Chinese Journal of Chemistry, **2004**, *22*, 434—436 **Article**

Synthesis, Crystal Structures and Characterization of $Ba_5LiTiNb_9O_{30}$

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A new niobate compound with the chemical composition of $Ba_5LiTiNb_9O_{30}$ was synthesized by doping Li^+ into the system BaO-TiO_2-Nb_2O_5 in conventional solid state reaction method. The crystalline structure was determined by X-ray diffraction analysis (XRD). The results showed that crystal structure of $Ba_5LiTiNb_9O_{30}$ belongs to tetragonal tungsten bronze structure with space group P4*bm* and its unit cell parameters: $a=b=1.2512(2)$ nm, $c=0.4008(5)$ nm. The microstructure of reaction products was observed by scanning electron microscopy (SEM).

Keywords niobate, tungsten bronze structure, XRD, solid state reaction, SEM

Introduction

Perovskite-type compounds are a kind of materials which could be used as candidate for functional materials such as dielectric materials, piezoelectric materials, ferroelectric materials *etc*.[1-5] Complex titanates, tantalates, and niobates display important dielectric properties that are exploitable, for example, in wireless communication applications. The research work includes materials design, chemical synthesis, characterization, processing, and phenomenology of the new compounds with unusual and promising electronic properties.

As part of a continuing program people try to elucidate phase relations, crystal chemistry, and the occurrence of new compounds in this class of ceramic oxides. The structure has great impact in its ferroelectrics capability and other functions. Neurgaonkar[6] synthesized a new niobate $Ba_6Ti_2Nb_8O_{30}$ by doping Ti^{2+} into the system BaO-Nb_2O_5. Many researchers paid attention to the research of syntheses and properties for new compounds and crystalline in order to get new crystalline structure compounds and find new properties.[7-10] In this research work we try to synthesize a new niobate structure compound $Ba_5LiTiNb_9O_{30}$ by doping Li^+ into the system BaO-TiO_2-Nb_2O_5. The crystalline structures and their micrograph were analyzed in detail by X-ray diffraction analysis (XRD), and scanning electron microscopy (SEM) respectively.

Experimental

According to the composition of $Ba_5LiTiNb_9O_{30}$, stoichiometric amounts of analytically pure $BaCO_3$, Li_2CO_3, TiO_2, Nb_2O_5 were mixed with a 5% excess of Li_2CO_3 to compensate for loss of Li^+ in the high temperature. The solid chemical reaction would happen at high temperature through the ionic diffusion, and the samples were prepared by a conventional solid-state reaction method in this paper. The samples were heated in a corundum crucible at 1200 ℃ for 2 h, followed by cooling to room temperature in furnace. Reaction products were washed thoroughly to remove un-reacted Li_2CO_3. Due to the weight loss in the reaction, the composition of the product should be investigated so that we could know the chemical composition of the reaction products, so quantitative analysis of elements including wet chemical method and electron probe X-ray microanalysis (EPMA) which is of JCXA-733 type were employed. X-ray powder diffraction data were collected on a Rigaku D/MAX-RB diffractometer equipped with Cu Kα radiation ($\lambda=0.154060$ nm) and graphite monochromator. Typical scans were collected in continuous mode from 5°—70° at a scan rate of 0.02 (°)/s using silicon as external standard. The unit cell parameters were refined by least-squares method. The microstructures of the reaction products were detected by scanning electronic microscopy.

Results and discussion

Solid state reaction for the synthesis of $Ba_5LiTiNb_9O_{30}$

Based on stoichiometric amounts of the composition, the mixture was heated at 1200 ℃. Due to the high reaction temperature, some of the composition like Li^+ would be not as accurate as the original. The reaction would happen at high temperature due to solid-state

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Received July 15, 2003; revised and accepted January 5, 2004.
Project supported by the National Natural Science Foundation of China (Grant No. 20371038), and Ministry of Education of China.

diffusion. $BaCO_3$, Li_2CO_3, TiO_2, and Nb_2O_5 belonged to carbonates or metal oxides, and simple solid-state reaction would happen when they were mixed well and heated together. The reaction is as follows:

$$Li_2CO_3 \rightarrow Li_2O + CO_2 \uparrow \quad (1)$$

$$BaCO_3 \rightarrow BaO + CO_2 \uparrow \quad (2)$$

$$Li_2O + 10BaO + 2TiO_2 + 9Nb_2O_5 \rightarrow 2Ba_5LiTiNb_9O_{30} \quad (3)$$

The solid-state phase reaction could be completed at high temperature.

Characterization of $Ba_5LiTiNb_9O_{30}$

In order to make clear what of reaction product we obtained the composition of the reaction products should be determined. EPMA method and chemical analysis method were employed to the determine composition of reaction compounds. The results of quantitative analysis of chemical compositions were shown in Table 1. The results of the composition by EPMA and chemical analysis were almost the same, showing the products were corresponding to the formula $Ba_5LiTiNb_9O_{30}$ as the composition.

Table 1 Results of quantitative analysis of elements

Method	Ba/ wt%	Li/ wt%	Ti/ wt%	Nb/ wt%	Chemical formula
Chemical analysis	32.58	0.33	2.27	39.63	$Ba_5Li_{0.99}Ti_{1.01}Nb_{9.03}O_{30.08}$
EMPA	32.52	0.31	2.29	39.95	$Ba_5Li_{0.99}Ti_{1.02}Nb_{9.07}O_{30.17}$

Based on the XRD recorded data, the X-ray diffraction peaks of $Ba_5LiTiNb_9O_{30}$ in Figure 1 were indexed by WDS11 program adapted by Shen Jinquan *et. al.*, China University of Geosciences. The calculation results were given in Table 2. Each diffraction peak got better indexed, and the quality gene $F_{16}=75$(0.007,00). Phase of the sample synthesized in present study was pure. Crystal cell parameters, rectified by least square method are as follows: $a=b=1.2512(2)$ nm, $c=0.4008(5)$ (nm) and space group P4*bm*.

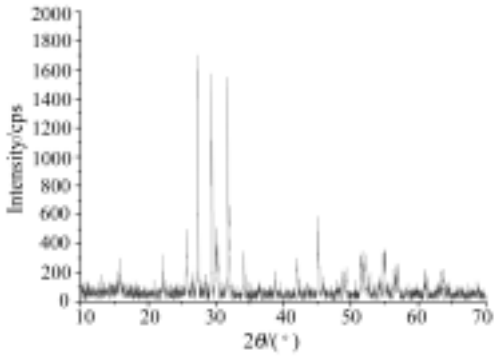

Figure 1 XRD pattern of $Ba_5LiTiNb_9O_{30}$.

Table 2 X-ray powder diffraction data of $Ba_5LiTiNb_9O_{30}$

D /(10^{-1} nm)	I/I_0	*hkl*	D (10^{-1} nm)	I/I_0	*hkl*
5.590	15	210	2.8159	100	311
4.008	14	001	2.6236	22	321
3.4706	30	320	2.3234	12	520
3.2586	98	211	2.1458	17	530
3.1280	12	400	2.0042	32	002
3.0346	88	410	1.7695	20	550
2.9704	32	221	1.6724	21	412
2.9491	23	330	1.5176	10	522

Compared with the X-ray diffraction data of niobate $Ba_6Ti_2Nb_8O_{30}$ with the structure of square tungsten bronze, it could be found that both the position and intensity distribution on of their X-ray patterns were identical, which denoted that their crystal structure was the same as that of square tungsten bronze.

There are three different types of interstices, A_1(pentagon), A_2(quadrangle), C(triangle) constituted by arrangement of oxygen octahedron in TB structure (Figure 2). The formula of structure is $(A_1)_4(A_2)_2C_1(B')_2(B'')_3O_{30}$, in which A_1, A_2, C_1, B′, B″ could be filled by cations with different valence to form niobate in TB structure. B′, B″ could be occupied by Nb^{5+}, and A_1, A_2, C_1 could be filled with alkaline metal atom. Based on the crystal field theory, Ti^{4+} was strongly selected as octahedron coordinate to form a stable octahedron structure radical like Nb^{5+} and O^{2-}. When the third group TiO_2 was led into BaO-Nb_2O_5 system, Ti^{4+} could occupy the site of octahedron coordinate instead of Nb^{5+}. So the electrovalence was lower than Ti^{4+} and Nb^{5+} formed relationship of different valence isomor-

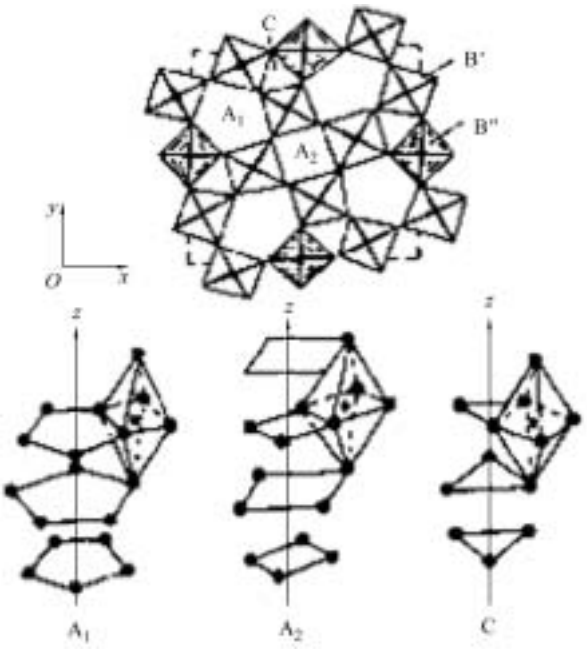

Figure 2 Tungsten bronze structure.

phism substitution. Due to requiring of balance of electrovalence, Ti^{4+} and Nb^{5+} formed relationship of different valence isomorphism substitution and entered octahedron, and additional Ba^{2+} and Li^{+} can compensate the deficient electrovalence. This replacement relationship could be expressed as: $Ti^{4+} + Ba^{2+} \rightarrow Nb^{5+} + Li^{+}$. Then Ba^{2+} and Li^{+} could occupy the vacant A in TB structure.

The micrograph of SEM for $Ba_5LiTiNb_9O_{30}$ was presented in Figure 3. The square crystal structure was clearly shown in the picture. Niobate compound with composition of $Ba_5LiTiNb_9O_{30}$ was synthesized by doping Li^{+} into the system $BaO\text{-}TiO_2\text{-}Nb_2O_5$ using conventional solid state reaction method.

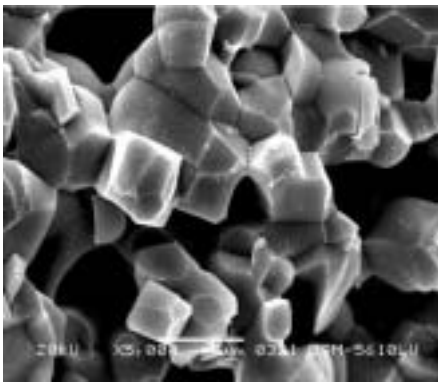

Figure 3 Micrograph of $Ba_5LiTiNb_9O_{30}$.

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(E0307152 ZHAO, X. J.)