Effects of iron substitution and anti-site disorder on crystal structures, vibrational, optical and magnetic properties of double perovskites Sr2(Fe1-xNix)TeO6

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Electronic supplementary information:

Experimental:

The Goldschmidt tolerance factor for a double perovskite, $A_2BB'O_6$ as follows:

$$t = \frac{r_A + r_O}{\sqrt{2}(\frac{r_B}{2} + \frac{r_{B'}}{2} + r_O)} \tag{1}$$

where r_A, r_B, $r_{B'}$, and r_O are the ionic radii as taken from Shannon [1] for the *A*, *B*, *B′* cations and oxygen anions, respectively. This parameter provides a measure of how well the *A*-site cations fits the twelve-fold (cubo-octahedral) coordination space within the corner-shared octahedral network formed by the *B*-site cations. It is well known that this tolerance factor depends on the size of ions located in *A* and *B* sites of double-perovskite structure. If the size of the *A* cation is greater than the size of the *B* cation, this factor is > 1. In contrast, $t < 1$ when the size of *A* cations is smaller than *B* cations. For $t = 1$ the structure is cubic [2].

The optical properties of the materials were studied by diffuse reflectance UV/Vis spectroscopy (DR-UV/Vis) with a Shimazdu, UV2600 spectrometer. Spectra were recorded over a wavelength range of 200 - 850 nm at room temperature. Barium sulfate was used as a standard. The band-gap energy was obtained from the reflectance spectra by employing Tauc's method [3] to transform the function:

$$\alpha(\frac{hc}{\lambda}) \approx B\, (\frac{hc}{\lambda} - E_g)^n \tag{2}$$

into the Kubelka - Munk function [4] to obtain the function *F(R)*, which is related to the absorption and scattering coefficients *k(λ)* and *s(λ)*:

$$F(R) = \frac{[1-R(\lambda)]^2}{2R(\lambda)} = \frac{k(\lambda)}{s(\lambda)} \tag{3}$$

where *F(R)* is the Kubelka-Munk absorption, '*R*' is the diffuse reflectance, *h* is the Planck constant, *c* is the speed of light, *λ* is the wavelength of the impinging light, and E_g is the optical band gap in eV, *B* is a proportionality constant. The exponent n is the type of transition: n = 2 for indirect transitions, n = 1/2 for direct transitions [3 - 5]. Nevertheless, from such a treatment it can often be difficult to determine the nature of the optical transition and therefore an accurate band gap energy. An alternative is to apply a derivation of absorption spectrum fitting (DASF) [6] without knowing if the transition is direct or indirect, which is expressed by the following equation:

$$A(\lambda) = D\lambda\, (\frac{1}{\lambda} - \frac{1}{\lambda_g})^n \tag{4}$$

where $D = B(hc)^{n-1}z/2.303$, *z* is thickness of the reflecting layer, *A* is the absorbance at a wavelength *λ*, λ_g is the wavelength for corresponding band-gap energy. We can also use this Equation (3) in the followed form:

$$\frac{d[\ln (A(\lambda/\lambda)]}{d(1/\lambda)} = \frac{n}{(\frac{1}{\lambda} - \frac{1}{\lambda_g})} \tag{5}$$

In this method, the Kubulka-Munk function *F(R)* (equation 3) is assumed to be correlated to the absorption spectrum $A(\lambda)$ [$A(\lambda) = F(R)$], that is by means of the scattering coefficient $s(\lambda)$ which can be expressed as follow $s(\lambda) = s$ (this coefficient can be independent of the wavelength). Consequently, the obtained data from the transformed reflectance of Kubelka-Munk function can be utilized to estimate transition wavelength [7].

The equation (5) helps to calculate the absolute value of band-gap energy E_g, which could be expressed by: $Eg = \frac{hc}{\lambda_g} = \frac{1239.81}{\lambda_g}\ [eV]$ [8]. The idea is to get rid of the fixed transition exponent "n" by calculating the derivative of the absorption spectrum [8]. To its original successful use with thin films, this method was recently utilized for powders to determine the band gap energy [8]. The experimental work described herein demonstrates the possibility of employing the Reflectance-Absorption-Tauc-DASF (RATD) method [6], for deriving the transition types and band-gap energies of a series of isostructural compounds with varying composition.

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