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Preparation and crystal structure of H-$BaTa_2O_6$-type $K_{1.83}Ba_{4.17}Nb_{12.18}O_{36}$ and dielectric properties of the related compounds

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Abstract

Single crystal of a novel compound, $K_{1.83}Ba_{4.17}Nb_{12.18}O_{36}$, has been synthesized in the course of investigation on the K_2O–BaO–Nb_2O_5 system. The crystal structure was determined by single crystal X-ray diffraction data. The space group of this compound was found to be *P6/mmm* (#191) with the lattice parameters of $a = 21.109(4)$ and $c = 3.967(1)$ Å. The final *R*-factors were $R = 0.039$ and $R_w = 0.042$ for unique 508 reflections. The crystal structure had the same tunnel structure as that of hexagonal $BaTa_2O_6$ (H-$BaTa_2O_6$), which is the high temperature form in three modifications of $BaTa_2O_6$. The chemical composition of $K_{1.83}Ba_{4.17}Nb_{12.18}O_{36}$ was close to that of the tetragonal tungsten bronze (TTB) type $KBa_2Nb_5O_{15}$ and the powder samples within this composition were prepared so as to clarify the boundary between H-$BaTa_2O_6$ and TTB-type structures. The H-$BaTa_2O_6$-type structure appears in (K + Ba)/Nb ≤ 0.500 and the TTB-type structure is in (K + Ba)/Nb ≥ 0.575. The dielectric constants of these samples were measured from room temperature to 500 °C for sintered body. The TTB-type compounds exhibited ferroelectric temperature dependence with the Curie points of 284–372 °C and the H-$BaTa_2O_6$-type compounds were not ferroelectrics as predicted from the crystal structure analysis.

Keywords: A. Oxides; C. X-ray diffraction; D. Ferroelectricity

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1. Introduction

Barium niobates and tantalates, BaM_2O_6 (M = Nb, Ta), have been investigated with respect to their polymorphs [1–8]. In 1959, Ismailzade reported $BaTa_2O_6$ with the tetragonal cell of $a = 17.80$ and $c = 7.84$ Å [1,2]. Subsequently, Galasso et al. have prepared the single crystal of TTB-type $BaTa_2O_6$ with the lattice constants of $a' = 12.60$ and $c' = 3.95$ Å which were related with Ismailzade's data by $a' = a/\sqrt{2}$ and $c' = c/2$ [3]. Further, in 1967 Layden reported that $BaTa_2O_6$ existed in three polymorphs based on his studies on BaB_2O_4–$BaTa_2O_6$ system: the orthorhombic cell below 1150 °C, the TTB-type structure at 1150–1300 °C and the hexagonal cell (H-$BaTa_2O_6$) above 1300 °C. The crystal structure of H-$BaTa_2O_6$ was determined by X-ray powder diffraction data [5]. He also determined the crystal structure of the high temperature form of $BaNb_2O_6$ by X-ray powder diffraction data [6]. It also had three polymorphs and the crystal structures of the other modifications were reported by Sirotinkin et al. [7,8]. The crystal structures of BaM_2O_6 (M = Nb, Ta) are shown in Fig. 1. The common structure is the orthorhombic phase, which has a zig–zag pattern formed by edge-sharing pairs of MO_6 octahedra. Although the TTB-type structure is not adopted for $BaNb_2O_6$, in the K_2O–BaO–Nb_2O_5 system two compounds, $KBa_2Nb_5O_{15}$ [9] and $KBa_3Nb_7O_{21}$ [10], have the TTB-type structure. In particular, $KBa_2Nb_5O_{15}$ is a ferroelectric compound with the $T_c = 392$ °C and the related compounds, $AB_2Nb_5O_{15}$ (A = Na, K, Rb; B = Sr, Ba), and the solid solutions were investigated by Giess et al. [9]. However, there were few reports for the preparation in the K_2O–BaO–Nb_2O_5 system, and then we attempted to prepare new compounds in this system. Single crystals of a new compound, $K_{1.83}Ba_{4.17}Nb_{12.18}O_{36}$, with H-$BaTa_2O_6$-type structure were obtained and the crystal structure was refined by using single crystal X-ray diffraction data. Powder samples were prepared so as to clarify the boundary between H-$BaTa_2O_6$ and TTB-type structures and the crystallographic difference was discussed.

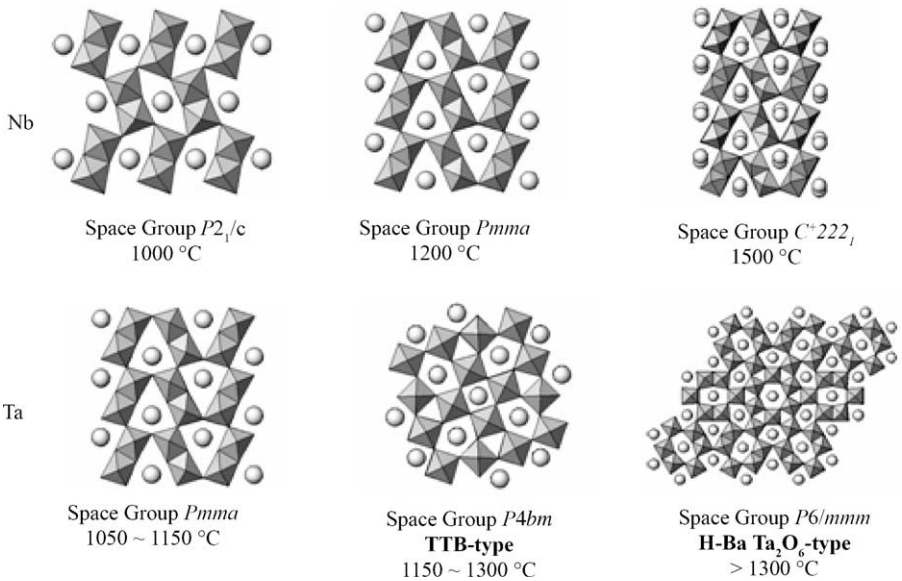

Fig. 1. Crystal structures of BaM_2O_6 (M = Nb, Ta).