^{2-}) to the central vanadium cation (V^{5+}) [12]. The emission spectra ($\lambda_{ex} = 340 \text{ nm}$) expound a bright green emission, the maximum being positioned at 560 nm ($^3\text{T}_2 \rightarrow ^1\text{T}^1$) [10, 11]. It is known that vanadates present luminescence without any addition of dopant, fact that can be explained by the presence of local defects which induce new energy levels in the band gap [11].

The most efficient phosphor is the sol-gel LZV powder thermally treated at 600 °C, with a maximum emission intensity almost double compared to the following emission curve (Fig. 5b). This behaviour shows that the material purity and its crystallinity degree play an important role in the photoluminescence processes. Further analysing the emission intensity, it can be noticed that the sol-gel LZV powders calcined at 500 or 550 °C exhibit lower intensities than the conventional LZV powder thermally treated at 700 °C; moreover, the increase of the calcining temperature has a negative influence, as Hsiao *et al.* [12] reported, aspect related to the defect density and surface roughness.

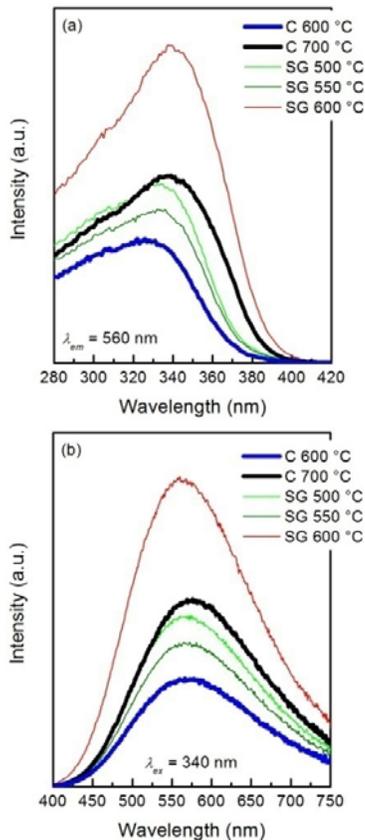


Fig. 5. (a) Excitation and (b) emission spectra of LZV powders (C - conventional, SG - sol-gel).

Considering the dielectric properties at low frequencies, LZV ceramics present a regular behaviour: the dielectric constant increases with temperature increasing and decreases with frequency increasing (Fig. 6), while the dielectric loss is around 10^{-4} for most frequencies. The sol-gel LZV ceramics exhibit smaller values for the dielectric constant in comparison with the conventional LZV ceramic, for all sintering temperatures and frequencies; for example, at 20 °C and for 100 kHz frequency, we have 8.6 (Fig. 6a) as against 7.3 (Fig. 6b) and 7.2 (Fig. 6c). This can be assigned to a better densification of the conventional LZV ceramic, as SEM

images indicate (Figs. 2b, 4c and 4d). In the case of the sol-gel method, the increase of the sintering temperature with 100 °C causes almost no change in the dielectric properties at low frequencies.

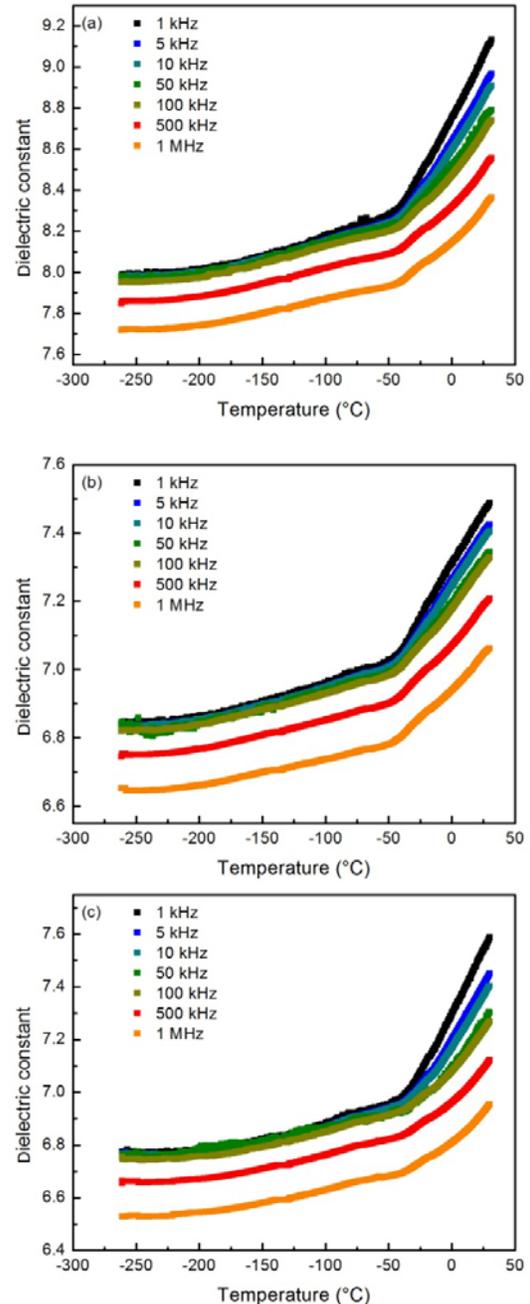


Fig. 6. Dielectric constant variation with temperature for: (a) the conventional LZV ceramic sintered at 700 °C and the sol-gel LZV ceramics sintered at (b) 600 °C and (c) 700 °C, for all frequencies.

The microwave measurements were performed in the 5 - 12 GHz frequency range. The shrinkage, density and dielectric constant values are lower in the case of the sol-gel LZV ceramic (Table 1), being well known the difficulty

of uniaxial pressing powders obtained by soft chemistry methods. The conventional LZV resonator presents the highest value for the $Q \times f$ product, 37900 GHz, a good result if we take into consideration the fact that the sintering process was performed at a relatively low temperature, 700 °C.

Table 1. Shrinkage (C), density (ρ), dielectric constant (ϵ_r), resonant frequency (f) and $Q \times f$ product values for LZV ceramics sintered at 700 °C.

Sample	C (%)	ρ (g/cm ³)	ϵ_r	f (GHz)	$Q \times f$ (GHz)
Conventional LZV	16.58	3.22	7.5	11.4	37909
Sol-gel LZV	11.17	2.94	6.8	12.5	6096

4. Conclusions

LiZnVO₄ ceramics with rhombohedral structure were prepared by the conventional solid-state reaction method, the sintering treatment being performed at 700 °C, 5 h. Moreover, LiZnVO₄ powders with a low content of secondary phases, but with a high crystallinity degree were synthesized by the sol-gel method, being calcined at 500 or 550 °C, 2 h; the sintering process at 600 or 700 °C, 5 h, made possible the obtaining of single phase LiZnVO₄ ceramics.

The emission spectra exhibit a bright green emission, with maximum at 560 nm ($\lambda_{ex} = 340$ nm), attributed to [VO₄]³⁻ anionic group. The most efficient phosphor is the sol-gel LiZnVO₄ powder thermally treated at 600 °C, the emission intensity being double compared to the one of the conventional LiZnVO₄ powder thermally treated at 700 °C. This behaviour shows that the material purity and its crystallinity degree play an important role in the photoluminescence processes.

At low frequencies, LiZnVO₄ ceramics obtained by the sol-gel method display dielectric constant values lower than the conventional LiZnVO₄ ceramic, while the dielectric loss is around 10⁻⁴ for most frequencies. The conventional LiZnVO₄ resonator sintered at 700 °C presents the highest value for the $Q \times f$ product, 37900 GHz at 11.4 GHz, with a dielectric constant value of 7.5.

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