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Gel combustion synthesis of transition metal ions doped Zn_2SiO_4 powder

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We present here the synthesis procedure for obtaining Zn_2SiO_4:M^{2+} (M = Mn, Ni, Co) powder based on the combination of sol-gel and combustion methods. Combustion is performed both in a conventional furnace and in a microwave oven in order to evaluate the influence of combustion conditions on the properties of synthesized material. X-ray diffraction analysis confirmed that obtained material has crystallized in rhombohedral structure of Zn_2SiO_4 (willemite) with traces of ZnO. The effects of combustion conditions are investigated further by means of thermogravimetric analysis, differential thermal analysis, infrared spectroscopy, diffuse reflectance optical spectroscopy and photoluminescence spectroscopy. Based on these results we could conclude that microwave combustion synthesis can be successfully applied for Zn_2SiO_4-based products.

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1. Introduction

Zn_2SiO_4 is very good host material for rare earth ions and transition metal ions, providing excellent luminescence in the blue, green and red part of the visible electromagnetic spectrum. It is well known that α-Zn_2SiO_4 (willemite) is extensively used as a host material for cathode ray tubes phosphors [1], and more recently in electroluminescence devices [2, 3]. It is an important crystalline phase in glass ceramics [4], glazes and pigments [5, 6]. Structural ordering and particle morphology affect luminophor optical characteristics and for these reasons it is still of practical importance to do research on Zn_2SiO_4 doped with transition metal ions.

Traditionally, this phosphor is prepared by solid phase reaction method. The sol-gel technology offers several processing advantages over many materials production methods. This method is important for the synthesis of luminophors as being able to ensure complete and controlled mixing of the starting components (including dopants) in the preliminary stage, and to prove an ordering of the forming structure under relatively mild conditions. Also, the combination of the sol-gel and combustion techniques has been proven to be sucessful for the synthesis of phosphor particles [7].

The present work describes the synthesis of willemite powders doped with divalent transition metal ions (Mn^{2+}, Co^{2+} and Ni^{2+}) using salted sol-gel technique in combination with combustion processing initiated in conventional oven and in microwave oven. Microwave processing of materials is different from conventional thermal processing in terms of the heat generation mechanism. In a microwave oven heat is generated within the sample itself by interaction of microwaves with material [8]. In conventional oven heat is generated by heating elements and then transferred to the sample surfaces [9]. Many investigations suggest that heating treatment is an important factor for controlling size and crystalline structure of the products. In this work we analyzed how the difference between combustion processes performed with conventional and microwave heating is affecting structural and optical properties of 3d metal doped willemite powders.

2. Experimental

2.1 Materials and samples preparation

Three samples of Zn_2SiO_4 doped with 3 at% of Co^{2+}, Ni^{2+} and Mn^{2+} were prepared using polymer modified salted sol-gel method. Tetraethyl orthosilicate (TEOS) (Aldrich, 98%), zinc-oxide (Alfa Aesar, p.a.) and nitrates of cobalt (Alfa Aesar, p.a.), zinc (Alfa Aesar, p.a.) and manganese (Aldrich, 99%) were used as the starting materials, while ethanol was used as solvent. Polyethylene glycol with average molecular weight 200 (PEG 200, Alfa Aesar) was used not only as chelating agent and a raisin vehicle, but also as fuel to provide the combustion reaction. Aqueous solutions containing appropriate concentrations of zinc nitrate and nitrates of cobalt, nickel or manganese were prepared by dissolving zinc-oxide in 6M nitric acid and adequate 3d-metal nitrates in water. Ethanolic solutions of equimolar TEOS were added to all three mixtures. In the resulting sols PEG 200 was added in 1:1 mass ratio to the expected mass of the final product, and obtained mixtures were stirred for 60 minutes at room temperature. Their acidity was adjusted to pH ≈ 6 by slowly adding ammonia solution and stirring until gels were derived. After drying at 100ºC for 5 days obtained dry gels were fired in two ways: in conventional furnace (at 600 ˚C for 10 min) and in microwave (800 W for 5 min), and then thermally treated in furnace at 1180˚C for 1h.

2.2 Characterization techniques

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) measurements have been performed on the SETARAM Setsys Evolution-1750 instrument. Powder samples of about 20 mg, obtained after combustion of gel, were heated from 500 ^{o}C to 1400 ^{o}C at the heating rate of 10 ^{o}C min^{-1} in air atmosphere with the gas flow rate of 16 ml min^{-1}. X-ray diffraction measurements are obtained by Philips PW 1050 instrument, using Ni filtered Cu $K_{\alpha1,2}$ radiation. Diffraction data were recorded in a 2θ range from 10° to 80° counting for 20 s in 0.05° steps. Infrared spectroscopy (IR) measurements were made with Thermo Nickolet Corporation Model 380 FTIR instrument. Luminescence emission and excitation spectra are measured using Perkin-Elmer Luminescent Spectrophotometer LS45 equipped with a red-sensitive R928 photomultiplier tube. Diffusion reflectance spectroscopy (DRS) measurements are performed with Perkin-Elmer Lambda 35 Spectrometer equipped with integrating sphere based diffuse reflectance accessory. The composition of the samples was determined by X-ray microanalysis unit (Oxford Instruments) on SEM (scanning electron microscop) acquiring an EDX (energy dispersive X-ray spectroscopy) spectrum for 120 s (live time) at the accelerating voltage of 25 kV. For this analysis powder was cold-pressed into pellets of 13 mm diameter under a load of about 3 tons and left uncoated. The spectra obtained from EDX analysis qualitatively confirmed the purity of investigated materials. Quantitative EDX analysis verified successful doping with 3d metals: the elemental ratio of Zn/M ≈ 8.8 is obtained for all samples that is close to value expected for a solid solution of $Zn_{1.79}M_{0.21}SiO_4$ composition (M = Co, Ni, Mn).

For EDX, diffuse reflectance and luminescence experiments we prepared pellets from the powders, without any additives and under the load of 5 tones. The pellets are shown in Fig. 1.

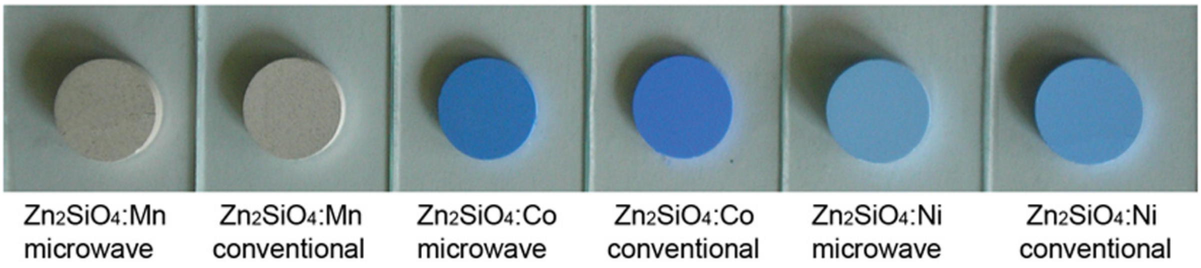

Fig. 1 The pellets of Zn_2SiO_4 powders prepared with cold pressing under the load of 5 tones.

3. Results and discussion

3.1 Thermal analysis

The DTA curves of powders obtained after the gel combustion are presented on Fig. 2. One can observe two exothermic peaks at 778 and 895°C for the case of microwave combustion, and at 788 and 905°C for the case of combustion in conventional oven. These peaks could be assigned to the crystallization of β-willemite and its transformation to α-phase, respectively [10]. The crystallization temperature of β-willemite and the temperature of transformation into the α-phase of the microwave derived product are 10°C lower than those obtained with the conventional combustion. The reason for observed difference is the thermal shock created simultaneously through the volume of the sample during the microwave combustion reaction, making the microwave-derived willemite slightly more reactive compared to the conventional one. Thermogravimetric analysis (graphs not presented here) of conventionally combusted sample showed no weight loss in the applied temperature range while for the microwave combusted sample minute weight loss is observed in the 500-700°C interval, probably duo to oxidation of residual organic groups.

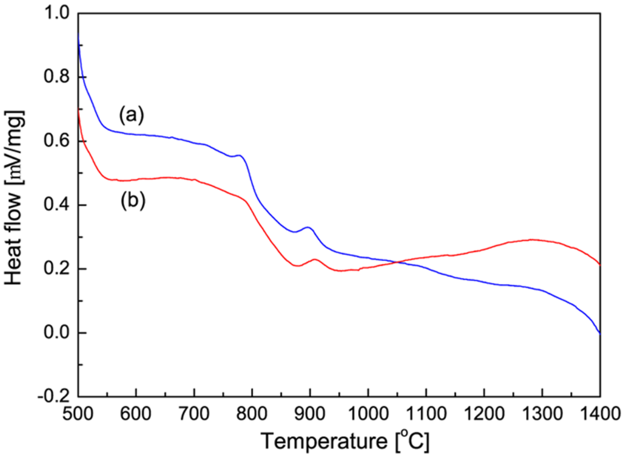

Fig. 2 Differential thermal analysis of powders obtained after the gel combustion: (a) microwave combustion and (b) conventional combustion.

3.2 X-ray diffraction analysis

Zn_2SiO_4 under ordinary conditions crystallizes in phenacite structure and belongs to the rhombohedral structure, space group R3, with both Zn^{2+} and Si^{4+} ions coordinated tetrahedrally to four oxygen atoms. X-ray diffraction patterns of obtained manganese doped willemite powders are presented on Fig. 3, where the pattern marked with (a) belongs to powder combusted in microwave oven and (b) belongs to one combusted in conventional oven. These samples are chosen as representative given that we did not observe any change in diffraction patterns when willemite was doped with cobalt or nickel. The results are in agreement with the JCPDS No. 37-1485 data, presented on Fig. 3 (c), and with those reported in literature [11-13]. A small quantity of ZnO (marked with ▼ on Figure 3 (a) and (b) on the basis of JCPDS No. 36-1451) can be observed. This fraction is smaller in microwave combusted sample. The average particle sizes of both powders, according to the Debye-Scherrer equation, are calculated to be around 50 nm, quite similar to the results obtained earlier by Yang *et al* [14] for the samples produced with sol-gel-microwave heating method.

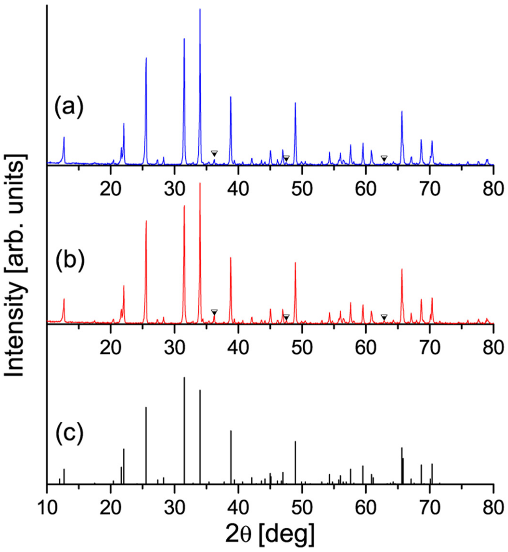

Fig. 3. X-ray diffraction patterns of Zn_2SiO_4 : (a) sample obtained with microwave induced combustion, (b) sample obtained with conventional induced combustion, (c) JCPDS No. 37-1485 data; ▼ indicates diffraction peaks of ZnO impurity phase (JCPDS No. 36-1451).

3.3 Infrared spectroscopy

The Fig. 4 shows FTIR spectra of powders after microwave induced combustion (A), and calcination at 1180 °C (C) and conventional combustion (B) and calcination at 1180 °C (D). Spectra C and D are almost identical and give characteristic willemite vibrational modes: 866 cm^{-1} (ν_1 SiO_4); 901, 931 and 977 cm^{-1} (ν_3 SiO_4); 460 cm^{-1} (ν_4 SiO_4); 573 cm^{-1} (ν_1 ZnO_4); and 613 cm^{-1} (ν_3 ZnO_4), where ν_1 stands for totally symmetric stretching, ν_3 is asymmetric stretching and ν_4 asymmetric deformation [15-18]. The IR spectrum of the powder after microwave combustion (Fig. 4A) exhibits additional absorption band at 1384 cm^{-1} which can be ascribed to the CH_3 deformation of residual organic groups/molecules. This result correlates well with observed small weight loss during TG measurement of same sample, and displays somewhat incomplete decomposition of organic phases through the microwave combustion process.

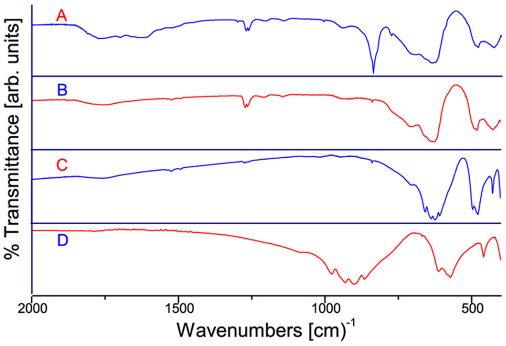

Fig. 4 FTIR spectra of powders after microwave induced combustion (A), conventional combustion (B), microwave combustion and calcination at 1180 °C (C) and conventional combustion and calcination at 1180 °C (D).

3.4 Diffuse reflectance spectroscopy

In the Zn_2SiO_4 structure both the Zn^{2+} and the Si^{4+} ions are tetrahedrally coordinated by four oxygen atoms, with two nonequivalent crystallographic Zn sites [11]. Due to the different charge and smaller ionic radius of Si^{4+} it is safe to assume that Co^{2+} and Ni^{2+} cations isomorphously replace Zn^{2+} ions in two nonequivalent Zn^{2+} sites [19, 20]. According to the literature [8, 21, 22], in the case of tetrahedrally coordinated Co^{2+} ($3d^7$ configuration) and Ni^{2+} ($3d^8$ configuration) there are three spin-allowed absorption bands. Two of them fall in the infrared region while one is present in the visible and gives rise to the blue coloration see (Fig. 1).

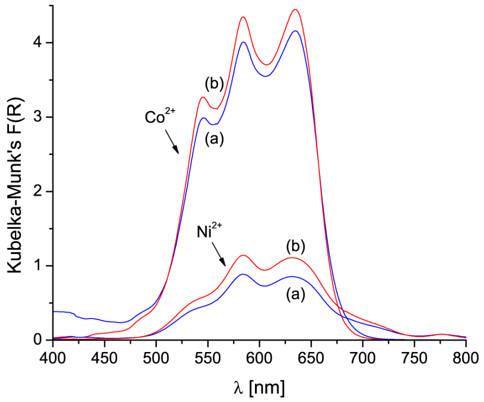

Fig. 5 Kubelka-Munk's reemission measured by diffuse reflectance on $Zn_2SiO_4:Co^{2+}$ and $Zn_2SiO_4:Ni^{2+}$ samples prepared with microwave combustion (a) and conventional combustion (b).

The Fig. 5 gives Kubelka-Munk's reemission function measured by diffuse reflectance spectroscopy on samples prepared with microwave combustion (a) and conventional combustion (b). The spectra of Zn_2SiO_4:Co^{2+} shows a broad intense band with absorption maxima at 546, 584, and 634 nm, which could be assigned to $^4A_2(F) \rightarrow {}^4T_1(P)$ d-d electronic transition in the tetrahedral environment. The spectrum of Zn_2SiO_4:Ni^{2+} also exhibits a wide, intense band with absorption maxima at 534, 584, and 631 nm, which correspond to $^3T_1(F) \rightarrow {}^3T_1(P)$ d-d transition. The high intensity of these bands is a consequence of the interaction of the 3d orbitals with the 4p orbitals and the orbitals of the ligands. There are no changes in the spectral shape and maxima positions between samples prepared with different combustion techniques. This clearly indicates identical metal cation coordination in both types of samples. However, one can notice a bit stronger reemission from samples conventionally prepared (label (a) on Fig. 5), and this stronger coloration is also visually observed as the variations of blue color (Fig.1).

3.5 Luminescence spectroscopy

Luminescence due to Mn^{2+} is known to occur in more than 500 compounds. The Mn^{2+} has five electrons occupying the outermost 3d electron orbitals of the ion ($3d^5$ configuration). In tetrahedral coordination (weak crystal field) Mn^{2+} exhibits green luminescence from $^4T_1(G) \rightarrow {}^6A_1(S)$ transition. The position of the luminescence band maximum is influenced by the coordination change (covalency, interatomic distances, etc.) and by the concentration of Mn^{2+} in the host. Luminescence of Zn_2SiO_4:Mn^{2+} powders prepared with microwave (a) and conventional (b) combustion is presented on Fig. 6. Both spectra show characteristic emission band with the maximum situated at 528 nm. The emission is almost identical with insignificant difference in intensity suggesting, like in the case of diffuse reflectance results, identical cation coordination in both samples.

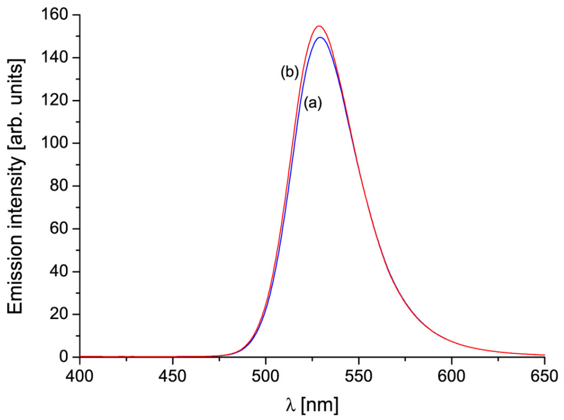

Fig. 6. Luminescence emission of Zn_2SiO_4:Mn^{2+} powders prepared with (a) microwave triggered combustion and (b) by conventional combustion.

4. Conclusions

Structural and optical properties of Zn_2SiO_4:M^{2+} (M = Mn, Co, Ni) powders, prepared using salted sol-gel method in combination with combustion processing, are studied. The objective was to investigate feasibility of the substitution of the combustion triggered with conventional heat with one initiated with microwaves. Microwave-heating has many advantages over conventional heating methods; some of the most important are reduced processing time and energy saving [23] which may be valuable for the large scale production of investigated materials.

Two sets of samples were prepared; the only difference in synthesis was variation of combustion process step. We find out that both procedures lead to structurally and morphologically identical materials (α-Zn_2SiO_4 well crystallized phenacite structure with crystallite sizes of around 50 nm). ZnO impurity phase is present in small quantities in conventionally combusted samples, while it is barely discernible in samples processed by microwaves. Lower temperature of β-phase crystallization and temperature of its transformation to α-phase are found for microwave combusted sample, suggesting that more reactive material is formed by microwave processing. In given experimental conditions microwave processing fail to decompose all organic phases from starting gel as seen from FTIR and TGA results. However, this did not influence properties of final product since organic residue decomposes completely at annealing stage. Characteristic optical properties, coloration for Co^{2+} and Ni^{2+} doped Zn_2SiO_4 and luminescence emission for Mn^{2+} doped Zn_2SiO_4 showed no discrepancies between samples prepared in two different ways. Based on these results we may conclude that microwave combustion can be successfully used in synthesis of Zn_2SiO_4-based products.

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