JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 4, April 2008, p. 887 - 890

Synthesis of sillenite-type compounds from zeolite precursors: XRPD and SEM/EDS analyses

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The paper analyze the possibility of using LTA zeolite as a precursor for obtaining sillenite phase ($Bi_{12}MO_{20}$, M=Si, Ti, Ge) by hydrothermal synthesis process. The synthesis procedure involves mixing of zeolite (Na-LTA) water solution with native bismuth in autoclave at 170°C for 7 days. As-prepared sample contains sillenite $Bi_{12}SiO_{20}$ and nepheline (Na_2AlO_6) phases. The structures of sillenite and nepheline phases were determined by XRPD methods, and their quantitative amounts were calculated by Rietveld method. These structures were refined with agreement factors: R_p= 7.21, R_{wp}= 9.25 and R_{bragg} = 6.14 for a cubic structure sillenite and R_{bragg} = 18.6 for nepheline phases. The weight fractions were 36.73% for sillenite and 63.72% for nepheline. The shape, morphology and chemical composition of investigated phase are done by means of scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS).

(Received February 25, 2008; accepted April 2, 2008)

Keywords: Sillenite, Zeolite precursor, XRPD, SEM, EDS

1. Introduction

The structural family of bismuth silicate with sillenite structure is of interest due to some special physical properties (photorefraction, piezoelectricity, optical activity) [1-2]. The general formula of the sillenite compounds was $Bi_{12}MO_{20}$, with the cation M = Ge, Si, Ti or the cation in the form of isomorphic mixtures M = (Bi, Ga), (Bi, V), (Bi, Zn), (Bi, Fe), (Fe, P) [3-4]. Several methods have been used to synthesize compounds with sillenite structure: solid-state reaction [5, 6], sol-gel processing [7], and aqueous solution synthesis [8]. Usual, the Czochralski growth process was used for synthesis of single crystal sillenite structure [1].

There has been intense activity over the last three decades in the area of preparation of various ceramic materials using synthetic zeolites as precursors [9-12]. It is well known that the zeolites are crystalline alumosilicates with an open framework structure and general formula $M^{n+}_{2/n}$ Al_2O_3 $x SiO_2$ H_2O, was used as precursor powders. Aqueous ion exchange can be preformed to incorporate a variety of other metals, typically alkali and alkaline earth for the M^{n+} cation. Upon heating, the zeolite structure collapses and forms a glass that then crystallizes into the composition predicted by the starting chemical composition and equilibrium phase diagram [13].

In this paper, we present the results of using zeolite LTA – framework topology as a precursor for obtaining sillenite phase together with XRPD, SEM/EDAX and DTA/TG characterization of titled compounds.

2. Experimental part

The sodium form of synthetic zeolite LTA, manufactured by Union Carbide Co., was used as starting material. The content of Na^+ cation is 11.6 wt. % and exchange capacity (CEC) of this zeolite was 5.1meq/g. The process of synthesis was preformed as follows: 5g of the Na-LTA zeolite were contacted overnight with 0.1 dm^3 of water solution with 0.5g of native Bi in autoclave at about 190 °C. This sample was marked as Na_{LTA}+Bi.

The results of atomic absorption spectrophotometer (ASS) by using a Perkin-Elmer 390 spectrophotometer are shown in Table 1. Using EDAX method we controlled the presence of Si, Al, Na and Bi cations in chemical composition of synthesized compounds. The first exothermic peak in the DTA/TG curves was in temperature range of 344°C. The new synthesized materials (Bi+zeolite $_{LTA}$ topology) were annealed up to 350°C for 1h and its structural transformation to sillenite and nepheline phase was confirmed by X-ray powder diffraction (XRPD) analysis. This new materials was marked as Bi_{LTA}.

The XRPD patterns were obtained on a Philips PW-1710 automated diffractometer using a Cu tube operated at 40 kV and 30 mA. For a Rietveld profile fitting method the XRPD data were collected by using the step scanning mode in the range of Bragg angle 2Θ = 4-65° at each 0.02 step counting for 12.5 sec. Collected data were refined by using the FullProff program [14]. The XRPD patterns measurements were performed *ex situ* at the room temperature in a stationary sample holder. For the Rietveld refinement procedure was used the published results for nepheline [10] and sillenite [6] crystal structures, respectively. The alignment of the diffractometer was checked by means of a standard Si powder material.

Investigations of crystal morphology and chemical composition of sample was carried out using a LINK AN 1000 EDS microanalyses attached to a JEOL JSM–6460 LV scanning electron microscope. The ZAF-4/FLS software provided by LINK was used for corrections.

A NETZSCH STA 409EP simultaneous differential thermal and thermogravimetric analyzer was used. A 200 mg sample was heated at 1000 °C in a Pt-Ir crucible at 10 °C/min. Powdered corundum was used as a reference material.

3. Results

3.1 Chemical and SEM/EDX analysis

Chemical composition of starting zeolite and thermal treated new phase (Bi_{LTA}) is presented in Table 1. EDS patterns yielded composition results in agreement with chemical analysis, see Table 1.

Table 1. Chemical analysis results of starting zeolite and synthesized Bi_{LTA} phase.

Composition (wt %)					
Sample	SiO_2	Al_2O_3	BiO	Na_2O	H_2O
Na_{LTA}	34	31	-	16	19
Bi_{LTA300}	17	16	34.5	12	18
Results of EDX analysis					
Composition (wt %)					
	Si	Al	Bi	Na	O
Na_{LTA}	15.8	16	-	10.65	57.45
Bi_{LTA300}	7.73	8.30	32	8.8	43.20

The crystal morphology of staring zeolite$_{LTA}$ – framework topology and thermal trated phase of Bi_{LTA} was presented on SEM images in Fig. 1 (a-d). Observed initial zeolites with developed cubic crystal forms are present in Fig. 1a. A predominately rounded grain forms, observed in Fig. 1b-d, show the form of new synthesis phase Bi_{LTA}. The SEM microphotography show average smaller grain size of synthesis material.

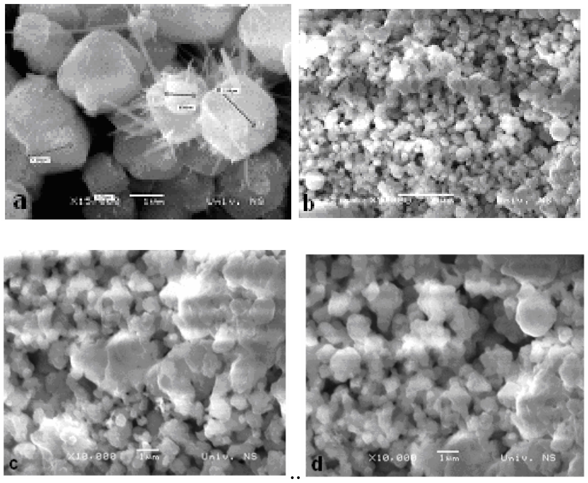

Fig. 1. Scanning electron images (a) of initial LTA-framework zeolite (b, c, d), thermal treated Bi_{LTA} phase.

3.2 DTA/TG and XRPD analysis

The thermal behavior of sample Na_{LTA}+Bi was observed with differential thermal analysis. Figure 2 shows the DTA/TG curve obtained for the sample (presented in XRPD diagram in Figure 3b). DTA curve shows the typical endothermic dehydration peaks for frist zeolitic water in temperature 102°C. An additional endothermic peak was observed in 609°C, 792°C, 891°C and two exothermic peak in temperature rang 344°C and 804°C. The polymorphic transformation for sillenite materials are observed in this temperature range [15, 16].

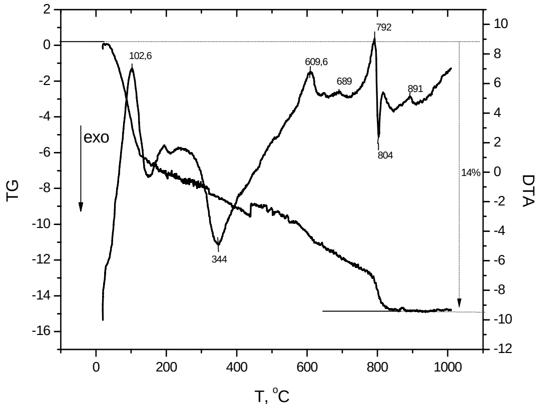

Fig. 2. DTA/TG curve of compounds Na_{LTA}+ Bi

Based on the results of Chehab at al. [16] the $Bi_{12}SiO_{20}$ appear at 600°C. The exothermic peak at 344°C (figure 2) corresponds the crystallization of sillenite phase ($Bi_{12}SiO_{20}$) and that was confirm in X-ray pattern (figure 3c).

The observed other thermal peaks is very difficulty to be attributed, because they present composite of zeolite$_{LTA}$ and native Bi.

The diffraction patterns of the zeolite$_{LTA}$, hydrothermal exchange Na$_{LTA}$+ Bi and thermal treated composite sample are presented in Figure 3. The XRPD patterns (figure 3a, 3b) show a decrease in crystallinity of zeolite Na-LTA phase due to the presence of Bi. Also, in this diagram (figure 3b) was presented the reflection of native Bi (d=3.27, 2.36, 2.26).

Thermal treatments at 350°C for 1h of Bi+ zeolite $_{LTA}$ sample, results in crystallization of sillenite phase, as it is showed from the XRD patterns (Figure 3c). The d-values of the synthesized sillenite phase were 3.19, 2.70, 1.73, 1.98, 1.68, 1.63 Å and the line intensities were in good agreement with data of JCPDS base (PDF number 37-0485). The second phase was mineral nepheline (d-values were 4.30, 3.82, 3.26, 2.98, 2.33 Å).

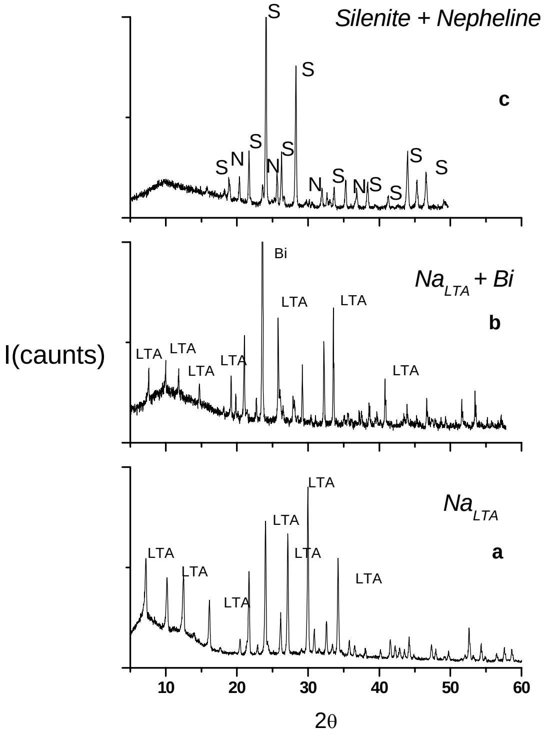

Fig. 3. XRPD patterns of investigation samples

4. Discussion

Stoichiometric sillenites $Bi_{12}MO_{20}$ contain tetravalent atoms, e.g., Si, Ge, Ti, wich occupy position (*2a*) in space group *I23* with ideal tetrahedral coordination by oxygen [6].

The sillenite phase was refined in the cubic space group *I23*, for different distributions of Si and Bi over the cation sites [6]. Cubic unit-cell parameters (*I23*) of sillenite yielded the best refinement agreement R-factors (R_p= 7.21, R_{wp}= 9.25, R_{exp} = 7.05 and R_{bragg} = 6.14, *ch2* =1.72). Hexagonal unit-cell parameters, space group P63 was used to determined nephelin phase. Quantitative volume fraction (*) and unit-cell parameters of thermal treated Bi$_{LTA}$ sample and second phase mineral nepheline obtained from Rietveld refinement are presented in Table 2.

Background values were determined by linear interpolation between consecutive breakpoints in the pattern. Intensities within eight times the full width at half maximum of a peak were considered to contribute to the central reflexion. The pseudo-Voigt function was chosen for the simulation of the peak shape, with two parameters defining the Lorentzian and Gaussian character of the peaks as a function of 2θ.

Table 2. The lattice parameters and the reliability factore, obtained from Rietveld refinement.

	Sillenite	Nepheline
a (Å)	10.1109(4)	9.97243(2)
b (Å)	10.1109(4)	9.97243(2)
c (Å)	10.1109(4)	8.30669(2)
β (°)	90	100.91(1)
Reliability factors (%)		
R_B	6.13	18.6
R_F	3.79	13.8
* (wt %)	36.72	63.28

Starting values for the fractional atomic coordinates were taken from Delicat at all.[6]. The observed results indicate the stoichiometric formula $Bi_{12}SiO_{20}$ was present. The Si cation occupies the tetrahedral coordinated on the Wyckoff position 2a (0, 0, 0). The refined fractional atomic coordinates are listed in Table 3.

Table 3.The final atomic coordinates and occupations factors for sillenite (S.G. I23).

Atom	*x*	*y*	*z*
Bi1	0.1756 (2)	0.31741 (2)	0.01592 (1)
Si1	0	0	0
O(1)	0.1348 (3)	0.2523(3)	0.2138 (2)
O(2)	0.1950 (3)	0.1950 (3)	0.1950 (2)
O(3)	0.9059 (2)	0.9059 (3)	0.9059 (2)

A comparison between the observed and calculated powder patterns is given in Fig. 4.

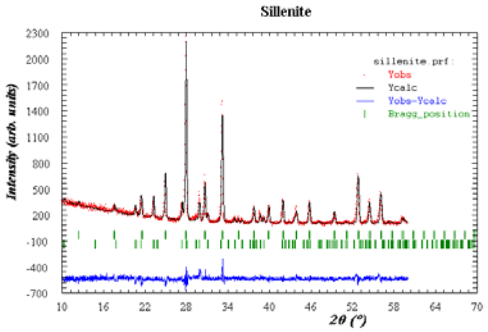

Fig. 4. The observed (circles), calculated (continuous line) and difference powder diffraction profiles for thermal treated LTA+Bi compuonds. Vertical bars mark Bragg peak positions of sillenite and nephelin phase.

5. Conclusion

The above data showed that sillenite phase can be obtained by using zeolite LTA as a precursor. The synthesis procedure involves mixing of zeolite (Na-LTA) water solution with native bismuth in autoclave at 170^{o}C for 7 days. The synthesized materials (Bi+zeolite$_{LTA}$ topology) annealed up to 350^{o}C for 1h, was transformation to sillenite and nepheline phases. The presence of the above phases was confirmed by X-ray powder diffraction (XRPD) analysis. These structures were refined with reliability factors: R_p= 7.21, R_{wp}= 9.25 and R_{bragg} = 6.14 for a cubic structure sillenite and R_{bragg} = 18.6 for nepheline phases. The weight fractions were 36.73% for sillenite and 63.72% for nepheline.

Acknowledgments

The authors are grateful for financial support of the Ministry of Science of Republic Serbia (project number 142016).

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