Metathesis microwave synthesis, Rietveld refinement and optical studies of metal orthovanadates, MVO_4 (M = Cr, Fe, Co, Ni, Cu)

G. ÇELIK GÜL*
Department of Chemistry, Balikesir University, 10145, Balikesir, Turkey

Metathesis microwave synthesis (MMS) of metal orthovanadates (MVO_4, M = Cr, Fe, Co, Ni, Cu) are realized with by-product NaCl having high lattice energy driven in the forward direction of the MMS reaction based on ionic exchange. The synthesis procedure is applied at 850 W powers in a domestic oven for a short time as 10 minutes. The structural, morphological and optical properties of synthesized powders are determined by powder X-ray diffraction (XRD), Rietveld analysis, fourier transform infrared spectroscopy (FTIR), scanning electron microscopy/energy dispersive X-ray analysis and photoluminescence spectroscopy (PL). The unit cell parameters and crystal systems of the products are identified by Rietveld refinement method one by one.

(Received March 24, 2017; accepted February 12, 2018)

Keywords: Metathesis microwave synthesis, Metal orthovanadate, Lattice energy, Rietveld refinement method, Powder X-ray diffraction

1. Introduction

The family of ABX_4 type compounds is interesting candidates in such areas: solid state scintillator materials, laser host materials, in opto-electronic devices, etc. Zircon [1], orthovanadates [2,3], chromates [4], phosphates [5], fluorides [6], orthotungstates [7,8], and molybdates [9] are the intensively studied systems of this family. Most of these compounds crystallize either in zircon with space group I41/amd, Z ¼ 4 or scheelite structure with space group I41/a, Z ¼ 4 [10] at ambient conditions. Among these systems the metal orthovanadates with the general formula MVO_4 (M = Cr, Mn, Fe, Co, Ni, Cu, Zn, Sn) represent optical, magnetic and electronic properties [11,12]. In addition, given their incomparable properties, chemical stability, and non-toxicity, orthovanadate can be used in biomedical applications [13]. The scientists began to resolve the crystal structure and group theory of MVO_4, to find the cause of the unique features obtained when the metals orthovanadates coexist [14]. Milligan and Vernon [15] reported structural studies of a group of MVO_4 which was synthesized by a previously described route containing mixed ammonium metavanadate with the oxide of a metal [16], and exposed that the crystals had crystallised in body-centred tetragonal systems of space group I41/amd (1 41) [15]. In 1958, Carron et al. [17] emphasized that acorrelation exist between ionic radii and the crystalline structures of vanadates. Also, Chakoumakos et al. [18] considered the same pathway, and managedto find relations between size limits and structures of MVO_4 synthesized homogeneous co-precipation in molten urea. The average V–O bond lengths for all synthesized heavy metals were similar with a small shortening with decreasing the atomic size of HM [19,20]. On the other hand, colloidal synthesis [21], conventional solid state synthesis [10-12,22], flux technique [23,24], sol-gel method [25,26] and polyacrylamid gel method [27] were used to obtain metal orthovanadates.

The above mentioned syntheses methods have some disadventages. For example, conventional high temperature solid state reactions need high temperature ranging from 450–1100 °C and long reaction time between 3–72 hours, and also produce both oxygen deficiency and large graing size materials. In precipation method, pH regulation must be under proper control to overcome the formation of respective phase of the hydroxide. The other wet processes need longer reaction time, expensive equipment, complicated processing and produce poor yield [28]. A novel microwave metathesis synthesis (MMS) reaction driven by microwave energy is emerging as a altervative method of synthesis of inorganic solids such as oxides, chalcogenides, oxide superconductors, metal halides, nitrides, etc. [29-37]. For example, $K_2La_2Ti_3O_{10}$, $Ca_2La_2CuTi_2O_{10}$, $LaMO_3$ (M = Co, Mn), $ATiO_3$ (A = Ca, Sr and Ba) and $Ba_3M^IM^{II}{}_2O_9$ (M^I = Mg, Ni, Zn; M^{II} = Nb, Ta) were synthesized via this process by Gopalakrishnan et al [38-41]. Additionally, Kaner et al. have synthesized oxides of Zr, Hf and Cu using this approach [42,43]. Parhi et al. have synthesized $Zn_3(PO_4)_2$ [43], LMO_4 (L = Y, La and M = V, P) [28] and MWO_4, (M = Zn) at room-temperature using this procedure [43].

Microwaves are electromagnetic radiation with frequency range of 0.3-300 GHz. In the microwave heating purposes, narrow frequency window is only used and at least one of the reactants must be ineraction to microwave field [44]. Although, microwave ovens are prefered to use in laboratory scale, large industrial types of microwave furnaces have been applied to obtain large quantities of production of many chemicals [45-51]. There are featured advantages of microwave heating such as improved product uniformity, higher yield, energy saving, shorter processing time, and controlled microstructure resulting obtaining of fresh materials with superior properties [28,34,40,43,49-54]. The most fateful property of a metathetic reaction is the formation of high lattice energy by-product (such as NaCl) ensured a local source of energy which acts as the fundamental driving force for the reaction in a short amount of time [55]. When we take into account these adventages, selecting solid-state metathesis reactions become inevitable. We have used a combination of MMS and solid state synthesis for obtaining of $M\mathrm{VO}_4$ (M = Cr, Fe, Co, Ni, Cu) with matchless properties in a simpleway. Reaction-referrer by-product NaCl has been obtained by hydrous metal chloride and sodium orthovanadate. In this medium, hydrous metal chloride acts both microwave active material and chloride source, and sodium orthovanadate plays bor sodium and vanadium source. The extraordinary side of this study is microwave metathesis synthesis of metal orthovanadates ($M\mathrm{VO}_4$, M = Cr, Fe, Co, Ni, Cu) and calculation of unit cell parameters by Rietveld refinement method for the first time as far as we know. The morphological, vibrations of interatomic bonds and optical properties of CrVO_4, FeVO_4, CoVO_4, NiVO_4 and CuVO_4 powders have been tested for brighten of structural and optical nature.

2. Experimental section

All chemical were used without further purification. Anhydrous metal chloride and sodium orthovanadate were employed for preperation of the title compounds. The prepartion of chromium orthovanadate was carried out by grinding chromium chloride and $\mathrm{Na_3VO_4}$ as 1:1 molar ratio in an agate mortar followed by microwave treatment in a domestic microwave oven (2.45 GHz, 850 W powers) for 10 min. The X-ray powder diffraction pattern of the final product was get two times; without washing and after washing with distilled hot water and recrystallized at 400 ºC. All heavy metal orthovanadates were obtained in a same metathetic pathway.

Powder X-ray diffraction (XRD) measurements were carried out by Panalytical X'Pert Pro Diffractometer and CuK_α radiation (λ=1.54056 Ǻ, 40 mA, 50 kV) with a scan rate of 1º/min with step size 0.02º. The Rietveld analyses of the samples were done by using the High Score Plus (HS+) Program (License number: 92000029). A Siemens V12 domestic microwave oven was used as the microwave source. Recrystallization process was achieved in a Protherm conventional furnace. Fourier transform infrared spectroscopy (FTIR) was on a Perkin Elmer Spectrum 100 FTIR Spectrometer from 4000 to 650 cm^{-1}. Scanning electron microscopy/energy dispersive X-ray analyses were achieved in SEM JEOL 6390-LV/EDX. The luminescence properties were measured by Andor Solis Sr 500i spectrophotometer (PL) at grating 1200 and 100 µm slit conditions.

3. Results and discussion

Fig. 1 shows the powder XRD of CrVO_4 (V1), FeVO_4 (V2), CoVO_4 (V3), NiVO_4 (V4) and CuVO_4 (V5) without washing (Fig. 1a), after washing (Fig. 1b) and after heat treatment (Fig. 1c). The by-product NaCl (ICSD:98-005-3815) is marked with " * " in Fig 1a. The formation of NaCl confirm the reactions have progressed in a metathetic pathway as described previous studies [43,55-57]. The equation of the reaction between metal chloride and sodium orthovanadate to form $M\mathrm{VO}_4$ (M = Cr, Fe, Co, Ni, Cu) is indicated as follows:

$$M\mathrm{Cl}_3 + \mathrm{Na_3VO_4} \rightarrow M\mathrm{VO}_4 + 3\mathrm{NaCl}$$

The reaction equations for the other compounds can be formed by taking into account of the above equation. Sodium chloride with high lattice energy drives the related reaction to product direction. Therefore, metal orthovanadates, are synthesized by driving force of NaCl. Therefore, target compounds have been obtained by MMS reaction. The removal process of the by-product contains washing hot distilled water three times and dried at 80 ºC to remove the water. The products which are amorphous caused by sudden temperature changes under microwave energy and washing process have been subjected to heat treatment at 800 ºC to get best crystallization and remove excess water (Fig. 1c). The unit cell parameters of the recrystallized compounds are calculated by High Score Plus program with Rietveld refinement method (Table 1).

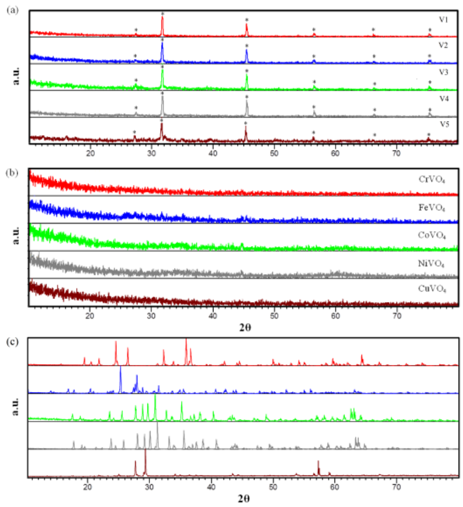

Fig. 1. Powder X-ray diffraction pattern of the samples (a) without washing, (b) after washing, (c) after heat treatment

Table 1. Crystal system and unit cell parameters of MVO_4 (M=Cr, Fe, Co, Ni, Cu) calculated by Rietveld refinement method using X-ray powder diffraction data

Reactants		Product	Crystal system	Unit cell parameters		
				a (Å)	b (Å)	c (Å)
$CrCl_3$	Na_3VO_4	$CrVO_4$	orthorombic	5.5684	8.6842	6.5645
$FeCl_3$	Na_3VO_4	$FeVO_4$	orthorombic	6.1784	9.1258	7.0529
$CoCl_2$	Na_3VO_4	$CoVO_4$	orthorombic	5.8784	8.6710	6.6290
$NiCl_2$	Na_3VO_4	$NiVO_4$	orthorombic	5.9014	8.6659	6.5464
$CuCl_2$	Na_3VO_4	$CuVO_4$	orthorombic	6.0382	8.6106	6.7646

The FTIR spectrums of the samples are shown in Fig. 2. The vibrations of V=O [58] and V–O [59] bonds of orthovanate group are also listed in Table 2. These vibration values are overstated evidence of formation of the related compounds.

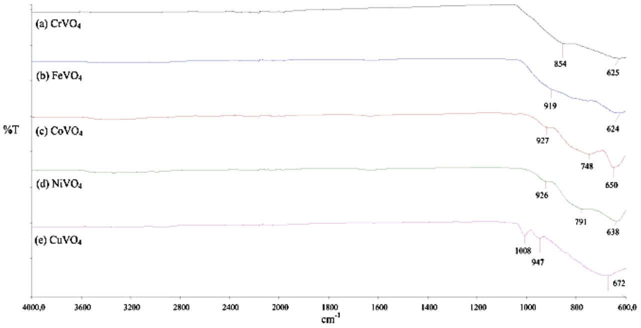

Fig. 2. The FTIR spectrum of (a) $CrVO_4$, (b) $FeVO_4$, (c) $CoVO_4$, (d) $NiVO_4$ and (e) $CuVO_4$

Table 2. Frequency data of sub-vibrations of orthovanadate group at FTIR spectrum

Assignment	Frequency (cm^{-1})
V=O	970-920
V-O	756-631

Scanning electron microscopy and energy dispersive X-ray analysis are given in Fig. 3. SEM micrograph and EDX analyses are used to determine surface morphology and crystal composition of the samples. The SEM photographs of the samples show that homogeneous particle with a flate-like aspect which is composed of a large number of small grains, except $FeVO_4$ with needle-like morphology. The molar ratios metal to vanadium calculated via EDX pattern are given in Table 3. The EDX results of the samples exhibit a good agreement with the XRD database.

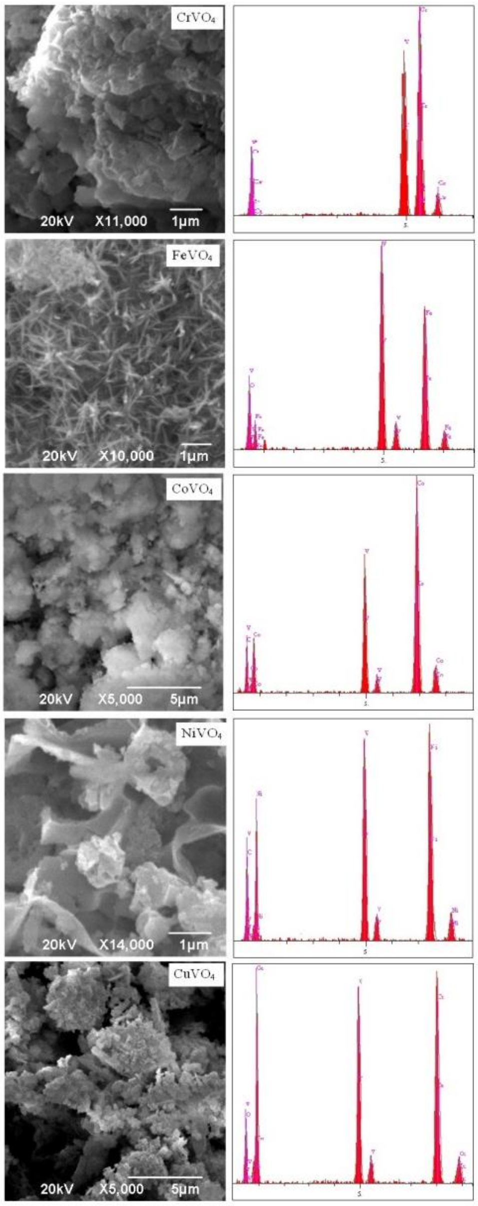

Fig. 3. Scanning electron micrograph images and EDX analysis of (a) $CrVO_4$, (b) $FeVO_4$, (c) $CoVO_4$, (d) $NiVO_4$ and (e) $CuVO_4$

Table 3. The metal to vanadium ratios from EDX

Compound	Ratio (M:V)
$CrVO_4$	1.1:1
$FeVO_4$	1.1:1
$CoVO_4$	1.3:1
$NiVO_4$	1.2:1
$CuVO_4$	1.0:1

In Fig. 4, the PL emissions of $CrVO_4$, $FeVO_4$, $CoVO_4$, $NiVO_4$ and $CuVO_4$ powders can be seen in order. All the emission spectra consist of a broad band ranging from 350 to 600 nm with a maximum at about 470 nm with several shifts, which can be attributed to a one-electron charge-transfer process like in other self-activated vanadate phosphors [60-62]. In a general aspect, compounds exhibit blueshift except $CrVO_4$ with a redshift. On the other hand, $CoVO_4$ has the most intensive radiation.

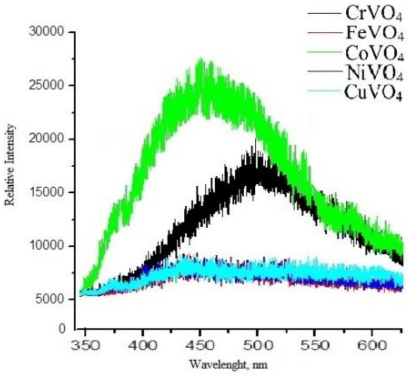

Fig. 4. Photoluminescent spectrum of (a) $CrVO_4$, (b) $FeVO_4$, (c) $CoVO_4$, (d) $NiVO_4$ and (e) $CuVO_4$

4. Conclusion

In this study, metal orthovanadates, MVO_4 (M = Cr, Fe, Co, Ni, Cu) are synthesized by microwave metathesis synthesis via driving force to product direction of by-product NaCl with high lattice energy. The synthesis process is achieved at 850 W powers for 10 minutes in a domestic oven with starting materials sodium orthovanadate and metal chlorides. Besides, the volumetric heating ability of microwaves allows for more rapid and uniform heating, resulting in decreased processing time, and often enhanced material properties. The calculations of unit cell parameters are realized by Rietveld method using powder XRD pattern. Structural, morphological and optical properties also support the formation of these metal orthovanadates. In a general aspect, compounds exhibit blueshift except $CrVO_4$, and homogeneous view in surface images.

Acknowledgement

This work has been financially supported by Balıkesir University with research project foundation and Scientific and Technological Research Council of Turkey. We want to thank to Prof. Dr. Figen Kurtuluş and Dr. M. Burak Çoban for scientific support.

References

[1] E. Knittle, Q. Williams, Am. Mineral. **78**, 245 (1993).
[2] A. Jayaraman, G. A. Kourouklis, G. P. Espinosa, A. S. Cooper, L. G. V. Uitert, J. Phys. Chem. Solids **48**, 755 (1987).
[3] S. J. Duclos, A. Jayaraman, G. P. Espinosa, A. S. Cooper, R. G. Maines Sr., J. Phys. Chem. Solids **50**, 769 (1989).
[4] Y. W. Long, L. X. Yang, Y. Yu, F. Y. Li, R. C. Yu, Y. L. Liu, C. O. Jin, J. Appl. Phys. **103**, 093542 (2008).
[5] F. X. Zhang, M. Lang, R. C. Ewing, J. Lian, Z. W. Wang, J. Hu, L. A. Boatner, J. Solid State Chem. **181**, 2633 (2008).
[6] A. Grzechnik, K. Syassen, I. Loa, M. Hanfland, J. Y. Gesland, Phys. Rev. B **65**, 104102 (2002).
[7] D. Errandonea, J. Pellicer-Porres, F. J. Manjon, A. Segura, Ch. Ferrer-Roca, R. S. Kumar, O. Tschauner, P. Rodriguez-Hernandez, J. Lopez-Solano, S. Radescu, A. Mujica, A. Munoz, G. Aquilanti, Phys. Rev. B **72**, 174106 (2005).
[8] D. Errandonea, J. Pelliser-Porres, F. J. Manjon, A. Segura, Ch. Ferrer-Roca, R. S. Kumar, O. Tschauner, J. Lopez-Solano, P. Rodriguez-Hernandez, S. Radescu, A. Mujica, A. Munoz, G. Aquilanti, Phys. Rev. B **73**, 224103 (2006).
[9] D. Christofilos, A. Arvanitidis, E. Kampasakali, K. Papagelis, S. Ves, G. A. Kourouklis, Phys. Status Solidi B **241**, 3155 (2004).
[10] R. Rao, A. B. Garg, T. Sakuntala, S. N. Achary, A. K. Tyagi, J. Solid State Chem. **182**, 1879 (2009).
[11] Y. Liang, P. Chui, X. Sun, Y. Zhao, F. Cheng, K. A. Sun, J. Alloys Compd. **552**, 289 (2013).
[12] C. T. G. Petit, R. Lan, P. I. Cowin, S. Tao, J. Solid State Chem. **183**, 1231 (2010).
[13] W. O. Milligan, L. W. Vernon, J. Phys. Chem. **56**, 145 (1952).
[14] W. O. Milligan, L. M. Watt, H. H. Rachford, J. Phys. Colloid Chem. **53**, 227 (1949).
[15] M. K. Carron, M. E. Mrose, K. J. Murata, Am. Mineral. **43**, 985 (1958).
[16] B. C. Chakoumakos, M. M. Abraham, L. A. Boatner, J. Solid State Chem. **109**, 197 (1994).
[17] M. M. Abraham, L. A. Boatner, T. C. Quinby, D. K. Thomas, M. Rappaz, Radioactive Waste Manage. **1**, 181 (1980).
[18] B. C. Sales, L. A. Boatner, Radioactive waste forms for the future, W. Lutze, R.C. Ewing (Eds.), Elsevier, New York, 1988.
[19] V. Klochkov, J. Photochem. Photobio. A: Chem. **310**, 128 (2015).
[20] T. V. Gavrilovic, D. J. Jovanovic, V. M. Lojpur, V. Dordevic, M. D. Dramicanin, J. Solid State Chem. **217**, 92 (2014).
[21] U. G. Nielsen, H. J. Jakobsen, J. Skibsted, Solid State Nucl. Magn. Reson. **23**, 107 (2003).

[22] C. C. Santos, I. Guedes, C.-K. Loong, L. A. Boatner, Vibra. Spect. **45**, 95 (2007).

[23] D. F. Mullica, E. L. Sappenfield, M. M. Abratmm, B. C. Chakoumakos, L. A. Boamer, Anorg. Chim. Acta **248**, 85 (1996).

[24] N. Cimino, F. Artuso, F. Decker, B. Orel, A. Surca Vuk, R. Zanoni, Solid State Ionics **165**, 89 (2003).

[25] B. Orel, A. Surca Vuk, U. Opara Krasovec, G. Drazic, Electrochim. Acta **46**, 2059 (2001).

[26] H. Zhang, X. Fu, S. Niu, G. Sun, Q. Xin, J. Solid State Chem. **177**, 2649 (2004).

[27] P. Parhi, V. Manivannan, Solid State Sci. **10**, 1012 (2008).

[28] P. R. Bonneau, R. F. Jarvis, R. B. Kaner, Nature **349**, 510 (1991).

[29] P. Parhi, A. Ramanan, A. R. Ray, Mater. Lett. **58**, 3610 (2004).

[30] P. Parhi, A. Ramanan, A. R. Ray, Mater. Lett. **60**, 218 (2006).

[31] T. K. Mandal, J. Gopalakrishnan, Chem. Mater. **17**, 2310 (2005).

[32] J. Gopalakrishnan, T. Sivakumar, K. Ramesha, V. Thangadurai, G. N. Subbanna, J. Am. Chem. Soc. **122**, 6237 (2000).

[33] A. M. Nartowski, I. P. Parkin, M. MacKenzie, A. J. Craven, I. Macleod, J. Mater. Chem. **9**, 1275 (1999).

[34] L. Rao, E. G. Gillan, R. B. Kaner, J. Mater. Res. **10**, 353 (1995).

[35] R. E. Treece, J. A. Conklin, R. B. Kaner, Inorg. Chem. **33**, 5701 (1994).

[36] D. Mingos, P. Michael, Adv. Mater. **5**, 857 (1993).

[37] B. Vaidhyanathan, M. Ganguli, K. J. Rao, Mater. Res. Bull. **30**, 1173 (1995).

[38] T. Sivakumar, S. E. Lofland, K. V. Ramanujachary, K. Ramesha, G. N. Subbanna, J. Gopalakrishnan, J. Solid State Chem. **177**, 2635 (2004).

[39] T. K. Mandal, J. Gopalakrishnan, J. Mater. Chem. **14**, 1273 (2004).

[40] R. Mani, N. S. P. Bhuvanesh, K. V. Ramanujachary, W. Green, S. E. Lofland, J. Gopalakrishnan, J. Mater. Chem. **17**, 1589 (2007).

[41] E. G. Gillan, R. B. Kaner, J. Mater. Chem. **11**, 1951 (2001).

[42] J. B. Wiley, E. G. Gillan, R. B. Kaner, Mater. Res. Bull. **28**, 893 (1993).

[43] P. Parhi, V. Manivannan, Bull. Mater. Sci. **31**, 885 (2008).

[44] M. A. Janney, H. D. Kimrey, Ceramic Powder Science, 919 (1988).

[45] G. Link, V. Ivanov, S. Paranin, V. Khrustov, R. Bohme, G. Muller, G. Schumacher, M. Thumm, Mater. Res. Soc. Symp. Proc. **430**, 157 (1996).

[46] T. T. Meek, R. D. Blake, J. Petrovic, J. Ceram. Eng. Sci. Proc. **8**, 861 (1987).

[47] Y. V. Bykov, A. G. Eremeev, V. V. Holoptsev, C. Odemer, A. I. Rachkovskii, H. J. R. Kleissi, Ceram. Trans. **80**, 321 (1997).

[48] K. E. Haque, Int. J. Miner. Process. **57**, 1 (1999).

[49] P. D. Ramesh, B. Vaidhyanathan, M. Ganguli, K. J. Rao, J. Mater. Res. **9**, 3025 (1994).

[50] Q. Zang, J. Luo, E. Vileno, S. L. Suib, Chem. Mater. **9**, 2090 (1997).

[51] H. Guler, F. Kurtulus, Mater. Chem. and Phy. **99**, 394 (2006).

[52] P. Parhi, A. Ramanan, A. R. Ray, J. Am. Ceram. Soc. **90**, 1237 (2007).

[53] V. Thangadurai, C. Knittlmayer, W. Weppner, Mater. Sci. Eng. B **106**, 228 (2004).

[54] S. M. Montemayor, A. F. Fuentes, Ceram. Int. **30**, 393 (2004).

[55] J. Guo, C. Dong, L. Yang, G. Fu, J. Solid State Chem. **178**, 58 (2005).

[56] K. Uematsu, K. Toda, M. Sato, J. Alloys Compd. **389**, 209 (2005).

[57] H. Y. Xu, H. Wang, Y. Q. Meng, H. Yan, Solid State Commun. **130**, 465 (2004).

[58] M. I. Kohan, T. Hope, S. Tabassum, Solid State Sci. **1**, 163 (1999).

[59] D. Xiao, S. Wang, Y. Hou, E. Wang, Y. Li, H. An, L. Xu, C. Hu, J. Mol. Struc. **692**, 107 (2004).

[60] H. Ronde, G. Blasse, J. Inorg. Nucl. Chem. **40**, 215 (1978).

[61] G. Blasse, Springer-Verlag, Berlin, 1 (2006).

[62] Y. A. Barykina, N. I. Medvedeva, V. G. Zubkov, D. G. Kellerman, Journal of Alloys and Compounds, in press.

---

[*] Corresponding author: gulsahcelik@balikesir.edu.tr