A study of the sillenite phase in the system Bi_2O_3-Nb_2O_5

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Bismuth oxide (Bi_2O_3) is strongly polymorphic, being known α-, β-, γ-, and δ-forms. Two of them, α- and δ-forms, are thermodynamically stable. The α-phase is the low temperature stable monoclinic structure, which undergoes a phase transition at 730°C to the high temperature cubic δ-form that melts at 825 °C. The other two phases, β-tetragonal and γ-body-centered cubic, are both metastable phases and only can be formed on specific conditions depending on the sample thermal history [1]. However, the metastable β- and γ-forms, as well as the high temperature stable δ-phase, can be stabilized at room temperature by addition of some metal oxides [2-4]. Room temperature stabilized δ-form is interesting because of its high ionic conductivity [3, 4]. The γ-bcc phase has a structure called sillenite exhibiting attractive optical properties, with special interest for the combination of electro-optical and photoconductive properties resulting in the so-called photorefractive effect, making the sillenite crystals useful for many advanced and promising applications, such as reversible recording medium for real-time holography or image processing [6].

Many oxides with metal cation in a large range of ionic radii and valence states are effective for stabilizing the γ-phase of Bi_2O_3. Depending on the metal ion used the general formulae of the resulting sillenite compounds can be written as $Bi_{12}MO_{20}$, with *M* cations such as Ge, Si, Ti, or with the *M* cation in the form of mixtures such as (Bi, Zn), (Ga, P), (Bi, V), (Bi, Ga), and others, including in many cases a fraction of vacancies. Concerning the γ-phase in the binary system Bi_2O_3-Nb_2O_5 exist few studies and there is some controversy regarding its composition and thermal stability. In this work, a detailed screening of composition in the Bi-rich region of the binary Bi_2O_3-Nb_2O_5 system was done by solid state reaction synthesis. The synthesized powders were characterized by room and high temperature X-ray diffraction and thermal analysis, aiming to clarify the thermal behavior and composition of sillenite phase in this system.

KEYWORDS: Bismuth niobium oxide, Sillenite structure, metastable structure.

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