Effect of barium titanate on the unit cell parameter of $\text{Nd}_{0.5}\text{Li}_{0.5}\text{TiO}_3$

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Abstract. Structural characteristics of new type of perovskites with formula $\text{Ba}_x(\text{Nd}_{0.5}\text{Li}_{0.5})_{1-x}\text{TiO}_3$ ($0 \leq x \leq 1$) are reported. $\text{Nd}_{0.5}\text{Li}_{0.5}\text{TiO}_3$ crystallises with orthorhombic distorted perovskite structure, while $\text{Ba}_x(\text{Nd}_{0.5}\text{Li}_{0.5})_{1-x}\text{TiO}_3$ crystallises with tetragonal distorted perovskite structure.

Keywords. X-ray diffraction; perovskite; orthorhombic; tetragonal; barium titanate; tolerance factor.

1. Introduction

Perovskite-like compound of the type ABO_3 can be obtained with A and B ions which have ionic radii within fairly wide limits (Jona and Shirane 1962). The same type can be found in solid solution of the type $\text{A}(\text{B}_i\text{B}_j)\text{O}_3$ (Jaffe *et al* 1955), $(\text{A}_i\text{A}_j)\text{BO}_3$ (Shirane and Suzuki 1951) and even in the quaternary systems of the general type $(\text{A}_i\text{A}_j)(\text{B}_i\text{B}_j)\text{O}_3$ (Chincholkar *et al* 1969). Accordingly, one can consider the preparation of perovskite-type compounds with more complicated combination of atoms than these provided the charge neutrality is preserved. Such complex type compositions crystallising with perovskite structure have been reported (Patil and Chincholkar 1970). We have prepared the compounds of $(\text{A}_i\text{A}_j)\text{BO}_3$ type by using Ba^{2+} , Nd^{3+} and Li^+ ions at A sites. These compounds have the general formula $\text{Ba}_x(\text{Nd}_{0.5}\text{Li}_{0.5})_{1-x}\text{TiO}_3$ ($0 \leq x \leq 1$). The structure of the compounds was determined by using x-ray powder diffraction technique.

2. Method

The compounds were prepared by using constituent oxides of AR grade, each oxide was weighed on a Mettler single-pan balance, in a weighing bottle. The substance was then transferred into an agate mortar. The mixture was ground in mortar for 30 min using acetone (AR grade) to ensure effective mixing. The compounds thus obtained were heated in the platinum crucible at 1200°C for 12 hr and cooled to room temperature in air.

X-ray diffraction patterns of the compounds were taken on Philips x-ray diffractometer (PW 1051) using Cu-K α radiation filtered suitably. The diffraction patterns were used to determine crystallographic parameters. The densities of the substances were determined using carbon tetrachloride.

3. Results and discussion

Pure Nd_{0.5}Li_{0.5}TiO₃ crystallises with the orthorhombic structure with $a = 5.441$ Å, $b = 5.573$ Å and $c = 7.753$ Å. The pure compound has a tolerance factor (t) 0.761 so that the structure could be visualised as orthorhombic distortion of the cubic perovskite structure. This observation agrees with that of Schreider *et al* (1961) who placed a lower limit of 0.78 for the rare-earth mixed oxide and that of Keith and Roy (1954) who placed a lower limit of 0.77 for the perovskite structures of the A²⁺B⁴⁺O₃²⁻ type. Table 1 shows the variation in unit cell parameters, tolerance factor values and density values of the system.

It can be seen that the orthorhombic strain ($b/a = 1.024$) present in the pure phase disappears by the addition of 20 mol % of BaTiO₃ since the tolerance factor values of the composition increases to 0.796. The c/a value goes on decreasing as the Ba²⁺ concentration increases in contrast to the normal increase in tetragonality (c/a) with increase in size of the ion (Ba²⁺ = 1.32 Å, Nd³⁺ = 1.08 Å, Li⁺ = 0.60 Å). This discrepancy could be understood by comparing the t value of different composition in the series.

It is also seen that there is an increase in the value of t with Ba²⁺ concentration so that the structure gradually changes to that of the perovskite lattice, where the tetragonality (c/a) is nearly 1.01 for pure BaTiO₃. This may be ascribed to the polarization of the constituent ions (Roberts 1949, 1951) which might play an important role in determining the symmetry formed by a given perovskite structure. The measured density gave a Z value of 4 for the Nd_{0.5}Li_{0.5}TiO₃ phase which reduces to 1 for and beyond 20 mol % BaTiO₃ incorporation into this lattice.

Table 1. Unit cell parameters, tolerance factor and density values of Ba (Nd_{0.5}Li_{0.5})_{1-x}TiO₃ system.

Composition	Sym- metry	a	b	c	c/a	b/a	t	D_M	D_{cal}	Z
		Å						g.ml ⁻¹	(x-ray) g. ml ⁻¹	
Nd _{0.5} Li _{0.5} TiO ₃	O	5.441	5.573	7.753	1.425	1.024	0.761	4.30	4.48	4
Ba _{0.2} Nd _{0.4} Li _{0.4} TiO ₃	T	3.28	4.69	1.429			0.796	5.98	6.030	1
Ba _{0.4} Nd _{0.3} Li _{0.3} TiO ₃	T	3.95	4.60	1.164			0.831	4.23	4.526	1
Ba _{0.6} Nd _{0.2} Li _{0.2} TiO ₃	T	4.097	4.64	1.154			0.865	4.25	4.440	1
Ba _{0.8} Nd _{0.1} Li _{0.1} TiO ₃	T	3.97	4.13	1.040			0.900	5.31	5.616	1
BaTiO ₃	T	3.99	4.01	1.010			..	..	..	..

O = Orthorhombic T = Tetragonal.

Density values do not suggest any deviation from the stoichiometric compositions.

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