

DISTORTIONS IN THE Sr_2TiO_4 AND $\text{Sr}_3\text{Ti}_2\text{O}_7$ STRUCTURES AND THEIR SPECTROSCOPIC DETECTION

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It is shown that distortions in Sr_2TiO_4 - and $\text{Sr}_3\text{Ti}_2\text{O}_7$ -like structures can be predicted from Pauling's electrostatic valence principle. It is discussed in how far these distortions can be observed spectroscopically.

1. Introduction

Recently the crystal structures of $\text{SrLa}_2\text{Al}_2\text{O}_7$ and $\text{SrGd}_2\text{Al}_2\text{O}_7$ [1] and $\text{BaLa}_2\text{Fe}_2\text{O}_7$ and $\text{SrTb}_2\text{Fe}_2\text{O}_7$ [2] have been described. They can be considered as distorted forms of the $\text{Sr}_3\text{Ti}_2\text{O}_7$ structure [3]. As a result the Al^{3+} ion has a tetragonal-pyramidal five-coordination, although Ti^{4+} in $\text{Sr}_3\text{Ti}_2\text{O}_7$ is in octahedral six-coordination.

On the other hand spectroscopic evidence has been presented that in NaLnTiO_4 (superstructure of Sr_2TiO_4) the Ti^{4+} ions are in the pyramidal five-coordination [4]. Pauling's electrostatic valence principle [5] was used to account for this fact.

It is the purpose of this paper to show that this principle can be applied more generally to predict the coordination of the smaller cations in Sr_2TiO_4 - and $\text{Sr}_3\text{Ti}_2\text{O}_7$ -like structures and to discuss in how far spectroscopic methods can be used to measure this coordination.

2. Distortions and Pauling's electrostatic valence principle

If we consider NaLnTiO_4 with the ideal Sr_2TiO_4 structure, the Ti^{4+} would be in octahedral coordination. None of the surrounding oxygen ions obeys Pauling's electrostatic valence principle: the electrostatic bond strength s (which should be 2), is $2\frac{2}{3}$ for the four oxygen ions in the titanate layer, $2\frac{1}{3}$ for the

oxygen belonging to the $\text{Ln}-\text{O}$ layer and only $1\frac{2}{3}$ for the oxygen belonging to the $\text{Na}-\text{O}$ layer. This poor charge balance is partly removed by a displacement of the Ti^{4+} ion from the centre of the octahedron to the O^{2-} ion with $s = 1\frac{2}{3}$. Pyramidal five-coordination of the Ti^{4+} ion and a high-wavenumber frequency for the $\text{Ti}-\text{O}$ vibration results [4].

In $\text{SrGd}_2\text{Al}_2\text{O}_7$ with ordered $\text{Sr}_3\text{Ti}_2\text{O}_7$ structure the situation is similar. The Al^{3+} ion is found in five coordination. This can be explained as follows: in the ideal $\text{Sr}_3\text{Ti}_2\text{O}_7$ arrangement for $\text{SrGd}_2\text{Al}_2\text{O}_7$ the Al^{3+} ion would occupy octahedral sites with $s = 1\frac{2}{3}$ for the oxygen ion in the centre of the perovskite layer, $s = 2$ for the four oxygen ions in the $\text{Ti}-\text{O}$ layer and $s = 2\frac{1}{6}$ for the oxygen ions in the $\text{Gd}-\text{O}$ layer. A better charge balance results if the Al^{3+} ion moves to the oxygen ion with $s = 1\frac{2}{3}$ as observed experimentally. This has also been observed for $\text{BaLa}_2\text{Fe}_2\text{O}_7$ and $\text{SrTb}_2\text{Fe}_2\text{O}_7$ [2]. The electrostatic valence principle seems to be a guide in predicting distortions in Sr_2TiO_4 - and $\text{Sr}_3\text{Ti}_2\text{O}_7$ -like structures.

It is interesting to note that the ideal structures are not stable without distortion: compounds $\text{SrLn}_2\text{Cr}_2\text{O}_7$ and $\text{BaLn}_2\text{Cr}_2\text{O}_7$ do not exist [2]. Here distortion would cost a large amount of extra energy due to the well-known preference energy of Cr^{3+} for octahedral coordination.

Due to the distortions the compounds contain Ln_2O_2 layers perpendicular to the tetragonal axis. Layers of this type have been found for a number of Ln^{3+} compounds and especially for a number of Bi^{3+}

compounds [6,7]. The most well-known examples are LnOCl and BiOCl .

3. Spectroscopic methods

The use of vibrational spectra to distinguish between five- and six-coordination for the smaller cation has been discussed before [4]. For the Ti^{4+} ion this method is applicable, since the titanate stretching modes can be considered in good approximation as internal vibrations of the titanate group. In NaLnTiO_4 the highest stretching mode is situated at about 900 cm^{-1} (five-coordination), in Sr_2TiO_4 at about 600 cm^{-1} (six-coordination). This method will not be of great use for the aluminates, since the approach of internal vibrations is likely to break down.

Fava and Le Flem [1] used the luminescence of Eu^{3+} in $\text{SrLa}_2\text{Al}_2\text{O}_7$ and $\text{SrGd}_2\text{Al}_2\text{O}_7$ to observe structural details and especially to find out whether the trivalent rare earths occupy positions in the centre of the perovskite layer (12-coordinated sites with D_{4h} symmetry) or positions in between the perovskite layers (9-coordinated sites with C_{4v} symmetry). The Eu^{3+} ions on the former sites are expected to emit mainly $^5D_0-^7F_1$ magnetic dipole emission (due to inversion symmetry), whereas the Eu^{3+} ions on the latter sites are expected to emit mainly $^5D_0-^7F_2$ forced electric dipole emission [8]. The authors excite into the 5L_7 level (3965 Å excitation) and observe mainly $^5D_0-^7F_2$ emission so that they conclude that the Eu^{3+} ions occupy the 9-coordinated sites. This, however, is questionable since the excitation transition is also a forced electric dipole transition which will have a much higher oscillator strength for 9 than for 12 coordination. Consequently the 9-coordinate Eu^{3+} is excited preferentially and emission from a possible 12-coordinated Eu^{3+} ion will not be observed.

We feel that the Eu^{3+} emission spectra can be used in a different way to elucidate structural details of compounds as those under discussion, viz., by considering the intensity of the $^5D_0-^7F_0$ emission relative to that of the $^5D_0-^7F_1$ emission. The latter is used as a reference, since it will not be influenced strongly by the Eu^{3+} surroundings (being a magnetic dipole emission) [8].

In table 1 this ratio is given for several compounds. The relatively high intensity of the $^5D_0-^7F_0$ emission

Table 1

Ratio of the intensities of the $^5D_0-^7F_0$ and $^5D_0-^7F_1$ transitions in the Eu^{3+} emission in several compounds

Compound	Crystal structure	Ratio	Ref.
Sr_2TiO_4 (Eu^{3+} , Na)	Sr_2TiO_4	1.65	[9]
NaLaTiO_4 (Eu)	ordered Sr_2TiO_4	0.4	[10]
NaGdTiO_4 (Eu)	ordered Sr_2TiO_4	0.1	[10]
NaYTiO_4 (Eu)	ordered Sr_2TiO_4	0.02	[10]
SrLaAlO_4 (Eu)	disordered Sr_2TiO_4	0.09	[9]
SrGdAlO_4 (Eu)	disordered Sr_2TiO_4	0.09	[9]

has been ascribed to the presence of a linear crystal field term [11]. Its presence in the structures under consideration can be ascribed to the fact that in the 9-coordinated site the cation has one anion above and four anions below itself. The four other anion neighbours form a square perpendicular to the tetragonal c axis and do not contribute, because the cation occupies the centre of this square. This is the situation in the ideal Sr_2TiO_4 and $\text{Sr}_3\text{Ti}_2\text{O}_7$ structures. In the distorted versions the square moves to the site where only one anion is situated [1,2], so that the strength of the linear crystal field term decreases.

The luminescence and structure data that are now available confirm this qualitative picture. In undistorted Sr_2TiO_4 the ratio $^5D_0-^7F_0$ to $^5D_0-^7F_1$ intensity is unusually high (1.65; table 1). In the ordered compounds NaLnTiO_4 this ratio is much lower: the Sr-O layer of Sr_2TiO_4 is distorted in such a way that the oxygen anions move to the lanthanides. It is not unreasonable that this distortion is the stronger, the smaller the lanthanide ionic radius. The compounds SrLaAlO_4 and SrGdAlO_4 are difficult to discuss because the Sr^{2+} and La^{3+} (Gd^{3+}) ions do not order. According to ref. [1] the emission spectra of Eu^{3+} in $\text{SrLa}_2\text{Al}_2\text{O}_7$ and $\text{SrGd}_2\text{Al}_2\text{O}_7$ are very similar to those of Eu^{3+} in SrLaAlO_4 and SrGdAlO_4 , so that we may take the ratio $^5D_0-^7F_0$ to $^5D_0-^7F_1$ intensity about 0.1 in the case of $\text{SrLa}_2\text{Al}_2\text{O}_7$. The compound $\text{SrGd}_2\text{Al}_2\text{O}_7$ is ordered so that we have the same Gd_2O_2 layer as in NaGdTiO_4 . In fact the intensity ratios are equal for these compounds. $\text{SrLa}_2\text{Al}_2\text{O}_7$ is reported to be disordered. For ordered $\text{SrLa}_2\text{Al}_2\text{O}_7$ the intensity ratio should be about 0.4.

We conclude that in a qualitative way the relative intensity of the Eu^{3+} $^5D_0-^7F_0$ emission reveals structural details of the Ln_2O_2 layer in Sr_2TiO_4 - and

$\text{Sr}_3\text{Ti}_2\text{O}_7$ -like compounds and, consequently, the coordination of the smaller cation: relatively high intensity forms evidence for six-coordination, relatively low intensity for five-coordination.

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ERRATUM

J. Hendeković, Some aspects of the complex molecular orbitals method, *Chem. Phys. Letters* 32 (1975) 597.

The denominator in the third line of eq. (16) should be replaced by

$$[\text{Re}(1 + e^{2i\phi_\lambda} D_\lambda)]^{-1}$$

The last sentence on page 600 should read:
Thus the CMO energy decrease with respect to the LCAO MO energy was reduced for about 20%.