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Next neighbors effect along the Ca–Sr–Ba-åkermanite join: Long-range vs. short-range structural features

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ABSTRACT

An original approach has been developed herein to explore the correlations between short- and long-range structural properties of solid solutions. X-ray diffraction (XRD) and electronic absorption spectroscopy (EAS) data were combined on a $(Ca,Sr,Ba)_2(Mg_{0.7}Co_{0.3})Si_2O_7$ join to determine average and local distances, respectively. Instead of varying the EAS-active ion concentration along the join, as has commonly been performed in previous studies, the constant replacement of Mg^{2+} by a minimal fraction of a similar size cation (Co^{2+}) has been used to assess the effects of varying second-nearest neighbor cations (Ca, Sr, Ba) on the local distances of the first shell. A comparison between doped and un-doped series has shown that, although the overall symmetry of the Co-centered *T1*-site was retained, greater relaxation occurs at the CoO_4 tetrahedra which become increasingly large and more distorted than the MgO_4 tetrahedra. This is indicated by an increase in both the quadratic elongation (λ_{T1}) and the bond angle variance (σ^2_{T1}) distortion indices, as the whole structure expands due to an increase in size in the second-nearest neighbors. This behavior highlights the effect of the different electronic configurations of Co^{2+} ($3d^7$) and Mg^{2+} ($2p^6$) in spite of their very similar ionic size. Furthermore, although the overall symmetry of the Co-centered T1-site is retained, relatively limited (<10 deg) angular variations in O–Co^{2+}–O occur along the solid solution series and large changes are found in molar absorption coefficients showing that EAS Co^{2+}-bands are highly sensitive to change in the local structure.

1. Introduction

A fundamental problem in determining the chemical and physical properties of a crystal structure is the precise distribution of the atoms in its lattice. In early X-ray diffraction applications, Vegard observed that the lattice constant linearly scales with composition in many cubic ionic salts [1,2]. In the hypothetical case of a solid solution which obeys Vegard's law, it is reasonable to assume that mean atomic bond distances also vary linearly as a function of composition. Therefore, the constituent atoms of every compound belonging to the solid solution will be located at a lattice site whose size stems from the composition-averaged structure, ignoring any local displacement (i.e. the structure will follow the virtual-crystal approximation model, VCA) [3]. On the other hand, almost all compounds belonging to a solid solution deviate from the VCA model, as their properties differ from the linearity predicted by Vegard's law. Since no single experimental method can determine an average long-range crystal structure and, at the same time, give indications on local distances between the central ion and its surrounding atoms, the *long-range* vs. *short-range* properties of a crystal structure along a binary join have to be obtained through a combination of diffraction and spectroscopy techniques [4–6].

When access to large scale facilities is not possible and hence EXAFS cannot be performed, electronic absorption spectroscopy (EAS) is the most common technique applied to gain local structural information [7–12]. Local metal–oxygen distances in a solid solution investigated through EAS are derived by means of the crystal field parameter 10*Dq*. According to the crystal field theory [13,14], in an oxygen-based structure, the 10*Dq* value depends on the mean metal–oxygen bond distances ⟨*M*–O⟩ through the relationship:

$$10Dq = 5/3 \times Q \times \langle \mathrm{r} \rangle^4 \langle M\text{–O} \rangle^{-5} \tag{1}$$

where both the effective charge on ligands, Q, and the average radius of *d* orbitals, ⟨r⟩, can be considered constant for the same metal ion in the same ligand environment [7,13–15]. The local ion–oxygen distance, $\langle M\text{–O}\rangle_x{}^{\mathrm{local}}$, can be calculated for each term *x* of a $M_x\mathrm{O}\text{–}M'_{1-x}\mathrm{O}$ solid solution by [5–7]:

$$\langle M\text{–O}\rangle_x{}^{\mathrm{local}} = \langle M'\text{–O}\rangle \cdot \left[(10DqM')/(10DqM)_x\right]^{1/5} \tag{2}$$

In this study, a first attempt has been made to obtain information on the deviation between *long-range* and *short-range* properties using a “*probe cation*”. The solid solution here chosen is based on compounds with a melilite-type structure which is characterized by a tetragonal lattice (space group $P\text{-}42_1m$), with the general formula $^{[8]}X_2{}^{[4]}T1^{[4]}T2_2A_7$ (where *X* is a large mono- to tri-valent

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Table 1
Quantitative phase analysis, agreement factors and refinement details, unit-cell parameters, mean metal–oxygen bond distances, bond angles, and tetrahedral distortion indices for the (Ca,Sr,Ba)$_2$(Mg$_{0.7}$Co$_{0.3}$)Si$_2$O$_7$ samples. Standard deviations are reported in parentheses.

(Ca,Sr,Ba)$_2$(Mg$_{0.7}$Co$_{0.3}$)Si$_2$O$_7$							
Nominal ionic radius of the cations hosted at the *X* site, ir_X (Å)							
	1.12	1.19	1.26	1.34	1.38	1.42	1.42
Sample label	**Ca**	**CaSr**	**Sr**	**SrBa**	**Sr$_{0.5}$Ba$_{1.5}$**	**Ba-S**[a]	**Ba-E**[a]
Main phases space group	*P*-42$_1$*m*	*P*-42$_1$*m*	*P*-42$_1$*m*	*P*-42$_1$*m*	*P*-42$_1$*m*	*P*-42$_1$*m*	*P*-42$_1$*m*
Quantitative phase analysis (mol)							
Main phases	92.52(4)	100.00	97.19(1)	88.24(3)	91.59(2)	–	–
Other							
CaMgSi$_2$O$_6$	7.48(5)	–	–	–	–	–	–
SrSiO$_3$	–	–	2.81(1)	–	–	–	–
Sr$_2$SiO$_4$	–	–	–	11.76(3)	8.41(3)	–	–
Agreement factors and refinement details							
Chi^2	1.524	1.485	1.438	2.227	2.080	–	–
R_{wp}	0.1278	0.1375	0.1185	0.1118	0.1140	–	–
R_p	0.0965	0.1006	0.0857	0.0777	0.0761	–	–
No. of variables	63	41	46	63	63	–	–
R(*F*)	0.0543	0.0446	0.0307	0.0306	0.0265	–	–
R(*F*^{2})	0.0889	0.0737	0.0574	0.0509	0.0449	–	–
No. of reflections	364	356	284	415	422	–	–
Unit-cell parameters							
$a=b$ (Å)	7.8325(3)	7.9291(2)	8.0161(1)	8.1070(1)	8.1532(1)	8.2036(4)	8.1709(7)
c (Å)	5.0124(2)	5.0837(1)	5.1648(1)	5.2666(1)	5.3273(1)	5.4058(4)	5.3374(7)
V (Å^3)	307.51(3)	319.62(2)	331.88(1)	346.14(1)	354.13(2)	363.81(2)	356.34(6)
Mean metal–oxygen bond distances (Å)							
⟨*X*–O⟩	2.580(4)	2.624(4)	2.673(4)	2.732(6)	2.758(7)	2.793(4)	2.763(5)
⟨*T1*–O⟩	1.915(1)	1.929(2)	1.942(1)	1.952(2)	1.960(2)	1.966(4)	1.964(4)
⟨Si–O⟩	1.616(2)	1.618(1)	1.617(2)	1.620(2)	1.626(2)	1.635(4)	1.633(5)
Bond angles (deg)							
O3–*T1*–O3 [*x*4]	108.02(4)	106.64(5)	105.22(4)	104.24(7)	103.89(7)	103.8(1)	103.9(1)
O3–*T1*–O3 [*x*2]	112.42(7)	115.29(12)	118.36(8)	120.54(17)	121.33(17)	121.6(2)	121.2(2)
⟨O3–*T1*–O3⟩	109.49(5)	109.52(8)	109.60(6)	109.67(11)	109.70(11)	109.7(1)	109.7(1)
T1–O3–Si	118.90(10)	120.99(14)	122.85(11)	124.13(20)	124.63(21)	124.6(2)	123.8(2)
Tetrahedral distortion indices[b]							
λ_{T1}	1.0013	1.0052	1.0124	1.0194	1.0224	1.0232	1.0220
σ^2_{T1} (deg^2)	5.17	19.95	46.12	70.89	81.26	84.11	79.77
λ_{Si}	1.0103	1.0088	1.0079	1.0059	1.0065	1.0065	1.0081
σ^2_{Si} (deg^2)	44.48	38.38	34.00	26.06	28.29	28.26	35.92

[a] Data reported for samples labeled as Ba–S and Ba–E refer to those achieved from the single-crystal refinements of tetragonal Ba$_2$MgSi$_2$O$_7$ and Ba$_2$CoSi$_2$O$_7$, respectively [32,33].
[b] Both tetrahedral quadratic elongation (λ) and bond angle variance (σ^2) were computed according to Robinson et al. [24].

cation: Na, Ca, Sr, Ba, Y,…; *T1* and *T2* are small di- to tetra-valent cations: *T1*=Be, Mg, Al, Co, Zn,…; *T2*=Al, Si, Ge,…; and *A* is an anion, frequently O, but also F or S). The melilite structure can be described as sheets of linked tetrahedra (*T2*$_2$O$_7$ dimers corner-sharing with four-coordinated *T1* cations) connected together by *X* cations accommodated in a distorted eight-coordinated antiprismatic polyhedron [16,17].

Differently to what is commonly put forward in the literature, where increasing concentrations of EAS-active cations (i.e. “chromophores” which exhibit electronic absorption transitions in the UV–visible–NIR spectrum) replace the starting cation in the same polyhedron (e.g. usually octahedron or tetrahedron) [7–12,18–20], in the present study, the *long*- vs. *short*-range mismatch has been evaluated by studying the structural properties along a Ca–Sr–Ba-åkermanite solid solution characterized by a *constant concentration* of Co^{2+} (i.e. the “probe cation”) which substitutes for 0.3 mol of Mg^{2+} at *T1* tetrahedron. In this way, local information on the effect of the second-nearest neighbors, induced by the replacement of Ca^{2+} with bigger ions (Sr^{2+} and Ba^{2+}) at *X* site, will be gained using an innovative, simple method by investigating the (Ca,Sr,Ba)$_2$(Mg$_{0.7}$Co$_{0.3}$)Si$_2$O$_7$ join as a case-study by means of an X-ray powder diffraction (XRPD) and electronic absorption spectroscopy (EAS) combined approach.

2. Experimental section

2.1. Sample preparation

Six polycrystalline samples with a melilite structure were obtained through solid state reaction synthesis to cover all the Ca$_2$(Mg$_{0.7}$Co$_{0.3}$)Si$_2$O$_7$–Sr$_2$(Mg$_{0.7}$Co$_{0.3}$)Si$_2$O$_7$–Ba$_2$(Mg$_{0.7}$Co$_{0.3}$)Si$_2$O$_7$ solid solution. One further composition was synthesized for reference: Ca$_2$CoSi$_2$O$_7$ (Co-åkermanite).

Stoichiometric quantities of high purity carbonates (CaCO$_3$, SrCO$_3$, and BaCO$_3$) and oxides (MgO, Co$_3$O$_4$, and SiO$_2$), used as raw materials, were mixed in ethanol, dried in the oven at 105 °C, pulverized in an agate mortar and pelletized using a piston cylinder press till ~80 MPa. Subsequently, each pellet was calcined in a sealed alumina crucible in an electric kiln with static air at a maximum temperature of 1200 °C for several hours applying a heating rate of 3 °C/min. Calcined samples underwent pulverization in an agate mortar until passing through a 50 μm sieve.

2.2. XRD data collection and structural refinements

Data collection was performed at room temperature on a Bruker D8 Advanced diffractometer equipped with an Si(Li) solid-state