The local crystal chemistry and dielectric properties of the cubic pyrochlore phase in the Bi_2O_3-M^{2+}-Nb_2O_5 (M^{2+}=Ni^{2+} and Mg^{2+}) systems

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A compositionally and displacively disordered, Bi-based pyrochlore phase found in a range of ternary Bi_2O_3 - $M^{2+}O$ - Nb_2O_5 systems has been the subject of much recent interest as a result of its relatively low sintering temperatures and often excellent dielectric properties including electric field tuneability. In this study, two such $A_2B_2O(1)_6O(2)_1$ pyrochlore type phases of stoichiometry $(Bi_{0.825}Ni_{0.125}<>_{0.05})_2(Ni_{0.25}Nb_{0.75})_2O_7$ (BNN) and $(Bi_{0.835}Mg_{0.085}<>_{0.08})_2(Mg_{0.235}Nb_{0.765})_2O_7$ (BMN) have been synthesized via solid-state reaction. Their average as well as disordered local structures have been investigated by means of Rietveld refinement of neutron powder diffraction data combined with electron diffraction studies of structured diffuse intensity. The refined average structures of both phases show large amplitude Atomic Displacement Parameters (ADP's) for the atoms occupying the *A* and O(2) sites of the ideal pyrochlore structure type. A disordered model, involving splitting of the Bi^{3+}/M^{2+} atoms on the *A* site from the 16*d* to the 96*h* sites and of the O(1) atoms from the 8*b* on to the 32*e* sites was found to significantly improve the average structure refinements as well as substantially reduce the refined *A*-site ADP's. A highly structured characteristic diffuse intensity distribution was found in electron diffraction patterns of both phases and partially interpreted in terms of large amplitude, β - cristobalite-type tetrahedral rotations of the O(2)A_2 tetrahedral framework sub-structure of the ideal pyrochlore structure type. The BNN and BMN, Bi-based pyrochlore phases with the above compositions show relatively high dielectric permittivities of 116 and 151 respectively at 1MHz and room temperature, respectively. Their dielectric loss tangents under the same conditions were also very good *i.e.* as low as 0.00065 and 0.00042, respectively.