

APPLICATION OF BOND VALENCE MODEL TO STABILITY OF RE OXYCOMPOUNDS*

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The bond valence model was used to study the stability of the non-stoichiometric $\text{LaO}_{1-x}\text{F}_{1+2x}$ phases, the solid solubility in the $(\text{La}_{1-x}\text{Gd}_x)\text{OCl}$ system and the phase transformation in the REOCl ($\text{RE}^{3+} = \text{La}^{3+} - \text{Nd}^{3+}$, $\text{Sm}^{3+} - \text{Gd}^{3+}$, Ho^{3+} , and Y^{3+}) series. The stability of the non-stoichiometric $\text{LaO}_{1-x}\text{F}_{1+2x}$ ($0 \leq x \leq 0.3$) phase decreases with increasing excess fluoride. The global instability index values close to 0.2 indicate the instability of the non-stoichiometric phase. The relative stability of the $(\text{La}_{1-x}\text{Gd}_x)\text{OCl}$ ($0 \leq x \leq 1.0$) solid solutions achieved its minimum in the middle of the series. However, the X-ray powder diffraction results indicated complete solid solubility in the whole $(\text{La}_{1-x}\text{Gd}_x)\text{OCl}$ series and no phase separation was observed. The bond valence model was used to explain the structural transformation from the tetragonal oxychlorides, REOCl ($\text{RE} = \text{La} - \text{Er}$, and Y), to hexagonal beyond ErOCl . The calculated global instability index values did not show any clear trend across the REOCl series probably due to the inaccuracies and incoherencies in the original structural data.

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1. Introduction

The bond valence model provides a useful and quantitative description of the internal strains in bonding [1, 2], particularly in inorganic compounds with bonds of intermediate strength (e.g. the oxides and halides of di- and trivalent cations). The relaxation of the strain can result in non-stoichiometry, stabilization of unusual oxidation states, distortion of bonding environments and lowering of

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crystal symmetry [3]. With the aid of the bond valence concept, detailed insight to the inherent stability of a compound, or the stability of a crystal structure *vis-à-vis* to another polymorph can be estimated for an individual compound or for a series of compounds [4].

In this work, the bond valence model was used to study the stability of the non-stoichiometric $\text{LaO}_{1-x}\text{F}_{1+2x}$ ($0 \leq x \leq 0.3$) system, the cation solid solubility in $(\text{La}_{1-x}\text{Gd}_x)\text{OCl}$ ($0 \leq x \leq 1.0$) and the tetragonal to hexagonal phase transformation in the REOCl ($\text{RE}^{3+} = \text{La}^{3+}\text{-Nd}^{3+}, \text{Sm}^{3+}\text{-Gd}^{3+}, \text{Ho}^{3+}, \text{and Y}^{3+}$) series. The structural information used in the bond valence model calculations was based on the experimental X-ray powder diffraction data treated by the Rietveld profile refinement method [5] for the $\text{LaO}_{1-x}\text{F}_{1+2x}$ and the $(\text{La}_{1-x}\text{Gd}_x)\text{OCl}$ systems while for the REOCl series the structural data from different literature sources were employed [6–12].

2. Experimental

2.1. Sample preparation and diffraction measurements

The lanthanum oxyfluorides $\text{LaO}_{1-x}\text{F}_{1+2x}$ ($0 \leq x \leq 0.3$) were prepared by the solid state reaction between the high-purity (99.99%) La_2O_3 and ammonium fluoride at 1050°C for 1.5 h in static ambient atmosphere. The $(\text{La}_{1-x}\text{Gd}_x)\text{OCl}$ ($0 \leq x \leq 1$; step 0.2) powder samples were prepared by the solid state reaction between the high-purity sesquioxide mixture and NH_4Cl at 900°C for one hour in an inert nitrogen atmosphere.

The room temperature X-ray powder diffraction (XPD) patterns of the $\text{LaO}_{1-x}\text{F}_{1+2x}$ and the $(\text{La}_{1-x}\text{Gd}_x)\text{OCl}$ samples were measured with a ENRAF-NONIUS PDS120 X-ray powder diffractometer ($\text{Cu } K_{\alpha 1}$ radiation, $\lambda = 1.5406 \text{ \AA}$) equipped with a INEL CPS120 position sensitive detector. Silicon powder (NBS standard 640b) was used as an external standard.

2.2. Structural data

The stoichiometric RE oxyfluorides belong to the hexagonal crystal system throughout the whole RE series [13]. The stoichiometric LaOF crystallizes in the hexagonal system with a SmSI -type structure (space group: $R\bar{3}m$; $Z = 6$). In addition to the stoichiometric hexagonal REOF form, the RE oxyfluorides are also known to exhibit non-stoichiometry with the formation of $\text{REO}_{1-x}\text{F}_{1+2x}$ phases with excess fluoride [14]. Some of the phases in this system have been assigned to different crystal systems, e.g. compositions $\text{LaO}_{0.65}\text{F}_{1.70}$ and $\text{SmO}_{0.70}\text{F}_{1.60}$ to the tetragonal [15] and orthorhombic [16] structures, respectively.

The Matlockite-type PbFCl structure of the lighter REOCl ($\text{RE} = \text{La-Er}$, and Y) belongs to the tetragonal crystal system with $P4/nmm$ ($Z = 2$) as the space group [6]. The overall structure is formed of alternating layers of $[\text{REO}]_n^+$ complex cations and Cl^- anions. ErOCl as well as the heavier oxychlorides crystallize in the hexagonal system with the space group $R\bar{3}m$ ($Z = 6$) [17].

2.3. Theoretical considerations of the bond valence model

In the bond valence model, the bond valence calculated from the experimental structural data for each ion in the structure is compared to the nominal valence. The bond valences, s_{ij} , for each cation-anion pair were obtained from the experimental interatomic bond distances R_{ij} and the characteristic distance R_0 according to Eq. (1) [18, 19]

$$s_{ij} = \exp [(R_0 - R_{ij}) / B]. \quad (1)$$

In this equation, B is an universal constant equal to 0.37 [18]. The R_0 values can be found in tabulated form for the most frequent cation-anion pairs [2, 20]. The more the s_{ij} value deviates from the ideal value, R_0 , the more important strains exist in the bonding around the atom.

The global instability index (GII) value (Eq. (2)) which can be used to estimate the total structural strains and thus the stability of the structure studied is defined by a comparison between the calculated valence sums s_{ij} and the formal valence V_i of all the species N in the asymmetric unit of the crystal structure

$$\text{GII} = \sqrt{\sum_{i=1}^N [(\sum_j s_{ij} - V_i)^2 / N]}. \quad (2)$$

The global instability index describes strains in the structure and puts thus a limit to the maximum allowable distortions. According to an empirical formulation, if GII exceeds 0.2 the structure becomes unstable and faces a possible collapse or a phase transformation [1, 19].

3. Results and discussion

3.1. Non-stoichiometry in $\text{LaO}_{1-x}\text{F}_{1+2x}$

The structure of the stoichiometric LaOF changes drastically to the non-stoichiometric $\text{LaO}_{1-x}\text{F}_{1+2x}$ ($0.05 \leq x \leq 0.3$) phases even with a few mole per cent of excess fluoride introduced. The changes in the powder diffraction patterns are less pronounced, except for a slight splitting of the most intense reflections. The low intensity reflections move not more than slightly in the 2θ scale.

The X-ray diffraction data measured at room temperature in the 2θ range between 6.5 and 121° were analyzed with the Rietveld profile refinement method. The structural parameters were then utilized as input data for the bond valence model calculations. The global instability index as a function of the x value in $\text{LaO}_{1-x}\text{F}_{1+2x}$ ($0 \leq x \leq 0.3$) increases with increasing excess fluoride indicating diminishing stability with increasing non-stoichiometry. The GII value for each $\text{LaO}_{1-x}\text{F}_{1+2x}$ composition is significantly greater than that for the stoichiometric LaOF, and exceeds the limit (*ca.* 0.2) which indicates the possible breakdown of the tetragonal structure (Fig. 1). This was effectively shown by the thermogravimetric (TGA) measurements since the thermal decomposition of the non-stoichiometric phases yielded always the stoichiometric LaOF as an intermediate phase [21].

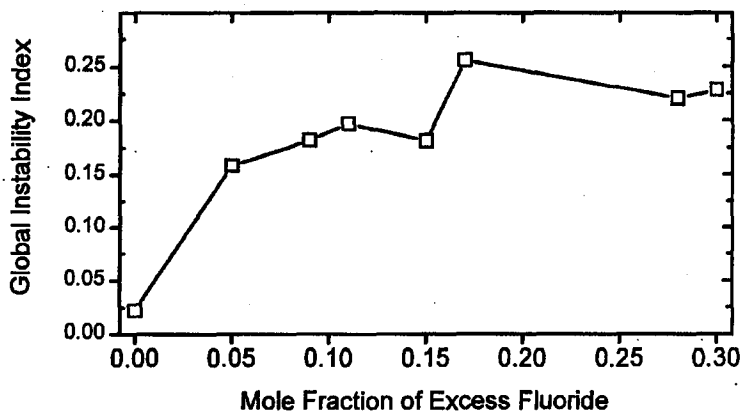


Fig. 1. Evolution of the global instability index in the $(LaO_{1-x}F_{1+2x})$ series.

3.2. Solid solubility in $(La_{1-x}Gd_x)OCl$

The formation of the solid solutions in the $(La_{1-x}Gd_x)OCl$ series was studied by the X-ray powder diffraction at room temperature in the 2θ region between 6.5 and 120° . The Rietveld profile refinement analyses of the XPD patterns were carried out with the background, unit cell, atomic position, isotropic temperature, and Gaussian profile form parameters refined freely. All $(La_{1-x}Gd_x)OCl$ samples possessed the tetragonal $PbFCl$ -type structure with $P4/nmm$ as the space group ($Z = 2$). The unit cell parameters a and c evolve smoothly through the series and no clustering of the Gd^{3+} ions was thus observed according to the Vegard law. It was concluded that solid solubility exists throughout the whole series.

The bond valence model was used to estimate the relative stabilities of the $(La_{1-x}Gd_x)OCl$ solid solutions. The GII value achieved its maximum in the middle of the series for the $(La_{0.4}Gd_{0.6})OCl$ composition (Fig. 2). However, from the X-ray

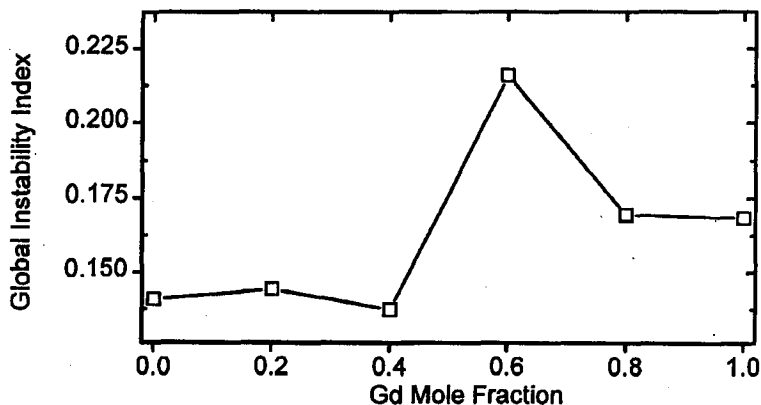


Fig. 2. Evolution of the global instability index in the $(La_{1-x}Gd_x)OCl$ series.

powder diffraction results it was concluded that complete solid solubility exists in the $(\text{La}_{1-x}\text{Gd}_x)\text{OCl}$ series and no phase separation was observed though the GII value exceeded the approximate limit of 0.2. The diffraction reflections were found somewhat broader in the middle of the series indicating possible local distortion or disorder.

3.3. Phase transition in REOCl

The bond valence model was thought to explain the structural change from the tetragonal PbFCl-type REOCl to the hexagonal SmSI-type. By using the structural data from different sources [6–12] the calculated global instability index values did not show any clear trend across the REOCl series and thus no further conclusions could be drawn (Fig. 3). Reasons to the irregular behavior could include the inaccuracies and incoherencies in the original structural data due to the different experimental and data treatment procedures.

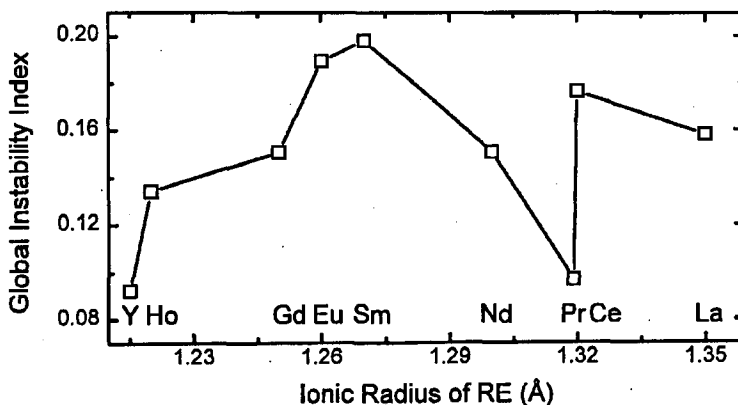


Fig. 3. Evolution of the global instability index in the REOCl series.

4. Conclusions

The bond valence model was proved useful in the characterization of the cation solid solubility in the $(\text{La}_{1-x}\text{Gd}_x)\text{OCl}$ series, the stability being lowest in the middle of the series for the $(\text{La}_{0.4}\text{Gd}_{0.6})\text{OCl}$ composition. Also the investigation of the non-stoichiometry in the $\text{LaO}_{1-x}\text{F}_{1+2x}$ system could be carried out successfully, with the stability of the non-stoichiometric $\text{LaO}_{1-x}\text{F}_{1+2x}$ ($0.05 \leq x \leq 0.3$) phases decreasing with the increasing content of the excess fluoride. The stability is always lower than that of the stoichiometric phase. However, the consistent experimental conditions and data treatment procedures proved to be of primordial importance when the phase transformation in the REOCl series was investigated. Due to the structural data from different sources no consistent results were obtained with the bond valence calculations.

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