

and cation vacancies were found at the octahedral cation site (B site). Change in cell dimension was smooth and monotonous, while structure refinements utilizing only high angle data (147 out of 182 Bragg points with $\sin\theta/\lambda \geq 0.6$) showed that the most of structural parameters have different trends with Ti doping higher and lower than 2%.

Anisotropy in ADPs at the octahedral cation site (B site) was high in the stoichiometric specimen [1] and this high anisotropy was kept in Ti 2% specimen. This anisotropy, however, got smaller with increasing Ti doping as it was reported on cation-deficient magnetite [2]. ADPs at the tetrahedral cation site (A site) and that at the oxide ion site along $\langle 111 \rangle$ increased steeply with Ti doping at concentrations higher than 5%.

As it has been repeatedly reported, the A-O and B-O distances in magnetite are longer and shorter than ${}^{\text{iv}}\text{Fe}^{2+}$ -O and average of ${}^{\text{vi}}\text{Fe}^{2+}$ -O and ${}^{\text{vi}}\text{Fe}^{3+}$ -O distances, respectively, in hitherto reported Fe-bearing spinels [3]. The A-O distance increased moderately with Ti doping, indicating transfer of remnant electron from the B site due to substitution of Fe^{2+} by Ti^{4+} . Change in the B-O distance showed convex feature with an amount of Ti: the B-O distance abruptly increased with Ti doping from 0 to 2%, then it turned into moderate convex trend with further Ti doping. Intercept at $\text{Ti} = 0\%$ extrapolated from Ti 5% and 10% data [$d(\text{B-O}) = 2.0610(6) \text{ \AA}$ at $\text{Ti} = 5\%$ and $2.0607(6) \text{ \AA}$ at $\text{Ti} = 10\%$] was 2.0615 \AA . While the value (2.0615 \AA) was still smaller than the average of $d({}^{\text{iv}}\text{Fe}^{2+}\text{-O})$ and $d({}^{\text{vi}}\text{Fe}^{3+}\text{-O})$ estimated from bond-valence scheme (2.078 \AA), this trend itself indicated change in nature of Fe-O bonding in the B-O bond (semi-metallic to ionic nature) with a little amount of Ti doping.

Difference Fourier synthesis on the stoichiometric specimen showed positive residues on B-O bonds, particularly in the vicinity of the B site (at $1/2, 1/2, 1/2$), and also positive residues on non-bonding directions in the vicinity of the A site. These features, however, were not clearly seen on Ti 2% and 5% specimens and vanished on Ti 10% specimen.

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Structural properties of gahnite doped with cobalt, manganese or titanium

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Oxide spinels include a very large group of structurally related compounds having a considerable technological importance. Among them, zinc aluminate (ZnAl_2O_4), known by the mineral name gahnite, is of interest due its good combination of semiconducting and optical properties which makes it useful in various photoelectronic devices [1]. When doped with some transition-metal cations or rear-earth cations, it exhibits luminescence and can be used as a cathodoluminescence material [2]. Gahnite possesses a cubic spinel-type structure, space group $Fd\bar{3}m$ [3]. Although gahnite doped with various cations already has wide applications, some cases of doping are not completely elucidated.

Three series of nanocrystalline powder gahnite samples were

prepared by a sol-gel technique: (i) samples doped with 0-100 at% Co (substituted for Zn), (ii) samples doped with 0-60 at% Mn (substituted for Zn), (iii) samples doped with 0-12.5 at% Ti (substituted for Al). Structural changes due to Co, Mn and Ti incorporation in the gahnite lattice were studied by XRD. Crystal structures were refined by the Rietveld method [4], including the analysis of diffraction line broadening. Valence state and location of dopant cations in the gahnite lattice were determined by EPR spectroscopy.

Unit-cell parameter of gahnite increased on doping with Co, Mn and Ti. Doping with cobalt and manganese induced a partial inverse spinel structure, with Co^{2+} and Mn^{2+} cations residing on both tetrahedral and octahedral cation sites of the gahnite structure respectively. On the other hand, Ti^{4+} dopant cations occupied only octahedral sites substituting for Al^{3+} . In the latter case the excess Zn^{2+} cations (included during the synthesis procedure) were also situated on octahedral cation sites due to charge compensation. On cobalt doping as well on titanium doping, the metal-oxygen distances in gahnite structural tetrahedra decreased while in structural octahedra increased. In the case of manganese doping the situation is just opposite: metal-oxygen distances in structural tetrahedra increased and in structural octahedra decreased. Such behavior is a consequence of ionic radii of involved dopant cations and their contents on the respective cation sites.

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Structure and spectroscopic study of $\text{A}_{0.50}\text{SbFe}(\text{PO}_4)_3$ (A = Mn, Ca, Cd, Sr) Nasicon phosphates series

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The Nasicon-type family has been the subject of intensive research due to its potential applications as solid electrolyte, electrode material, low thermal expansion ceramics and as storage materials for nuclear waste [1-4]. The structure of such materials with general formula $\text{A}_x\text{XX}'(\text{PO}_4)_3$ consists of a three-dimensional network made up of corner-sharing $\text{X}(\text{X}')\text{O}_6$ octahedra and PO_4 tetrahedra in such a way that each octahedron is surrounded by six tetrahedra and each tetrahedron is connected to four octahedra. Within the Nasicon framework, there are interconnected interstitial sites usually labelled M1 (one per formula unit) and M2 (three per formula unit) through which A cation can diffuse, giving rise to a fast-ion conductivity. The crystallographic formula can be written as $[\text{M1}][\text{M2}]_3\text{XX}'(\text{PO}_4)_3$.

$\text{A}_{0.50}\text{SbFe}(\text{PO}_4)_3$ (A = Mn, Ca, Cd, Sr) samples were obtained by solid state reaction in air. The structural characteristics by powder X-ray diffraction (XRD) study using the Rietveld method show that $\text{A}_{0.50}\text{SbFe}(\text{PO}_4)_3$ (A = Mn, Ca, Cd, Sr) compounds are isostructural and crystallise in the $R\bar{3}$ space group. In all samples, A^{2+} cations occupied one-half of the M1 sites and the Sb^{5+} and Fe^{3+} cations are orderly distributed within the $\text{SbFe}(\text{PO}_4)_3$ framework. A globally structural comparison between $\text{A}_{0.50}\text{SbFe}(\text{PO}_4)_3$ phases are presented. In order to obtain further structural information about the nature of bonding in studied phosphates an assignment of Raman and Infrared bands was also realised.