Phase equilibria in the BaO–MgO–Ta$_2$O$_5$ system

Taras Kolodiazhnyi,[*a] Alexei A. Belik,[b] Tadashi C. Ozawa[b] and Eiji Takayama-Muromachi[ab]

We report on the phase relation in the BaO–MgO–Ta$_2$O$_5$ system equilibrated at 1450 °C. We found three ternary phases, namely 3:1:1 perovskite Ba$_3$MgTa$_2$O$_9$, 9:1:7 TTB (tetragonal tungsten bronze)-type Ba$_9$MgTa$_{14}$O$_{45}$ and 4:1:5 Ba$_4$MgTa$_{10}$O$_{30}$ closely related to the tungsten bronze structure. Another ternary phase, Ba$_{10}$Mg$_{0.25}$Ta$_{7.9}$O$_{30}$, with a 10 layer hexagonal perovskite structure can be only obtained after equilibration at 1600 °C. MgO solubility in the TTB-like Ba$_4$Ta$_{10}$O$_{29}$, BaTa$_4$O$_{11}$ and Ba$_{6.63}$Ta$_{34.95}$O$_{95}$ does not exceed 2.0 mol%. Only the hexagonal polymorph of the BaTa$_2$O$_6$ phase was found along the Mg$_4$Ta$_2$O$_9$–BaTa$_2$O$_6$ join. Measurements of dielectric properties in the 20 Hz–2 MHz range revealed that Ba$_9$MgTa$_{14}$O$_{45}$ has a dielectric constant of 99 with no frequency dispersion and low dielectric loss. We have also clarified several contradictory reports related to the ternary and binary phases in the BaO–MgO–Ta$_2$O$_5$ composition field.

1. Introduction

Low-loss dielectric ceramics are used as passive components in satellite and terrestrial wireless communication systems operating in the microwave (MW) frequency range. Utilization of these ceramics brings significant reduction in the weight and size of the MW electronic components. Driven by their exceptional technical importance, one of the most extensively studied compounds is a family of complex perovskites, namely Ba$_3$M'M''$_2$O$_9$ where M' = Mg, Zn, Co and M'' = Nb, Ta.[1–7]

Analysis of the literature data on Ba$_3$M'M''$_2$O$_9$ ceramics reveals that in addition to the target phase, in many cases, small amounts of secondary phases are present.[8,9] Appearance of the secondary phases may be caused by accidental or intentional deviation from stoichiometry, incomplete reaction of starting precursors, or high-temperature decomposition of the main phase. A well-known example is Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$ where Zn loss at high temperature leads to the formation of small volumes of the Ba$_8$ZnTa$_6$O$_{24}$ secondary phase. A large body of literature has been dedicated to the effect of the secondary phases and non-stoichiometry on the dielectric properties of the Ba$_3$M'M''$_2$O$_9$ ceramics.[10–13] A comprehensive analysis of the effect of the non-stoichiometry on the dielectric properties and cation ordering in Ba(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ has been published recently by Wu and Davies.[14]

Despite the high cost of tantalum, dielectric resonators based on Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ will be viable in future applications as we are facing increasing shortages (and cost) of available electromagnetic frequency space. The Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ ceramics have the lowest dielectric loss (i.e., highest Q-factor) and therefore offer the most efficient utilization of the allocated electromagnetic frequency window, i.e., they provide the largest number of communication channels within a fixed frequency band.

Preparation of high quality Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ ceramics has proven to be challenging and only a few academic groups were able to achieve Q-factors exceeding 25 000 at 10 GHz. In contrast to the intuitive perception that the lowest dielectric loss should be attained in ideally stoichiometric Ba$_3$M'M''$_2$O$_9$ compounds, recent findings reveal that a small deviation from stoichiometry enhances the M':M'' cation ordering and yields the highest Q-factors.[12,14] Even more surprising, the highest Q-factor in Ba(Co$_{1/3}$Nb$_{2/3}$)O$_3$ is found beyond a single phase composition range.[15] In light of these new findings, it seems imperative to have a clear understanding of the phase equilibria in the BaO–MgO–Ta$_2$O$_5$ ternary system. Several ternary phases, including Ba$_{10}$Mg$_{0.25}$Ta$_{7.9}$O$_{30}$, Ba$_9$MgTa$_{14}$O$_{45}$, Ba$_3$MgTa$_2$O$_9$, Ba$_8$Mg-Ta$_6$O$_{24}$, Ba$_4$MgTa$_{10}$O$_{30}$, Ba$_9$Mg$_4$Ta$_{20}$O$_{63}$, reportedly exist in the BaO–MgO–Ta$_2$O$_5$ ternary system,[16,19] yet their phase relationship has not been clarified. Although a tentative BaO–MgO–Ta$_2$O$_5$ phase diagram at 1450 °C has been proposed by Roth,[17] a complete phase equilibrium in the BaO–MgO–Ta$_2$O$_5$ composition field has never been reported. The present paper attempts to fill this gap.

2. Experimental

Chemical compositions in the BaO–MgO–Ta$_2$O$_5$ field were prepared from 99.99% BaCO$_3$ (Wako, Japan), 99.99% MgO and 99.9% Ta$_2$O$_5$ (Kanto Chem., Japan) precursors. Before preparation of the target compositions, the precursors were heat-treated in air up to 900 °C to ensure that their composition corresponds to the chemical formula. In total, around 40 chemical compositions were analyzed in this study. The powders were mixed in ethanol medium using high density alumina mortar. After drying, the samples were pressed into pellets using a tungsten carbide (Fuji Die Co., Japan) die, and then fired at 1450 °C for 20 hours in 99.9% pure Al$_2$O$_3$ crucibles covered with lids. After firing, the samples were cooled to 900 °C within 1 hour and then withdrawn from the furnace and air cooled. In most cases, this procedure was repeated three times after which no changes in the powder X-ray diffraction patterns were observed.

[a]National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan. E-mail: kolodiazhnyi.taras@nims.go.jp
[b]International Center for Materials Nanoarchitectonics (MANA), 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan

However, for compositions along the $Mg_4Ta_2O_9$–$BaTa_2O_6$ and the $Ba_3MgTa_2O_9$–$Ba_5Ta_4O_{15}$ tie lines the re-grinding and re-sintering were repeated four times to reach an equilibrium phase composition. In addition, selected compositions were sintered at 1600 °C for 5 hours. Phase identification and lattice parameters were examined with a Rigaku Ultima III X-ray diffractometer (Cu Kα radiation). Rietveld refinement of the crystal structures was performed using RIETAN 2000.[20] Dielectric properties at room temperature were measured in the 20 Hz–2 MHz range using an Agilent E4980 Precision LCR Meter.

3. Results and discussion

The overall phase relationship between the BaO:MgO:Ta_2O_5 compositions equilibrated at 1450 °C is shown in Fig. 1. Although it carries some similarities with the tentative BaO–MgO–Ta_2O_5 phase diagram proposed by Roth[17] one may also notice substantial differences. For samples equilibrated in air at 1450 °C there are only three ternary compounds. These include a 3:1:1 $Ba_3MgTa_2O_9$ perovskite, a 9:1:7 $Ba_9MgTa_{14}O_{45}$ phase with tetragonal tungsten bronze (TTB) structure[21] and a 4:1:5 orthorhombic $Ba_4MgTa_{10}O_{30}$ phase.[18]

In the 9:1:7 phase Ba atoms occupy tetragonal and pentagonal channels whereas Mg and Ta atoms are randomly distributed inside the corner-sharing oxygen octahedra. This phase belongs
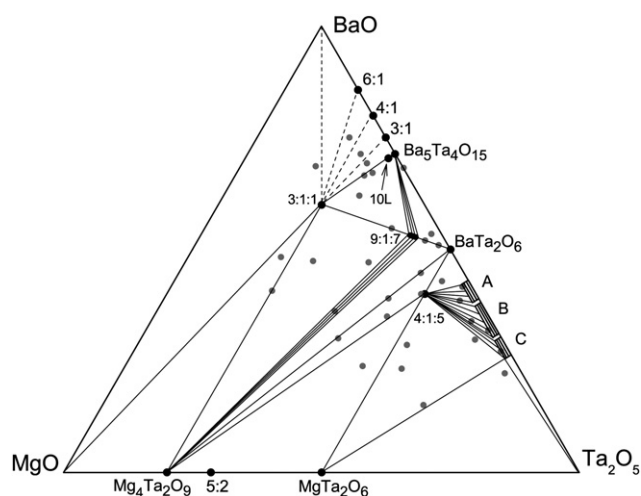
Fig. 1 Subsolidus phase diagram of BaO–MgO–Ta_2O_5 obtained for samples prepared in air at 1450 °C. The 10-layer (10L) hexagonal $Ba_{10}Mg_{0.25}Ta_{7.9}O_{30}$ phase included in the figure appears only at 1600 °C and cannot be obtained at 1450 °C. Grey dots are the compositions prepared in this study. Formulae and numbers designate distinct phases. At 1450 °C only three ternary compounds were identified, *i.e.*, 3:1:1 = $Ba_3MgTa_2O_9$, 9:1:7 = $Ba_9MgTa_{14}O_{45}$ and 4:1:5 = $Ba_4MgTa_{10}O_{30}$. In agreement with ref. 31 we found that BaO-rich phases, such as 3:1, 4:1 and 6:1 along the BaO–Ta_2O_5 binary, are unstable at room temperature. The 3:1:1 phase forms tie lines with $Mg_4Ta_2O_9$ and 9:1:7 phases. Compositions along the $Mg_4Ta_2O_9$–$BaTa_2O_6$ join contain a hexagonal polymorph of the $BaTa_2O_6$ phase. Phases labeled A, B, and C are TTB-type compounds described in detail in ref. 31; A = $Ba_xTa_{(10-2x)/5}[Ta_{10}O_{30}]$ where $3.40 \leq x \leq 3.93$, B = $Ba_yTa_{(14-2y)/5}[Ta_{22}O_{62}]$ where $5.11 \leq y \leq 6.77$, C = $Ba_zTa_{(18-2z)/5}[Ta_{34}O_{94}]$ where $6.17 \leq z \leq 7.42$.

to a large family of the $A_6B_{10}O_{30}$ TTB compounds intensively studied during the 'ferroelectric boom' in the second half of the last century.[22] A number of the compounds in this family show ferroelectric properties including Nb analogues of the 9:1:7 phase, *e.g.*, $Ba_9MgNb_{14}O_{45}$ ($T_C \approx 248$ K) and $Sr_9MgNb_{14}O_{45}$ ($T_C \approx 283$ K).[23] In agreement with earlier reports,[23] we found that the TTB $Ba_9MgTa_{14}O_{45}$ phase is not exactly a point compound. It appears to have a finite solubility range of *ca.* 2–3 mol% extending along both sides of the 9:1:7 composition towards the $Ba_3MgTa_2O_9$ and $BaTa_2O_6$ end members. Rietveld refinement confirmed earlier reports that the TTB 9:1:7 compound is isostructural with the TTB $BaTa_2O_6$ polymorph[24] as well as with its reduced analogues, *e.g.*, $Ba_3Ta_5O_{15}$ and $Ba_3Nb_5O_{15}$; all of them crystallize in the same $P4/mbm$ space group.[25,26] For initial refinement of the 9:1:7 phase we have used atomic coordinates of the tetragonal $BaTa_2O_6$ polymorph.[24] Table 1 shows lattice parameters of the 9:1:7 phase as a function of the BaO:MgO:Ta_2O_5 composition. The unit cell volume increases with an increase in the occupation of the Ta sites with slightly larger Mg^{2+} ions.

There are several important differences between this study and the BaO–MgO–Ta_2O_5 phase equilibria at 1450 °C reported by Roth.[17] In contrast to ref. 17, we could not find a tie line between the MgO and the TTB 9:1:7 phase; neither we can confirm a join between MgO and $BaTa_2O_6$. Instead, we found that the $Ba_3MgTa_2O_9$ phase forms tie lines with the $Mg_4Ta_2O_9$ and TTB 9:1:7 phases. In fact, $Ba_3MgTa_2O_9$ is the only ternary phase that forms along the join between corundum-like $Mg_4Ta_2O_9$ and an unstable $Ba_4Ta_2O_9$. Furthermore, in contrast to ref. 17, we could not confirm the existence of the hexagonal 9:4:10 $Ba_9Mg_4Ta_{20}O_{63}$ phase along the $Mg_4Ta_2O_9$–$BaTa_2O_6$ line. All three intermediate compositions along the $Mg_4Ta_2O_9$–$BaTa_2O_6$ join turned out to be mixtures of the end members: $Mg_4Ta_2O_9$ (space group $P\bar{3}c1$) and a hexagonal polymorph of $BaTa_2O_6$ (space group $P6/mmm$).

A variety of layered hexagonal perovskites have been reported along the tie line connecting the 3:1:1 cubic perovskite $Ba_3M'M''_2O_9$ and 5-layer hexagonal $Ba_5Ta_4O_{15}$ ($Ba_5Nb_4O_{15}$) end members.[16,27–30] For example, in the BaO–ZnO–Ta_2O_5 system these include 8-layer 'twin'-type hexagonal $Ba_8ZnTa_6O_{24}$ and 10-layer hexagonal $Ba_{10}Zn_{0.25}Ta_{7.9}O_{30}$ phases,[28] whereas in the BaO–CoO–Nb_2O_5 system an 8-layer 'shift'-type hexagonal $Ba_8CoNb_6O_{24}$ has been identified.[29] Remarkably, we were not able to synthesize an 8-layer hexagonal $Ba_8MgTa_6O_{24}$ phase in the BaO–MgO–Ta_2O_5 system in agreement with earlier reports by Mallinson *et al.*[16] and Kawaguchi *et al.*[30] The X-ray analysis of the compound with the $Ba_8MgTa_6O_{24}$ target composition sintered at 1450 °C revealed a mixture of $Ba_3MgTa_2O_9$ and $Ba_5Ta_4O_{15}$ phases. The same target compound equilibrated at 1600 °C resulted in a mixture of cubic $Ba_3MgTa_2O_9$ and 10-layer (10L) hexagonal $Ba_{10}Mg_{0.25}Ta_{7.9}O_{30}$ perovskite in agreement with ref. 16.

The Ta-rich region of the BaO–Ta_2O_5 binary has been recently revised by Vanderah *et al.*[31] during a comprehensive study of the BaO–TiO_2–Ta_2O_5 ternary system. In contrast to the earlier report,[32] the authors of ref. 31 have found that three TTB related phases with extended solid solution exist within the $26 \leq BaO \leq 43$ mol% range. To avoid oxygen deficiency,[31] these phases have been formulated as $Ba_xTa_{(10-2x)/5}[Ta_{10}O_{30}]$ where $3.40 \leq x \leq 3.93$ (space group $P4bm$), $Ba_yTa_{(14-2y)/5}[Ta_{22}O_{62}]$ where $5.11 \leq y \leq 6.77$ (space group $P4bm$) and $Ba_zTa_{(18-2z)/5}[Ta_{34}O_{94}]$ where

Table 1 Lattice parameters of the TTB-type 9:1:7 phase solid solution $Ba_{9+1.5x}Mg_{1+x}Ta_{14-x}O_{45}$ refined within the $P4/mbm$ space group. The pattern (R_p) and weighted pattern (R_{wp}) are reliability factors of the Rietveld refinement

x value	Composition [mol $BaO:MgO:Ta_2O_5$]	Secondary phases [weight %]	a [Å]	c [Å]	Vol [Å³]	R_p [%]	R_{wp} [%]
−0.725	50.93:1.77:47.31	hex-$BaTa_2O_6$ [32%]	12.588(4)	3.957(8)	627.1(9)	8.12	11.37
−0.367	51.96:3.89:44.15		12.598(1)	3.961(4)	628.7(2)	5.21	7.06
0	52.94:5.88:41.18		12.625(5)	3.972(0)	633.1(6)	4.55	5.93
0.645	54.72:9.03:36.26	$Ba_3MgTa_2O_9$ [15%]	12.630(5)	3.977(0)	634.4(5)	5.84	7.43
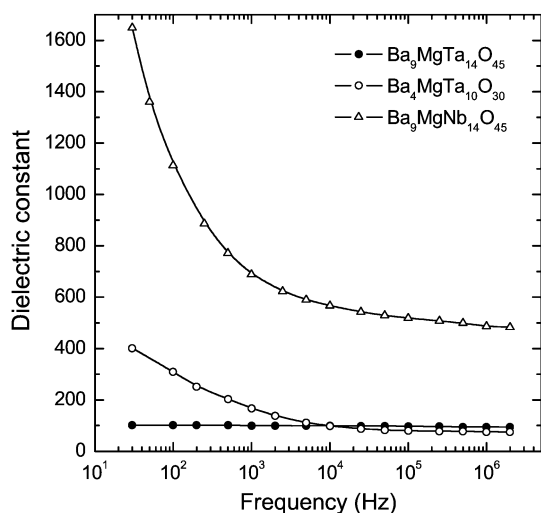
Fig. 2 Room temperature frequency dependence of the dielectric constant of $Ba_9MgTa_{14}O_{45}$, $Ba_4MgTa_{10}O_{30}$ and $Ba_9MgNb_{14}O_{45}$ ceramics of 97–98% density.

$6.17 \leq z \leq 7.42$ (space group $Pbam$). The ability of these TTB related phases to incorporate substantial amount of foreign ions was demonstrated in the example of the $BaO–TiO_2–Ta_2O_5$ system, where the TTB phases extend into the ternary region and dissolve up to 12 mol% of TiO_2.[31] Our analysis of the similar composition region in the $BaO–MgO–Ta_2O_5$ system confirmed the existence of the TTB-related phases along the $BaO–Ta_2O_5$ binary. Moreover, we have found that these phases slightly extend into the ternary region by dissolving up to 1.5–2.0 mol% of MgO. In this case, much lower solubility of MgO as compared to TiO_2 is not unexpected. Assuming that $Mg^{2+}(Ti^{4+})$ substitutes Ta^{5+}, the charge compensation of the Mg''_{Ta} defects would require 3 times more oxygen vacancies than that required for compensation of the Ti'_{Ta} defects. A high concentration of oxygen vacancies will eventually destabilize the TTB crystal structure.

Another ternary phase with a close relationship to the tungsten bronze type structure is 4:1:5 $Ba_4MgTa_{10}O_{30}$ (space group $Amm2$, $a = 3.90$, $b = 10.22$, $c = 14.97$ Å). It forms along the $MgTa_2O_6–BaTa_2O_6$ join and it is isostructural with $Ba_4Co-Ta_{10}O_{30}$ and $Ba_4NiTa_{10}O_{30}$.[18]

Although both 9:1:7 $Ba_9MgTa_{14}O_{45}$ and 4:1:5 $Ba_4MgTa_{10}O_{30}$ phases have been known for a number of years, their dielectric properties have not been reported so far. Fig. 2 shows the frequency dependence of the dielectric constant of $Ba_9Mg-Ta_{14}O_{45}$ and $Ba_4MgTa_{10}O_{30}$ ceramics. For comparison, we have also prepared and measured a $Ba_9MgNb_{14}O_{45}$ ceramic that is

isostructural with $Ba_9MgTa_{14}O_{45}$. We find that the room temperature dielectric constant of $Ba_9MgTa_{14}O_{45}$ shows a value of 98–99 without any noticeable frequency dispersion. Moreover, the dielectric loss of this compound was below the detection limit of the LCR Meter (i.e., tanδ < 0.002). Providing a temperature stable dielectric constant, the $Ba_9MgTa_{14}O_{45}$ compound with TTB structure may find technical applications as a compact dielectric resonator for the 1–2 GHz range. In contrast to $Ba_9MgTa_{14}O_{45}$, its Nb analogue shows a rather large dielectric constant ($ε' \approx 1200$ at 100 Hz) with a very strong frequency dependence and large dielectric loss (e.g., tanδ ≈ 0.05 at 2 MHz), consistent with typical ferroelectric relaxor behavior. The dielectric constant of $Ba_4MgTa_{10}O_{30}$ has a noticeable frequency dependence below 100 kHz. At higher frequency, $ε'$ of $Ba_4Mg-Ta_{10}O_{30}$ levels off at around 79. The low frequency dispersion of $ε'$ may be associated with a slow ionic conductivity or with a possible ferroelectric ground state. To clarify these assumptions, a detailed temperature characterization of dielectric properties is under way.

In conclusion, we have studied the phase equilibrium in the ternary $BaO–MgO–Ta_2O_5$ composition field. We confirmed only three ternary compounds (i.e., $Ba_3MgTa_2O_9$, $Ba_9MgTa_{14}O_{45}$ and $Ba_4MgTa_{10}O_{30}$) that form upon equilibration at 1450 °C. We found no evidence of the hexagonal $Ba_9Mg_4Ta_{20}O_{63}$ phase,[17] nor can we confirm the existence of the $Ba_7Ta_6O_{22}$ phase reported in ref. 19. TTB-type $Ba_9MgTa_{14}O_{45}$ forms along the $BaTa_2O_6–Ba_3MgTa_2O_9$ join. We found that only the hexagonal polymorph of the $BaTa_2O_6$ phase exists along the $Mg_4Ta_2O_9–BaTa_2O_6$ tie line. We also found that the MgO solubility in the TTB-like $Ba_4Ta_{10}O_{29}$, $BaTa_4O_{11}$ and $Ba_{6.63}Ta_{34.95}O_{95}$ is less than 2.0 mol%. For the first time we have reported the dielectric properties of the $Ba_9MgTa_{14}O_{45}$ and $Ba_4MgTa_{10}O_{30}$ phases and found that the TTB $Ba_9MgTa_{14}O_{45}$ shows a promising combination of relatively large dielectric constant and low dielectric loss which makes it an attractive candidate for passive microwave devices.

Acknowledgements

References

1 S. Nomura, *Ferroelectrics*, 1983, **49**, 61.
2 M. Bieringer, S. M. Moussa, L. D. Noailles, A. Burrows, C. J. Kieley, M. J. Rosseinsky and R. M. Ibberson, *Chem. Mater.*, 2003, **15**, 586.
3 M. W. Lufaso, *Chem. Mater.*, 2004, **16**, 2148.
4 M. A. Akbas and P. K. Davies, *J. Am. Ceram. Soc.*, 1998, **81**, 670.

5 M. Barwick, F. Azough and R. Freer, *J. Eur. Ceram. Soc.*, 2006, **26**, 1767.

6 T. V. Kolodiazhnyi, A. Petric, G. P. Johari and A. G. Belous, *J. Eur. Ceram. Soc.*, 2002, **22**, 2013.

7 T. Kolodiazhnyi, A. Petric, A. Belous, O. V'yunov and O. Yanchevskij, *J. Mater. Res.*, 2002, **17**, 3182.

8 H.-J. Youn, K.-Y. Kim and H. Kim, *Jpn. J. Appl. Phys.*, 1996, **35**, 3947.

9 L.-C. Tien, C.-C. Chou and D.-S. Tsai, *J. Am. Ceram. Soc.*, 2000, **83**, 2074.

10 C.-H. Lu and C.-C. Tsai, *J. Mater. Res.*, 1996, **11**, 1219.

11 J. H. Paik, S. Nahm, J. D. Bylin, M. H. Kim and H. J. Lee, *J. Mater. Sci. Lett.*, 1998, **17**, 1777.

12 K. P. Surendran, M. T. Sebastian, P. Mohanan, R. L. Moreira and A. Dias, *Chem. Mater.*, 2005, **17**, 142.

13 I. T. Kim, K. S. Hong and S. J. Yoon, *J. Mater. Sci.*, 1995, **30**, 514.

14 H. Wu and P. K. Davies, *J. Am. Ceram. Soc.*, 2006, **89**, 2250.

15 Dr B. Jancar, personal communication.

16 P. Mallinson, J. B. Claridge, D. Iddles, T. Price, R. M. Ibberson, M. Allix and M. J. Rosseinsky, *Chem. Mater.*, 2006, **18**, 6227.

17 R. S. Roth, '*Phase Equilibria of Experimental Ceramic Systems*', NIST Project Report, Report No. 1, Contract No. SB1341-02-W-0787, National Institute of Standards and Technology, Ceramics Division; Gaithersburg, Maryland; 2 pp. (2003).

18 R. Brandt and H. Mueller-Buschbaum, *Z. Anorg. Allg. Chem.*, 1987, **551**, 13.

19 J. S. Kim, J.-W. Kim, C. I. Cheon, Y.-S. Kim, S. Nahm and J. D. Byun, *J. Eur. Ceram. Soc.*, 2001, **21**, 2599; C.-M. Cheng, Y.-T. Hseih and C.-F. Yang, *Ceram. Int.*, 2002, **28**, 255; X. M. Chen, Y. Suzuki and N. Sato, *J. Mater. Sci.: Mater. Electron.*, 1994, **5**, 244.

20 F. Izumi and T. Ikeda, *Mater. Sci. Forum*, 2000, **321–324**, 198.

21 V. G. Kryshtop, R. U. Devlikanova, V. S. Filip'ev and E. G. Fesenko, *Inorg. Mater.*, 1983, **19**, 851.

22 T. Ikeda, T. Haraguchi, Y. Onodera and T. Saito, *Jpn. J. Appl. Phys.*, 1971, **10**, 987 and references therein.

23 N. N. Krainik, V. A. Isupov, M. F. Bryzhina and A. I. Agranovskaya, *Sov. Phys. Crystallogr.*, 1964, **9**, 281.

24 G. K. Layden, *Mater. Res. Bull.*, 1967, **2**, 533.

25 C. R. Feger and R. P. Ziebarth, *Chem. Mater.*, 1995, **7**, 373.

26 B. Hessen, S. A. Sunshine, T. Siegrist, A. T. Fiory and J. V. Waszczak, *Chem. Mater.*, 1991, **3**, 528.

27 A. M. Abakumov, G. Van Tendeloo, A. A. Scheglov, R. V. Shpanchenko and E. V. Antipov, *J. Solid State Chem.*, 1996, **125**, 102.

28 S. M. Moussa, J. B. Claridge, M. J. Rosseinsky, S. Clarke, R. M. Ibberson, T. Price, D. M. Iddles and D. C. Sinclair, *Appl. Phys. Lett.*, 2003, **82**, 4537.

29 P. M. Mallinson, M. M. B. Allix, J. B. Claridge, R. M. Ibberson, D. M. Iddles, T. Price and M. J. Rosseinsky, *Angew. Chem., Int. Ed.*, 2005, **44**, 7733.

30 S. Kawaguchi, H. Ogawa, A. Kan and S. Ishihara, *J. Eur. Ceram. Soc.*, 2006, **26**, 2045.

31 T. A. Vanderah, R. S. Roth, T. Siegrist, W. Febo, J. M. Loezos and W. Wong-Ng, *Solid State Sci.*, 2003, **5**, 149.

32 L. M. Kovba, L. N. Lykova, M. V. Paramova, L. M. Lopato and A. V. Shevchenko, *Russ. J. Inorg. Chem.*, 1977, **22**, 2845.

This journal is © The Royal Society of Chemistry 2009

J. Mater. Chem., 2009, **19**, 8212–8215 | 8215