JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 8, August 2008, p. 2142 - 2145

Phase formation in the section Bi_2MoO_6-$Bi_4Ti_3O_{12}$ by the melt quenching method

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Compositions from the section Bi_2MoO_6-$Bi_4Ti_3O_{12}$ of the Bi_2O_3-MoO_3-TiO_2 system were investigated by the melt quenching method. During slow cooling of the melts, a $Bi_4Ti_3O_{12}$ phase crystallizes mainly in compositions containing above 30 mol % TiO_2. In compositions with higher MoO_3 content, Bi_2MoO_6 polymorphous crystallized. A route based on the melt quenching technique was suggested for the preparation of composite materials containing both phases, Bi_2MoO_6 and $Bi_4Ti_3O_{12}$.

(Received February 25, 2008; accepted June 30, 2008)

Keywords: Melts, Quenching, Phase formation

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1. Introduction

The Aurivillius family of layered bismuth oxides with the general formula $(Bi_2O_2)^{2+}(Bi_{n-1}B_nO_{3n+1})^{2-}$, where $B=Ti^{4+}$ or Nb^{5+}, and n=1, 2, 3, …, are a class of ferroelectrics whose properties were widely studied in the beginning of the 50-s [1, 2]. These ceramics were described recently as superior candidates for lead-free piezoelectric materials [3, 4] and important computer components such as non-volatile memories [5]. On the basis of the new results [6, 7] it can be expected that mixing of Aurivillius type compounds, could improve the materials properties. It was established that the reason for that could be the formation of solid solutions, for example $Bi_2Mo_{1-x}W_xO_6$ (0<x<1) [6] and other more complicated compounds, such as $Ba_{1.2}Bi_{2.8}Nb_{1.2}Ti_8O_{12}$ with compositional inhomogeinity and disorder at a local scale [8, 9]. The other possibility is to obtain composite materials by mixing two or more independent Aurivillius phases, which is a typical solution in the ceramic materials science. In our case, two model compounds, Bi_2MoO_6 and $Bi_4Ti_3O_{12}$ were selected. The Bi_2MoO_6 phase was found to be catalytically active [10-12] and it is also a high oxide ion conductor [13]. Three polymorphous modifications of Bi_2MoO_6 were established: γ(L), γ(H) and γ(I) [14, 15], in agreement with the labeling used by Kodama and Watanabe. Both, γ(L) and γ(I) phases belong to the Aurivillius family with n=1. Their crystalline structure has been determined [16-18]. Up to now Bi_2MoO_6 has been obtained by several methods, such as mechanochemically assisted solid state synthesis, hydrothermal route and solid state synthesis [6, 12 and 19]. The $Bi_4Ti_3O_{12}$ compound belongs to the Aurivillius family, with n=3 [1, 2]. At room temperature its structure is orthorhombic but above 670^0C it undergoes transformation into tetragonal. Bismuth titanate has a high potential for device applications (optical memory, piezoelectric and electro-optic devices) because of its relatively high dielectric constant, high Curie temperature and high breakdown strength. It has been obtained by various methods and a survey in which more than 50 papers are analyzed concerning this problem will be published soon. For the purpose of this study, only a few methods will be mentioned: mixing of oxides following the conventional solid state reaction method [20, 21], microwave assisted sintering [22] and especially the melt quenching method [23-25]. By crystallization of amorphous samples, $Bi_4Ti_3O_{12}$ was obtained in the binary system Bi_2O_3-TiO_2 [23] as well as in the three component systems Bi_2O_3-TiO_2-B_2O_3 [24, 25] and Bi_2O_3-TiO_2-SiO_2 [26]. It is well known that the melt quenching method is suitable for improving the homogeneity of the mixture on a molecular level and for accelerating the phase synthesis. Up to now this technique has been applied to determine the glass formation regions in the systems Bi_2O_3-TiO_2 [27, 28], Bi_2O_3-MoO_3 [29] and in more complicated systems Bi_2O_3-MoO_3-M_nO_m (M_nO_m=Fe_2O_3, V_2O_5, WO_3 and PbO) [29-32]. The results obtained motivated us to investigate the section Bi_2MoO_6-$Bi_4Ti_3O_{12}$ as part of the three-component system Bi_2O_3-MoO_3-TiO_2.

The purpose is to study the phase formation by the melt quenching method using mixtures of initial oxides (Bi_2O_3, TiO_2 and MoO_3) in different ratios situated in the section Bi_2MoO_6-$Bi_4Ti_3O_{12}$.

Table 1. Compositions from the section Bi_2MoO_6-$Bi_4Ti_3O_{12}$.

No	composition	nominal composition of the compounds, mol %	nominal composition of oxides, mol %	crystal phases, detected by *melt quenching method*	crystal phases, detected by *solid state reaction*
1.	A	Bi_2MoO_6	$50Bi_2O_3.50MoO_3$	γ (I)	γ (H) and γ(L)
2.	B	$90Bi_2MoO_6/10Bi_4Ti_3O_{12}$	$48Bi_2O_3.5TiO_2.47MoO_3$	γ (H) and γ(L)	-
3.	C	$82Bi_2MoO_6/18Bi_4Ti_3O_{12}$	$48Bi_2O_3.10TiO_2.42MoO_3$	γ (H) and γ(L)	-
4.	D	$67Bi_2MoO_6/33Bi_4Ti_3O_{12}$	$46Bi_2O_3.20TiO_2.34MoO_3$	γ(L)	-
5.	E	$50Bi_2MoO_6/50Bi_4Ti_3O_{12}$	$45Bi_2O_3.30TiO_2.25MoO_3$	γ(L) and $Bi_4Ti_3O_{12}$	γ(L) and $Bi_4Ti_3O_{12}$ (texture)
6.	F	$34Bi_2MoO_6/66Bi_4Ti_3O_{12}$	$43Bi_2O_3.40TiO_2.17MoO_3$	γ (H) and $Bi_4Ti_3O_{12}$ (texture)	-
7.	G	$12Bi_2MoO_6/88Bi_4Ti_3O_{12}$	$41Bi_2O_3.54TiO_2.5MoO_3$	$Bi_4Ti_3O_{12}$ (texture)	-
8.	H	$Bi_4Ti_3O_{12}$	$40Bi_2O_3.60TiO_2$	$Bi_4Ti_3O_{12}$ (oriented)	$Bi_4Ti_3O_{12}$ (texture)

2. Experimental

Different compositions from the section (1-x)Bi_2MoO_6.x$Bi_4Ti_3O_{12}$ of the Bi_2O_3-MoO_3-TiO_2 system were investigated (Table 1). All batches were prepared using pure MoO_3 (Aldrich), Bi_2O_3 (Merck) and TiO_2-anatase (Merck) as starting materials. The melting was performed in alumina crucibles for 15 min in air at 900 to 1150^{0}C. The melting temperatures were chosen taking into account the liquidus temperature of the phase diagrams Bi_2O_3-MoO_3 and Bi_2O_3-TiO_2. It was established that both compounds were incongruently melting, with a 970^{0}C peritectic temperature (T_m) of the Bi_2MoO_6 compound and a liquidus temperature (T_L) at about 1000^{0}C [33], while for $Bi_4Ti_3O_{12}$ the peritectic temperature was T_m =1200^{0}C and T_L at about 1300^{0}C [34, 35]. Fast cooling by the roller-quenching technique (10^4-10^5K/s) and slow cooling (10^2-10^3K/s) achieved by pouring the melts on the metal plate, were used. Heat treatment of selected compoitions for 1 to 5 hours at 500^{0}C was applied also. The phase transformations were verified by X-ray diffraction (Bruker D8 Advance with Cu Kα radiation) at room temperature in the 10° < 2θ < 80° range. The structure refinement was carried out with the Rietvield profile refinement technique, by means of the program "PowderCell" [36]. The differential thermal analyses and thermogravimetry (DTA-TG) were carried out on a Stanton Redcroft STA 780 apparatus with a heating rate of 10^o/min in air stream using Al_2O_3 as reference material.

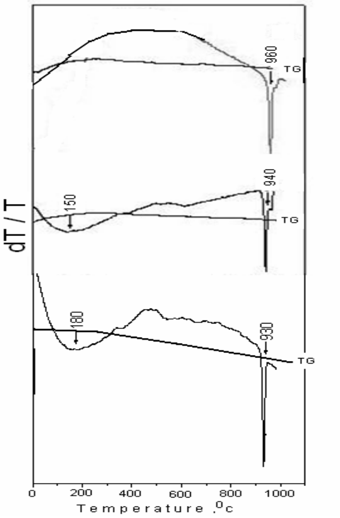

Fig.1. DTA of the crystallized samples from the section Bi_2MoO_6-$Bi_4Ti_3O_{12}$: a) $45Bi_2O_3.30TiO_2.25MoO_3$, b) $48Bi_2O_3.10TiO_2.42MoO_3$ and c) $50Bi_2O_3.50MoO_3$.

3. Results and discussion

Fig. 1 shows the DTA results of selected compositions from the section investigated. As is seen, all samples demonstrate a strong endothermic effect at about 930-960^{0}C, which is an indication of the liquid phase appearance. These experimental data along with data for the binary phase diagrams [33-35] were used to determine the maximal melting temperature of the batches (1200-1250^{0}C). The XRD patterns of the terminal samples A and H (Table 1), corresponding to the Bi_2MoO_6 and $Bi_4Ti_3O_{12}$ compounds are presented in fig. 2. Peaks corresponding to the metastable γ (I) Bi_2MoO_6 phase (JCPDS 33-0208) were only found in the melt quenched sample A (fig. 2). The results obtained were proved by the Rietvield profile method (fig. 3, sample A). The solid state reaction of the same composition (5h at 600^{0}C) led to formation of two phases γ (H) (JCPDS 22-0112) and γ (L) (koechlinite) (JCPDS 21-0102) (fig. 2). In the melt-quenched sample H, an orthorhombic $Bi_4Ti_3O_{12}$ phase was obtained (JCPDS 72-1019) (fig. 2), with a dominant peak near 30, 2θ degree (117), corresponding to the randomly oriented crystals [37, 38]. After a solid state reaction, a texture was observed along the "c" axis. A measure for that is the increased intensity of (00l) series of peaks. For example such peaks are in the range 16-22, 2θ degree: (004), (008) and (006). Fig. 4 shows the XRD patterns of the other compositions after quenching of the melts. The addition of TiO_2 (5 mol %, sample B, fig. 4) leads to appearance of a second γ (H) polymorphous in addition to the γ (I)-Bi_2MoO_6. The further addition of TiO_2 (10 and 20 mol %, samples C and D, fig. 4) stimulates the appearance of the low-temperature γ (L)- Bi_2MoO_6. Under these experimental conditions the bismuth titanate phase is not detected. In the next sample E, containing 30 mol % TiO_2, a $Bi_4Ti_3O_{12}$ phase is found along with both polymorphous modifications, γ (H) and γ

(L). The quantities of the phases were determined by Rietvield analysis: 21 % $Bi_4Ti_3O_{12}$, 36 % γ (H)-Bi_2MoO_6 and 43 % γ (L)-Bi_2MoO_6 (fig. 3, sample E). This peculiarity is due to the non-equilibrium experimental conditions (fast quenching technique). The XRD pattern of sample F contains interplanar distances for both phases - γ (H) Bi_2MoO_6 and textured $Bi_4Ti_3O_{12}$. The Rietvield refinements confirmed their presence (fig. 3, sample F). In both samples, G and H (fig. 4), the $Bi_4Ti_3O_{12}$ texture phase crystallized only. Molybdate phases were not detected.

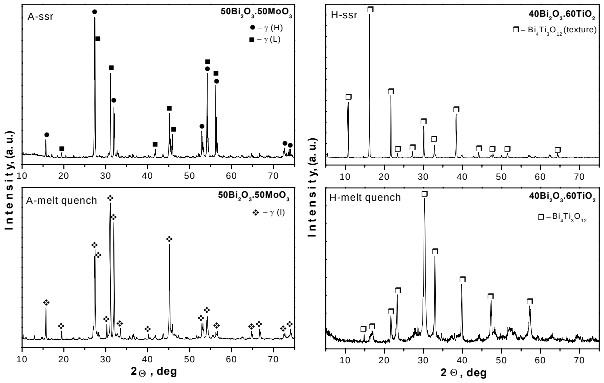

Fig. 2. X-ray diffraction patterns of the samples A ($50Bi_2O_3.50MoO_3$) and H ($40Bi_2O_3.60TiO_2$): A-melt quench – sample A, obtained by melt quenching method; A-ssr – sample A obtained by solid state reaction; H-melt quench - sample H, obtained by melt quenching method; H-ssr – sample H, obtained by solid state reaction.

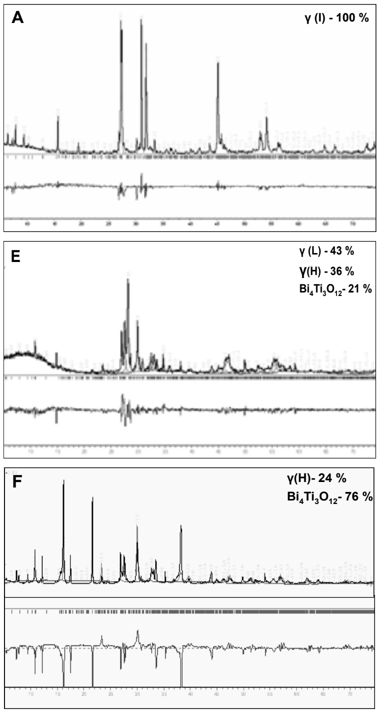

Fig. 3. Rietvield refinements of the samples A-$50Bi_2O_3.50MoO_3$, E-$45Bi_2O_3.30TiO_2.25MoO_3$ and F-$43Bi_2O_3.40TiO_2.17MoO_3$.

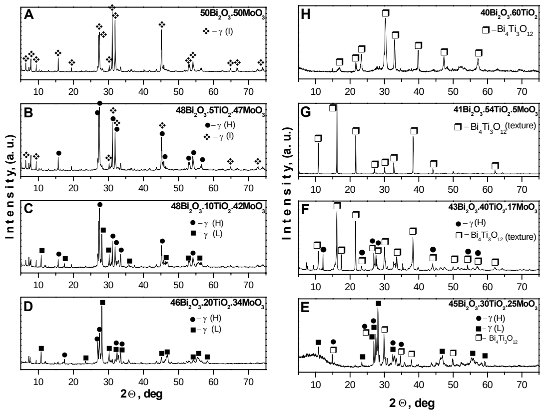

Fig. 4. X-ray diffraction patterns of the melt quenched samples from the section Bi_2MoO_6-$Bi_4Ti_3O_{12}$: γ (H) – high temperature Bi_2MoO_6, γ (L) - low temperature Bi_2MoO_6 and γ (I) metastable Bi_2MoO_6 polymorphous.

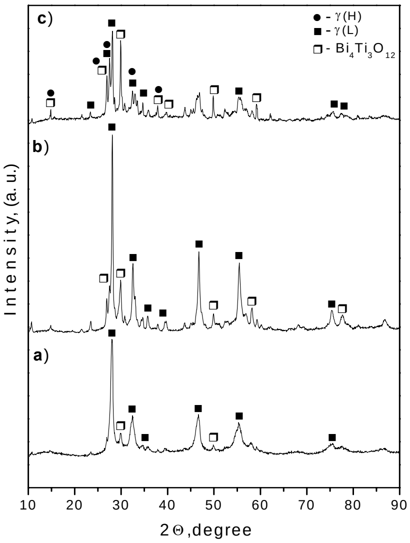

Fig. 5. X-ray diffraction patterns of the sample with composition $45Bi_2O_3.30TiO_2.25MoO_3$: a) fast-quenched sample; b) crystallization at 500^0C (5 h) and c) slow-cooled sample.

Special attention was paid to the sample $45Bi_2O_3.30TiO_2.25MoO_3$, situated in the central part of the investigated section (fig. 5). The fast-quenched sample was partially amorphous, containing mainly γ (L)-Bi_2MoO_6 crystals (fig. 5a). In the XRD pattern of the slowly cooled sample an increase of the tendency to crystallization was observed (fig. 5c). Heat treatment of the fast quenched sample at 500^0C for 5h led to crystallization of the both stable phases γ (L) Bi_2MoO_6 (JCPDS 21-0102) and orthorhombic $Bi_4Ti_3O_{12}$ (JCPDS 72-1019) (fig. 5b).

In the three-component system Bi_2O_3-MoO_3-TiO_2, the section Bi_2MoO_6-$Bi_4Ti_3O_{12}$ is not a quazibinary one, because the initial crystal phases are incongruently melting compounds but in this polytermic section a chemical reaction was not established and phases Bi_2MoO_6 and $Bi_4Ti_3O_{12}$ crystallized only. That is why the investigated compositions are suitable for preparation of composite materials.

4. Conclusions

The melt quenching method stimulates obtaining γ (I)-Bi_2MoO_6 metastable phase. The formation of the low temperature γ (L)-Bi_2MoO_6 phase was established in three-component compositions containing up to 30 mol % TiO_2. The MoO_3 addition favors the formation of textured $Bi_4Ti_3O_{12}$. The performed experiments showed that the melt quenching method allows controlling the order of precipitated crystal phases. It was proved that this method is appropriate and promising one for obtaining new multifunctional composite materials containing both phases, Bi_2MoO_6 and $Bi_4Ti_3O_{12}$.

Acknowledgments

Thanks are due to the Financial Support of Bulgarian National Science Fund, Ministry of Education and Science Grants: TK-X-1718/07.

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