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Note

The system $KNbO_3 + BaTiO_3$

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$BaTiO_3$ and $KNbO_3$ are ferroelectric materials which crystallise in the perovskite structure. Furthermore, both show the same sequence of phase transitions with increased temperature, i.e. $R3m \rightarrow Bmm2 \rightarrow P4mm \rightarrow Pm3m$. The temperatures corresponding to these transitions on heating are: $T_1 = 263$ K, $T_2 = 498$ K and $T_3 = 708$ K for $KNbO_3$ [1]; and $T_1 = 193$ K, $T_2 = 278$ K and $T_3 = 393$ K for $BaTiO_3$ [2]. All transitions are of first-order, as revealed by their pronounced thermal hysteresis. The first systematic investigation of the $BaTiO_3$–$KNbO_3$ system was made by Bratton and Tien [3]; between 4 and 90 mol% $KNbO_3$, they observed a continuous series of solid solutions with cubic symmetry. Their interpretation of the data seems to be inconsistent. We reinvestigated this system in the course of our studies on Nb_2O_5-based phase diagrams.

The experimental equipment and the method used have already been described [4]. The starting materials for the preparation of the samples were K_2CO_3, $BaCO_3$, TiO_2 and Nb_2O_5, all at least 99.9% purity. The required amounts of the powdered materials were mixed and equilibrated at 873 and 1273 K for 14 days in platinum crucibles. Samples of each preparation were characterised by DTA and X-ray powder diffractometry.

The phase diagram of the $BaTiO_3$–$KNbO_3$ system, which was constructed from the data obtained is shown in Fig. 1. $KNbO_3$ decomposes in a peritectic reaction; therefore the system is not quasi-binary. However, below the decomposition temperature of $KNbO_3$ only two phases were found. The first of these was $KNbO_3$ with orthorhombic symmetry and lattice parameters $a = 569.7$ (1), $b = 397.8$ (1) and $c = 572.0$ (1) pm, in good agreement with the data of Katz and Megaw [5] ($a = 569.74$, $b = 397.1$ and $c = 572.23$ pm). No solid solutions were observed in the $KNbO_3$-rich part of the system. The transition temperatures T_2 and T_3 were lowered sharply by addition of less than 1 mole.% $BaTiO_3$ and, on further addition of $BaTiO_3$, remain at constant temperatures of $T_2 = 450$ K and $T_3 = 638$ K. The second phase was a solid solution, based on $BaTiO_3$. At 1273 K, it has a homogeneity region which extends up to 33 mol.% $KNbO_3$. At elevated temperatures this solid solution undergoes a phase transformation from the tetragonal to the cubic

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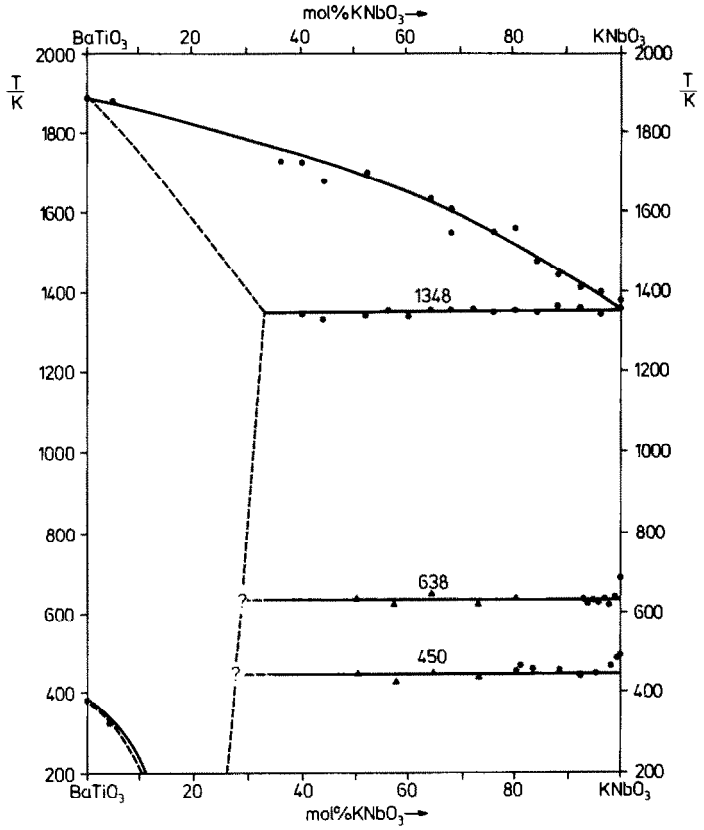

Fig. 1. The phase diagram of the $BaTiO_3$–$KNbO_3$ system: ●, DTA; ▲, dilatometry. (The system is constructed as a quasi-binary system. The deviations in the liquidi at its $KNbO_3$ side, due to the incongruent melting of $KNbO_3$, are neglected.)

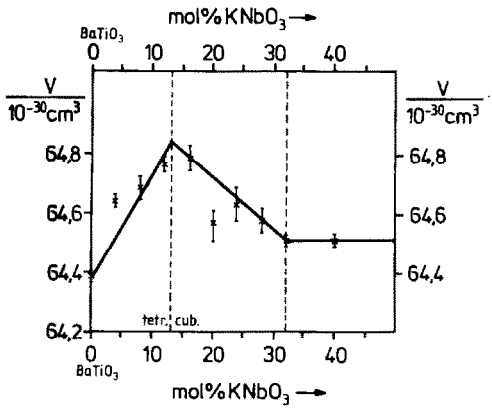

Fig. 2. Cell volumes of $BaTiO_3$-based solid solutions in the $BaTiO_3$–$KNbO_3$ system.

TABLE 1

Lattice parameters of $BaTiO_3$–$KNbO_3$ solid solutions

Composition (mol.% $BaTiO_3$)	*a* (pm)	*c* (pm)
100 (tetrag.)	399.57 (4)	400.30 (8)
	398.9 [a]	402.9
96	400.9 (2)	402.2 (6)
92	401.0 (3)	402.3 (6)
88	401.2 (2)	402.5 (5)
84	401.5 (4)	
82	401.2 (1)	
76	401.3 (1)	
72	401.18 (7)	
68	401.05 (3)	
60	401.04 (3)	
$BaTiO_3$ (cub.)	403.1 [b]	

[a] Ref. 6. [b] Ref. 7.

form of perovskite. The transformation temperatures decrease with increasing content of $KNbO_3$. The lattice constants and the volumes of the elementary cell of $BaTiO_3$-based solid solutions are given in Table 1. Solid solutions with tetragonal symmetry were observed between 0 and 12 mol.% $KNbO_3$. The volume of their elementary cells increased on addition of $KNbO_3$. In the solid solutions between 14 and 33 mol.% $KNbO_3$, a decrease in the volume of the cubic elementary cell was observed (Fig. 2).

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