

Effects of iron substitution and anti-site disorder on crystal structures, vibrational, optical and magnetic properties of double perovskites Sr₂(Fe_{1-x}Ni_x)TeO₆

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Experimental:

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

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

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 Shimadzu, 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:

$$\alpha\left(\frac{hc}{\lambda}\right) \approx B \left(\frac{hc}{\lambda} - E_g\right)^n \quad (2)$$

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

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

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:

$$A(\lambda) = D\lambda \left(\frac{1}{\lambda} - \frac{1}{\lambda_g}\right)^n \quad (4)$$

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:

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

In this method, the Kubelka-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: $E_g = \frac{hc}{\lambda_g} = \frac{1239.81}{\lambda_g}$ [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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