Bull. Mater. Sci., Vol. 23, No. 6, December 2000, pp. 495–498. © Indian Academy of Sciences.

Influence of strontium on the cubic to ordered hexagonal phase transformation in barium magnesium niobate

M THIRUMAL and A K GANGULI*

Department of Chemistry, Indian Institute of Technology, New Delhi 110 016, India

MS received 5 June 2000

Abstract. Oxides of the type $Ba_{3-x}Sr_xMgNb_2O_9$ were synthesized by the solid state route. The $x = 0$ composition ($Ba_3MgNb_2O_9$) was found to crystallize in a disordered (cubic) perovskite structure when sintered at 1000C. For higher Sr doping ($x \geq 0{\cdot}5$), there was clearly the presence of an ordered hexagonal phase indicated by the growth of superstructure reflections in the powder X-ray diffraction patterns. In all the compositions there was the presence of a minor amount of $Ba_{5-x}Sr_xNb_4O_{15}$ phase which increased with Sr substitution up to $x = 1$ and then it remained nearly constant at about 5%. Samples sintered at 1300C showed the hexagonally ordered phase for the entire range of composition ($0 \leq x \leq 3$). The degree of ordering being considerably greater than in the 1000C heated samples as evidenced by several superstructure reflections.

Keywords. Oxides; X-ray diffraction; ordering; dielectric materials.

1. Introduction

Among various families of oxides studied for the microwave dielectric applications, the oxides of the type $A(B_{1/3}B'_{2/3})O_3$ have been particularly of interest. Oxides with A = Ba, Sr; B = Zn, Mg and B^1 = Nb and Ta have been found to have appropriate dielectric properties. $Ba_3ZnTa_2O_9$ was first reported to show extremely low dielectric loss at microwave frequencies (Kawashima *et al* 1983). Several studies on related oxides have been carried out on other tantalates. $Ba_3MgTa_2O_9$ has been studied extensively for its microwave properties (Nomura *et al* 1982; Desu and O'Bryan 1985; Vincent *et al* 1993). The $A(B_{1/3}B'_{2/3})O_3$ or $A_3BB^1_2O_9$ type of perovskite oxides were first prepared by Roy (1954) and Galasso *et al* (1959). These crystallize in a disordered cubic structure or in a hexagonally ordered structure. The ordered structure results from the 1 : 2 ordering of the B and B^1-cations (–B–B^1–B^1–B–) along the [111] direction of the cubic perovskite cell. It is now known that the B-site ordering has a significant influence on the dielectric loss at microwave frequencies.

BMT ($Ba_3MgTa_2O_9$) is disordered at low temperatures and becomes ordered at high temperatures (around 1600C) (Desu and O'Bryan 1985). Ordering is also influenced by the addition of small quantities of dopants such as $BaZrO_3$ in $Ba_3MgTa_2O_9$ (Tamura *et al* 1984). Compared to BMT, the niobium analogue $Ba_3MgNb_2O_9$ (BMN) has been studied to a much lesser extent. It is reported to have a hexagonally ordered perovskite structure (Galasso and Pyle 1963) when sintered at 1400C and its dielectric properties show comparatively higher losses than BMT (Nomura 1983). In our studies we decided to investigate the influence, if any, of A-site substitution on the B-site ordering in an attempt to obtain ordered perovskites at relatively low temperatures (1300C). Note that both BMN and SMN ($Sr_3MgNb_2O_9$) are reported to be hexagonally ordered at 1400C. An earlier study (Onoda *et al* 1982) of a related system, $Ba_{3-x}Sr_xZnNb_2O_9$, gives some evidence of the presence of ordered structures at high Sr concentration for samples sintered at 1500C. Recent studies on Sr-doping in $Ba_3ZnNb_2O_9$ (Colla *et al* 1993) and $Ba_3MgTa_2O_9$ (Sugiyama and Nagai 1993; Nagai *et al* 1997) have also shown the presence of a new type of ordering of the octahedras leading to a lower symmetry (monoclinic) for the Sr-rich phases.

We have synthesized solid solutions for the first time between $Ba_3MgNb_2O_9$–$Sr_3MgNb_2O_9$. In this paper we report the synthesis, structural studies and phase relations at 1000C and 1300C.

2. Experimental

The starting materials were $BaCO_3$, $SrCO_3$, MgO and Nb_2O_5. Stoichiometric quantities were weighed, ground and calcined at 1000C for 30 h with two intermittent grindings. The calcined powder was ground, pressed into pellets with 5% polyvinylalcohol (PVA) solution and at 4 ton pressure. These pellets were sintered at 1000C for

*Author for correspondence

48 h followed by sintering at 1200C for 24 h and 1300C for 12 h. Powder X-ray diffraction (PXRD) was carried out using a Scintag–XDS 3000 and Rigaku RU 200 D-Max diffractometer with Cu-K*a* radiation. Lattice parameters were calculated by a least square fit to the observed *d* values.

3. Results and discussion

Powder X-ray diffraction patterns for $Ba_3MgNb_2O_9$ ($x = 0{\cdot}0$) synthesized at 1000C could be indexed on a cubic unit cell. For the $x = 0{\cdot}5$ composition in $Ba_{3-x}Sr_xMgNb_2O_9$, we clearly see the growth of the superstructure line at $d \sim 5{\cdot}0$ A (figure 1) corresponding to the (100) reflection of the hexagonally (1 : 2) ordered structure. The other superstructure lines however are not observed clearly. The $(100)_{(hex)}$ reflection grows in intensity with 'Sr' concentration and the $(100)_{(cubic)}$, which corresponds to the $(101)_{(hex)}$ reflection, decreases in intensity as is observed in hexagonally ordered structures. There is a gradual shift of the peaks towards higher $2q$ indicating the gradual decrease in the lattice parameters on Sr-substitution.

A small amount (5%) of a $Ba_5Nb_4O_{15}$ related phase occurs in all the samples. There appears to be a shift towards lower *d* values for this phase suggesting Sr doping in Ba sites in this impurity phase. Another cubic phase is present at higher Sr doping ($x \geq 1$) and is a maximum (~ 15%) at $x = 2$ (figure 2) after which it decreases. A close look at the *d* values of the lines corresponding to the cubic impurity phase in the $x = 1{\cdot}0$ loaded composition suggests that this impurity phase might be of the type $Ba_3Mg_{1-x}Sr_xNb_2O_9$ since the reflections occur at higher *d* values (2·920, **110**) compared to the parent $Ba_3MgNb_2O_9$ (2·900, **110**) phase. This is possible only if the larger ion (Sr^{2+}) substitutes on the Mg^{2+} site. However there is a gradual shift to lower *d* values with increase in Sr concentration. This could be explained if we consider

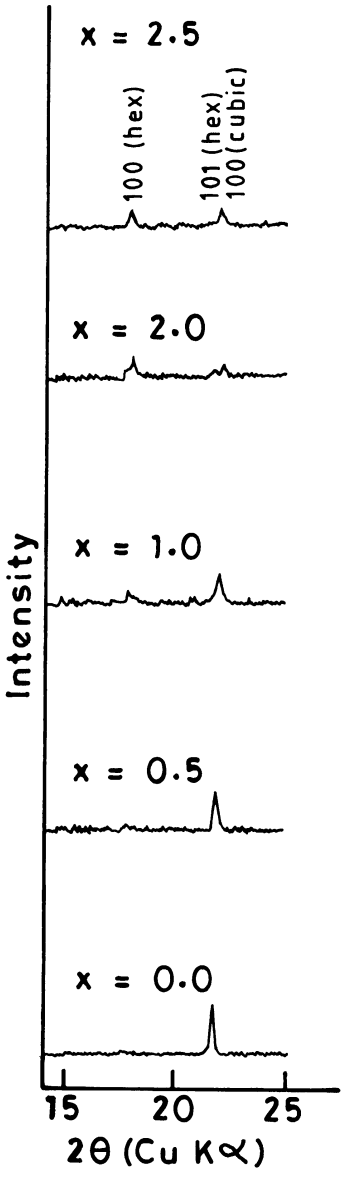

Figure 1. XRD of $Ba_{3-x}Sr_xMgNb_2O_9$ sintered at 1000C. (Note the increase in the intensity of the low $(100)_{hex}$ line with increase in *x*).

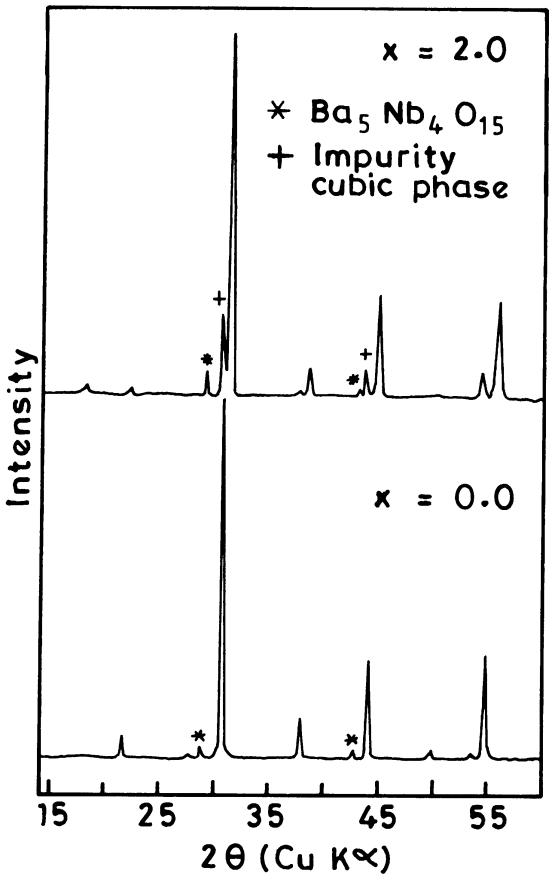

Figure 2. XRD of $Ba_3MgNb_2O_9$ ($x = 0$) and $BaSr_2MgNb_2O_9$ ($x = 2{\cdot}0$) sintered at 1000C.

Sr also substitutes on the Ba site at higher Sr concentration in addition to initially substituting on the Mg sites. This impurity phase would thus belong to a family of the type $Ba_{3-x}Sr_xMg_{1-y}Sr_yNb_2O_9$.

The $Ba_{3-x}Sr_xMgNb_2O_9$ compositions when further sintered at 1300C were found to have the 1 : 2 ordered structure for the entire range of composition ($0 \leq x \leq 3$) and the powder X-ray diffraction patterns (figure 3) can be indexed on a hexagonal cell. A small amount (5–10%) of $Ba_5Nb_4O_{15}$ related phase persists in all the compositions as earlier found in the 1000C heated samples. The $x = 0$ composition, $Ba_3MgNb_2O_9$ also shows additional weak peaks (5%) corresponding to *a*-$Ba_4Nb_2O_9$ (figure 3). However there are no extra peaks corresponding to the minor cubic phase tentatively ascribed to the formula $Ba_{3-x}Sr_xMg_{1-y}Sr_yNb_2O_9$ as found in the 1000C heated samples. The oxides at 1300C are clearly more ordered as evidenced from a large number of superstructure reflections (figure 3) compared to the corresponding compositions heated at 1000C where only the (100) reflection of the hexagonally ordered structure is observed (figures 1 and 2). The lattice parameters of $Ba_3MgNb_2O_9$ (**a** = 5·800(4), **c** = 7·090(3)) and $Sr_3MgNb_2O_9$ (**a** = 5·681(2), **c** = 6·942(1)) are close to those reported earlier (Galasso and Pyle 1963). Table 1 shows the indexed diffraction pattern for an ordered hexagonal phase. The hexagonal lattice parameters show a decrease with an increase in the Sr content (figure 4). This decrease in lattice parameter can be attributed to the smaller size of Sr^{2+} ion (ionic radii of Ba^{2+} (XII) is 1·61 and for Sr^{2+} (XII) is 1·44). In an earlier study (Onoda *et al* 1982) on the related $Ba_{3-x}Sr_xZnNb_2O_9$ system (sintered at 1500C for 1 h) there is evidence for ordering with increase in Sr concentration (for $x \geq 0{\cdot}8$) into 1 : 2 type hexagonally ordered perovskite from the broadening of high angle lines in the X-ray diffraction pattern. This value of x is close to what we also observe ($x \geq 0{\cdot}5$) in our studies on $Ba_{3-x}Sr_xMgNb_2O_9$. However, we observe ordering behaviour at temperatures as low as 1000C whereas the Zn analogue was sintered at 1500C (Onoda *et al* 1982). The broad lines observed in the earlier study (Onoda *et al* 1982) indicate the presence

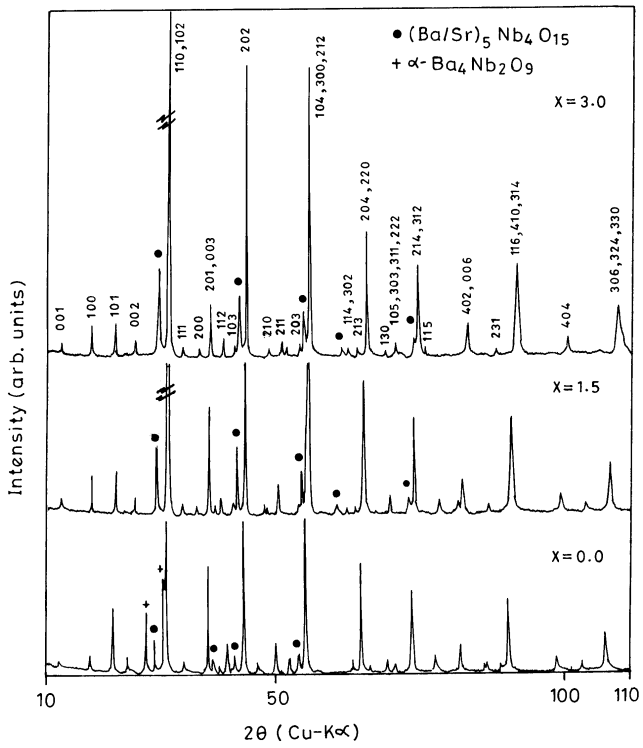

Figure 3. XRD pattern of $Ba_3MgNb_2O_9$, $Ba_{1·5}Sr_{1·5}MgNb_2O_9$ and $Sr_3MgNb_2O_9$ sintered at 1300C.

Table 1. Indexed X-ray powder diffraction pattern of $Ba_{1·5}Sr_{1·5}MgNb_2O_9$ (1300C) indexed on a hexagonal cell, a = 5·748(2) Å, c = 7·0299(7) Å unindexed lines belong to $(Ba/Sr)_5Nb_4O_{15}$.

d (obs)	*d* (cal)	I/I_0	*hkl*
7·104	7·030	2	001
4·993	4·978	4	100
4·074	4·063	4	101
3·531	3·515	2	002
3·071	–	11	–
2·878	2·871, 2·874	100	102, 110
2·657	2·660	1	111
2·486	2·489	1	200
2·345	2·346, 2·343	10	201, 003
2·288	–	1	–
2·226	2·225	2	112
2·125	2·120	1	103
2·095	–	6	–
2·032	2·031	30	202
1·899		1	–
1·877	1·881	1	120
1·814	1·816, 1·816	3	113, 211
1·707	1·706	1	203
1·691	–	4	–
1·657	1·659, 1·657, 1·659	28	300, 104, 212
1·534	–	1	–
1·499	1·499, 1·500	1	114, 302
1·467	1·467	1	213
1·436	1·436, 1·437	12	204, 220
1·352	1·353, 1·354, 1·355	2	105, 303, 311
1·298	1·285	2	132
1·284	1·284	9	124
1·224	1·224, 1·225, 1·225	2	205, 223, 401
1·182	1·190	1	133
1·181	–	1	–
1·176	–	1	–
1·172	1·173	3	402
1·169	1·172	2	006
1·124	1·126, 1·127	1	125, 231
1·094	1·099	1	403
1·091	–	1	–
1·085	1·085, 1·086, 1·086, 1·086	9	116, 134, 232, 140
1·015	1·016	2	404
1·013	1·004, 1·005	1	007, 225
0·984	0·984, 0·985, 0·986, 0·986	1	107, 135, 143, 501
0·961	0·959	1	502
0·958	0·958, 0·958	3	234, 330
0·956	0·957	5	306
0·954	0·949	3	331

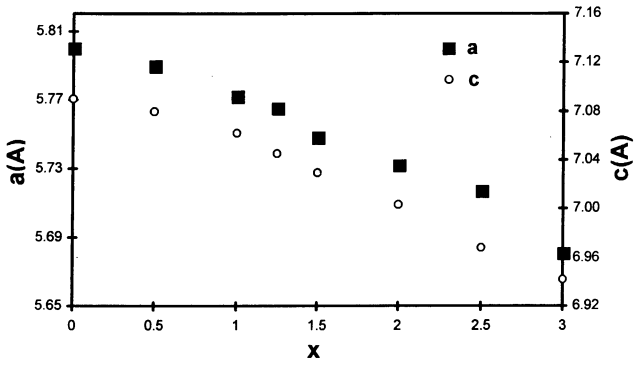

Figure 4. Plot of the variation of the hexagonal lattice parameters with Sr concentration (x) for samples sintered at 1300C.

of both ordered and disordered phase coexisting together, whereas, in our investigations of the 1300C sintered phases we clearly observe sharp lines including all superstructure reflections indicating a purely hexagonal structure. The transformation from a purely cubic structure to an ordered structure is usually influenced by the size and charge difference of the B and B^1 ions in the $A_3BB^1_2O_9$ type of oxides and to a much lesser extent by A-site substitution. We have tried to look for any lower symmetry reflections in our X-ray diffraction patterns corresponding to the monoclinic superstructure reported for the Sr-doped $Ba_3MgTa_2O_9$ and $Ba_3ZnNb_2O_9$ phases (Colla *et al* 1993; Sugiyama and Nagai 1993). The weak superstructure lines could not be clearly ascertained due to the presence of $(Ba/Sr)_5Nb_4O_{15}$ type of phases in the Sr-doped $Ba_3MgNb_2O_9$ system studied by us.

4. Conclusions

Various members of $Ba_{3-x}Sr_xMgNb_2O_9$ family were synthesized by the normal solid state method. There is a clear growth of the hexagonally ordered perovskite phase for those compositions with $x \geq 0{\cdot}5$ at 1000C evidenced by the presence of one superstructure line in the powder X-ray diffraction patterns of the 1000C heated samples. Thus Sr substitution helps in obtaining ordered structures at low temperature (1000C). At 1300C the entire range of oxides ($0 \leq x \leq 3$) are fully ordered as observed by powder X-ray diffraction and can be indexed satisfactorily to a hexagonal cell. There are two impurity phases present at 1000C, a $Ba_{5-x}Sr_xNb_4O_{15}$ type and another cubic phase (possibly of the type $Ba_{3-x}Sr_xMg_{1-y}Sr_yNb_2O_9$). At 1300C this impurity cubic phase disappears although the presence of the $Ba_{5-x}Sr_xNb_4O_{15}$ type phase (~ 5%) seems to persist in all samples.

We thus conclude that at temperatures of 1000C, Sr predominantly substitutes the A-site of the $A(B_{1/3}B^1_{2/3})O_3$ structure, although a small fraction does substitute the B-site (giving the impurity cubic phase). At 1300C only the A-site is substituted resulting in the absence of the cubic phase of the type $Ba_{3-x}Sr_xMg_{1-y}Sr_yNb_2O_9$.

Acknowledgements

Financial assistance to AKG from BRNS (DAE), Mumbai, is gratefully acknowledged.

References

Colla E L, Reaney I M and Setter N 1993 *J. Appl. Phys.* **74** 3414

Desu S B and O'Bryan H M 1985 *J. Am. Ceram. Soc.* **68** 546

Galasso F and Pyle J 1963 *J. Phys. Chem.* **67** 1561

Galasso F, Katz L and Ward R L 1959 *J. Am. Chem. Soc.* **81** 820

Kawashima S, Nishida M, Ueda I and Ouchi H 1983 *J. Am. Ceram. Soc.* **66** 421

Nagai T, Sugiyama M, Sando M and Niihara K 1997 *Jpn J. Appl. Phys.* **36** 1146

Nomura S 1983 *Ferroelectrics* **49** 61

Nomura S, Toyama K and Kaneta K 1982 *Jpn J. Appl. Phys.* **21** L624

Onoda M, Kuwata J, Kaneta K, Toyama K and Nomura S 1982 *Jpn J. Appl. Phys.* **21** 1707

Roy R 1954 *J. Am. Ceram. Soc.* **27** 581

Sugiyama M and Nagai T 1993 *Jpn J. Appl. Phys.* **32** 4360

Tamura H, Konoike T, Sakabe Y and Wakino K 1984 *J. Am. Ceram. Soc.* **67** C-59

Vincent H, Perrier C, Theritier P and Labeyrie M 1993 *Mater. Res. Bull.* **28** 951